
What Humans Contribute to Atmospheric CO₂: Comparison of Carbon Cycle Models with Observations

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Abstract: The Intergovernmental Panel on Climate Change assumes that the inclining atmospheric CO₂ concentration over recent years was almost exclusively determined by anthropogenic emissions, and this increase is made responsible for the rising temperature over the Industrial Era. Due to the far reaching consequences of this assertion, in this contribution we critically scrutinize different carbon cycle models and compare them with observations. We further contrast them with an alternative concept, which also includes temperature dependent natural emission and absorption with an uptake rate scaling proportional with the CO₂ concentration. We show that this approach is in agreement with all observations, and under this premise not really human activities are responsible for the observed CO₂ increase and the expected temperature rise in the atmosphere, but just opposite the temperature itself dominantly controls the CO₂ increase. Therefore, not CO₂ but primarily native impacts are responsible for any observed climate changes.

Keywords: Carbon Cycle, Atmospheric CO₂ Concentration, CO₂ Residence Time, Anthropogenic Emissions, Fossil Fuel Combustion, Land Use Change, Climate Change

1. Introduction

Following the interpretation of the Intergovernmental Panel on Climate Change (IPCC) the inclining atmospheric CO₂ concentration over recent years is assumed to result almost exclusively from anthropogenic emissions, and as a consequence of the greenhouse effect this increase is made responsible for the rising temperature over the Industrial Era (see, 5th Assessment Report, AR5 [1]). These predictions are based on more or less refined theoretical models of the carbon cycle and their comparison with observations. But good agreement between calculations and observations is only a necessary, not sufficient prerequisite for reliable simulations, they must also be in conformity with all natural causalities. Because of the expected far reaching consequences of anthropogenic carbon on future climate changes this was motivation enough to critically scrutinize the main assumptions used in these carbon cycle models.

In this contribution we consider three theoretical approaches, which find favor with the IPCC and predominantly focus on the influence of human activities caused by Land Use Change (LUC) (see e.g., Le Quéré et al.

[2]; CICERO [3]) and the Fossil Fuel Emissions (FFE) (CDIAC [4]), while environmental effects are supposed to have been constant over the last 270 yr. We show that the main consequence of isolating the anthropogenic carbon cycle from the natural cycle is to introduce a new time scale, the adjustment time, which differs significantly from the residence time, the latter characterizing the natural uptake of CO₂ from the atmosphere by extraneous reservoirs.

We compare respective simulations of these approaches with actual observations at Mauna Loa (Keeling et al. [5]; AR5 [1] Chap.6-Fig.6.3, p. 476), and we contrast them with our alternative description of the atmospheric carbon cycle (Harde [6]), which is based on a first order absorption process for the full cycle with only one time scale, the residence time, and additionally including temperature dependent natural variations of the emission and uptake of CO₂.

We do not model carbon in the complete Earth-Atmosphere System, we only focus upon CO₂ in the atmosphere, which is controlled by the governing Conservation Law.

Based on this fundamental relation of mass conservation and a first order absorption process, we show that human activities have a minor influence on the CO₂ increase in the atmosphere, while the main contribution has to be explained

by natural effects, particularly the temperature, which is responsible for more than 85% of the CO₂ increase since the Industrial Revolution. Therefore, not CO₂ but primarily native impacts control any observed climate changes.

2. Physical Concept

The basis of our considerations is the balance for the influx of CO₂ into the atmosphere and the outflux from the atmosphere to extraneous reservoirs, by which the CO₂ concentration C in the atmosphere is controlled. This can well be compared with a swimming pool (see also Salby [7]) with an influx f_{in} and an outflux f_{out} , for which the changing amount of water dm_W in the pool over the time interval dt is given by the difference of these fluxes:

$$\frac{dm_W}{dt} = f_{in} - f_{out} \quad (1)$$

From a simple flux consideration we get the average turnover or residence time τ_R it takes to completely exchange the water in the pool. Under steady state conditions for $f_{in} = f_{out}$ then the total amount of water in the pool m_W is exchanged within

$$\tau_R = \frac{m_W}{f_{in}} = \frac{m_W}{f_{out}} \quad (2)$$

and the other way round is this an important measure for the outflux rate

$$f_{out} = \frac{m_W}{\tau_R} \quad (3)$$

In the same way as for the pool we can consider the balance for atmospheric CO₂ with a total emission rate $e_T(t)$ of CO₂ from the surface to the atmosphere, and reversely a total absorption rate $a_T(t)$ of the extraneous reservoirs (Figure 1). Generally the influx can be split into natural emissions with a rate $e_N(t)$ and an additional anthropogenic emission rate $e_A(t)$, which on its part results from fossil fuel emissions and land use changes. The outflux is determined by temporary or continuing absorption of CO₂ by oceans and the land. Incidentally the total absorption rate $a_T(t)$ is also separated into a fraction $a_N(t)$, characterizing an uptake that can be addressed to the amount of natural emissions, and another contribution, $a_A(t)$, caused by the additional anthropogenic emissions. This results in a total mass balance, the Conservation Law:

$$\frac{dC(t)}{dt} = \frac{dC_N(t)}{dt} + \frac{dC_A(t)}{dt} = e_T(t) - a_T(t), \quad (4)$$

$$= e_N(t) + e_A(t) - a_N(t) - a_A(t)$$

which governs the atmospheric CO₂ concentration.

Generally all these fluxes are changing with time and also depend on the actual concentration $C(t)$, which virtually may be considered to consist of a time dependent fraction $C_N(t)$, caused by native emissions, and of a time dependent anthropogenic portion $C_A(t)$, with $C(t) = C_N(t) + C_A(t)$. Thus, usually

this equation has to be solved numerically.

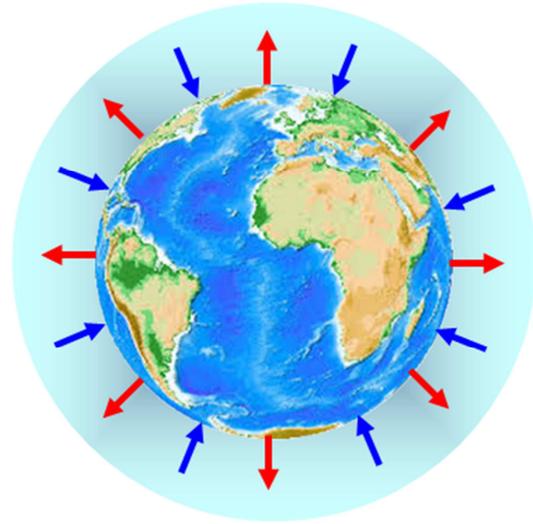


Figure 1. Emissions of CO₂ from the surface to the atmosphere (Red Arrows) and absorption of CO₂ by the surface (Blue Arrows).

In analogy to the pool example it follows that an exchange of CO₂ in the atmosphere takes the time

$$\tau_R = \frac{C(t)}{e_T(t)} = \frac{C(t)}{a_T(t)} \quad (5)$$

the so called residence time of CO₂ in the atmosphere, and the absorption rate is

$$a_T(t) = \frac{C(t)}{\tau_R} \quad (6)$$

With (4) we do not model the carbon cycle in the complete Earth-Atmosphere System (EASy). That would require a wider analysis, accounting for processes within extraneous systems and exchanges between them. Our analysis focuses upon CO₂ in the atmosphere, which is controlled by the governing conservation law. Incidentally this physical law is characterized as a flawed one-box description (see e.g., Köhler et al. [8]), because a single balance equation - so the argument - does not account for details in other reservoirs, systems that are extraneous to the atmosphere. As will be shown, such interpretation is confused. With the inclusion of surface fluxes e_T and a_T , which account for influences on the atmosphere, the balance equation (4) entirely determines the evolution of CO₂. Details of extraneous systems, which are largely unobservable, are then irrelevant.

Atmospheric CO₂ is fully described by this single equation for a reason. It follows from the 3-dimensional continuity equation, the physical law that governs the global distribution of atmospheric CO₂. In flux form, the continuity equation is given by

$$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{v}c) = c \nabla \cdot \mathbf{v}, \quad (7)$$

where the local CO₂ concentration c is transported with

velocity \mathbf{v} . When integrated over the volume of the atmosphere and subjected to the divergence theorem, (7) reduces to the governing balance equation (4) for globally averaged CO₂.

If this would be flawed, then so would be the fundamental physical law from which it follows.

The anthropogenic emissions $e_A(t)$ as the sum of the Land Use Change (LUC) (see e.g., Le Quéré et al. [2]; CICERO [3]) and the Fossil Fuel Emissions (FFE) (CDIAC [4]) are displayed in Figure 2. While LUC (Red-Brown) almost stays constant over the last 170 years, FFE (Blue) is rapidly increasing over recent years.

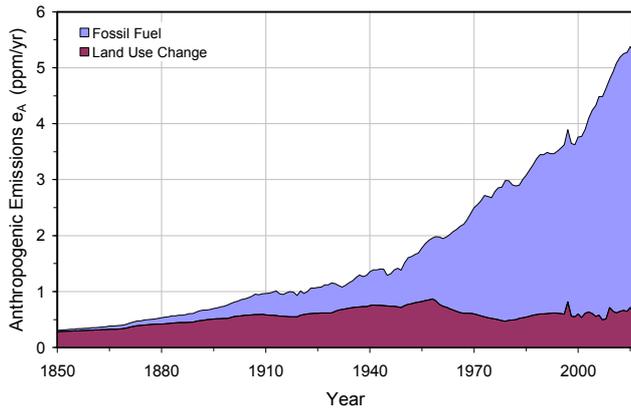


Figure 2. Total anthropogenic emissions $e_A(t)$ due to land use change (Red-Brown) and fossil fuel emissions (Blue). Data from Le Quéré et al. [2] and CDIAC [4] displayed as stacked representation.

Figure 3 shows again the total anthropogenic emissions (Red Squares) together with the temperature anomaly $\Delta T(t)$ (Blue Triangles) of the global annual station temperature data from the Goddard Institute for Space Studies (GISS) [9].

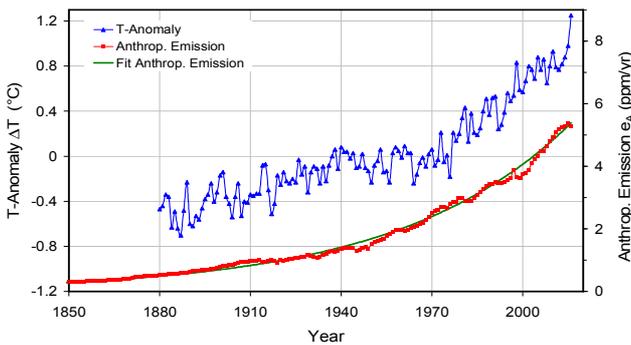


Figure 3. Anthropogenic emissions $e_A(t)$ (Red Squares) with exponential fit (Green Graph) and global temperature anomaly (GISS-data, Blue Triangles).

The anthropogenic emissions can be well approximated by an exponential of the form

$$e_A(t) = e_{A0} \cdot (e^{(t-t_0)/\tau_e} + b) \quad (8)$$

with parameters: $e_{A0} = 0.026 \text{ ppm/yr}$, $\tau_e = 50 \text{ yr}$, $t_0 = 1750 \text{ yr}$ and $b = 4$. The integral over the emission rate agrees within a few % with the integral of the estimated observations.

On first glance the almost synchronous evolution of the

fossil fuel emissions and temperature anomaly looks to be a strong indicator for the human influence as the driving force for a globally increasing temperature. But a closer look already reveals some systematic discrepancies, particularly between 1940 and 1970, where the emissions are further increasing, while the temperature stagnates or even slightly decreases. This has to be considered in some more detail, in particular by directly comparing model calculations of the CO₂ increase, based on the fossil fuel emissions and land use change, with the actual observations at Mauna Loa since 1958 (Keeling et al. [5]; AR5 [1] Chap.6-Fig.6.3, p. 476).

Therefore, in this contribution we first investigate the carbon cycle based on the IPCC's assumptions that the human emissions are the dominant cause of the CO₂ increase, before we extend the balance to the full carbon cycle also including natural variations with their temperature dependence (see also: Harde [6]; Salby [7, 10, 11]).

3. Anthropogenic Carbon Cycles

To explain the CO₂ increase over recent years and to predict its further progression, the IPCC assessment reports emanate from equation (4), but they are using some restricting assumptions (see AR5 [1] Chap.6), which can be summarized by the following statements:

1. Before 1750 and in first approximation also before 1850 steady state conditions are presupposed with a CO₂ concentration of $C_{N0}(1750) \approx 280 \text{ ppm}$, which is determined by constant natural emission and absorption rates $e_{N0} = a_{N0}$ of about 93 ppm/yr (AR5 [1] Chap.6-Fig.6.1).
2. At this concentration and with these fluxes it follows from (5) an average residence time τ_R (at pre-industrial times: τ_{R0}) of CO₂ in the atmosphere of

$$\tau_{R0} = \frac{C_{N0}}{e_{N0}} = \frac{C_{N0}}{a_{N0}} = 3.0 \text{ yr} \quad (9)$$

Note: The same result is found from (4) for the in- and outfluxes in equilibrium and with an absorption rate equivalent to (6), which is scaling proportional to the concentration C_{N0} :

$$\frac{dC_{N0}}{dt} = e_{N0} - a_{N0} = e_{N0} - \alpha_{R0} \cdot C_{N0} = e_{N0} - \frac{C_{N0}}{\tau_{R0}}, \quad (10)$$

with $\alpha_{R0} = 1/\tau_{R0}$ as the absorptivity and τ_{R0} now as the e-folding residence time.

3. It is assumed that an increasing CO₂ concentration over the last 170 years is almost exclusively caused by anthropogenic emissions from fossil fuel combustion and land use change, while the natural emissions over this period are supposed to have been the same as in pre-industrial times.

The increasing concentration is attributed to only partial re-absorption of the anthropogenic emissions, from which a fraction, the so-called Airborne Fraction $AF =$

$\Delta e_A/e_A$, is assumed to remain in the atmosphere. Then

$$\Delta e_A(t) = AF \cdot e_A(t) \tag{11}$$

is the non-absorbed portion, which cumulates in the atmosphere and

$$a_A(t) = e_A(t) - \Delta e_A(t) = e_A(t) \cdot (1 - AF) \tag{12}$$

represents the absorbed fraction of the anthropogenic emissions. Actually the IPCC emanates from an airborne fraction of $AF = 44\%$ (AR5 [1] Chap.6, p. 495; Le Quéré et al. [12]).

4. To account for a changing uptake of extraneous reservoirs with increasing atmospheric concentration the absorption is supposed to consist of a series of different exponential decay terms representing the uptake of the different reservoirs with different time constants. This absorption is considered to be proportional to the human emissions, not the actual concentration C (see (12)).

Based on these assumptions more or less sophisticated approaches are known to explain the increasing CO_2 concentration in the atmosphere. Three of them will be briefly characterized and discussed in this contribution. They all emanate from the same basic concept to isolate the natural carbon exchange between atmosphere and extraneous reservoirs and only to consider the anthropogenic cycle.

3.1. Constant Airborne Fraction

With a constant natural emission and absorption rate over the Industrial Era ($e_{N0} = a_{N0}$) and also a constant airborne fraction over this period the balance equation (4) reduces to the simple form

$$\frac{dC(t)}{dt} = \Delta e_A(t) = AF \cdot e_A(t) \tag{13}$$

and changes synchronously with $e_A(t)$. The concentration as a function of time is found by simply integrating (13) over the Industrial Era:

$$C(t) = C(1750) + AF \cdot \int_{1750}^t e_A(t') dt'. \tag{14}$$

From the carbon budget over the last 270 years we derive an airborne fraction of $AF = 42\%$ (see Le Quéré et al. [2], Table 9). Then, with an initial concentration of $C(1750) = C_{N0} = 280$ ppm this results in a progression as shown in Figure 4 (Green Line), which for the last 60 yr can directly be compared with measurements (Blue Diamonds) at Mauna Loa (Tans & Keeling [13]). This comparison shows generally too high concentrations, particularly for past periods. This might be caused by a too large initial concentration in 1750, but also the slope does not fit very well. More likely is a too large emission rate, especially due to LUC, which anyway is only known with an accuracy of about $\pm 50\%$.

A surprisingly good agreement can be found with an anthropogenic emission rate $e'_A(t)$, which as average over the considered period is reduced by 0.21 ppm/yr, and using an

airborne fraction of 48% (Green Crosses), 6% larger than the average fraction over the Industrial Era. The smooth shape of the fits is the result of an integration over the full anthropogenic emissions since 1750, where the soft increase of the curves is dominated by the 'average' emission rate, while even larger emission events are strongly flattened.

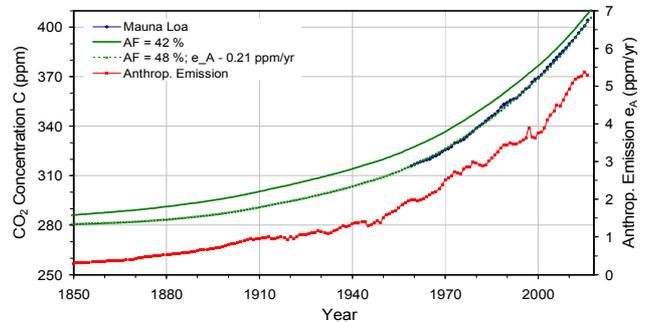


Figure 4. Calculated CO_2 concentration with an airborne fraction of 42% (Green Line) compared with observations at Mauna Loa (Blue Diamonds). A simulation with $AF = 48\%$ and reduced emissions is plotted as Green Crosses. Also shown are the anthropogenic emissions $e_A(t)$ (Red Squares).

3.2. Bern Model

A more advanced approach to describe the carbon cycle, is the so-called Bern Model of CO_2 absorption (e.g., Joos et al. [14]), a prototype of similar treatments in other models. It distinguishes between different sinks on different time scales and assumes a multi-exponential decay to re-equilibrate after a perturbation, e.g., caused by a transient spike of CO_2 added to the atmosphere. Using the five-term fit to the Bern carbon cycle model (Joos et al. [14]; Hansen et al. [15, 16]) the adjustment following a δ -pulse perturbation Δe_p from equilibrium emission e_{eq} is supposed to be:

$$R(t) = (e(t) - e_{eq}) / \Delta e_p = 0.18 + 0.14 \cdot e^{-t/420} + 0.18 \cdot e^{-t/70} + 0.24 \cdot e^{-t/21} + 0.26 \cdot e^{-t/3.4} \tag{15}$$

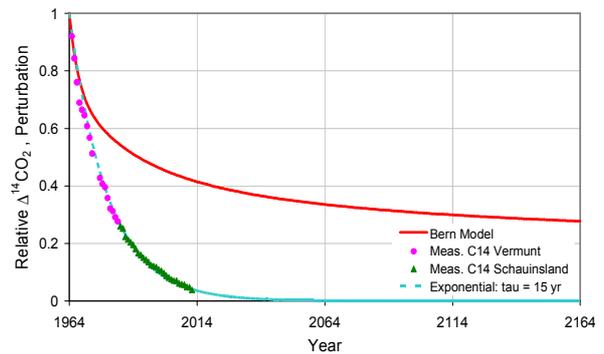


Figure 5. Decay of perturbation predicted by the Bern Model (Red Graph) as calculated from (15). Also shown is the observed ^{14}C decay (Circles and Triangles) and an exponential fit with a decay time $\tau = 15$ yr (Dashed Blue).

Figure 5 shows the adjustment of the relative perturbation $R(t)$ over 200 yr (Red). Also displayed is the observed $^{14}CO_2$ decay at Vermont and Schauinsland (Levin et al. [17]) after the stop of the atomic bomb tests, shown as relative

fractionation-corrected ‰-deviation $\Delta^{14}\text{CO}_2$ from the Oxalic Acid standard. This decay is well represented by a single exponential with a decay constant of only 15 yr (Dashed Blue). Almost identical $\Delta^{14}\text{CO}_2$ decays of 16.5 yr can be found from the data of Hua et al. [18] and Turnbull et al. [19].

For calculating the atmospheric CO₂ concentration by the Bern Model (e.g., Joos [14]), the emission of anthropogenic CO₂ into the atmosphere is considered as a series of consecutive pulse inputs. Then the atmospheric CO₂ concentration $C(t)$ at time t is assumed to be the sum of earlier emissions $e_A(t')$ at time t' multiplied by the fraction, now a time dependent airborne fraction, which is still available in the atmosphere after the time $t - t'$ and which is given by the pulse response function $R(t - t')$ of (15). With an anthropogenic emission rate, which can well be approximated by (8) (see Figure 3), it follows:

$$\begin{aligned} C(t) &= C(t_0) + \int_{t_0}^t e_A(t') \cdot R(t-t') \cdot dt \\ &= C(t_0) + e_{A0} \cdot \left[c_e \cdot e^{-(t-t_0)/\tau_e} - c_0 - c_1 \cdot e^{-(t-t_0)/\tau_1} \right. \\ &\quad \left. - c_2 \cdot e^{-(t-t_0)/\tau_2} - c_3 \cdot e^{-(t-t_0)/\tau_3} \right. \\ &\quad \left. - c_4 \cdot e^{-(t-t_0)/\tau_4} + 0.18 \cdot b \cdot (t-t_0) \right] \end{aligned} \quad (16)$$

with:

$$\begin{aligned} c_e &= 0.18 \cdot \tau_e + 0.14 \cdot \tau_{e1} + 0.18 \cdot \tau_{e2} + 0.24 \cdot \tau_{e3} + 0.26 \cdot \tau_{e4}; \\ c_0 &= 0.18 \cdot \tau_e - b \cdot (0.14 \cdot \tau_1 + 0.18 \cdot \tau_2 + 0.24 \cdot \tau_3 + 0.26 \cdot \tau_4); \\ c_1 &= 0.14 \cdot (\tau_{e1} + b \cdot \tau_1); \quad c_2 = 0.18 \cdot (\tau_{e2} + b \cdot \tau_2); \\ c_3 &= 0.24 \cdot (\tau_{e3} + b \cdot \tau_3); \quad c_4 = 0.26 \cdot (\tau_{e4} + b \cdot \tau_4); \\ \tau_{ei} &= \tau_e \cdot \tau_i / (\tau_e + \tau_i); \quad \tau_e = 50 \text{ yr}; \quad \tau_1 = 420 \text{ yr}; \\ \tau_2 &= 70 \text{ yr}; \quad \tau_3 = 21 \text{ yr}; \quad \tau_4 = 3.4 \text{ yr}; \quad b = 4; \end{aligned}$$

This approach also presupposes an equilibrium CO₂ concentration C_{eq} in 1750 of $C_{eq} = 280 \text{ ppm}$, and it excludes any further variations in the natural emission rate over the Industrial Era.

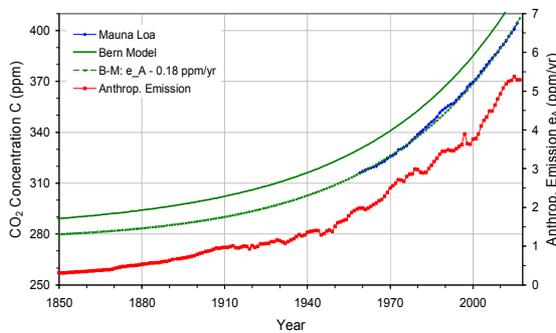


Figure 6. Comparison of the Bern Model (Green Graph) with the Mauna Loa data (Blue Diamonds). A simulation with reduced emission $e_A(t) - 0.18 \text{ ppm/yr}$ is displayed as Green Crosses. Also shown are the original data of anthropogenic emissions $e_A(t)$ (Red Squares).

The calculated atmospheric CO₂ concentration as given by (16) is displayed in Figure 6 (Solid Green). The Bern Model shows the same tendency of too large calculated concentrations as this was already found for the much simpler model of constant airborne fraction (AF Model).

With a reduced average anthropogenic emission rate, in this case of 0.18 ppm/yr , again a very good agreement with the Mauna Loa data can be observed.

But from basic causalities there exist some fundamental problems with the AF and the Bern Model:

1. Additional emissions to the atmosphere even at a constant rate will never attain a new equilibrium.
2. These emissions will further accumulate in the atmosphere, in the Bern Model 18%, in the simple AF Model even 48%, emissions which will stay for ever in the atmosphere.
3. This is a consequence of the defect, that these models essentially add up additional emissions deviating from pre-industrial times, and they only consider partial uptake, which is scaling *proportional with the emission rate* – and not with the concentration.
4. The Bern Model uses different time scales for the uptake, although the ¹⁴C-decay shows a single exponential decay of only 15 yr or shorter.
5. Even natural year-to-year variations of only 1%, El Niños and volcanic activities comparable or even larger than the human emissions, will cumulate in the atmosphere, since only additional emissions but not adequate sinks are considered in these models.

To avoid some of these deficits another class of models uses a first order absorption process, but applies this only to concentration changes $C_A(t)$ caused by anthropogenic emissions.

3.3. Absorption Scales with Concentration

Since the anthropogenic absorption rate $a_A(t)$, by presumption, is proportional to the man-made emission rate $e_A(t)$ (see Eq.(12)) and this rate on its part directly determines the anthropogenically induced fraction of the CO₂ concentration $C_A(t)$, in analogy to (6) or (10) we infer:

$$a_A(t) = e_A(t) \cdot (1 - AF) \Rightarrow \frac{C_A(t)}{\tau_A}, \quad (17)$$

which converts the absorption term in (4) to a first order process scaling proportional to the anthropogenic fraction $C_A(t)$ of the concentration (for a similar approach see e.g.: Siegenthaler & Sarmiento [20]; Dietze [21]; Cawley [22]; Lüdecke & Weiss [23]). For $e_{N0} = a_{N0}$ this results in the balance equation:

$$\frac{dC(t)}{dt} = \frac{dC_A(t)}{dt} = e_A(t) - \frac{C_A(t)}{\tau_A} = e_A(t) - \frac{C(t) - C_{N0}}{\tau_A} \quad (18)$$

with τ_A as the respective absorption time of molecules in the atmosphere, which in the IPCC terminology controls the

'adjustment' of the atmosphere only due to anthropogenic emissions. From Figure 4 and with (17) we can estimate this 'adjustment' time, which for $C_A = (393-280) \text{ ppm} = 113 \text{ ppm}$, $e_A = 4.7 \text{ ppm/yr}$ (all values averaged over 10 years from 2007-2016, see Le Quéré et al. [2], Table 7) and the fitted $AF = 48\%$ from Figure 4 gives

$$\tau_A = \frac{C_A(t)}{e_A(t)(1-AF)} = 46 \text{ yr} \quad (19)$$

Numerical integration of (18) with this 'adjustment' time, with the given emission rate $e_A(t)$ and a native concentration $C_{N0} = 280 \text{ ppm}$ is shown in Figure 7 (Green Line). For a corrected emission rate $e'_A(t) = e_A(t) - 0.3 \text{ ppm/yr}$ and the 'adjustment' time from (19) also this accounting scheme (Green Crosses) gives good agreement with the observations at Mauna Loa (Blue Diamonds). This absorption time is almost identical with an adjustment time of 48 yr as derived from a simple flux calculation presented in Harde [6], Eq. (9).

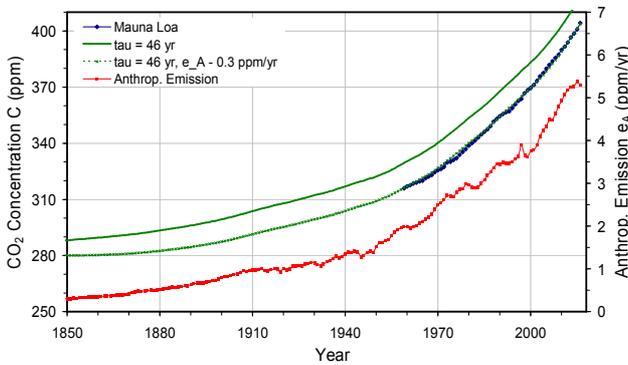


Figure 7. Calculation of the CO_2 concentration for an adjustment time $\tau_A = 46 \text{ yr}$ (Green Line) and comparison with observations at Mauna Loa (Blue Diamonds). A simulation with reduced emissions is displayed as Green Crosses. Also shown are the anthropogenic emissions $e_A(t)$ (Red Squares).

3.4. Influence of Native Effects

So, with the right parameters all investigated approaches can reproduce the observations at Mauna Loa very well. But all these models are based on different hypotheses and boundary conditions, some of them are even in contradiction to each other. Therefore, only one or none of them may be right. Good conformity with observations alone is not a sufficient criterion for testing the validity of a model, it must also be in agreement with basic physical principles. They alone can give us the physically consistent explanations for a carbon cycle, which is dominated by more than 95% of native emissions and underlies continuous environmental impacts. It is also evident that this cycle is governed by the same principles at paleoclimatic times as today with human emissions.

Thus, for the further considerations it seems reasonable first to concentrate on three basic questions:

1. How could nature be in equilibrium before the Industrial Era?

Some climate scientists consider the natural carbon

exchange as a closed cycle, which happened in this way unaffected over thousands of years without larger variations. But when looking to the glacial and interglacial periods or only to the Holocene we have to recognize that the atmospheric CO_2 concentration was always varying over longer and shorter periods. Slow variations per se are no sign of non-equilibrium, they can also result from varying emission strengths over time. But an adaptation to such natural variations is not possible, when emissions are only cumulating, as this is assumed in the AF and Bern Models for anthropogenic emissions, which never come to equilibrium. Thus, an adaptation to volcanic activities, temperature variations or even to the seasonal variations requires an absorption process for the native cycle, which behaves more or less proportional to the respective concentration $C_P(t)$ at pre-industrial times, in a similar way as considered in the 3rd model for the anthropogenic emissions.

So, it is close by to presuppose also a first order process for the native cycle, and the respective balance equation for pre-industrial times then assumes the form, analogous to (10):

$$\frac{dC_P(t)}{dt} = e_P(t) - \frac{C_P(t)}{\tau_{RP}} \quad (20)$$

with $e_P(t)$ as the emission rate and τ_{RP} as the residence time at pre-industrial times. Equilibrium is achieved when the left side of (20) is zero. Then the residence time becomes $\tau_{RP} = C_P(t)/e_P(t)$.

The same relation was found from the simple flux model with a residence time $\tau_{R0} = 3 \text{ yr}$ at 1750. Such a residence or absorption time for the natural cycle is in good agreement with the observed seasonal variations and is also supported by the ^{14}C -decay as will be discussed in detail in subsection 5.7.3.

When CO_2 concentrations were continuously changing in pre-industrial times we also have to inquire:

2. Can the natural cycle really be assumed to have been constant over the last 270 yr?

Almost every day we recognize natural phenomena and processes in form of significant perturbations or variations, e.g., volcanic eruptions, earthquakes, El Niño - La Niña events, internal and external oscillations, global warming or seasonal variations.

All these phenomena have a direct influence on the naturally caused fraction $C_N(t)$ of CO_2 in the atmosphere. Therefore, the balance for the natural cycle also over the Industrial Era has to be expressed explicitly by a time dependent emission rate $e_N(t)$ and also a time dependent residence time $\tau_R(t)$. The latter can slightly be affected by internal or external variations, but should not significantly deviate from pre-industrial times or 1750. Otherwise the balance must obey the same principal relation as in pre-industrial times with:

$$\frac{dC_N(t)}{dt} = e_N(t) - \frac{C_N(t)}{\tau_R(t)} \quad (21)$$

Finally we have to ask:

3. Can the anthropogenic cycle be considered separately from a natural cycle?

From the preceding discussion one may conclude that the total balance equation for the respective models looks like

$$\frac{dC(t)}{dt} = \frac{dC_N(t)}{dt} + \frac{dC_A(t)}{dt} \tag{22}$$

$$= \left(e_N(t) - \frac{C_N(t)}{\tau_R(t)} \right) + \begin{cases} e_A(t) \cdot AF & AF Model \\ e_A(t) \cdot R(t-t) & Bern Model \\ e_A(t) - C_A / \tau_A & 1. Order Mod \end{cases}$$

In all cases is this equation controlled by two or more independent time scales, a fast scale with $\tau_R \approx 3 \text{ yr}$ for the absorption of natural emissions and a slow scale with an infinite decay for 48% of emissions in the AF Model, with 5 decay times for different sinks in the Bern Model, and an adjustment time of 46 yr in the 3rd model, all for the adaptation of the atmosphere to additional anthropogenic emissions.

At least here it gets obvious that naturally and human emitted molecules cannot be treated differently. As long as no saturation in the uptake is observed, which is not the case (see Appendix A), an additional emission by humans must underlie the same absorption process as the natural emissions. A separation is in startling contradiction to the Equivalence Principle, and as a consequence of this principle only one absorption time, τ_R , with the same absorption behavior for human and native emissions must exist.

4. Complete Carbon Cycle

The preceding considerations show that a realistic analysis of the CO₂ exchange between the atmosphere and its adjacent reservoirs has also to include natural variations due to temperature effects or temporal events. It has also to consider a common absorption of all natural and human contributions, which are scaling proportional to the apparent CO₂ concentration and which are represented by one unique decay time (see also: Essenhig [24]; Salby [7, 10]; Harde [6]; Berry [25]).

We summarize the main deviations from the previously discussed accounting schemes by the following fundamental principles:

1. Changes in the natural carbon cycle, which are due to a continuous temperature increase over the Industrial Era, are included in the balance equation (4) by a temperature dependent term for the natural emissions and also a term for the temperature dependent absorption.
2. Perturbations from an equilibrium concentration C_{eq} due to natural changes or additional anthropogenic emissions are compensated for or controlled in the carbon cycle by an absorption rate, which changes proportional to the actual concentration C (first order process, see Eq. (6)).
3. Molecules emitted to the atmosphere can have a number of different sources, natural and man-made sources, but (up to now) they have only common natural sinks in form of the oceans and continents, which do not differentiate between the native or anthropogenic origin.

4. There exists no evidence that the absorption was suddenly saturating and the residence time τ_R jumping up by one or two orders of magnitude from τ_{R0} to τ_A , when the atmospheric concentration exceeded a level of 280 ppm. τ_R can only have changed continuously from pre-industrial to present times from 3 to 4 yr, synchronously with the atmospheric concentration and in agreement with (5) and (9).
5. The observed exponential decay of ¹⁴C in the atmosphere after the stop of the atomic bomb tests in 1963 is a strong indication for a first order absorption process of CO₂ by land and oceans with a unique time constant determined by the gross flux of CO₂ from the atmosphere to the reservoirs (see Figure 5). Only such an absorption ensures that the carbon cycle can stabilize and react adequately on any temporal perturbations like seasonal variations or volcanic activities.
6. For parallel absorption processes by the oceans, by the biosphere or rock weathering the absorptivity α is given as the sum of the individual channels α_i with $\alpha_R = \alpha_1 + \alpha_2 + .. + \alpha_N$ and $\tau_R = 1/\alpha_R$. The uptake is not restricted by the slowest process as assumed in the Bern Model, but by the sum of all processes with one unique absorptivity α_R for all molecules. The reciprocal of α_R is the residence time τ_R of CO₂ in the atmosphere.

These principles are incorporated in a balance equation, the General Conservation Law, which on the one side includes temperature dependent and, thus, time dependent natural and anthropogenic emissions, and on the other side considers a temperature dependent unique residence time τ_R , which describes the collective or net absorption of all molecules. It does not differentiate between a residence or adjustment time:

$$\frac{dC(t)}{dt} = e_N(T(t)) + e_A(t) - \frac{C(t)}{\tau_R(T(t))} \tag{23}$$

In first order the natural emission rate and the residence time can be assumed to increase linearly with the temperature anomaly ΔT :

$$\begin{aligned} e_N(T(t)) &= e_{N0} + \beta_e \cdot \Delta T(t) \\ \tau_R(T(t)) &= \tau_{R0} + \beta_\tau \cdot \Delta T(t) \end{aligned} \tag{24}$$

β_e and β_τ are the temperature coefficients of the natural emission and the absorption time. In the general case of a saturating uptake by the extraneous reservoirs τ_R will additionally change with C . But up to now any unequivocal saturation effects cannot be identified (see Appendix A).

With the temperature anomaly $\Delta T(t)$ and the anthropogenic emissions $e_A(t)$ as represented in Figure 3, Eq.(23) can be solved numerically.

Figure 8 shows the simulated CO₂ concentration in the atmosphere (Green Graph) over a time period 1880 - 2016, for which reliable temperature data are available (GISS [9]), whereas the direct CO₂ measurements at Mauna Loa (Blue Diamonds) started not before 1958. The temperature data were used as moving average over $\pm 5 \text{ yr}$. We achieve good

agreement with the observations for a natural emission rate $e_{N0} = 93.3 \text{ ppm/yr}$, $\tau_{R0} = 3 \text{ yr}$ (both in agreement with (9)) and temperature coefficients $\beta_e = 10 \text{ ppm/yr/}^\circ\text{C}$ and $\beta_\tau = 0.37 \text{ yr/}^\circ\text{C}$. Similar good results are obtained with larger β_e (up to $24 \text{ ppm/yr/}^\circ\text{C}$) and smaller β_τ ($\rightarrow 0$) or vice versa with β_τ (up to $0.74 \text{ yr/}^\circ\text{C}$) and smaller β_e ($\rightarrow 0$). Thus, we have to assert that as long as the natural and anthropogenic emission rates and at least one of the temperature coefficients are not more accurately known, we can only determine a combination of these parameters, not their absolute values.

Figure 8 also displays a simulation for which the anthropogenic emissions were set to zero (Magenta).

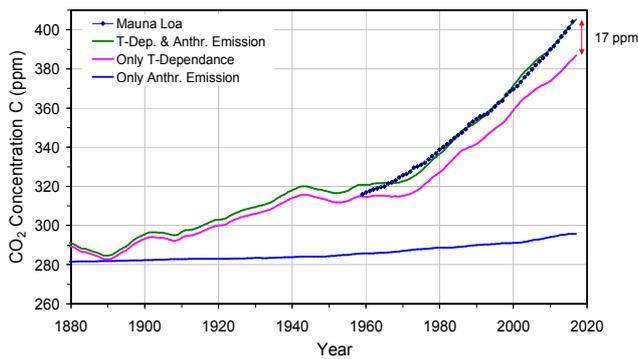


Figure 8. Calculated CO_2 concentration with temperature-dependent emission and absorption (Green). Compared against the observed record of CO_2 from Mauna Loa (Blue Diamonds). Simulation without anthropogenic emissions (Magenta), and only human activities (Blue).

The difference between both curves results from the human activities. These graphs evidently show that, based on (23), the anthropogenic contribution to the observed CO_2 increase over the last 150 years is significantly less than the natural influence. So, as an average over the period 2007- 2016 the anthropogenic emissions were contributing not more than 4.3% to the total concentration of 393 ppm and thus, their fraction to the atmospheric increase since 1750 of 113 ppm is not more than 17 ppm or 15%. The dominating contribution with 85% is determined by natural influences, in Figure 8 represented as difference of the Magenta Graph to the 280 ppm grid-line.

The pure anthropogenic contribution to the atmospheric concentration, which would result without temperature effects, is shown by the Blue Graph on a constant background of 280 ppm. With a residence time of $\tau_{R0} = 3 \text{ yr}$ human emissions cannot contribute more than 14.5 ppm, and with an increasing τ_R over the Industrial Era due to the temperature influence it will slightly increase to 17 ppm, as displayed by the difference between the Green and Magenta Graphs (see red arrow). At equilibrium the relative contribution of human activities to the total CO_2 concentration is always determined by the anthropogenic to the total emission rate, independent of the actual residence time (Eq.(23); Harde [6], Eq.(14)).

Note, a simulation without anthropogenic emissions, but slightly increased temperature coefficients ($\beta_\tau = 0.48 \text{ yr/}^\circ\text{C}$ or $\beta_e = 13.3 \text{ ppm/yr/}^\circ\text{C}$) lifts the Magenta curve to coincide almost exactly with the Green graph. Thus, the observed

evolution at Mauna Loa could also be reproduced without involvement of $e_A(t)$, contrary to the IPCC interpretations.

Up to now we were only considering the seasonally averaged CO_2 measurements, but it is also worthwhile to look closer to the monthly data at Mauna Loa (see Keeling et al. [5]; AR5 [1] Chap.6-Fig.6.3, p. 476) as displayed in Figure 9 (Magenta Diamonds). The “sawtooth” curve is an obvious indication for the direct variation of the CO_2 emission and uptake rates, driven by the solar activity and the temperature over the seasons. Generally this modulation is attributed to the greater land mass on the Northern Hemisphere, where the uptake by photosynthesis predominantly occurs during the growing season, while CO_2 release by heterotrophic processes is more dominant over the other seasons.

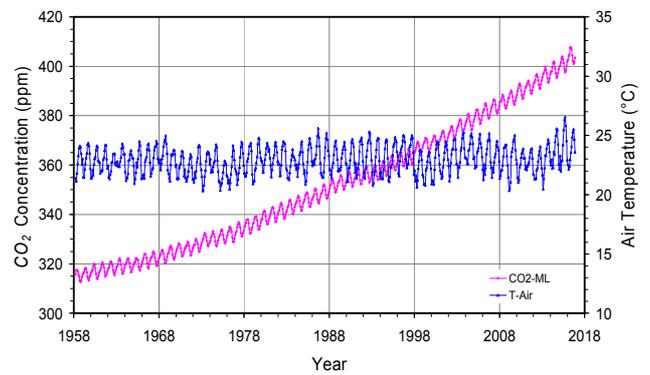


Figure 9. Monthly time series of measured CO_2 concentration at Mauna Loa (Magenta Diamonds) and air temperature record at Hawaii (Blue Triangles).

However, apparently also local effects have a direct influence on this record. Figure 9 shows also the monthly averaged air temperature at Hawaii (Blue Triangles) with seasonal variations of 3 - 4°C (NOAA [26]). Almost synchronous changes are found for the sea surface temperature (NOAA [27]). The CO_2 concentration follows these temperature variations with a delay of 6 - 7 months (see also Salby [7]).

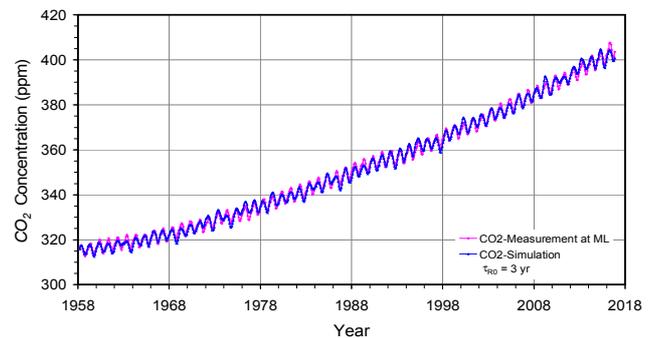


Figure 10. Monthly CO_2 concentration integrated from the balance equation with temperature-dependent emission and absorption and an initial residence time of 3 years (Blue Triangles). Compared against the observed record of CO_2 from Mauna Loa (Magenta Diamonds).

A calculation with human emissions included and using the modulated air temperature anomaly $\Delta T(t)$ at Hawaii (NOAA [26]) is shown in Figure 10 (Blue Diamonds). This excellent

agreement with the monthly Mauna Loa CO₂ measurements (Magenta Diamonds) is obtained by applying a linear response of the natural emissions to the modulated temperature anomaly, and assuming a residence time with an initial value of $\tau_{R0} = 3 \text{ yr}$ and an averaged slightly nonlinear temperature increase $\Delta T^{l.5}(t)$, which accounts for the nonlinear response of oceanic emissions and the uptake of CO₂ (see Subsection 5.6). It should be mentioned that the averaged air temperature at Hawaii is distinguished by a quite linear increase over time. Therefore, different to Figure 8 also smaller deviations at about 1970 are completely disappearing.

A detailed analysis of the Mauna Loa curve (Salby [7, 10, 11]) and independent cross-correlation investigations of thermally induced emission (Humlum et al. [28]) indicate that the actual absorption time of 3-4 yr, as derived from (9) and based on the IPCC's own estimates, may even be significantly shorter, as short as only 8-12 months, this at least over the vegetation growths' periods on land and in oceans, but also in areas such as the North Atlantic with cold downwelling waters. Under such conditions, in the same way as the residence time is getting shorter, the total emission rate gets larger (generally the most uncertain parameter of the guessed rates). As the admixture of human generated CO₂ is given by the percentage of anthropogenic to total emissions, also this fraction further decreases. So, with an absorption time of $\tau_{R0} = 1 \text{ yr}$ and a total emission rate of $e_T = 298 \text{ ppm/yr}$ the anthropogenic emissions of 4.7 ppm/yr do not contribute more than 1.6% or 6 ppm to the atmospheric CO₂. However, for a more conservative assessment and in agreement with the IPCC's estimates (AR5 [1], Chap.6-Fig. 6.1) we further emanate from conditions as derived from the simulations of Figures 8 and 10 with $\tau_{R0} = 3 \text{ yr}$.

5. Discussion

All presented schemes for simulating the atmospheric CO₂ concentration are based on the balance equation considering the fluxes from extraneous reservoirs to the atmosphere and vice versa. However, as widely used in the literature, the approaches in Section 3 restrict these fluxes on anthropogenic emission-absorption cycles, whereas natural emissions and their uptake are supposed to be the same since 270 years, and thus, any changes in these fluxes are simply disregarded in the total balance. In addition, two of these approaches use a unilateral balance for this cycle, only controlled by the influxes and independent of the actual atmospheric concentration. These deficits have some fatal consequences in the further interpretation of the carbon cycle.

5.1. New Time Scale

Sole consideration of anthropogenic fluxes is identical with the introduction of a new time scale for the uptake of man-made emissions (see subsection 3.4). Since these emissions and also their changes are more than one order of magnitude too small to explain directly the observed concentration changes over recent years, carbon-cycle models just introduce an additional buffer factor, the 'adjustment' time. Such new

time scale ensures a sufficiently long cumulation time of the molecules in the atmosphere to attain a concentration level, which is in agreement with the observations. But it looks quite dubious that 280 ppm, equivalent to the environmental fraction, are exchanged with extraneous reservoirs within 3-4 yr, and for about 45% of additional human emissions an accumulation over thousands of years in the atmosphere is assumed.

Effectively represents an 'adjustment' time τ_A nothing more than an amplification factor for the anthropogenic emission rate to fit with the observations. This is obvious for the approach described in subsection 3.3 (see Eqs.(18) and (19)), where the integrated net flux is proportional to $e_A(t)$ and τ_A . But implicitly this is also concealed in the other two schemes.

In the case of a constant airborne fraction the 'adjustment' time for the fraction $\Delta e_A = AF \cdot e_A(t)$, cumulating in the atmosphere, is even infinite. Under such conditions already any additional constant emission contributes to a linear increase of the concentration, whereas any changes in the emission rate only slightly affect the further shape of this increase. In such case - with an infinite lifetime of additionally emitted molecules in the atmosphere and a given emission rate for FFE from CDIAC [4] and for LUC from Le Quéré et al. [2] (see Figure 2) - AF is now the only free parameter controlling the size and steepness of the concentration growth rate (see (14)).

From a simple balance of the increasing concentration and the total emissions we derive a value for AF of 42%. A realistic model then should reproduce the observations with this airborne fraction. But our previous simulations (see Figure 4) showed that this does not fit in size and shape. The discrepancy would even further increase, when additional natural emissions due to a globally increasing temperature have to be considered. Good consistency can only be found with a reduced anthropogenic emission rate and a further adapted AF .

In the more elaborate Bern Model not only one, but even five new time scales are introduced. This is expressed by the response function with its five decay times (see (15)). While the last term in (15) is similar to the decay described by the residence time τ_R , the others shall represent the limited uptake by different extraneous reservoirs with different time constants, one also infinite. A simulation with this response function, which is equivalent with a time dependent airborne fraction, reproduces quite well the general trend of the increasing concentration (see Figure 6), but in direct analogy to 3.1 and 3.3 satisfactory agreement with the free-air measurements at Mauna Loa is only obtained when reducing the official anthropogenic emissions and neglecting any additional natural emissions.

5.2. First Order Absorption Process

Approaches 3.1 and 3.2 use a quite exceptional definition for the in- and outfluxes between the atmosphere and adjacent reservoirs. The respective absorption rates are considered to be independent of the actual atmospheric concentration, instead they are supposed to scale in direct proportion to the

emission rate either with fixed or time variable airborne fraction. As long as this emission is not zero, the atmospheric concentration further increases, independent of its actual level; and also at constant emissions the system never reaches steady state.

However, when such unusual correlation between emission and absorption rates would really exist, this cannot only be restricted to anthropogenic emissions and switched off for native emissions. Due to the equivalence principle it should be valid for both. *Also for times before 1750 the absorption process cannot have been completely different to that over the Industrial Era or was suddenly changing with the first anthropogenic emissions.*

The dramatic consequences when applying the Bern Model to the total emissions are illustrated in Figure 11. This would result in an exploding atmospheric CO₂ concentration (Green Line) up to levels found 500 Mio. yr ago, and it would never allow steady state conditions as supposed before 1750. In average such an increase over the last 270 yr is equivalent to an $AF = 35\%$.

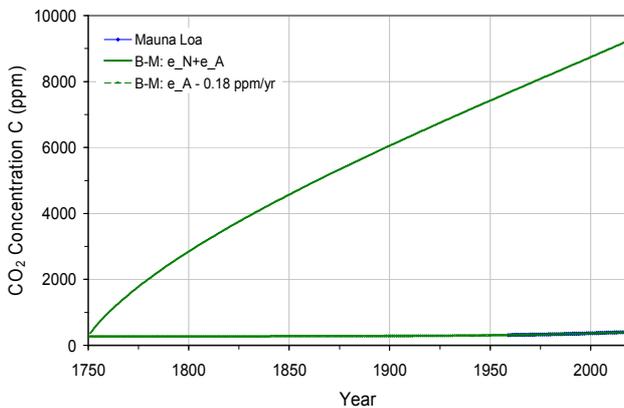


Figure 11. Simulation of the CO₂ concentration based on the Bern Model assuming the total emissions (Green). Also shown is a calculation for only anthropogenic emissions (Green Crosses). Compared against the observed record of CO₂ from Mauna Loa (Blue Diamonds).

An uptake process only scaling with the emission rate and not the concentration looks completely unrealistic (see also subsection 3.4). It must be dismissed, even when the simulation for the anthropogenic emissions alone (Green Crosses) pretends good agreement with the Mauna Loa observations (Blue Diamonds).

A balance which only adds up net emissions, and denies an increasing absorption rate with inclining atmospheric concentration, is in contradiction to real observations and hurts fundamental physical laws. CO₂ is not a noble gas, which indifferently accumulates in an open compartment after an emission, but it is dissolved in oceans and converted via photosynthesis to organic molecules. This uptake obeys a first order absorption process and scales with the actual concentration or the difference to an external reservoir¹. It

prevails as long as its concentration C or the difference remains nonzero, i.e., indefinitely.

Different to subsections 3.1 and 3.2 approach 3.3 already emanates from a first order absorption process, but it is also restricted only to anthropogenic concentration changes. Basically an 'ansatz' in (22), third case, and considering changes relative to some reference concentration is correct, when this also includes natural variations over the considered time period. But the fundamental flaw in 3.3 is to introduce a new, independent absorption constant, the adjustment time, for the uptake of the additional emissions instead of using the same absorption process, which already controls more than 95% of the carbon cycle, and this - due to physical causalities - at pre- industrial times in the same manner as over the Industrial Era.

5.3. Environment as a Net Sink

From the observations of the atmospheric concentration and estimates of anthropogenic emissions it is widely inferred that not natural but anthropogenic origin is responsible for the increasing atmospheric CO₂. Writing the global atmospheric carbon budget in the form (see e.g., Cawley [22])

$$\frac{dC}{dt} - e_A(t) = e_N - a_T < 0, \tag{25}$$

it is obvious that the net environmental flux, $e_N - a_T$ can quite well be assessed without needing to know the absolute magnitudes of e_N or a_T , quantities which on their parts are highly uncertain. Since the concentration changes dC/dt are smaller than the anthropogenic emission rate, the left side of (25) is negative and thus, the environmental uptake a_T must be larger than the natural emissions e_N . From this correct statement that the environment has acted as a net sink throughout the Industrial Era, however, often wrong conclusions are derived that nature cannot be the reason for any observed CO₂ increase.

For a moment let us assume e_N may be the emission rate at which the system was in balance, and e_A may represent an additional rate of human or native emissions or of both. In reality and in all discussed models with airborne fraction or with first order uptake the concentration growth rate develops slower than these additional emissions and thus, a_T gets larger than e_N . So, with both sides of (25) getting negative this only means that with additional emissions, native or humans, nature also acts as a further increasing sink (compared to a previous equilibrium). As long as any arbitrary fraction of human emission is involved, the environment is always a net sink. This is true per definition, since up to now no artificial uptake exists. But this does not say anything about any additional native emissions over the Industrial Era, since emission and uptake are largely independent processes and the absorption does not impede nature from increasing its own emissions.

A similar strange logic is used by Richardson [29], who

¹ Diffusion processes which act proportional to the concentration difference between two reservoirs, can be assumed to consist of an outflux proportional to the atmospheric concentration C_a and an influx proportional to the concentration of the

reservoir C_r .

considers mean values of the net atmospheric accumulation $\langle dC/dt \rangle = 1.7 \text{ ppm/yr}$ and of the human emissions $\langle dC_A/dt \rangle = e_A(t) = 3 \text{ ppm/yr}$ in a balance

$$\langle dC/dt \rangle - \langle dC_A/dt \rangle = \langle dC_N/dt \rangle < 0, \quad (26)$$

in which with $\langle dC_A/dt \rangle = e_A(t)$ a priori any anthropogenic absorptions are embezzled. From this relation it is also inferred that the average natural contribution $\langle dC_N/dt \rangle$ has been to remove CO₂ from the atmosphere, this with the same wrong conclusion as Cawley that the long term trend of rising CO₂ could not be explained by natural causes. This argument is disproved with Figures 8 and 10. The fact that the environment has acted as a net sink throughout the Industrial Era is a consequence of a dynamic absorption rate, which is only controlled by the total CO₂ concentration $C = C_N + C_A$. So, also with additional native emissions and/or temperature changes in the absorptivity the total uptake always tries - with some time delay - to compensate for the total emissions which, of course, also include the anthropogenic fraction. In other words: *Since nature cannot distinguish between native and human emissions, nature is always a net sink as long as human emissions are not zero.* Thus, except for shorter temporary events like volcanic activities the environment will generally act as a net sink even in the presence of increasing natural emissions.

To equate $\langle dC_A/dt \rangle$ in (26) exclusively with human emissions violates conservation of mass. Only when replacing $\langle dC_A/dt \rangle$ by $\langle e_A(t) - C_A/\tau_R \rangle$, eq.(26) satisfies the Conservation Law, and when additionally replacing $\langle dC_N/dt \rangle$ by $\langle e_N(t) - C_N/\tau_R \rangle$ eq.(26) converts to (23).

Again we emphasize that a separate treatment of the native and human cycle with their respective concentrations C_A and C_N is possible if and only if no contributions are missing and the two balances are linked together in one rate equation with only one unitary residence time.

5.4. Too Simple Model

Often climate scientists argue that changes of CO₂ in the atmosphere cannot be understood without considering changes in extraneous systems (see e.g., AR5 [1], Chap.6; Köhler et al. [8]), and they characterize the Conservation Law as a flawed 1-box description - because, a single balance equation would not account for details in other reservoirs. In particular, they refer to carbonate chemistry in the ocean, where CO₂ is mostly converted to bicarbonate ions. As only about 1% remains in the form of dissolved CO₂, they argue that only this small fraction could be exchanged with the atmosphere. Due to this so-called Revelle effect, carbonate chemistry would sharply limit oceanic uptake of anthropogenic CO₂.

In regard to understanding changes of CO₂ in the atmosphere, changes in extraneous systems are only qualifiedly of interest. The governing law of CO₂ in the atmosphere (4) and in more elaborate form (23) is self contained. With the inclusion of the surface fluxes $e_T(t)$ and $a_T(t) = C/\tau_R(t)$, which account for influences of the adjacent

reservoirs on atmospheric CO₂, details of other extraneous reservoirs of carbon are entirely irrelevant. This feature of the governing physics is not only powerful, but fortunate.

Concerning carbonate chemistry, it is noteworthy that, in the Earth's distant past, CO₂ is thought to have been almost 2000% as great as its present concentration (e.g., Royer et al. [30]). Most of that was absorbed by the oceans, in which carbon today vastly exceeds that in the atmosphere. According to the IPCC, even in modern times the oceans account for 40% of overall absorption of CO₂ (AR5 [1], Fig.6.1). In relation to other sinks, their absorption of CO₂ is clearly not limited (see Appendix A). Of that 40%, over the Industrial Era anthropogenic CO₂ represents less than 1%. Contrasting with that minor perturbation in absorption is oceanic emission of CO₂. Through upwelling of carbon-enriched water, the oceans significantly enhance natural emission of CO₂ (Zhang [31]).

Different to our approach, which takes into account human and also naturally varying emissions and absorptions, the models in Section 3 emanate from such a simple and apparently flawed description that over thousands of years CO₂ was circulating like an inert gas in a closed system, and only with the industrial revolution this closed cycle came out of control due to the small injections by human emissions.

5.5. Different Time Constants

The different time scales introduced with the models in Section 3 represent different absorption processes for the uptake of atmospheric CO₂ molecules by the extraneous reservoirs. From physical principles it is impossible that an absorption process would differentiate between naturally and anthropogenically emitted molecules. The temporal absorption or sequestration - except for smallest corrections due to isotopic effects - is for all molecules identical.

The absorption also cannot decline unexpectedly by more than one order of magnitude with the begin of the Industrial Era or because of an additional emission rate of a few %. Observations show that no noticeable saturation over recent years could be found (Appendix A).

Oceans and continents consist of an endless number of sources and sinks for CO₂ which act parallel, emitting CO₂ into the atmosphere and also absorbing it again. In the same way as the different emission rates add up to a total emission, the absorption rates with individual absorptivities α_i - and each of them scaling proportional to the actual CO₂ concentration - add up to a total uptake as a collective effect

$$\begin{aligned} a_T &= \alpha_1 C + \alpha_2 C + \dots + \alpha_N C \\ &= (\alpha_1 + \alpha_2 + \dots + \alpha_N) \cdot C = \alpha_R \cdot C \end{aligned} \quad (27)$$

Collective absorption thus leads to exponential decay of perturbation CO₂ at a *single* rate

$$\alpha_R = 1/\tau_R = \alpha_1 + \alpha_2 + \dots + \alpha_N \quad (28)$$

This decay rate is faster than the rate of any individual sink

and it prevails as long as its concentration C or its difference to external reservoirs remains nonzero (see: Harde [6]; Salby [11]).

The above behavior is a consequence of the Conservation Law and in contrast to the Bern Model, where decay proceeds at *multiple* rates. A treatment of CO_2 with a multiple exponential decay obeys the following:

$$\begin{aligned} C &= C_{10}e^{-\alpha_1 t} + C_{20}e^{-\alpha_2 t} + \dots + C_{N0}e^{-\alpha_N t} \\ &= C_1 + C_2 + \dots + C_N \end{aligned} \quad (29)$$

Then differentiation gives:

$$\begin{aligned} \frac{dC}{dt} &= -\alpha_1 C_{10}e^{-\alpha_1 t} - \alpha_2 C_{20}e^{-\alpha_2 t} \dots - \alpha_N C_{N0}e^{-\alpha_N t} \\ &= -\alpha_1 C_1 - \alpha_2 C_2 \dots - \alpha_N C_N \\ &\neq -(\alpha_1 + \alpha_2 + \dots + \alpha_N) \cdot C \end{aligned} \quad (30)$$

At multiple decay rates the corresponding sinks operate, not collectively, but independently. After a couple of their decay times, the fastest sinks become dormant. Overall decay then continues only via the slowest sinks, which remove CO_2 gradually. It is for this reason that such a treatment leaves atmospheric CO_2 perturbed for longer than a thousand years (Figure 5). In contrast, the behavior required by the Conservation Law decays as fast or faster than that of the fastest sink (see (28)).

The observed decay of ^{14}C shows that the corresponding absorption is determined by a single decay time and operates on a time scale of only about one decade (see Figure 5). This scale is the same for the natural carbon cycle as for the anthropogenic cycle. Therefore, it is unrealistic to differentiate between a residence time and different adjustment times.

In this context it should be noticed that due to re-emissions of $^{14}\text{CO}_2$ from extraneous reservoirs the real residence time of $^{14}\text{CO}_2$ in the atmosphere as well as that of the other isotopologues of CO_2 can only be shorter, even shorter than a decade (for details see subsection 5.7.3 and Appendix B).

5.6. Temperature Dependence

According to (9) or (10) we see that with increasing atmospheric concentration over the Industrial Era from 280 to 400 ppm either the residence time must be increased with temperature from 3 to about 4 yr, or τ_R is considered to be constant and the total emissions were rising from 93 to about 130 ppm/yr, synchronously increasing the concentration. Both these limiting cases are in agreement with a temperature anomaly of about 1.2 °C over this period (see GISS [9]), when we assume the maximum temperature coefficients $\beta_\tau = 0.74 \text{ yr}/^\circ\text{C}$ or $\beta_e = 24 \text{ ppm/yr}/^\circ\text{C}$. However, generally both temperature induced natural emissions as well as temperature dependent absorptions together will dictate the inclining concentration in the atmosphere.

In any way, as we see from Figure 8, is the CO_2 concentration dominantly empowered by the temperature increase; with only one unique decay process not human activities but almost only natural impacts have to be identified

as the main drivers for the observed CO_2 increase in the atmosphere and also for the continuous climate changes over the past and present times.

The various mechanisms, along with their dependence on temperature and other environmental properties, could not have remained constant during the pre-industrial era. This inconsistency invalidates the fundamental assumption, that natural emission and absorption during the pre-industrial period did remain constant. Even less this is valid over the Industrial Era, a period which is characterized by the IPCC as the fastest rise in temperature over the Holocene or even the last interglacial.

So, the CO_2 partial pressure in sea water approximately changes with temperature as $(p\text{CO}_2)_{\text{sw}}(T) = (p\text{CO}_2)_{\text{sw}}(T_0) \cdot \exp[0.0433 \cdot (T - T_0)]$ (see: Takahashi et al. [32]) and thus, an increase of 1 °C causes a pressure change of about 18 μatm , which amplifies the influx and attenuates the outflux. From observations over the North Atlantic Ocean (see, Benson et al. [33]) it can be estimated that a pressure difference $\Delta p\text{CO}_2$ between the atmosphere and ocean of 1 μatm contributes to a flux change of $\delta f_{\text{in}} \approx 0.075 \text{ mol/m}^2/\text{yr} = 3.3 \text{ g/m}^2/\text{yr}$. Therefore, with an Earth's surface of 320 Mio. km^2 covered by oceans and a pressure change of $\Delta p\text{CO}_2 = 18 \mu\text{atm}$, under conventional conditions the native influx from oceans to the atmosphere already increases by $\Delta f_{\text{in}} \approx 19 \text{ Pg/yr}$ or 2.4 ppm/yr for an average temperature incline of 1 °C. An even stronger variation can be expected for the land vegetation with an increased decomposition and reduced uptake of CO_2 at rising temperature (Lee [34]; Salby [11]).

Together this causes an incline of the atmospheric CO_2 level which is larger than all apparent human activities, but its contribution is completely neglected in the official accounting schemes.

Also melting permafrost and emissions of volcanoes on land and under water as well as any emissions at earthquakes are not considered. In addition, actual estimates of dark respiration suggest that under global warming conditions whole-plant respiration could be around 30% higher than existing estimates (Huntingford et al. [35]). This longer list of different native events and effects is completely embezzled in the favored IPCC models.

Equally inconsistent is the presumption that additional uptake of anthropogenic CO_2 , which represents less than 1% of the total over the Industrial Era, has, somehow, exceeded the storage capacity of oceans and other surface and sub-surface reservoirs, capacity which is orders of magnitude greater. *A reduced absorption is rather the consequence of global warming than of saturation.* Due to Henry's law and its temperature dependence not only the partial pressure in sea water increases, but also the solubility of CO_2 in water declines exponentially with temperature and, thus, reduces the CO_2 uptake. Often is this effect incorrectly misinterpreted as saturation caused by a limited buffer capacity and dependent on the concentration level. But here we consider an uptake changing with temperature, as this is known for chemical reactions, where the balance is controlled by temperature. How strongly the biological pump (see Appendix A) and

photosynthesis on land is also controlled by temperature, is only incompletely known, but obviously they are also varying slightly exponentially with temperature (Lee [34]).

Figure 12 displays a scatter plot supporting the close correlation of the atmospheric CO₂ concentration with the land-ocean temperature anomaly (GISS [9]). The latter is controlled by more than 60% by the solar influence and less than 40% by CO₂ as greenhouse gas feedback (Harde [36, 37]).

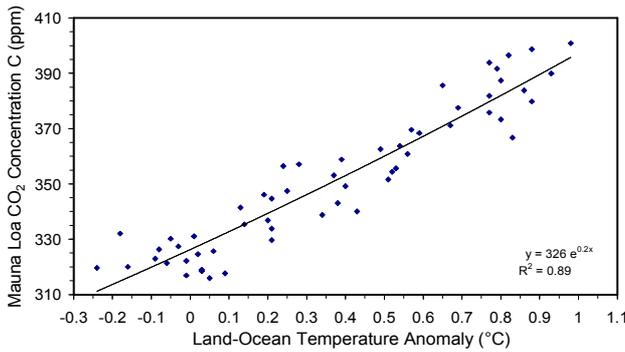


Figure 12. Scatter plot of Mauna Loa CO₂ concentration (Blue Diamonds) and trend curve (Black Graph) versus land-ocean temperature anomaly.

5.7. IPCC Arguments for a Human-Made CO₂ Increase

The preceding discussion has made clear that a consistent description of the carbon-cycle, which is in full agreement with all observations and physical relations, can only emanate from unitary treatment of all CO₂ molecules - native and human-caused ones. This means: the anthropogenic carbon cycle cannot be separated from the natural cycle; it exists only one single residence time of CO₂ molecules in the atmosphere; and the uptake of all these molecules obeys a first order principle.

But we still have to scrutinize how far this description is really in contradiction to the key arguments (lines of evidence) as adduced by the IPCC for a human caused CO₂ incline, or how far these arguments also hold for our alternative approach.

In AR5 [1], Subchap.6.3.2.3 we read:

"With a very high confidence, the increase in CO₂ emissions from fossil fuel burning and those arising from land use change are the dominant cause of the observed increase in atmospheric CO₂ concentration."

IPCC then lists five arguments to support this conclusion (references in the following IPCC-citations are not listed as additional references in this article).

5.7.1. Decrease in Atmospheric O₂

The observed decrease in atmospheric O₂ content over past two decades and the lower O₂ content in the northern compared to the SH are consistent with the burning of fossil fuels (see Figure 6.3 and Section 6.1.3.2; Keeling et al., 1996; Manning and Keeling, 2006)."

This is barely a supporting argument for a dominantly man-made CO₂ increase, since this 'line of evidence' is in the same way valid for our approach, which evidently includes the

same amount of anthropogenic emissions. Burning of fossil fuels removes oxygen from the atmosphere in a tightly defined stoichiometric ratio dependent on the fuel carbon content. This content is the same in our balance as in the IPCC models, therefore, the respective O₂ decay rate and on the other hand the CO₂ growth rate due to combustion is also the same, independent of any additional emissions of natural origin. The fundamental difference to the IPCC's assumption is that the anthropogenic emissions do not cumulate in the atmosphere for longer times or for ever. They have the same residence time as native CO₂, in average 4 yr or shorter, and therefore they only contribute 15% or even less to the observed increase since 1750.

In this context it should also be clear that CO₂ and O₂ behave just anti-cyclic in the photosynthesis and respiration cycle. Also the biochemical reactions in the atmosphere are completely different. CO₂ is a non-reacting gas in the atmosphere, while O₂ preferentially oxidizes other materials and is tied in chemical compounds. All these reactions are directly controlled by the temperature. Compared to the atmospheric oxygen content of about 21% a decrease of 80 ppm over 20 yr is relatively small, it is not more than 0.4‰. As long as this O₂ cycle is not better known, an observed decline in atmospheric oxygen gives only little evidence for a dominantly human caused CO₂ increase. At best it can confirm the CDIAC-data, which are the same in our approach as in the IPCC models.

5.7.2. Lower ¹³C/¹²C Isotope Ratio in Fossil Fuels

CO₂ from fossil fuels and from the land biosphere has a lower ¹³C/¹²C stable isotope ratio than the CO₂ in the atmosphere. This induces a decreasing temporal trend in the atmospheric ¹³C/¹²C ratio of atmospheric CO₂ concentration as well as, on annual average, slightly lower ¹³C/¹²C values in the NH (Figure 6.3). These signals are measured in the atmosphere."

Also this is no supporting argument for a dominantly man-made CO₂ increase, as with our approach we are also expecting such declining ¹³CO₂ concentration. The ¹³C/¹²C ratio in the atmosphere or its normalized ‰-difference ($\delta^{13}\text{C}_{\text{atm}}$) is measured at Mauna Loa and at the South Pole atmospheric station (see AR5 [1], Figure 6.3). At Mauna Loa, e.g., it shows an average decrease of 0.7‰ from -7.6‰ in 1980 to -8.3‰ in 2010. Over these 30 years was the anthropogenic emission rate increasing by 1.8 ppm/yr from 2.5 ppm/yr in 1980 to 4.3 ppm/yr in 2010 (CDIAC [4]). With respect to the total emission rate this corresponds to an increase of 1.8 %.

Owing to the equivalence principle fossil fuel emissions cannot cumulate in the atmosphere but will be absorbed with the same probability like naturally emitted CO₂ molecules. Thus, in first order the ¹³C/¹²C ratio in the atmosphere can only be diluted proportional to the leaner ¹³C concentration and proportional to the fraction of the man-made flux to the total flux. Smaller corrections will result from the fractionation for lighter molecules and a slightly higher emission probability for molecules, which were just taken up (re-emission, see next

item).

Since the fossil fuel emissions have a leaner difference $(\delta^{13}\text{C})_{\text{fuel-atm}} = -18\text{‰}$ compared to the atmosphere, or $(\delta^{13}\text{C})_{\text{fuel-VPDB}} = -25\text{‰}$ with respect to the international VPDB carbonate standard (Coplen [38]), the rising human emissions over the 30 yr interval can only have contributed to a decline of $\Delta = (\delta^{13}\text{C})_{\text{fuel-atm}} \times 1.8\% = -18\text{‰} \times 1.8\% = -0.32\text{‰}$ or a $(\delta^{13}\text{C})_{\text{atm}} = -7.92\text{‰}$ in 2010. Thus, the difference to -8.3‰ , which is more than 50%, in any case must be explained by other effects.

One possible explanation for a faster decline of $(\delta^{13}\text{C})_{\text{atm}}$ to -8.3‰ can be - even with oceans as source and an $^{13}\text{C}/^{12}\text{C}$ ratio in sea water greater than in air (particularly in the surface layer) - that the lighter $^{12}\text{CO}_2$ molecules are easier emitted at the ocean's surface than $^{13}\text{CO}_2$, this with the result of a leaner ^{13}C concentration in air and higher concentration in the upper water layer (see also: Siegenthaler & Munnich [39]). From water we also know that its isotopologues are evaporated with slightly different rates.

Such behavior is in agreement with the observation that with higher temperatures the total CO_2 concentration in the atmosphere increases, but the relative $^{13}\text{CO}_2$ concentration decreases. This can be observed, e.g., at El Niño events (see: M. L. Salby [40], Figure 1.14; Etheridge et al. [41]; Friedli et al. [42]).

We also remind at the Mauna Loa curve, which shows for the total emissions a seasonal variation with an increasing CO_2 concentration from about October till May and a decline from June to September. The increase is driven by respiration and decomposition mainly on the Northern Hemisphere (NH) as well as the temperature on the Southern Hemisphere (SH) and also local temperature effects. The $(\delta^{13}\text{C})_{\text{atm}}$ value is just anti-cyclic to the total CO_2 concentration (AR5 [1], Figure 6.3) with a minimum at maximum CO_2 concentration and with seasonal variations of 0.3 - 0.4‰, the same order of magnitude as the fossil fuel effect.

An increase of ^{13}C in the upper strata of oceans also results from an increased efficiency of photosynthesis for lighter CO_2 . Plankton accumulates this form and sinks to lower layers, where it decomposes and after longer times is emitted in higher concentrations with stronger upwelling waters particularly in the Eastern Tropic Pacific. It is also known that the ^{13}C concentrations are by far not equally distributed over the Earth's surface. Thus, it can be expected that with volcanic and tectonic activities different ratios will be released.

So, without any doubts fossil fuel emissions will slightly dilute the $^{13}\text{CO}_2$ concentration in air. But presupposing regular conditions for the uptake process (equivalence principle) they contribute less than 50% to the observed decrease. The difference has to be explained by additional biogeochemical processes. Particularly the seasonal cycles and events like El Niños are clear indications for a stronger temperature controlled modulation of the $(\delta^{13}\text{C})_{\text{atm}}$ value. Therefore is an observed decline of the $^{13}\text{C}/^{12}\text{C}$ ratio over recent years by far not a confirmation of an anthropogenic global warming (AGW) theory.

Also the widely spread but wrong declaration that "about

half of the emissions remained in the atmosphere since 1750" and "the removal of all the human-emitted CO_2 from the atmosphere by natural processes will take a few hundred thousand years (high confidence)" (see AR5 [1], Chap. 6-Summary and Box 6.1) can be simply refuted by the isotope measurements at Mauna Loa. If the 113 ppm CO_2 increase since 1750 (28.8% of the present concentration of 393 ppm - average between 2007 and 2016) would only result from human impacts and would have cumulated in the atmosphere, the actual $(\delta^{13}\text{C})_{\text{atm}}$ value should have dropped by $\Delta = (\delta^{13}\text{C})_{\text{fuel-atm}} \times 28.8\% = -18\text{‰} \times 28.8\% = -5.2\text{‰}$ to $(\delta^{13}\text{C})_{\text{atm}} \approx -7\text{‰} - 5.2\text{‰} = -12.2\text{‰}$, which by far is not observed. $(\delta^{13}\text{C})_{\text{atm}}$ in 1750 was assumed to have been -7‰ .

5.7.3. Fossil Fuels are Devoid of Radiocarbon

"Because fossil fuel CO_2 is devoid of radiocarbon (^{14}C), reconstructions of the $^{14}\text{C}/\text{C}$ isotopic ratio of atmospheric CO_2 from tree rings show a declining trend, as expected from the addition of fossil CO_2 (Stuiver and Quay, 1981; Levin et al., 2010). Yet nuclear weapon tests in the 1950s and 1960s have been offsetting that declining trend signal by adding ^{14}C to the atmosphere. Since this nuclear weapon induced ^{14}C pulse in the atmosphere has been fading, the $^{14}\text{C}/\text{C}$ isotopic ratio of atmospheric CO_2 is observed to resume its declining trend (Naegler and Levin, 2009; Graven et al., 2012)."

For ^{14}C we can adduce almost the same comments as listed for ^{13}C . Fossil CO_2 devoid of ^{14}C will reduce the $^{14}\text{C}/\text{C}$ ratio of the atmosphere, this is valid for our approach in the same manner as for the IPCC schemes. But, as no specific accumulation of anthropogenic molecules is possible (equivalence principle), this decline can only be expected proportional to the fraction of fossil fuel emission to total emission. Before 1960 this was not more than 1% and actually it is about 4.3%.

^{14}C is continuously formed in the upper atmosphere from ^{14}N through bombardment with cosmic neutrons, and then rapidly oxidizes to $^{14}\text{CO}_2$. In this form it is found in the atmosphere and enters plants and animals through photosynthesis and the food chain. The isotopic $^{14}\text{C}/\text{C}$ ratio in air is about $1.2 \cdot 10^{-12}$, and can be derived either from the radioactivity of ^{14}C , which with an average half-lifetime of 5730 yr decays back to ^{14}N by simultaneously emitting a beta particle, or by directly measuring the amount of ^{14}C in a sample by means of an accelerator mass spectrometer.

Fossil fuels older than several half-lives of radiocarbon are, thus, devoid of the ^{14}C isotope. This influence on radiocarbon measurements is known since the investigations of H. Suess [43] who observed a larger ^{14}C decrease (about 3.5%) for trees from industrial areas and a smaller decline for trees from unaffected areas. This so-called Suess or Industrial effect is important for reliable age assignments by the radiocarbon method and is necessary for respective corrections. But for global climate considerations it gives no new information, it only confirms the calculations based on the human to total emission rate (see above), and it clearly shows that an assumed accumulation of anthropogenic CO_2 in the

atmosphere contradicts observations.

More important for climate investigations is that after the stop of the nuclear bomb tests 1963 ¹⁴C could be used as a sensitive tracer in the biosphere and atmosphere to study temporal carbon mixing and exchange processes in the carbon cycle. As the bomb tests produced a huge amount of thermal neutrons and almost doubled the ¹⁴C activity in the atmosphere, with the end of these tests the temporal decline of the excess radiocarbon activity in the atmosphere can well be studied. This decline is almost completely independent of the radioactive lifetime, but practically only determined by the uptake through extraneous reservoirs.

Such decline has already been displayed in Figure 5 as fractionation-corrected ‰-deviations Δ¹⁴CO₂ from the Oxalic Acid activity corrected for decay, this for a combination of measurements at Vermunt and Schauinsland (Magenta Dots and Green Triangles; data from Levin et al. [17]). The decay is well represented by a single exponential with a decay constant of about 15 yr (Dashed Blue). For similar observations see also Hua et al. [18] and Turnbull et al. [19]. Thus, the decay satisfies the relation

$$\frac{dC'_{14}}{dt} = -\frac{1}{\tau_{14}} \cdot C'_{14}, \quad (31)$$

where C'_{14} represents the excess concentration of radiocarbon above a background concentration in the atmosphere. It corresponds to absorption that is proportional to instantaneous concentration with an apparent absorption time τ_{14} slightly more than a decade.

Because CO₂ is conserved in the atmosphere, it can change only through an imbalance of the surface fluxes e_T and a_T . This holds for all isotopologues of CO₂ in the same way. For this reason, its adjustment to equilibrium must proceed through those influences. They are the same influences that determine the removal time of CO₂ in the atmosphere. If CO₂ is perturbed impulsively (e.g., through a transient spike in emission), its subsequent decay must track the removal of perturbation CO₂, C' , which in turn is proportional to its instantaneous concentration. Determined by the resulting imbalance between e_T and a_T , that decay is governed by the perturbation form of the balance equation:

$$\frac{dC'}{dt} = -\frac{1}{\tau_R} \cdot C', \quad (32)$$

which is the same form as the observed decay of ¹⁴C following elimination of the perturbing nuclear source. But there is still one important difference between these equations.

Eq. (32) is the perturbation form of (23) with a decay time τ_R , the residence time, because $1/\tau_R$ describes the rate at which CO₂ is removed from the atmosphere, this as the result of the balance between all absorption and emission processes.

In contrast to this describes (31) a decay process, which implicitly also considers some back-pumping of radiocarbon to the atmosphere (see Appendix B, (37)). So, from all ¹⁴C that is removed from the atmosphere with the time constant τ_R - in the same way as all isotopes -, only some smaller fraction is

completely sequestered beneath the Earth's surface by a single absorption process. A substantial fraction is therefore returned to the atmosphere through re-emission (e.g., through decomposition of vegetation which has absorbed that ¹⁴C), and in average it takes several absorption cycles to completely remove that ¹⁴C from the atmosphere. This simply modifies the effective absorption for radiocarbon, but with a resulting decay which remains exponential (see Figure 5). Unlike any dilution effect by fossil fuel emission, which is minor (see Appendix B), this re-emission slows decay over what it would be in the presence of pure absorption alone. Therefore is the apparent absorption time - as derived from the ¹⁴C decay curve - longer than the actual absorption time.

In this context we emphasize that apart from some minor influence due to fractionation all CO₂ isotopologues are involved in the same multiple re-emission cycles. But in (23) or (32) this is already considered in the total balance via the emission rates, for which it makes no difference, if the same or meanwhile exchanged molecules are recycled to the atmosphere. In contrast to this are ¹⁴CO₂ isotopologues identified through their radioactivity, and in the worst case without any dilution or exchange processes in an external reservoir τ_{14} would approach the radioactive lifetime. On the other hand, at strong diffusion, dilution or sequestration of ¹⁴C in such reservoirs τ_{14} would converge to τ_R . Consequently it follows from the observed ¹⁴C decay shown in Figure 5 that this provides an upper bound on the actual absorption time τ_R , which can be only shorter. Both are tremendously shorter than the adjustment time requested by the IPCC.

The exponential decay of ¹⁴C with only one single decay time proves models with multiple relaxation times to be wrong. At the same time it gives strong evidence for a first order absorption process as considered in Section 4.²

5.7.4. Higher Fossil Fuel Emissions in the Northern Hemisphere

“Most of the fossil fuel CO₂ emissions take place in the industrialised countries north of the equator. Consistent with this, on annual average, atmospheric CO₂ measurement stations in the NH record increasingly higher CO₂ concentrations than stations in the SH, as witnessed by the observations from Mauna Loa, Hawaii, and the South Pole (see Figure 6.3). The annually averaged concentration difference between the two stations has increased in proportion of the estimated increasing difference in fossil fuel combustion emissions between the hemispheres (Figure 6.13; Keeling et al., 1989; Tans et al., 1989; Fan et al., 1999)”.

The strongest terrestrial emissions result from tropical forests, not industrial areas. The strongest oceanic emissions can be seen from the map of Takahashi et al. [32]. They are

² A calculation similar to Figure 8 but with a residence time of 15 yr as an upper bound would require to reduce the natural emissions at pre-industrial times from 93 ppm/yr to 19 ppm/yr. Then the anthropogenic contribution would supply 59 ppm, which is 15% of the total atmospheric concentration or 52% of the increase since 1850.

between 10°N and 10°S in the Eastern Tropic Pacific. Nevertheless, there is no doubt that industrial emissions endow their fingerprints in the atmosphere and biosphere (Suess effect). The influence and size of these emissions has already been discussed above, and their different impact on the two hemispheres can be estimated from Figure 6.3c of AR5 [1] indicating a slightly faster decline of $(\delta^{13}\text{C})_{\text{atm}}$ for the NH in agreement with predominantly located industrial emissions in this hemisphere. Even more distinctly this is illustrated by Figure 6.13 of AR5 [1] for the difference in the emission rates between the northern and SH with 8 PgC/yr, which can be observed as a concentration difference between the hemispheres of 3.8 ppm. But this is absolutely in no dissent to our result in Section 4 that from globally 4.7 ppm/yr FFE and LUC (average emission over 10 yr) 17 ppm or 4.3 % contribute to the actual CO₂ concentration of 393 ppm (average). This impact is of the same size as seasonal variations observed at Mauna Loa before flattening and averaging the measurements.

5.7.5. Human Caused Emissions Grew Exponentially

"The rate of CO₂ emissions from fossil fuel burning and land use change was almost exponential, and the rate of CO₂ increase in the atmosphere was also almost exponential and about half that of the emissions, consistent with a large body of evidence about changes of carbon inventory in each reservoir of the carbon cycle presented in this chapter".

The size and influence of FFE and LUC on the atmospheric CO₂ concentration has extensively been discussed in the preceding sections. Only when violating fundamental physical principles like the equivalence principle or denying basic causalities like a first order absorption process with only a single absorption time, the CO₂ increase can be reproduced with anthropogenic emissions alone.

In contrast to that we could demonstrate that conform with the rising temperature over the Industrial Era and in conformity with all physical legalities the overwhelming fraction of the observed CO₂ increase has to be explained by native impacts. Such simulations reproduce almost every detail of the observed atmospheric CO₂ increase (see Figures 8 and 10). And from observations of natural emissions it can be seen that they are increasing slightly exponential with temperature (Takahashi et al. [32]; Lee [34]).

Thus, no one of the preceding lines of evidence can really support the above statement that *"fossil fuel burning and land use change are the dominant cause of the observed increase in atmospheric CO₂ concentration."* In fact, they apply in the same way for our concept, and thus they are useless to disfavour our approach. The isotopic studies rather confirm our ansatz of a first order absorption process with a single absorption time, which is significantly shorter than one decade, and they refute the idea of cumulating anthropogenic emissions in the atmosphere.

6. Conclusion

The increase of CO₂ over recent years can well be explained

by a single balance equation, the Conservation Law (23), which considers the total atmospheric CO₂ cycle, consisting of temperature and thus time dependent natural emissions, the human activities and a temperature dependent uptake process, which scales proportional with the actual concentration. This uptake is characterized by a single time scale, the residence time of about 3 yr, which over the Industrial Era slightly increases with temperature. Only this concept is in complete conformity with all observations and natural causalities. It confirms previous investigations (Salby [7, 10]; Harde [6]) and shows the key deficits of some widespread but largely ad hoc carbon cycle models used to describe atmospheric CO₂, failures which are responsible for the fatal conclusion that the increase in atmospheric CO₂ over the past 270 years is principally anthropogenic.

For a conservative assessment we find from Figure 8 that the anthropogenic contribution to the observed CO₂ increase over the Industrial Era is significantly less than the natural influence. At equilibrium this contribution is given by the fraction of human to native impacts. As an average over the period 2007-2016 the anthropogenic emissions (FFE&LUC together) donated not more than 4.3% to the total concentration of 393 ppm, and their fraction to the atmospheric increase since 1750 of 113 ppm is not more than 17 ppm or 15%. With other evaluations of absorption, the contribution from anthropogenic emission is even smaller. Thus, not really anthropogenic emissions but mainly natural processes, in particular the temperature, have to be considered as the dominating impacts for the observed CO₂ increase over the last 270 yr and also over paleoclimate periods.

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Appendix

Appendix A

The absorption efficiency of extraneous reservoirs has been claimed to have decreased, based on changes in the arbitrarily-defined airborne fraction (e.g., Le Quére et al. [12]; Canadell et al. [44]). Such claims are dubious because they rely on the presumption that changes of CO₂ are exclusively of anthropogenic origin. Nor are the claims supported by recent atmospheric CO₂ data. Gloor et al. [45] found that decadal changes of AF followed from changes in the growth of anthropogenic emissions - not from changes in absorption efficiency, which were comparatively small. Further, uncertainties in emission and absorption exceeded any

changes in AF. Ballantyne et al. [46] arrived at a similar conclusion. They used global atmospheric CO₂ measurements and CO₂ emission inventories to evaluate changes in global CO₂ sources and sinks during the past 50 years. Their mass balance analysis indicates that net CO₂ uptake significantly increased, by about 0.18 Pg/yr (0.05 GtC/yr) and, between 1960 and 2010, that global uptake actually doubled, from 8.8 to 18.4 Pg/yr. It follows that, without quantitative knowledge of changes in natural emission, interpretations based on AF are little more than speculative.

The uptake and outgassing of atmospheric CO₂ by oceans is simulated with complex marine models. How much CO₂ enters or leaves the ocean surface is calculated from the difference between atmospheric and surface concentrations of CO₂, modified by the Revelle factor. However, most of these models involve assumptions which are not in agreement with observed behavior (see, e.g., Steele [47]). They assume that the surface layer absorbs CO₂ through equilibrium with atmospheric concentration. On this premise, they calculate how much Dissolved Inorganic Carbon (DIC) will be added to the ocean based on increased atmospheric CO₂ since pre-industrial times. In reality, the surface layer is not at equilibrium with the atmosphere. A difference in concentration results from conversion of CO₂ into organic carbon by photosynthesis. Organic carbon produced then sinks into the deep ocean, where it is sequestered. This downward transport to the deep ocean is known as the biological pump. In the Northeastern Atlantic basin, e.g., Benson et al. [33] report on seasonal pressure differences between the ocean and atmosphere of $\Delta pCO_2 = -70 \mu atm$ and an air-sea CO₂ flux of $220 g/m^2/yr$. Only in those regions where strong upwelling of DIC from the deep ocean exceeds sequestration of carbon via photosynthesis can CO₂ be outgassed to the atmosphere. The latter is found primarily in the tropical oceans (Takahashi et al. [32]; Zhang et al. [31]). Several models estimate that, without the biological pump, atmospheric CO₂ would be 200 to 300 ppm higher than current levels (see also Evans [48]).

With increasing primary production, carbon export to depth also grows. Arrigo et al. [49] reported that, since 1998, annual primary production in the Arctic has increased by 30%. Steinberg et al. [50] observed a 61% increase in meso-plankton between 1994 and 2006 in the Sargasso Sea. The North Atlantic coccolithophores have increased by 37% between 1990 and 2012 (Krumhardt et al. [51]). And Chavez et al. [52] found a dramatic increase in primary production in the Peru Current since the end of the Little Ice Age (LIA). Together, the increase in primary production and downward transport of organic carbon is sufficient to account for anthropogenic CO₂ that was absorbed from the atmosphere (Steele [47]).

Further, seasonal changes in surface CO₂ illustrate that absorption of CO₂ by the oceans and accumulation of DIC near the surface are determined, not by the Revelle factor, but by the biological pump. Evans et al. [48] found from buoy data off the coast of Newport, Oregon that each spring photosynthesis lowers ocean surface CO₂ to 200 ppm - far below current atmospheric concentrations and much lower than what would be expected from equilibrium with a pre-industrial

atmosphere. Anthropogenic CO₂ in surface water is then quickly removed. It is also well known that higher concentrations of CO₂ magnify photosynthesis. At increased atmospheric CO₂, the plankton community consumed 39% more DIC (Riebesell et al. [53]). During summer and autumn, surface CO₂ can rapidly increase to 1000 ppm - more than twice the concentration of CO₂ in the atmosphere. Surface water then significantly enhances natural emission to the atmosphere. Conversely, during winter, surface CO₂ remains at about 340 ppm. Despite reduced photosynthesis, CO₂ in surface water then remains below equilibrium with the atmosphere, reflecting efficient removal through downward transport by the biological pump. It is noteworthy that these strong seasonal variations of CO₂ in surface water are manifest in the record of atmospheric CO₂ (see Figures 9 and 10).

Under steady state conditions, diffusion of CO₂ into the ocean is believed to require about 1 year to equilibrate with an atmospheric perturbation. But, when increased sunlight enhances photosynthesis, such equilibration is no longer achieved. Perturbation CO₂ is then simply transported to depth, where it is sequestered from surface waters (McDonnell et al. [54]). Under such conditions uptake of CO₂ is not restricted by the Revelle factor but by the biological pump.

The foregoing processes are controlled essentially by sunlight and temperature. There is no reason to believe that net primary production, the biological pump, and sequestration of CO₂ below surface waters would be the same today as 270 years ago, when temperature and atmospheric CO₂ were likely lower.

In simulating transport of carbon in the ocean, complex models assume behavior that is found in tracers like chlorofluorocarbons (CFCs). Because those species accumulate near the ocean surface, models assume DIC does as well. But unlike CFCs, which are inert, CO₂ entering sunlit waters is quickly converted to organic matter by photosynthesis (Steele [47]). Although dissolved CFCs and dissolved carbon are passively transported in the same manner, particulate organic carbon (alive or dead) behaves very differently. It rapidly sinks, removing carbon from surface water through mechanisms which do not operate on CFCs.

The removal of carbon from surface water depends on the sinking velocity and also on how rapidly organic matter is decomposed. After descending below the pycnocline (depths of 500-1000 meters), carbon is effectively sequestered - because water at those depths does not return to the surface for centuries (Weber et al. [55]). For the atmosphere, this long-term sequestration translates into removal that is effectively permanent. Before such carbon can return to the atmosphere, fossil fuel reserves will have long since been exhausted.

The combination of sinking velocities and sequestration depth suggests that a significant fraction of primary production is sequestered in a matter of days to weeks (Steele [47]). Therefore, increasing primary production leads to a proportionate increase and rapid export of carbon to depth. If marine productivity has increased since pre-industrial times, it will

have also sequestered the respective anthropogenic carbon into the deeper ocean. Observations from ocean basins suggest that, since the Little Ice Age, marine productivity and carbon export have indeed increased as the oceans warmed (Chavez et al. [52]; Abrantes et al. [56]).

Appendix B

The bomb radiocarbon signal in the atmosphere is a sensitive tracer to study the fluxes in the carbon cycle, in particular to determine an upper bound for the residence time of CO₂ in the atmosphere and its uptake through extraneous reservoirs. Carbon 14 obeys the balance equation

$$\frac{dC_{14}}{dt} = e_{14} - \frac{C_{14}}{\tau_{14}} \tag{33}$$

with e_{14} as the emission rate, which follows from background emission of ¹⁴C as well as anthropogenic emission. The decay after the stop of the bomb tests in 1963 then satisfies the relation (see Subsection 5.7.3, (31))

$$\frac{dC'_{14}}{dt} = -\frac{1}{\tau_{14}} \cdot C'_{14}, \tag{34}$$

where C'_{14} represents the excess concentration of radiocarbon above background concentration in the atmosphere, and τ_{14} is the apparent absorption time of about 15 yr. Regularly not the absolute number of ¹⁴C but its ratio to ¹³C or ¹²C is measured, either as radioactivity or by accelerator mass spectrometry.

As the total CO₂ concentration is not constant over the observed decay period and this directly affects the relative ¹⁴C decay as well as the background level, the measured ¹⁴C activity has to be corrected for these variations to obtain the true C'_{14} concentration. Such corrections are important for age dating of materials and also for atmospheric ¹⁴C measurements. Without compensating for the varying total concentration, e.g., the ¹⁴C-decay and the background would be modified by several ten %.

Mostly the corrected data are specified as fractionation-corrected ‰-deviations from the Oxalic Acid standard activity corrected for decay (see Stuiver&Polach [57]):

$$\Delta^{14}C = \left[\frac{A_{SN}}{A_{ABS}} - 1 \right] \cdot 1000 \tag{35}$$

with A_{SN} as sampling activity normalized for isotope fractionation to ¹³C, and A_{ABS} as the absolute international standard activity (Oxalic Acid standard). A_{SN} relates to the measured sample activity A_S as

$$A_{SN} = A_S \left[1 - \frac{2(25 + \delta^{13}C)}{1000} \right], \tag{36}$$

where $\delta^{13}C$ is specified in ‰ with respect to the ¹³C VPDB standard.

This normalization procedure also accounts for fossil fuel emissions, which are devoid of ¹⁴C and also have a leaner ¹³C abundance. So, human emissions dilute the ¹⁴C/¹²C and

¹³C/¹²C ratio in the atmosphere. Such corrections are important for correct age assignments, but how much does this industrial effect and the observed dilution also affect the atmospheric ¹⁴C decay?

To answer this question we compare the original $\Delta^{14}CO_2$ data of Vermont and Schauinsland shown in Figure 5, with a hypothetical $\Delta^{14}CO_2$ -distribution, which is found for a fixed $\delta^{13}C$ -value over the full observation period, thus, assuming no further dilution. This requires first to recalculate the sampling activity A_S from (35) and (36) with the known $\delta^{13}C$ -record, e.g., from Mauna Loa (AR5 [1], Chap6, Figure 6.3c, missing data from 1964-1976 can be extrapolated from this record), and then to simulate the decay curve with new A_S activities, which are derived for a constant $\delta^{13}C(1964) = -7.4‰$.

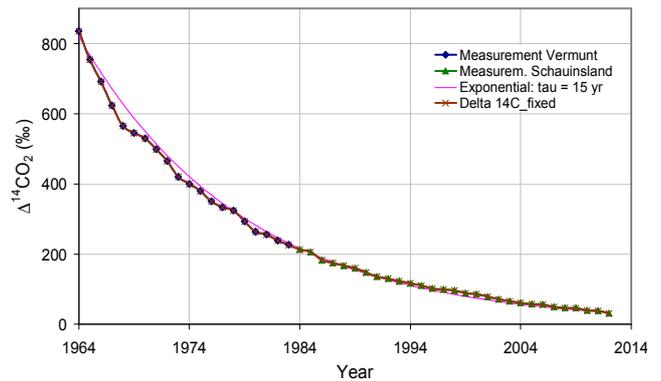


Figure 13. $\Delta^{14}CO_2$ -evolution for Vermont and Schauinsland (Magenta Dots and Green Triangles), compared with a recalculated decay neglecting dilution effects (Brown Crosses). Additionally shown is an exponential fit with an e-folding time of 15 yr (Magenta).

Figure 13 displays the normalized $\Delta^{14}CO_2$ -values of Vermont and Schauinsland (Blue Diamonds and Green Triangles; data from Levin et al. [17]) as reproduction of Figure 5 on a magnified scale.

It directly compares this with the hypothetical $\Delta^{14}CO_2$ decay curve (Brown Crosses). Deviations over the observed time period of 48 yr are smaller than 2‰ and the respective graphs completely coincide on this scale. They can well be approximated by a single exponential with a decay time of 15 yr (Magenta Line). Thus, any dilution effect of fossil fuel and natural emissions can well be neglected for the ¹⁴C-decay.

Far more influential is re-emission of ¹⁴C that was absorbed from the atmosphere. On the time scale of observed absorption, not all ¹⁴C is directly sequestered beneath the Earth's surface, but needs several cycles before being removed from the atmosphere. This can be described by a perturbation balance, which different to (33) now considers the regular absorption (characterized by the residence time τ_R) and takes account of an emission rate e'_{14} , now for re-emitted ¹⁴C from the upper Earth layer (e.g., through decomposition of vegetation which has absorbed that ¹⁴C), before it is sequestered or distributed:

$$\frac{dC'_{14}}{dt} = e'_{14} - \frac{C'_{14}}{\tau_R} \approx \left(\frac{C'_{14}}{\tau_R} - \frac{C'_{E,14}}{\tau_{14}} \right) - \frac{C'_{14}}{\tau_R} \approx -\frac{C'_{14}}{\tau_{14}} \tag{37}$$

Primed quantities are now referenced against unperturbed values before introduction of the nuclear source. From a balance for the Earth layer it follows that in good approximation e'_{14} opposes the atmospheric absorption rate C'_{14}/τ_R minus the sequestration rate $C'_{E,14}/\tau_{14}$, for which it is assumed that the concentration in the upper layer $C'_{E,14}$ is almost the same as the concentration C'_{14} in the atmosphere. Thus, re-emission simply modifies the effective absorption, which for ¹⁴C is controlled by the apparent absorption time τ_{14} and not the residence time τ_R in agreement with (34).

Unlike the dilution effect, which is minor, this slows decay over what it would be in the presence of absorption alone. The apparent absorption time is therefore *longer* than the actual absorption time, which must even be shorter than a decade. Integration of (37) or (34) exactly reproduces a pure exponential decay in Figure 13 with an e-folding time $\tau_{14} = 15 \text{ yr}$.

References

- [1] AR5, In: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M. (Eds.), "Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change", Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.
- [2] C. Le Quéré et al., "Global Carbon Budget 2017", Earth Syst. Sci. Data Discuss., <https://doi.org/10.5194/essd-2017-123>, Open Access Earth System Science Data Discussions, Manuscript under review for journal Earth Syst. Sci. Data, 2017.
- [3] CICERO, Center for International Climate Research, Oslo, R. Andrew: <http://folk.uio.no/roberan/GCP2017.shtml>. 2017.
- [4] CDIAC, 2017: Carbon Dioxide Information Analysis Center, http://cdiac.ornl.gov/trends/emis/glo_2014.html.
- [5] C. D. Keeling, S. C. Piper, R. B. Bacastow, M. Wahlen, T. P. Whorf, M. Heimann, H. A. Meijer, "Atmospheric CO₂ and ¹³CO₂ exchange with the terrestrial biosphere and oceans from 1978 to 2000: Observations and carbon cycle implications", In: Ehleringer, J. R., Cerling, T. E., Dearing, M. D. (Eds.), *A History of Atmospheric CO₂ and Its Effects on Plants, Animals, and Ecosystems*. Springer Science+Business Media, New York, NY, USA, and Heidelberg, Germany, pp. 83–113 (actualized by Scripps-Institutes, USA), 2005.
- [6] H. Harde, "Scrutinizing the carbon cycle and CO₂ residence time in the atmosphere", *Global and Planetary Change* 152, pp. 19–26, 2017. <http://dx.doi.org/10.1016/j.gloplacha.2017.02.009>.
- [7] M. L. Salby, "Atmospheric Carbon", Video Presentation, July 18, 2016. University College London. https://youtu.be/3q-M_uYkpT0.
- [8] P. Köhler, J. Hauck, C. Völker, D. A. Wolf-Gladrow, M. Butzin, J. B. Halpern, K. Rice, R. E. Zeebe, Comment on "Scrutinizing the carbon cycle and CO₂ residence time in the atmosphere" by H. Harde, *Global and Planetary Change* 164, pp. 67–71, 2017. <https://doi.org/10.1016/j.gloplacha.2017.09.015>
- [9] GISS, 2017: Goddard Institute for Space Studies: <https://data.giss.nasa.gov/gistemp/>.
- [10] M. L. Salby, "Relationship Between Greenhouse Gases and Global Temperature", Video Presentation, April 18, 2013. Helmut-Schmidt-University Hamburg https://www.youtube.com/watch?v=2ROw_cDKwc0.
- [11] M. L. Salby, "What is Really Behind the Increase of Atmospheric CO₂"? Helmut-Schmidt-University Hamburg, 10. October 2018, <https://youtu.be/rohF6K2avtY>
- [12] C. Le Quéré, M. R. Raupach, J. G. Canadell, G. Marland et al., "Trends in the sources and sinks of carbon dioxide", *Nature Geosci.*, 2, pp. 831–836, 2009. doi: 10.1038/ngeo689.
- [13] P. Tans, NOAA/ESRL and R. Keeling, Scripps Institution of Oceanography (scrippsco2.ucsd.edu), 2017. <https://www.esrl.noaa.gov/gmd/ccg/trends/data.html>.
- [14] F. Joos, M. Bruno, R. Fink, U. Siegenthaler, T. F. Stocker, C. Le Quéré, J. L. Sarmiento, "An efficient and accurate representation of complex oceanic and biospheric models of anthropogenic carbon uptake", *Tellus B* 48, pp. 397–417, 1996. doi: 10.1034/j.1600-0889.1996.t01-2-00006.x.
- [15] J. Hansen, M. Sato, P. Kharecha, G. Russell, D. W. Lea, M. Siddall, "Climate change and trace gases", *Phil. Trans. R. Soc. A* 365, pp. 1925–1954, 2007. doi: 10.1098/rsta.2007.2052.
- [16] J. Hansen, M. Sato, G. Russell, K. Pushker, "Climate sensitivity, sea level, and atmospheric CO₂", *Philos. Trans. R. Soc. A*, 371, 20120294, 2013. doi: 10.1098/rsta.2012.0294. <https://www.nasa.gov/>
- [17] I. Levin, B. Kromer, and S. Hammer, "Atmospheric $\Delta^{14}\text{CO}_2$ trend in Western European background air from 2000 to 2012", *Tellus B* 65, pp. 1–7, 2013.
- [18] Q. Hua, M. Barbetti, A. Z. Rakowski, "Atmospheric radiocarbon for the period 1950–2010". *RADIOCARBON* 55, pp. 2059–2072, (2013). Supplementary Material Table S2c, https://doi.org/10.2458/azu_js_rc.v55i2.16177
- [19] J. C. Turnbull, S. E. Mikaloff Fletcher, I. Ansell, G. W. Brailsford, R. C. Moss, M. W. Norris, K. Steinkamp, "Sixty years of radiocarbon dioxide measurements at Wellington, New Zealand: 1954–2014", *Atmos. Chem. Phys.* 17, pp. 14771–14784, 2017. <https://doi.org/10.5194/acp-17-14771-2017>.
- [20] U. Siegenthaler, J. L. Sarmiento, "Atmospheric carbon dioxide and the ocean", *Nature* 365, pp. 119–125, 1993.
- [21] P. Dietze, IPCC's Most Essential Model Errors, 2001. <http://www.john-daly.com/forcing/moderr.htm>; (Carbon Model Calculations, <http://www.john-daly.com/dietze/cmodcalc.htm>).
- [22] G. C. Cawley, "On the Atmospheric Residence Time of Anthropogenically Sourced Carbon Dioxide", *Energy Fuels* 25, pp. 5503–5513, 2011. dx.doi.org/10.1021/ef200914u
- [23] H.-J. Lüdecke, C. O. Weiss, "Simple Model for the Anthropogenically Forced CO₂ Cycle Tested on Measured Quantities", *JGEESI*, 8(4), pp. 1–12, 2016. DOI: 10.9734/JGEESI/2016/30532.
- [24] R. E. Essenhigh, "Potential dependence of global warming on the residence time (RT) in the atmosphere of anthropogenically sourced carbon dioxide", *Energy Fuel* 23, pp. 2773–2784, 2009. <http://pubs.acs.org/doi/abs/10.1021/ef800581r>.
- [25] E. Berry, "Human CO₂ has little effect on atmospheric CO₂", 2019. <https://edberry.com/blog/climate-physics/agw-hypothesis/contradictions-to-ipccs-climate-change-theory/>

- [26] NOAA, 2017: <https://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html>
<http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NCDC/.GHCN/.v2/?bbox=bb%3A-161.488%3A16.360%3A-150.062%3A23.051%3Abb>
- [27] NOAA, 2018: <http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NCDC/.ER SST/.version2/.SST/index.html>
<http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NCDC/.ER SST/.version2/.SST/X/%28164W%29VALUES/T/%28Jan%201938%29%28Dec%202009%29RANGEEDGES/Y/%2819N%29VALUES/datafiles.html>
- [28] O. Humlum, K. Stordahl, J. E. Solheim, "The phase relation between atmospheric carbon dioxide and global temperature", *Global and Planetary Change* 100, pp. 51-69, 2013.
- [29] M. Richardson, Comment on "The phase relation between atmospheric carbon dioxide and global temperature" by Humlum, Stordahl and Solheim, *Global and Planetary Change* 107, pp. 226-228, 2013.
- [30] D. L. Royer, R. A. Berner, I. P. Montañez, N. J. Tabor, D. J. Beerling, "CO₂ as a primary driver of Phanerozoic climate", *GSA Today* 14, no. 3, 2004.
doi: 10.1130/1052-5173(2004)014<4:CAAPDO>2.0.CO;2.
- [31] Y. G. Zhang, M. Pagani, J. Henderiks, H. Ren, "A long history of equatorial deep-water upwelling in the Pacific Ocean", *Earth and Planetary Science Letters* 467, pp. 1-9, 2017.
<http://dx.doi.org/10.1016/j.epsl.2017.03.016>.
- [32] T. Takahashi, S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely et al., "Climatological mean and decadal change in surface ocean pCO₂ and net sea-air CO₂ flux over the global oceans", *Deep-Sea Res. II*, 56, pp. 554-577, 2009.
doi:10.1016/j.dsr2.2008.12.009.
- [33] N. U. Benson, O. O. Osibanjo, F. E. Asuquo, W. U. Anake, "Observed trends of pCO₂ and air-sea CO₂ fluxes in the North Atlantic Ocean, *Intern. J. Marine Science* 4, pp. 1-7, 2014.
- [34] J.-S. Lee, "Monitoring soil respiration using an automatic operating chamber in a Gwangneung temperate deciduous forest", *J. Ecology & Field Biology* 34(4), pp. 411-423, 2011.
- [35] C. Huntingford, O. K. Atkin, A. Martinez-de la Torre, L. M. Mercado, M. A. Heskell, A. B. Harper, K. J. Bloomfield, O. S. O'Sullivan, P. B. Reich, K. R. Wythers, E. E. Butler, M. Chen, K. L. Griffin, P. Meir, M. G. Tjoelker, M. H. Turnbull, S. Sitch, A. Wiltshire, Y. Malhi, "Implications of improved representations of plant respiration in a changing climate", *NATURE COMMUNICATIONS* 8, 1602, 2017.
DOI: 10.1038/s41467-017-01774-z.
- [36] H. Harde, "Radiation Transfer Calculations and Assessment of Global Warming by CO₂", *International Journal of Atmospheric Sciences*, Volume 2017, Article ID 9251034, pp. 1-30, 2017. <https://doi.org/10.1155/2017/9251034>.
- [37] H. Harde, "Was tragen CO₂ und die Sonne zur globalen Erwärmung bei"? 12. Internationale EIKE Klima- und Energiekonferenz und 13th International Conference on Climate Change (ICCC-13), München, 23. u. 24. November, 2018, https://youtu.be/ldrG4mn_KCs.
- [38] T. B. Coplen, "Reporting of stable hydrogen, carbon and oxygen isotopic abundances", *Pure and Applied Chemistry* 66, pp. 273-276, 1994.
- [39] U. Siegenthaler, K. O. Münnich, "¹³C/¹²C fractionation during CO₂ transfer from air to sea", *In: Bolin, B. (Ed.): Carbon cycle modelling (SCOPE 16)*, John Wiley & Sons, pp. 249-257, 1981.
- [40] M. L. Salby, "Physics of the Atmosphere and Climate", Cambridge University Press, Cambridge 2012. (ISBN: 978-0-521- 76718-7).
- [41] D. M. Etheridge, L. P. Steele, R. L. Langenfelds, R. J. Francey, J.-M. Barnola, V. I. Morgan, "Natural and anthropogenic changes in atmospheric CO₂ over the last 1000 years from air in Antarctic ice and firm", *J. Geophys. Res.* 101, pp. 4115-4128, 1996.
- [42] Friedli H., H. Löttscher, H. Oeschger, U. Siegenthaler, B. Stauffer, 1986. Ice core record of the 13C/12C ratio of atmospheric CO₂ in the past two centuries, *Nature* 324, pp. 237-238.
- [43] H. Suess, "Radiocarbon Concentration in Modern Wood", *Science* 122, Issue 3166, pp. 415-417, 1955. DOI: 10.1126/science.122.3166.415-a
- [44] J. G. Canadell, Le Quéré, C., Raupach, M. R., Field, C. B., Buitenhuis, E. T., Ciais, P., Conway, T. J., Gillett, N. P., Houghton, R. A., and Marland G., "Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity, and efficiency of natural sinks", *P. Natl. Acad. USA*, 104(47), 18866-18870, 2007, doi:10.1073/pnas.0702737104.
- [45] M. Gloor, J. L. Sarmiento, and N. Gruber, "What can be learned about carbon cycle climate feedbacks from the CO₂ airborne fraction"? *Atmos. Chem. Phys.*, 10, pp. 7739-7751, 2010. <https://www.atmos-chem-phys.net/10/7739/2010/>, doi:10.5194/acp-10-7739-2010.
- [46] A. P. Ballantyne, C. B. Alden, J. B. Miller, P. P. Tans, J. W. C. White, "Increase in observed net carbon dioxide uptake by land and oceans during the past 50 years", *Nature* 488, pp. 70-73, 2012. doi:10.1038/nature11299
- [47] J. Steele, "How NOAA and Bad Modeling Invented an Ocean Acidification Icon", Part 2 – Bad Models, 2017. <https://wattsupwiththat.com/2017/03/02/how-noaa-and-bad-modeling-invented-an-ocean-acidification-icon-part-2-bad-models/>
- [48] W. Evans, B. Hales, P. G. Strat, "Seasonal cycle of surface ocean pCO₂ on the Oregon shelf", *J. Geophys. Research* 116, 2011, DOI: 10.1029/2010JC006625.
- [49] K. R. Arrigo, G. L. van Dijken, "Continued increases in Arctic Ocean primary production", *Progress in Oceanography* 136, pp. 60-70, 2015, <https://doi.org/10.1016/j.pocean.2015.05.002>.
- [50] D. K. Steinberg, M. W. Lomas, J. S. Cope, "Long-term increase in mesozooplankton biomass in the Sargasso Sea: Linkage to climate and implications for food web dynamics and biogeochemical cycling", *Global Biogeochemical Cycle* 26, 2012, DOI: 10.1029/2010GB004026.
- [51] K. M. Krumhardt, N. S. Lovenduski, N. M. Freeman, N. R. Bates, "Apparent increase in coccolithophore abundance in the subtropical North Atlantic from 1990 to 2014", *Biogeosciences* 13, pp. 1163-1177, 2016. doi:10.5194/bg-13-1163-2016, <http://www.biogeosciences.net/13/1163/2016/>.
- [52] F. P. Chavez, M. Messié, J. T. Pennington, "Marine Primary Production in Relation to Climate Variability and Change", *Annu. Rev. Mar. Sci.* 3, pp. 227-260, 2011, doi:10.1146/annurev.marine.010908.163917.

- [53] U. Riebesell, K. G. Schulz, R. G. J. Bellerby, M. Botros, P. Fritsche, M. Meyerhöfer, C. Neill, G. Nondal, A. Oeschies, J. Wohlers, E. Zöllner, "Enhanced biological carbon consumption in a high CO₂ ocean", *Nature* 450, pp. 545-548, 2007, doi:10.1038/nature06267.
- [54] A. M. P. McDonnell, K. O. Buesseler, "Variability in the average sinking velocity of marine particles", *Limnology and Oceanography* 55, pp. 2085–2096, 2010. DOI:10.4319/lo.2010.55.5.2085.
- [55] T. Weber, J. A. Cram, S. W. Leung, T. DeVries, C. Deutsch, "Deep ocean nutrients imply large latitudinal variation in particle transfer efficiency", *PNAS* 113 no. 31, pp. 8606–8611, 2016, doi: 10.1073/pnas.1604414113.
- [56] F. Abrantes, P. Cermenó, C. Lopes, O. Romero, L. Matos, J. Van Iperen, M. Rufino, V. Magalhães, "Diatoms Si uptake capacity drives carbon export in coastal upwelling systems", *Biogeosciences* 13, pp. 4099–4109, 2016, <https://doi.org/10.5194/bg-13-4099-2016>
- [57] M. Stuiver, H. A. Polach, "Discussion Reporting of ¹⁴C Data", *RADIOCARBON* 19, No. 3, pp. 355-363, 1977.