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Scrutinizing the Carbon Cycle and CO₂

Residence Time in the Atmosphere

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Climate scientists presume that the carbon cycle has come out of balance due to the increasing anthropogenic emissions from fossil fuel combustion and land use change. This is made responsible for the rapidly increasing atmospheric CO₂ concentrations over recent years, and it is estimated that the removal of the additional emissions from the atmosphere will take a few hundred thousand years. Since this goes along with an increasing greenhouse effect and a further global warming, a better understanding of the carbon cycle is of great importance for all future climate change predictions. We have critically scrutinized this cycle and present an alternative concept, for which the uptake of CO₂ by natural sinks scales proportional with the CO₂ concentration. In addition, we consider temperature dependent natural emission and absorption rates, by which the paleoclimatic CO₂ variations and the actual CO₂ growth rate can well be explained. The anthropogenic contribution to the actual CO₂ concentration is found to be 4.3%, its fraction to the CO₂ increase over the Industrial Era is 15% and the average residence time 4 years.

Key-words: Carbon cycle, atmospheric CO₂ concentration, CO₂ residence time, anthropogenic emissions, fossil fuel combustion, land use change, climate change

1. Introduction

The carbon cycle can be understood as a series of carbon reservoirs in the Earth-Atmosphere-System (EASy), which are connected to each other by exchange fluxes of carbon and its main bio-chemical compounds. For climate considerations especially atmospheric CO₂ as the main atmospheric phase of the global carbon cycle is of great importance due to its infrared active properties and its classification as the most dangerous greenhouse gas. Therefore, particularly the increase of CO₂ in the atmosphere, which climate scientists mainly trace back to growing anthropogenic emissions as well as a reduced uptake of CO₂ by oceans and land vegetation, are in the focus of many investigations.

In the 5th Assessment Report (AR5, 2013) of the Intergovernmental Panel on Climate Change (IPCC) we can read (AR5-Chap.12-FAQ 12.3, p. 1107): "Global temperature would not respond quickly to the greenhouse gas concentration changes... Eliminating CO₂ emissions only would lead to near constant temperature for many centuries (commitment from past emissions)... As a consequence of the large inertia in the climate and carbon cycle, the long-term global temperature is largely controlled by total CO₂ emissions that have accumulated over time, irrespective of the time when they were emitted."

So, the IPCC assumes that not only the Earth as a large heat storage but also the atmosphere as a big storage for CO₂, cumulating this greenhouse gas over many centuries, is responsible for a slow response of the global temperature. But obviously this response is assumed to work only in one direction. While the CO₂ increase of 100 ppm over the last century is made liable for a relatively fast increase of the temperature of about 0.8 °C over this period, eliminating further emissions are expected to lead to near constant temperatures for many centuries. The IPCC explains this with ‘extremely long
time scale processes involved into the removal of anthropogenic CO₂ emissions into the atmosphere, which makes the concept of a single, characteristic atmospheric lifetime not applicable to CO₂ (AR5-Chap.6-Box.6.1).

Because of the IPCC's interpretation of an extremely long atmospheric residence time together with a high climate sensitivity CO₂ is supposed to be the most dangerous component destabilizing our climate. Our own assessment of global warming by CO₂ (Harde, 2013; Harde, 2014; Harde, 2016) shows a less dramatic influence of CO₂ on the climate, yielding an equilibrium climate sensitivity (temperature increase at doubled CO₂) almost a factor of five smaller than published in AR5, and also a closer inspection of the residence time gives significantly different values than presented by the IPCC.

Therefore, it seemed worthwhile to scrutinize the carbon cycle and the different accounting schemes for the residence time with their individual assumptions in more detail and to identify the fundamental distinctions of these concepts. For a better comparison and deeper understanding we have tried to reproduce the IPCC's accounting scheme for the carbon cycle (see AR5-Chap.6) as far as possible, only supplemented by some own contemplations. This is presented in Section 2, while in Section 3 we contrast this to an alternative description, which is based on the balance equation and the empirical evidence that uptake rates scale proportional with the CO₂ concentration, in agreement with the observed exponential decay of ¹⁴C in the atmosphere. The balance equation is a fundamental law that must be obeyed by any legitimate model of CO₂. In addition, we consider temperature dependent natural emission and absorption rates, by which the paleoclimatic CO₂ variations and the actual CO₂ growth rate can well be explained. For these studies we have applied the IPCC's own estimates of natural absorption and emission, not because they are necessarily correct, but to demonstrate that, with those estimates, governing physical laws, lead to an explanation of increased CO₂ entirely different to the one advocated by the IPCC.

Previous critical analyses facing the IPCC's favored interpretation of the carbon cycle and residence time have been published, e.g., by Jaworowski et al. (1992), Segalstad (1998), Dietze (2001), Rösch et al. (2005) or Essenhigh (2009), and more recently by Humlum et al. (2013), or Salby (2013 and 2016). Although most of these analyses are based on different observations and methods, they all derive residence times (in some cases also differentiated between turnover and adjustment times) in part several orders of magnitude shorter than specified in AR5. As a consequence of these analyses also a much smaller anthropogenic influence on the climate than propagated by the IPCC can be expected.

2. IPCC Accounting Scheme

2.1 CO₂ Emission-Absorption-Balance

The total carbon emission rate is supposed to be between 200 and 220 GtC/yr, which corresponds to a CO₂ emission rate of \( E_T = 734 \cdot 807 \text{ Gt} / \text{yr} \) (transfer from C → CO₂ is a factor of 3.67). For our further considerations we calculate with a mean rate of \( E_T = 760 \text{ Gt} / \text{yr} = 760 \text{ Pg} / \text{yr} \). The IPCC estimates, that from this total rate a fraction \( E_A = 32.7 \text{ Pg} / \text{yr} \) (8.9 PgC/yr fossil fuels +1.1 PgC/yr net land use change) results from anthropogenic sources, while the rest with \( E_N = 727.3 \text{ Pg} / \text{yr} \) originates from natural sources (see Fig. 1). So, the anthropogenic part is just 4.3 % of the total emission rate.

Further the IPCC assumes, that from this anthropogenic portion a residual of 15 to 40 % remains longer than 1,000 years in the atmosphere (AR5-SPM, p.28; AR5-Chap.6-Box.6.1; AR5-Chap.12.5.3, p.1106; Hansen, 2007) and is not again reabsorbed like most of the naturally and anthropogenically generated CO₂. In Fig. 1 this residual is quantified as \( \Delta E_A = 14.7 \text{ Pg} / \text{yr} \) (4 PgC/yr), which is 1.9 % of the total emission rate. The respective emission-absorption balance, which determines the CO₂ concentration of the atmosphere, then may be expressed by a mass rate equation of the form:
\[ \frac{dM_{\text{CO}_2}}{dt} = \Delta E_A = E_T - A = (E_N + E_A) - (A_p + \Delta A) \]  

(1)

with \( dM_{\text{CO}_2} \) as the \( \text{CO}_2 \) mass change over the differential time interval \( dt \) (\( M_{\text{CO}_2} \) is the \( \text{CO}_2 \) mass in the atmosphere), and with \( A \) as an absorption rate, consisting of a constant uptake rate from pre-industrial times \( A_p \) and a smaller increase \( \Delta A \) of the absorption rate over the Industrial Era. In this accounting scheme the non-absorbed part \( \Delta E_A \) (actually 1.9 % of the total emission rate or 2 % of the total absorption rate) is made responsible to cumulate in the atmosphere and to cause the increasing \( \text{CO}_2 \) concentration since the Industrial Revolution. The ratio \( \Delta E_A/E_A \) is also known as airborne fraction. So, under the IPCC’s interpretation, before 1750 and in good approximation also before 1850 the rate between naturally produced and absorbed \( \text{CO}_2 \) is assumed to have been in balance, i.e. eq.(1) reduces for the pre-industrial time to

\[ \frac{dM_{\text{CO}_2}}{dt} = 0 = E_N - A_p \]  

(2)

with \( E_N = A_p \approx 727.3 \text{ Pg/yr} \), and for the Industrial Era, over which only the human influence is made responsible to have disturbed this balance, we get

\[ \frac{dM_{\text{CO}_2}}{dt} = \Delta E_A = E_A - \Delta A \]  

(3)

Eq. (3) is almost identical with the net balance for the anthropogenic emission and natural fluxes as specified in \( \text{AR5-Chap.6-Box-6.4} \) (p. 516, eqs (6.1) and (6.2)). Only, unfortunately, the absorption
changes $\Delta A$ over the Industrial Era are designated as "land_carbon_uptake + ocean_carbon_uptake", which can seriously be misinterpreted to represent the total absorption rate $A$ instead of the small changes actually of about $\Delta A = E_A - \Delta E_A = 32.7 - 14.7 \text{ Pg/yr} = 18 \text{ Pg/yr}$, representing only 2.4% of the total uptake rate.

For a compilation of the symbols and their size see Table 1.

Table 1: Compilation of used symbols and their size

<table>
<thead>
<tr>
<th>quantity</th>
<th>symbol</th>
<th>amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass of atmosphere</td>
<td>$M_{\text{air}}$</td>
<td>5,135 Eg</td>
</tr>
<tr>
<td>mol mass of air</td>
<td>$M_{\text{molair}}$</td>
<td>28.9 g/mol</td>
</tr>
<tr>
<td>mol number</td>
<td>$M_{\text{air}}/M_{\text{mol}}$</td>
<td>177.7 Emol</td>
</tr>
<tr>
<td>C in atmosphere - 1850</td>
<td>$M_C$</td>
<td>597 PgC</td>
</tr>
<tr>
<td>- 2012</td>
<td></td>
<td>830 PgC</td>
</tr>
<tr>
<td>CO$_2$ in atmosphere - 1850</td>
<td>$M_{\text{CO}_2}$</td>
<td>2,190 Pg</td>
</tr>
<tr>
<td>- 2012</td>
<td></td>
<td>3,050 Pg</td>
</tr>
<tr>
<td>mol mass of CO$_2$</td>
<td>$M_{\text{molCO}_2}$</td>
<td>44 g/mol</td>
</tr>
<tr>
<td>mol number</td>
<td>$M_{\text{CO}<em>2}/M</em>{\text{molCO}_2}$</td>
<td>69.3 Pmol</td>
</tr>
<tr>
<td>C emission rate - natural</td>
<td>$E_{\text{N}(C)}$</td>
<td>198.2 PgC/yr</td>
</tr>
<tr>
<td>- anthrop.</td>
<td>$E_{\text{A}(C)}$</td>
<td>8.9 PgC/yr</td>
</tr>
<tr>
<td>- total</td>
<td>$E_{\text{T}(C)}$</td>
<td>207.1 PgC/yr</td>
</tr>
<tr>
<td>CO$_2$ emission rate - natural</td>
<td>$E_{\text{N}}$</td>
<td>727.3 Pg/yr</td>
</tr>
<tr>
<td>- anthrop.</td>
<td>$E_{\text{A}}$</td>
<td>93.0 ppm/yr</td>
</tr>
<tr>
<td>- total</td>
<td>$E_{\text{T}}$</td>
<td>760.0 Pg/yr</td>
</tr>
<tr>
<td>CO$_2$ increase per year - anthr.</td>
<td>$\Delta E_{\text{A}(C)}$</td>
<td>4 PgC/yr</td>
</tr>
<tr>
<td>CO$_2$ absorption change - I.E.</td>
<td>$\Delta A$</td>
<td>18.0 Pg/yr</td>
</tr>
<tr>
<td>CO$_2$ growth rate 1850 - 2012</td>
<td>$\Delta e_{\text{A}} = \Delta C_{\text{CO}_2}/\Delta t$</td>
<td>0.68 ppm/yr</td>
</tr>
<tr>
<td>CO$_2$ concentration - 1850</td>
<td>$C_{\text{CO}_2}(1850)$</td>
<td>280 ppm</td>
</tr>
<tr>
<td>- 2012</td>
<td>$C_{\text{CO}_2}(2012)$</td>
<td>390 ppm</td>
</tr>
<tr>
<td>temperature coef.- resid. time</td>
<td>$\beta_t$</td>
<td>0.55 yr/$^o$C</td>
</tr>
<tr>
<td>- nat. emiss.</td>
<td>$\beta_e$</td>
<td>15.0 ppm/yr/$^o$C</td>
</tr>
<tr>
<td>CO$_2$ residence time</td>
<td>$\tau$</td>
<td>4.0 yr</td>
</tr>
</tbody>
</table>

In 1850 the mass of CO$_2$ in the atmosphere was about $M_{\text{CO}_2} = 2,190 \text{ Gt} = 2.19 \times 10^{15} \text{ kg} = 2,190 \text{ Pg}$, corresponding to a CO$_2$ concentration of

$$C_{\text{CO}_2} = \frac{M_{\text{CO}_2}}{M_{\text{air}}/M_{\text{mol}}(\text{air})} = \frac{(2,190 \text{ Pg})/(44 \text{ g/mol})}{(5,135 \text{ Eg})/(28.9 \text{ g/mol})} = 280 \text{ ppm},$$

where $M_{\text{air}}$ is the total air mass with $M_{\text{air}} = 5.135 \times 10^{15} \text{ kg} = 5,135 \text{ Eg}$ and $M_{\text{mol}}$ the mol mass of CO$_2$ resp.
of the air. The gain due to anthropogenic emissions then can be found by integrating eq.(1) or (3):

\[
\Delta M_{CO2} = \int_{1850}^{2012} \Delta E_A \, dt .
\]  

(5)

In 2012 \( M_{CO2} \) already increased up to \( M_{CO2} = 3,050 \) Pg, equivalent to a concentration of \( C_{CO2} = 390 \) ppm. Therefore, the average growth rate over this period was 0.68 ppm/yr, whereas the rate that would result from a non-absorbed portion of \( \Delta E_A = 14.7 \) Pg/yr (4 PgC/yr - see Fig.1) would be almost three times of this:

\[
\Delta e_A = \frac{\Delta C_{CO2}}{\Delta t} = \frac{\Delta E_A / M_{mol}(CO_2)}{M_{air} / M_{mol}(air)} = \frac{(14.7 \text{ Pg/yr})/(44 \text{ g/mol})}{(5,135 \text{ Eg})/(28.9 \text{ g/mol})} = 1.88 \text{ ppm/yr} .
\]  

(6)

### 2.2 CO₂ Residence Time in the Atmosphere

The rate equations in subsection 2.1 describing the CO₂ fluxes into and from the atmosphere go along with the principal question, how long CO₂ will stay in the atmosphere before it is re-absorbed, and how long it takes after some perturbation, till a new concentration equilibrium or the old concentration has adjusted. In this context the IPCC speaks about "Multiple Residence Times for an Excess of Carbon Dioxide Emitted in the Atmosphere", and in AR5-Chap.6-Box.6.1, p. 472, we can read: "On an average, CO₂ molecules are exchanged between the atmosphere and the Earth surface every few years. This fast CO₂ cycling through the atmosphere is coupled to a slower cycling of carbon through land vegetation, litter and soils and the upper ocean (decades to centuries); deeper soils and the deep sea (centuries to millennia); and geological reservoirs, such as deep-sea carbonate sediments and the upper mantle (up to millions of years) as explained in Section 6.1.1.1."

So, the idea is that due to the coupling of these cycles the cycle of CO₂ from the atmosphere is determined and limited by the slower processes. However, this will only be the case, when in the chain of these cycles all pre-connected faster responding reservoirs are already strongly saturated and have no further buffer capacity.

For the pre-industrial period, for which the system is assumed to be in quasi equilibrium, a quite reliable estimate of the average residence time or lifetime \( \tau_p \) can be derived from the simple relation, that under steady state (eq. (2)) the emission or absorption rate times the average residence time gives the total CO₂ amount in the atmosphere, equivalent to a pool with constant inflow and drain. So, with \( M_{CO2(1850)} = 2,190 \) Pg and \( A_p = E_N = 727.3 \) Pg/yr we find a residence time, also called turnover time, of:

\[
\tau_p = \frac{M_{CO2}}{A_p} = 3.0 \text{ yr} ,
\]  

(7)

where the slower carbon cycles through land vegetation up to the deep-sea sedimentation are also in equilibrium and are considered as small constant fluxes from one reservoir to another.

Over the Industrial Era the IPCC emanates from an excess of CO₂ emitted in the atmosphere as expressed by eq. (1) or (3). Nevertheless, more than 98 % of the total actual emission per year can be characterized by a residence time

\[
\tau_A = \frac{M_{CO2(2012)}}{A} = \frac{M_{CO2(2012)}}{E_T - \Delta E_A} = 4.1 \text{ yr} ,
\]  

(8)

which is larger than at pre-industrial times due to the meanwhile increased CO₂ level with \( M_{CO2(2012)} = 3,050 \) Pg, this despite the slightly larger absorption rate with \( A = E_T - \Delta E_A = 745.3 \) Pg/yr. The rate \( A \) already represents the sum of the different CO₂ absorption channels like plant photosynthesis with about 451 Pg/yr (123 PgC/yr) and ocean-atmosphere gas exchange with 294 Pg/yr (80 PgC/yr). These estimates of \( \tau_p \) and \( \tau_A \) rely upon the IPCC’s estimates of \( A \) during and even before the industrial era (see
For the remaining 1.9 %, which are not re-absorbed, the IPCC assumes that they cumulate in the atmosphere and "The removal of all the human-emitted CO₂ from the atmosphere by natural processes will take a few hundred thousand years (high confidence)" (see AR5-Chap.6-Executive-Summary and Box-6.1). Different to the turnover time this is often called the adjustment time.

So, obviously the IPCC presupposes, that not only the buffer capabilities of the faster but also the slower reservoirs through land vegetation, litter, soils and the upper ocean (decades to centuries) as well as those of the deeper soils and the deep sea (centuries to millennia) are already completely exhausted.

This interpretation is somewhat surprising, since over the last 160 years the absorption rate meanwhile increased from the pre-industrial rate \( A_e \) by the additional amount \( \Delta A = 18 \text{Pg/yr} \), which is an increase in the absorption of 2.4 %. When any further anthropogenic emissions could be switched off (i.e. \( E_A = 0 \)), a scenario always discussed by the IPCC in context with the adjustment of the atmosphere to pre-industrial times, from eq. (1) it follows for \( E_N = A_e \) that it would take not more than

\[
\tau_{\text{adjust}} = \frac{M_{\text{CO}_2}(2012) - M_{\text{CO}_2}(1850)}{\Delta A} = \frac{3,050 - 2,190 \text{Pg}}{18 \text{Pg/yr}} = 47.8 \text{ yr}
\]

9
to remove the additionally accumulated CO₂ from the atmosphere and, thus, to adjust to a new equilibrium. A similar value of 55 yr has been deduced by Dietze (2001) from his "waterbox-model". This adjustment time is at least more than three times faster than it took to build up this additional concentration. Even when the removal would slightly slow down with decreasing CO₂ concentration, this adjustment is orders of magnitude faster than assumed by the IPCC.

So, obviously the uptake rates by the oceans and plants, as compiled in Fig. 1, by no means are saturated, but just the opposite can be expected. On the one hand the exchange flux between the atmosphere and the ocean surface - driven by the partial CO₂ pressure difference between the air and the sea (see also Henry's law) - is even increasing; on the other hand also the plant growth and, thereby, autotrophic processes, converting atmospheric CO₂ together with water to higher organic molecules, are rising with a higher CO₂ concentration in the atmosphere (see also Keenan et al., 2016). As long as these fast uptake processes are not completely saturated, it cannot be expected that the slower carbon cycles determined by land vegetation or deep-sea sedimentation can significantly influence the CO₂ residence time.

A clear indication that the faster uptake processes still have enough absorption capabilities, is also the exponential removal of the \(^{14}\text{C}\) isotope from the atmosphere, which after the stop of the nuclear tests in 1963 disappears much faster than within one decade (see, e.g., Sundquist, 1985; Segalstad, 1998; Salby, 2016).

So in summary, the preceding accounting scheme brings up some general questions:

- Can it really be expected, that the pre-industrial absorption rate essentially was a constant and did not change with CO₂ concentration, humidity or temperature in the atmosphere over the whole Industrial Era or even larger periods of the Holocene?
- How could the Earth-Atmosphere-System respond to larger paleoclimatic CO₂ changes and still can react on actual natural variations, e.g., caused by volcanic activities, when the primary carbon reservoirs (ocean and land uptake) are coming so quickly to saturation?
- Why did the guessed absorption rate meanwhile increase by 2.5 % and is about 18 Pg/yr larger than 1850, although the absorption is assumed to be largely independent of concentration and temperature changes?
- How is this absorption change over the Industrial Era connected to anthropogenic emissions or is it even stimulated by these emissions?
- Why should not the absorption rate change by further 2.5 % or even more over the next hundred years and, therefore, at least partially compensate for additional emissions within the next years?
- How scientists know, that from an anthropogenic emission about half is removed within a few decades, but about 15 - 40 % of the CO₂ is still found in the atmosphere after 1,000 years (see AR5-Chap.12.5.3; Hansen et. al., 2007), when more than 98 % of the atmospheric CO₂ is exchanged within 4 years and due to eq.(9) the cumulating 2 % could also be absorbed within about 50 years?

3. Alternative Accounting Scheme

3.1 Balance Equation and CO₂ Residence Time

As already outlined in the preceding Section changes of CO₂ in the atmosphere on the one hand depend on the total emission rate \( E_T \) of CO₂ into the atmosphere and on the other hand on the re-absorption by plants or by the uptake in water. Since natural cycles like unsaturated absorption or decay processes are always characterized by an exponential relation (see, e.g., Lambert-Beer's law, scattering and decay processes), different to eq.(1) here we assume an absorption rate, which naturally scales with the actual CO₂ concentration. The more CO₂ molecules are available, the more they can be absorbed. Then we can express respective changes in the atmospheric CO₂ mass flux by a rate equation of the form:

\[
\frac{dM_{CO₂}}{dt} = E_T - \alpha \cdot M_{CO₂} = E_T - \frac{1}{\tau} M_{CO₂}
\]

where \( M_{CO₂} \) again represents the CO₂ mass in the atmosphere, \( \alpha = 1/\tau \) the absorption efficiency and \( \tau \) the average lifetime or residence time (decline to \( 1/e \)) of CO₂ in the atmosphere before it is re-absorbed. This approach is well justified by the observation of an exponential decay of \(^{14}\text{C}\) in the atmosphere (Essenhigh, 2009; Salby, 2016). It is also in qualitative agreement with the IPCC’s interpretation, that 60 - 85 % of the additional emissions can still be absorbed by the sinks, which at least since 1958 approximately followed the atmospheric rate of increase (see AR5-WG1-Chap.6-Executive-Summary). In the case of a fractional saturation of one of the reservoirs a delayed uptake of CO₂ is directly expressed by a smaller absorption efficiency, respectively a larger residence time and manifests itself in a larger CO₂ amount in the atmosphere. So, different to the IPCC’s approach, which uses one of the most speculative parameters, the adjustment time with values varying from 50 up to 100,000 years, in this concept such parameter has no longer any meaning but merges into a consistent residence time.

Eq.(10) can also be expressed for the CO₂ concentration \( C_{CO₂} \) as:

\[
\frac{dC_{CO₂}}{dt} = e_T - \alpha \cdot C_{CO₂} = (e_N + e_A) - \frac{1}{\tau} C_{CO₂}
\]

where \( C_{CO₂} = 390 \text{ ppm} \) corresponds to \( M_{CO₂} = 3,050 \text{ Pg} \), \( e_T = 97.2 \text{ ppm/yr} \) to \( E_T = 760 \text{ Pg/yr} \) and \( \Delta e_A = \Delta C_{CO₂} / \Delta t = 1.88 \text{ ppm/yr} \) to \( \Delta E_A = \Delta M_{CO₂} / \Delta t = 14.7 \text{ Pg/yr} \). Identical to the total emission rate for the mass fluxes also the rates for the concentration fluxes consist of 95.7 % natural emissions with \( e_N = 93 \text{ ppm/yr} \) and 4.3 % anthropogenic emissions with \( e_A = 4.2 \text{ ppm/yr} \).

Supposing the same natural emissions in 1850 like presently \( e_N = 93 \text{ ppm/yr} - \text{IPCC approach} \) and inserting a CO₂ concentration of \( C_{CO₂}(1850) = 280 \text{ ppm} \) in eq.(11), we find for pre-industrial times and under equilibrium conditions a residence time identical to eq.(7) of:

\[
\tau_p = \frac{C_{CO₂}(1850)}{e_N} = 3.0 \text{ yr}.
\]
whereas with an actual total emission rate \( e_T = 97.2 \text{ ppm/yr} \) and a concentration \( C_{CO2} = 390 \text{ ppm} \) we get a lifetime, representing the natural and anthropogenic absorptions, of:

\[
\tau_T = \frac{C_{CO2}(2012)}{e_T} = 4.0 \text{ yr}.
\]  

(13)

\( \tau_T \) is slightly shorter than derived from eq. (8), but would be the same for the non-equilibrium state, when inserting on the left side of eq.(11) \( dC_{CO2}/dt = \Delta e_n \).

A residence time of 4 yr is in close agreement with different other independent approaches for this quantity. So, investigations based on natural \(^{14}\text{C} \), on bomb \(^{14}\text{C} \), on the \(^{13}\text{C}/^{12}\text{C} \) mass balance, on \(^{222}\text{Ra} \), on the Suess Effect, or on solubility data on average give a value of about 5 yr (for a compilation of different methods see: Sundquist, 1985; Segalstad, 1998; for an analysis using the rate equation see also: Essenhigh, 2009).

Since all known uptake processes do not distinguish between naturally or anthropogenically emitted \( \text{CO}_2 \) molecules, both kinds in average can only survive 4 years in the atmosphere, before they are again absorbed. Also, when two or more different absorption processes with a fast absorption rate \( \alpha_F \) and slower rates \( \alpha_{S1}, \alpha_{S2}, \) etc. are present, the total rate \( \alpha \) as the sum of all is always larger than \( \alpha_F \) and the resulting residence time is always shorter than the shortest lifetime \( \tau_F \). So, as long as the faster absorption channels are not completely saturated and the total emission rate is not several orders of magnitude smaller than the numbers given in Fig. 1 (see also Riebeek, 2011), from this simple rate equation it already follows that a \( \text{CO}_2 \) lifetime of 1,000 years or more, seems completely impossible.

The general solution of eq.(11) is:

\[
C_{CO2}(t) = C_0 e^{-\tau/t} + (e_N + e_A) \cdot \tau \cdot (1 - e^{-\tau/t})
\]  

(14)

with \( C_0 \) as the initial concentration at a reference time \( t = 0 \).

From this equation it is also clear, that for a constant total emission rate \( e_T = e_N + e_A \) the \( \text{CO}_2 \) concentration should come to equilibrium within less than one decade. Then the natural emissions will contribute to a concentration of \( C_{CO2,N} = e_N \tau_T = 373 \text{ ppm} \) and the actual anthropogenic emissions deliver an additional fraction of \( C_{CO2,A} = e_A \tau_T = 17 \text{ ppm} \). Different to Section 2, as long as no significant saturation in the uptake rate can be observed, even over a period of 1,000 years a constant anthropogenic emission rate of \( e_A = 4.2 \text{ ppm/yr} \) could not further accumulate and increase the total concentration in the atmosphere.

### 3.2 Linear Temperature Dependence of Emission and Absorption

With this accounting method, however, it comes up the question, how the increasing concentration - actually 1.88 ppm/yr or over the last 160 years in average 0.7 ppm/yr - could climb up from 280 ppm to 390 ppm. When the anthropogenic emission rate of \( e_A = 4.2 \text{ ppm/yr} \) only contributes to a concentration increase over the Industrial Era of 17 ppm, the additional growth of 93 ppm obviously must result from declining natural absorptions and/or increasing natural emissions. With respect to eq.(14) this may be expressed by an increased residence time \( \tau \) and/or further native emissions \( e_n \) over this period.

Eq.(13) and almost equivalently eq.(8) already exclusively trace this increase of 93 ppm back to an ascending lifetime (for eq.(8) turnover time) of 1 yr over the Industrial Era, this in agreement with the IPCC’s assumption of a constant natural emission rate. But different to the IPCC, which assumes a rapidly saturating absorption, caused by the additional anthropogenic emissions, it appears much more plausible, that the increased lifetime finds its natural explanation in a temperature controlled uptake rate (see also Essenhigh, 2009). A saturating absorption, which more and more would become independent of the actual \( \text{CO}_2 \) concentration (different to eq. (11)), is in contradiction to the observed \(^{14}\text{C} \) decay and also the reported absorption increase, which follows the atmospheric emission rate (see AR5-WG1-
Chap.6-Executive-Summary).

Since the solubility of CO$_2$ in the oceans roughly scales inversely proportional with the temperature and also variations of the land sinks with temperature are expected (Keenan et al., 2016), as an approximation over some smaller interval we consider a linear dependence of the form:

$$\tau = \tau_0 + \beta_\tau \cdot (T_E - T_0) = \tau_0 + \beta_\tau \cdot \Delta T_E$$

(15)

with \(\tau_0\) as the lifetime at temperature \(T_0\) and \(\beta_\tau\) as the respective temperature coefficient. With \(\tau - \tau_0 = \tau_T - \tau_p = 1\) yr (see eqs (12) and (13)) and \(\Delta T_E = T_E(2012) - T_E(1850) = 0.9\) °C we deduce an average temperature dependence over the whole Industrial Era of \(\beta_\tau = 1.1\) yr/°C.

From paleoclimatic investigations (see, e.g.: Petit et al., 1999; Monnin et al., 2001; Caillon et al., 2003; Torn et al., 2006) and also from actual studies (Humllum et al., 2013; Salby, 2013; Salby, 2016) we know, that the natural emission rate - in agreement with typical biological and chemical processes - is also directly and indirectly controlled by the surface temperature \(T_E\). Therefore, considering additional changes in \(e_N\), which over smaller intervals are also assumed to scale proportional to variations in the temperature, with these impacts included, eq. (14) takes the form:

$$C_{CO_2}(t >> \tau, T_E, T_0) = (e_N(T_E) + e_A) \cdot \tau(T_E) = (e_{N0} + e_A + \beta_e \cdot \Delta T_E) \cdot (\tau_0 + \beta_\tau \cdot \Delta T_E).$$

(16)

with \(e_{N0}\) as the natural emission rate at \(T_0\) and \(\beta_e\) as the temperature coefficient of the emission rate. Due to the twofold temperature dependence the concentration increases quadratically with \(\Delta T_E = T_E - T_0\).

An obvious indication for the direct variation of the CO$_2$ emission and uptake rates is the time series of CO$_2$ at Mauna Loa since 1958 (see Fig. 2, Keeling et al., 2005; AR5-Chap.6-Fig.6.3, p. 476). Both, absorption and emission are varying over the seasons with the solar activity and, thus, with temperature and can be observed as a "sawtooth" curve. The CO$_2$ uptake by photosynthesis predominantly occurs during the growing season, whereas CO$_2$ release by heterotrophic processes is more dominant over the other seasons. The greater land mass in the Northern Hemisphere then imparts this characteristic sawtooth-cycle, which can be observed on top of the slowly increasing average concentration, caused by the dominating temperature dependent natural processes and the much smaller anthropogenic contributions.

![Fig. 2: Time series of the CO$_2$ concentration on Mauna Loa, Hawaii. Data downloaded from https://www.esrl.noaa.gov/gmd/ccgg/trends/data.html](https://www.esrl.noaa.gov/gmd/ccgg/trends/data.html)
With a temperature dependent native emission rate, i.e. $\beta_n > 0$, it is clear that eq.(16) can only be satisfied over the whole Industrial Era for a smaller rate $e_{n0}$ at pre-industrial times (the most uncertain parameter of the guessed IPCC rates) than present (93 ppm/yr) and for $\beta < 1.1$ yr/$^\circ$C. So, choosing $e_{n0} = 80$ ppm/yr and only half of the temperature sensitivity for $\tau$ with $\beta_t = 0.55$ yr/$^\circ$C, but an increased residence time at 1850 with $\tau_0 = 3.5$ yr ($e_{n0}$-$\tau_0$ then gives again $C_{CO2}(1850) = 280$ ppm), we deduce a temperature dependence for $e_n$ of $\beta_n = 15$ ppm/yr/$^\circ$C.

Of course, these parameters exactly reproduce the concentrations at 1850 and 2012. But also the measurements as well as the slightly nonlinear progression from 1960 - 2015, as represented by a smoothed Mauna Loa curve, can well be reconstructed by eq.(16). So, in 1960, e.g., with a temperature increase since 1850 of $\Delta T_E = 0.3$ °C and an anthropogenic emission rate of $e_A = 1.4$ ppm/yr (one third of the actual rate) we calculate a concentration of $C_{CO2}(1960) = 315$ ppm, or in 2000 with an increase $\Delta T_E = 0.74$ °C and $e_A = 3.0$ ppm/yr a concentration $C_{CO2}(2000) = 368$ ppm, both in full agreement with Fig. 2.

Nevertheless, it should be noticed, that as long as the natural and anthropogenic emission rates and at least one of the temperature coefficients are not more accurately known, we cannot really distinguish, what are the individual temperature induced contributions of the natural emission and the absorption. Only their product can quite well be determined with their quadratic influence on the CO$_2$ concentration. It can also be shown that this product has a close relation to similar studies of Salby (2012), p. 253.

Based on our considerations the actual contribution of anthropogenic emissions in the atmosphere with 17 ppm then causes not more than 15 % to the CO$_2$ increase of 110 ppm over the Industrial Era.

A detailed analysis of the sawtooth curve, and independently cross-correlation investigations of thermally induced emission, indicate that the actual absorption time may be significantly shorter than the absorption time of 4 years adopted from IPCC values, as short as only 8-9 months (for details see Salby, 2016). Again this indicates a non-saturated and even faster absorption than results from eq.(8) or (13) with the IPCC’s estimates of natural emission and absorption (Fig. 1). With an absorption time of only 8 months and an anthropogenic emission rate of $e_A = 4.2$ ppm/yr (IPCC value), the man-made fraction of CO$_2$ in the atmosphere would decline from 4.3% to 0.7%, which is not more than 2.8 ppm of the actual CO$_2$ concentration. With respect to the 110 ppm increase over the Industrial Era, the values would then give an anthropogenic fraction of only 2.5%.

### 3.3 Generalized Temperature Response of the CO$_2$ Concentration

Comparing the derived temperature response with paleoclimatic data over the last 400,000 years (Petit et al., 1999) or even over 800,000 years (Jouzel et al., 2007), we see that CO$_2$ variations of about 100 ppm between glacial and interglacial periods typically go along with temperature changes of about 8 °C, whereas our preceding estimates already gave a 110 ppm increase at a temperature boost of only 0.9 °C. So, on first glance some larger discrepancy and doubts are coming up that a temperature dependent emission and absorption rate could also explain the increasing CO$_2$ concentrations over ancient as well as over recent years.

Within smaller temperature intervals indeed we can assert, that the emission rate $e_n$ as well as the residence time $\tau$ can well be approximated to change linearly with the temperature, which together already contribute to a slightly quadratic increase. For larger intervals as they are observed from glacial up to present times, however, a stronger nonlinear response of the CO$_2$ concentration is expected. This can be seen when directly plotting the CO$_2$ concentration as a function of temperature (see Fig.3).

The total concentration $C_{CO2, T}$ as found from measurements is shown as red squares. Data derived from ice core proxies are indicated with estimated error bars, direct atmospheric measurements without bars due to the higher accuracy. Also the proxy data proceed quite smooth, but it should be noticed that their absolute values are by far not so accurately known as those from direct air samples because of distortion and diffusion errors with these proxies. So, in average ice core data show about 20-30 ppm
lower concentrations than derived, e.g., from fossil stomata analyses (see e.g. Wagner et al., 2004). In addition, they integrate over much longer time intervals than other techniques and, therefore, create the impression of predominantly stable CO₂ levels over longer eras. In contrast to this, studies of plant stomata, which can resolve quite well shorter climatic variations of one or a few centuries, show larger climate changes over the whole Holocene and at the same time indicate a close correlation between temperature and CO₂ (see, e.g., Wagner et al., 2002; Wagner et al., 2004; Kouwenberg et al., 2005; García-Amorena et al., 2008). Nevertheless, such ice core records allow an acceptable reconstruction of the general trend between temperature and CO₂ level, and this with the advantage to cover a period of almost one million years.

According to eq.(14) or (16) the natural contribution (blue triangles in Fig. 3) is derived by subtracting the temperature independent slightly increasing anthropogenic portion over the period 1850 - 2012.

For quasi equilibrium conditions (at times much larger than \( \tau \)) we can approximate the naturally generated fraction \( C_{\text{CO}_2,N} \) by an exponential of the form:

\[
C_{\text{CO}_2,N}(t \gg \tau, T_E) = e_N(T_E) \cdot \tau(T_E) = C_{\text{CO}_2,G} + \chi \cdot (e^{\gamma(T_G - T_E)} - 1). \tag{17}
\]

where \( C_{\text{CO}_2,G} \) and \( T_G \) are the concentration and temperature at glacial times. With \( C_{\text{CO}_2,G} = 200 \text{ ppm} \) and \( T_G = 8^\circ \text{C} \) (about 8 °C lower than present - see Petit et al., 1999) a fit based on eq.(17) with fit parameters \( \chi = 0.2 \text{ ppm} \) and \( \gamma = 0.845 \text{ °C}^{-1} \) shows excellent agreement (blue line) with the observations.

![Fig. 3: Total atmospheric CO₂ concentration \( C_{\text{CO}_2,T} \) (red squares) and natural fraction \( C_{\text{CO}_2,N} \) (blue triangles) with exponential fit (blue line) as a function of the Earth's temperature.](image)

This agreement illustrates that, for plausible temperature dependence, long term changes of CO₂ can be well accounted for by changes of natural emission and absorption. Since it is not clear if and how strong the paleoclimatic data are still superimposed by non-surface-temperature induced emissions like volcanic eruptions, it might be that \( C_{\text{CO}_2,G} \) still has to be corrected to lower values. Nevertheless, also with a significantly smaller glacial concentration, e.g., \( C_{\text{CO}_2,G} = 80 \text{ ppm} \), the observed data from 1850 to present can be well explained with the adopted temperature dependence of emission and absorption, only using modified parameters (\( \chi = 10.1 \text{ ppm}, \gamma = 0.424 \text{ °C}^{-1} \)).

In this context it should be noticed that our approach with eq.(17) again describes the product of two temperature dependent quantities but does not distinguish between their individual contributions.

So, all in all the temperature response of \( C_{\text{CO}_2,N} \) can be characterized by a soft, slow increase at lower
temperatures up to about 14 °C, while at higher temperatures, similar to a threshold process, it passes over to a steeper incline. On the one hand this may be explained by a further rising degassing of the oceans together with an activated vegetation and faster growing decomposition. All this contributes to increasing emissions of CO₂ and is even accelerated by a faster plant growth at higher CO₂ concentrations. On the other hand it can be forced by an increasing residence time with reduced solubility of CO₂ in oceans (T-dependence of Henry's law constant). Altogether this results in a nearly exponential increase with temperature.

Over smaller intervals eq.(17) can be approximated by the slope at temperature \( T_E \) with

\[
\Delta C^\text{eq}_{\text{CO2,N}} \bigg|_{T_E} = \chi \cdot \gamma \cdot e^{r(T_E-T_0)} \Delta T_E,
\]

and together with the anthropogenic contribution this reproduces the concentration changes over smaller intervals as observed between 1960 and 2000 (Mauna Loa curve) or the increase over the Industrial Era in good agreement with eq.(16).

The preceding considerations show, that the quantitative relation between CO₂ variations and the temperature can significantly differ between paleoclimatic and actual studies. However, both cases can be traced back to eq.(14), which is the direct consequence of mass conservation, and to the enlargement that the dependence of emission and absorption (in our description the natural emission rate and the residence time) both are assumed to vary with temperature. With this extension the steep increase of atmospheric CO₂ over recent years can well be explained in full agreement with all observations and natural causalities.

Our alternative accounting scheme does not need any postulate of saturated reservoirs (land and ocean sinks), which could not absorb more than 55 % of the anthropogenic emissions, while 45 % would be accumulated in the atmosphere and, therefore, should contribute to the fast increase (see AR5-WG1-Chap.6, p. 467). Different to the IPCC’s estimates our own considerations only show an anthropogenic contribution to CO₂ in the atmosphere of 17 ppm, i.e. 4.3 %, which causes a fraction of 15 % to the increase of 110 ppm over the Industrial Era. The other 85 % are explained due to the temperature dependence of the native emission rate and the residence time, the latter with an actual value of 4 years.

4. Conclusions

Climate scientists assume that a disturbed carbon cycle, which has come out of balance by the increasing anthropogenic emissions from fossil fuel combustion and land use change, is responsible for the rapidly increasing atmospheric CO₂ concentrations over recent years. While over the whole Holocene up to the entrance of the Industrial Era (1750) natural emissions by heterotrophic processes and fire were supposed to be in equilibrium with the uptake by photosynthesis and the net ocean-atmosphere gas exchange, with the onset of the Industrial Era the IPCC estimates that about 15 - 40 % of the additional emissions cannot further be absorbed by the natural sinks and are accumulating in the atmosphere. The IPCC further argues that CO₂ emitted until 2100 will remain in the atmosphere longer than 1000 years, and in the same context it is even mentioned that the removal of human-emitted CO₂ from the atmosphere by natural processes will take a few hundred thousand years (high confidence) (see AR5-Chap.6-Executive-Summary). Since the rising CO₂ concentrations go along with an increasing greenhouse effect and, thus, a further global warming, a better understanding of the carbon cycle is a necessary prerequisite for all future climate change predictions.

In their accounting schemes and models of the carbon cycle the IPCC uses many new and detailed data which are primarily focussing on fossil fuel emission, cement fabrication or net land use change (see AR5-WG1-Chap.6.3.2), but it largely neglects any changes of the natural emissions, which contribute to more than 95 % to the total emissions and by far cannot be assumed to be constant over longer periods (see, e.g.: variations over the last 800,000 years (Jouzel et al., 2007); the last glacial termination
Since our own estimates of the average $\text{CO}_2$ residence time in the atmosphere differ by several orders of magnitude from the announced IPCC values, and on the other hand actual investigations of Humlum et al. (2013) or Salby (2013, 2016) show a strong relation between the natural $\text{CO}_2$ emission rate and the surface temperature, this was motivation enough to scrutinize the IPCC accounting scheme in more detail and to contrast this to our own calculations.

Different to the IPCC we start with a rate equation for the emission and absorption processes, where the uptake is not assumed to be saturated but scales proportional with the actual $\text{CO}_2$ concentration in the atmosphere (see also Essenhigh, 2009; Salby, 2016). This is justified by the observation of an exponential decay of $^{14}$C. A fractional saturation, as assumed by the IPCC, can directly be expressed by a larger residence time of $\text{CO}_2$ in the atmosphere and makes a distinction between a turnover time and adjustment time needless.

Based on this approach and as solution of the rate equation we derive a concentration at steady state, which is only determined by the product of the total emission rate and the residence time. Under present conditions the natural emissions contribute 373 ppm and anthropogenic emissions 17 ppm to the total concentration of 390 ppm (2012). For the average residence time we only find 4 years.

The stronger increase of the concentration over the Industrial Era up to present times can be explained by introducing a temperature dependent natural emission rate as well as a temperature affected residence time. With this approach not only the exponential increase with the onset of the Industrial Era but also the concentrations at glacial and cooler interglacial times can well be reproduced in full agreement with all observations.

So, different to the IPCC's interpretation the steep increase of the concentration since 1850 finds its natural explanation in the self accelerating processes on the one hand by stronger degassing of the oceans as well as a faster plant growth and decomposition, on the other hand by an increasing residence time at reduced solubility of $\text{CO}_2$ in oceans. Together this results in a dominating temperature controlled natural gain, which contributes about 85 % to the 110 ppm $\text{CO}_2$ increase over the Industrial Era, whereas the actual anthropogenic emissions of 4.3 % only donate 15 %.

These results indicate that almost all of the observed change of $\text{CO}_2$ during the Industrial Era followed, not from anthropogenic emission, but from changes of natural emission. The results are consistent with the observed lag of $\text{CO}_2$ changes behind temperature changes (Humlum et al., 2013; Salby, 2013), a signature of cause and effect.

Our analysis of the carbon cycle, which exclusively uses data for the $\text{CO}_2$ concentrations and fluxes as published in AR5, shows that also a completely different interpretation of these data is possible, this in complete conformity with all observations and natural causalities.

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**References**


Salby, M., 2013. Relationship between Greenhouse Gases and Global Temperature, video presentation, April 18, 2013, Helmut-Schmidt-University Hamburg, https://www.youtube.com/watch?v=2ROw_cDKwc0


Graphical abstract
Scrutinizing the Carbon Cycle and CO₂ Residence Time in the Atmosphere

Highlights

- An alternative carbon cycle is presented in agreement with the carbon 14 decay.
- The CO₂ uptake rate scales proportional to the CO₂ concentration.
- Temperature dependent natural emission and absorption rates are considered.
- The average residence time of CO₂ in the atmosphere is found to be 4 years.
- Paleoclimatic CO₂ variations and the actual CO₂ growth rate are well reproduced.
- The anthropogenic fraction of CO₂ in the atmosphere is only 4.3%.
- Human emissions only contribute 15% to the CO₂ increase over the Industrial Era.