

Response to:

"Scrutinizing the carbon cycle and CO₂ residence time in the atmosphere" by Hermann Harde

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1. About the difference between residence time and relaxation time.

Many people don't see the distinction between residence time for a single molecule, whatever the source, and what the IPCC calls the "relaxation time", that is the time needed to remove any external extra mass of CO₂, whatever the source, injected into the atmosphere above the long term steady state of the carbon cycle.

Although Hermann Harde clearly knows the distinction between these two, in his final formula he implicitly used the residence time as a single reaction to any disturbance of the carbon cycles, while he should have used the relaxation time. That is a fundamental problem. I will try to illustrate that with a scheme, using the same fluxes from the IPCC as in the essay:

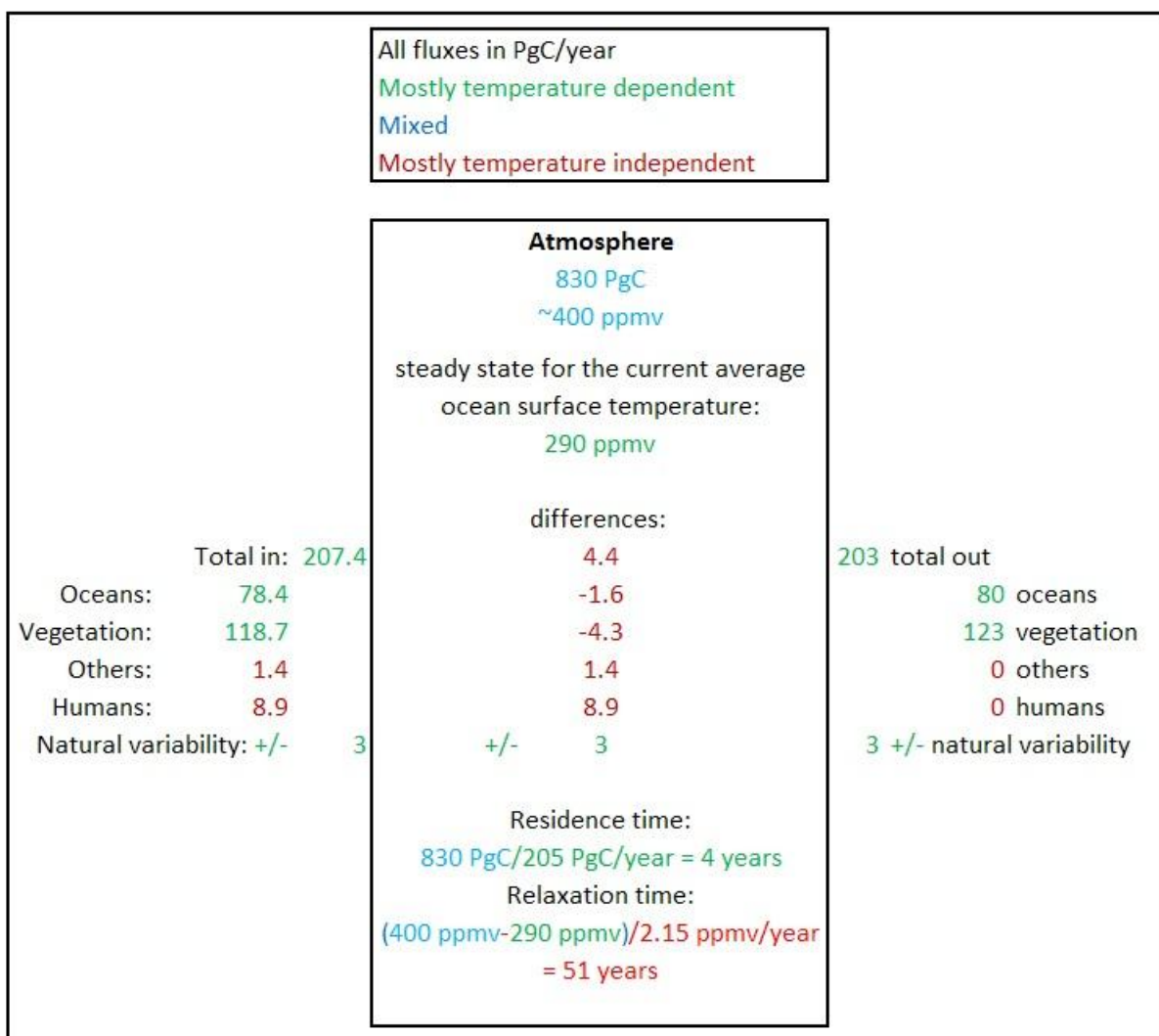


Figure 1. Amounts and fluxes from the IPCC graph [1], natural variability as is observed in the extremes.

Of all the used figures, only two are quite accurate: human emissions, based on fossil fuel sales (taxes!) and burning efficiency (+/- 0.5 PgC/year) and direct measurements of CO₂ in the atmosphere (+/- 0.4 PgC/year). Natural fluxes are rough estimates, based on local, seasonal and year by year changes in CO₂, O₂ and δ13C, which makes a separation between oceanic and biosphere CO₂ changes possible.

Because the human input and the increase in the atmosphere are known, the difference between these two is known and that is the net effect of what nature has done in any given year, whatever the natural fluxes in that year were.

The residence time is the total CO₂ mass in the atmosphere divided by the throughput of CO₂ in each year. That only influences the chance that an individual CO₂ molecule in the atmosphere is replaced by an individual CO₂ molecule from another reservoir. **That doesn't influence the total amount of CO₂ in the atmosphere**, but does influence the isotopic ratio, as other reservoirs have a different isotopic ratio than the atmosphere.

What does influence the total CO₂ mass in the atmosphere? The difference between the sum of all inputs and the sum of all outputs. That is much smaller than the throughput itself, but the only part of all in/out fluxes that influences the total quantity in any reservoir.

2. Temperature dependency.

Most natural fluxes are highly temperature dependent. That is the case for vegetation as well as for the ocean surface. With rough estimates:

Diurnal: +/- 60 PgC nightly plant/soil respiration and daily photosynthesis, these fast changes in general are only measurable locally over land in the first few hundred meters over the surface and not measurable after mixing into the bulk of the atmosphere.

Seasonal: +/- 60 PgC from vegetation growth in spring/summer and vegetation decay in fall/winter. +/- 40 PgC warming from ocean surfaces in summer, cooling in winter. As the changes are countercurrent, the net effect is that vegetation CO₂ changes dominate, which can be seen in the opposite changes of CO₂ and δ¹³C (mainly in the NH). If the changes were from the oceans, CO₂ and δ¹³C would parallel each other, as the δ¹³C levels of the ocean's surface are higher than in the current atmosphere (even including the water-air shift in δ¹³C level). Here for Mauna Loa and Barrow:

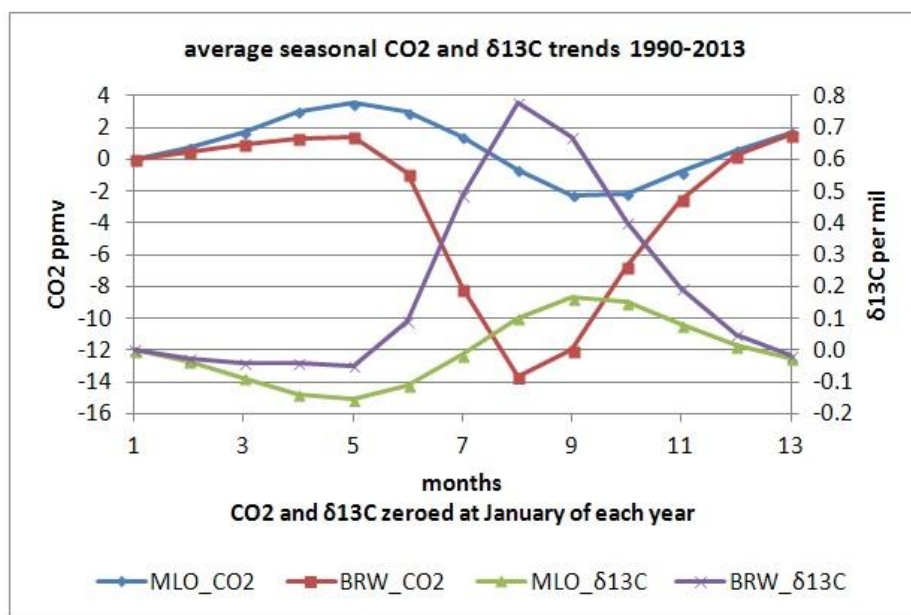


Figure 2. All monthly observations are from NOAA's Carbon tracker [2]

Global temperature influence ~5 ppmv/K with 2-3 months lag and NH and SH opposite to each other and a much smaller amplitude in the SH (more ocean, less vegetation).

Continuous: +/- 40 PgC/year between the upwelling zones near the equator and the sink zones near the poles. While there is some seasonal variation in it and a multiyear variation (El Niño), the average flux was calculated from the decay rate of the 14C level after the atomic bomb tests and the "thinning" of the δ¹³C "fingerprint" from the low-δ¹³C human emissions by the high-δ¹³C throughput from deep ocean waters.

Year by year variability: again mostly the influence of temperature on (this time tropical) vegetation. Largest influences +/- 3 PgC/year during huge events like the Pinatubo eruption and the 1998/2016 El Niño's. While the variability is huge, the effects last not more than 1-3 years:

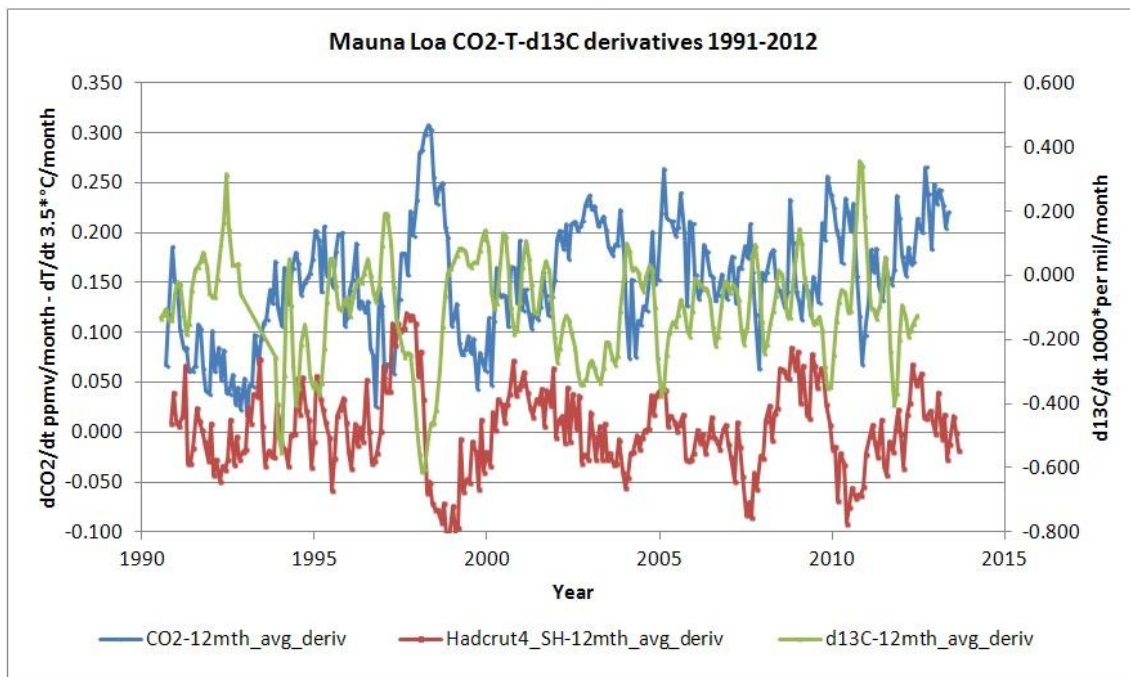


Figure 3. Variability in the 12-month moving average derivatives as taken from WFT [3], $\delta^{13}\text{C}$ from NOAA [2]

Again vegetation is the dominant cause as can be deduced from the opposite CO_2 and $\delta^{13}\text{C}$ changes. The CO_2 and $\delta^{13}\text{C}$ rates of change lag the temperature rate of change with several months. While the temperature rate of change has zero slope (only a small offset from zero), both the CO_2 rate of change (positive) and the $\delta^{13}\text{C}$ rate of change (negative) have a slope. Average variability is 4-5 ppmv/K with a lag of several months.

Temperature variability in vegetation surely is the main cause of the CO_2 and $\delta^{13}\text{C}$ variability in the derivatives (about 2/3) [4], but is not the cause of the long term increase in CO_2 or decrease of $\delta^{13}\text{C}$, as vegetation is a net absorber of CO_2 and preferably $^{12}\text{CO}_2$, thus leaving relative more $^{13}\text{CO}_2$ in the atmosphere [5].

Centuries to multi-millennia: mostly the influence of temperature on the (deep) oceans. Quite constant over the past 800,000 years with long lags: 800 +/- 600 years during the transition between a glacial and an interglacial period and several thousands of years during cooling after an interglacial. The long lags are explained by the very long distribution time between the atmosphere and the deep oceans. Average result ~16 ppmv/K.

3. Pressure dependency

Human emissions and a few natural emissions are temperature and pressure independent. For volcanoes the emissions are quite small, as measured during and after eruptions of mount Etna (~0.01 PgC/year [6]), one of the most active volcanoes in the world. Rock weathering is more substantial, but there is no reason to expect that it changed much (it depends on the water cycle) over the past 150 years, compared to the previous thousands of years.

Anyway, natural cycles, including one-way emissions like volcanoes and rock weathering simply followed Henry's law for the solubility of CO_2 in seawater over the past 800,000 years and there is no indication in any observation that they increased over the past 150 years, as human emissions did: a fourfold since 1959.

What does that imply for the removal of human emissions out of the atmosphere? In first instance not much will happen, with a relative stable long term seasonal temperature difference: nearly as much CO_2 is going in as out.

In the first years of human emissions, there was very little change in partial CO₂ pressure (pCO₂) in the atmosphere. As the release of CO₂ from the warm ocean upwelling and the withdrawal of CO₂ in the cold polar waters is directly proportional to the ΔpCO₂ between atmosphere and ocean surface, most did stay as mass in the atmosphere, as even with the current increase in atmospheric pCO₂ (~110 ppmv above steady state), not more than 2.15 ppmv/year is removed out of the atmosphere (factor ~0.02).

What remains in the atmosphere are not the original CO₂ molecules, as about 20% of all CO₂ each year is replaced by CO₂ from other reservoirs. Thus "human" CO₂ is fast redistributed from the atmosphere into other reservoirs (because of the short residence time), as can be followed by the δ¹³C "fingerprint".

If one looks at the current rates, humans emit around 9 PgC/year of CO₂. That increases the pCO₂ in the atmosphere with ~4.2 ppmv or ~4.2 μatm. The increase in pCO₂ meanwhile is 110 μatm above steady state, which is the dynamic equilibrium setpoint for the current (area weighted) average ocean surface temperature, that should be ~290 μatm. That is based on Henry's law for the solubility of CO₂ in seawater and confirmed by over 3 million seawater samples taken over the centuries.

The response of the net sink capacity is remarkably linear in ratio with the increased pressure in the atmosphere over the past decades with accurate measurements and good estimates of human emissions:

In 1959: 25 ppmv, 0.5 ppmv/year, 50 years, half life time 34.7 years

In 1988: 60 ppmv, 1.13 ppmv/year, 53 years, half life time 36.8 years

In 2012: 110 ppmv, 2.15 ppmv/year, 51.2 years or a half life time of 35.5 years.

That looks very linear, widely within the borders of accuracy of the emission inventories and natural sink capacity variability.

This all makes that the pressure related natural sink capacity is not capable of removing all human emissions (as mass, not as original molecules) in the same year as emitted and humans are the main cause of the CO₂ increase (and δ¹³C decline).

4. Problems in the essay in chapter 2.2.

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.

As showed before, one need to make a differentiation between temperature related processes and pressure related processes. The bulk of the fast exchanges is temperature related and these are hardly influenced by any extra CO₂ pressure in the atmosphere and get in fact "saturated" when the temperature changes again in opposite direction. That is the case for the seasonal changes: plant leaves growth and decay, warming and cooling ocean surface and largely the case for the permanent CO₂ flux between ocean upwelling near the equator and CO₂ uptake near the poles. Without huge changes in temperature (difference), these CO₂ fluxes and the net result doesn't change much over time.

Any extra pressure in the atmosphere above steady state only can be removed by pressure dependent processes. That is in average a lot smaller in mass transfer than for the temperature related processes.

Moreover, the fastest pressure dependent process is the exchange with the ocean surface: less than a year, but the ocean surface is quite fast saturated by a limiting factor: the Revelle/buffer factor at around ~10% of the change in the atmosphere [7].

The two remaining pressure related relaxation processes (deep oceans and vegetation) combined give the observed e-fold decay rate of ~51 years or a half life time of ~35 years.

the exponential removal of the ^{14}C isotope from the atmosphere, which after the stop of the nuclear tests in 1963 disappears much faster than within one decade

Unfortunately, the ^{14}C decline speed is much faster than for any extra bulk (near 99% as $^{12}\text{CO}_2$) decline speed. The problem is that what goes into the deep oceans is the momentary isotopic composition of the atmosphere (minus the air-water isotopic shift), also in 1960 at the height of the atomic bomb tests. What comes out of the oceans is the isotopic composition of ~ 1000 years ago (minus the water-air isotopic shift and the ^{14}C radiation decay over that time frame), thus from long before the bomb tests. Thus while in 1960 about 97.5% of $^{12}\text{CO}_2$ mass returned out of the oceans, only some 45% of $^{14}\text{CO}_2$ mass returned. Which leads to a much faster decay rate of an excess $^{14}\text{CO}_2$ than of an excess (bulk) $^{12}\text{CO}_2$ decay rate...

Here for the fluxes and reservoirs around 1960 (the diurnal CO_2 cycle of vegetation not included):

1960 distribution of CO_2 mass and $^{14}\text{CO}_2$ concentration

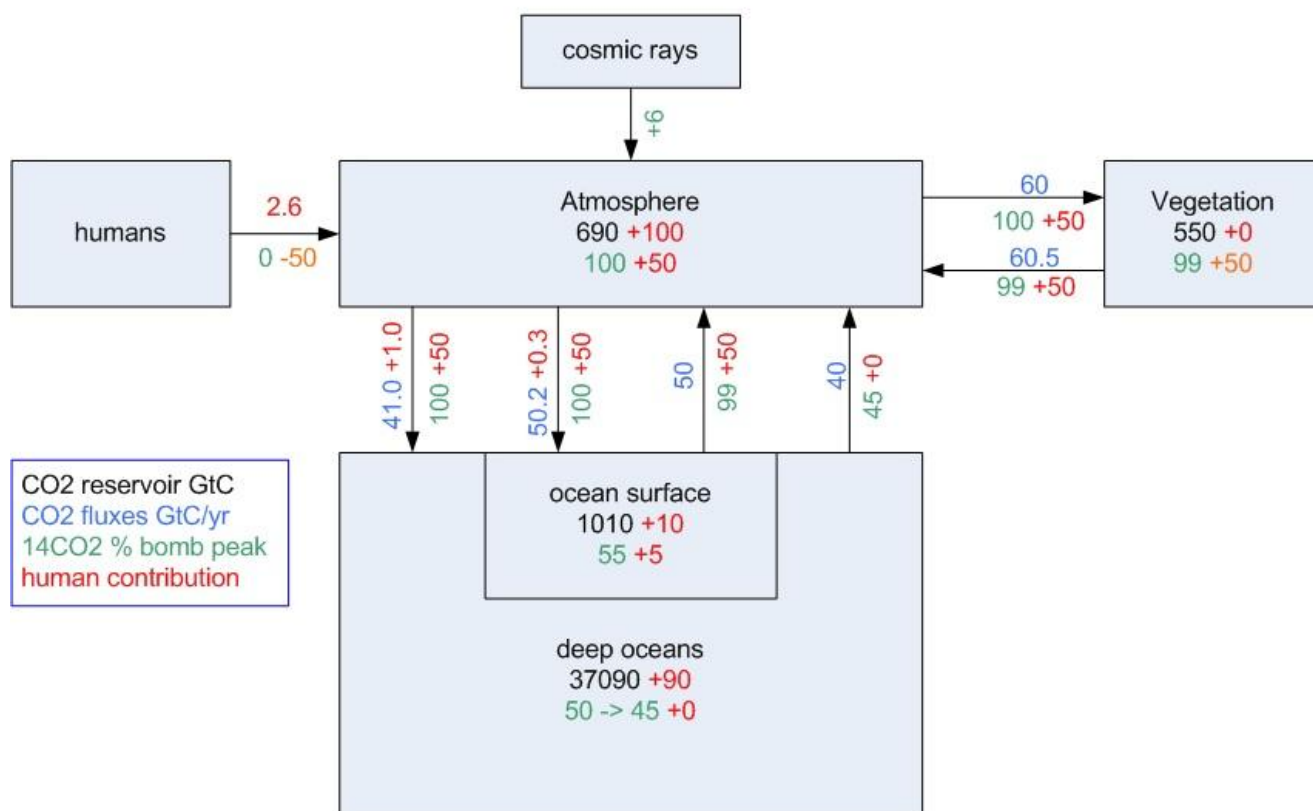


Figure 4. Rough estimates of bulk CO_2 reservoirs and fluxes and $^{14}\text{CO}_2$ percentages of the peak level in 1960 [8]

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?

As far as I know, the IPCC doesn't assume that the absorption rate is constant... If more plants grow thanks to higher temperatures, there will be certainly a larger seasonal amplitude and more pressure will certainly increase the net sink rate (as is observed). But the bulk of the temperature dependent CO_2 changes are quite constant over time...

How is this absorption change over the Industrial Era connected to anthropogenic emissions or is it even stimulated by these emissions?

Because the sink rate in oceans (and vegetation) is directly proportional to the extra pressure in the atmosphere above the steady state between ocean surface (temperature dependent at ~ 16 ppmv/K) and the atmosphere:

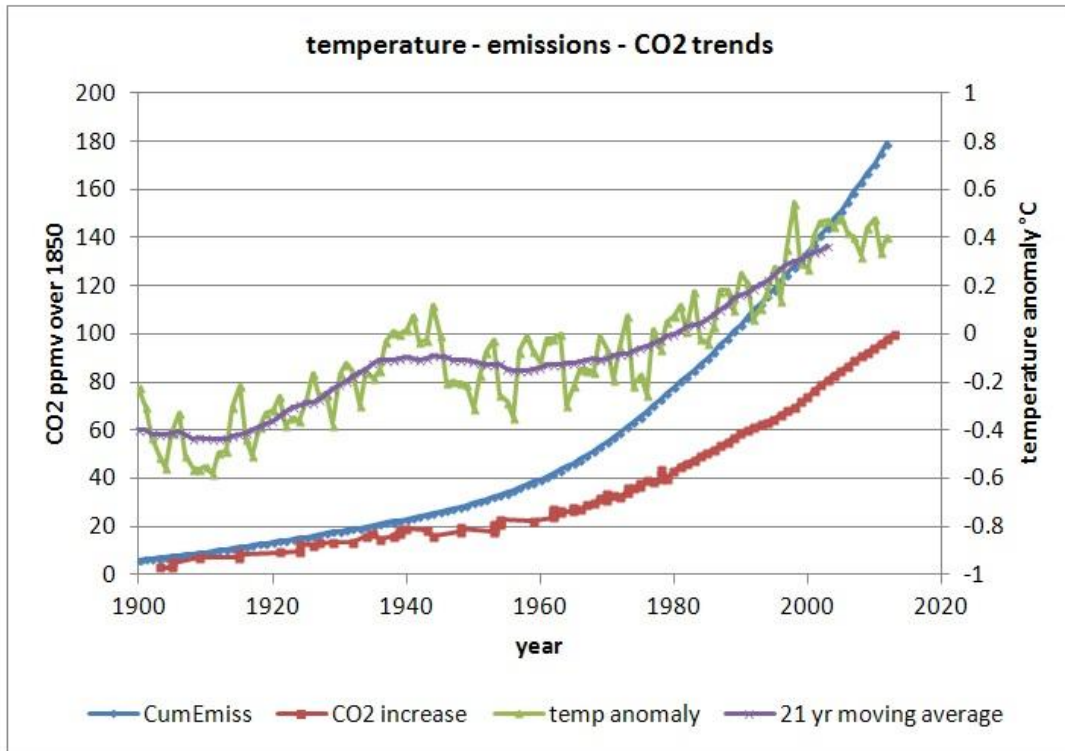


Figure 5. Total human emissions, increase in the atmosphere and temperature since 1900. From [3] and [10]

Or comparing total emissions with increase in the atmosphere (where the difference = accumulated net sink rate):

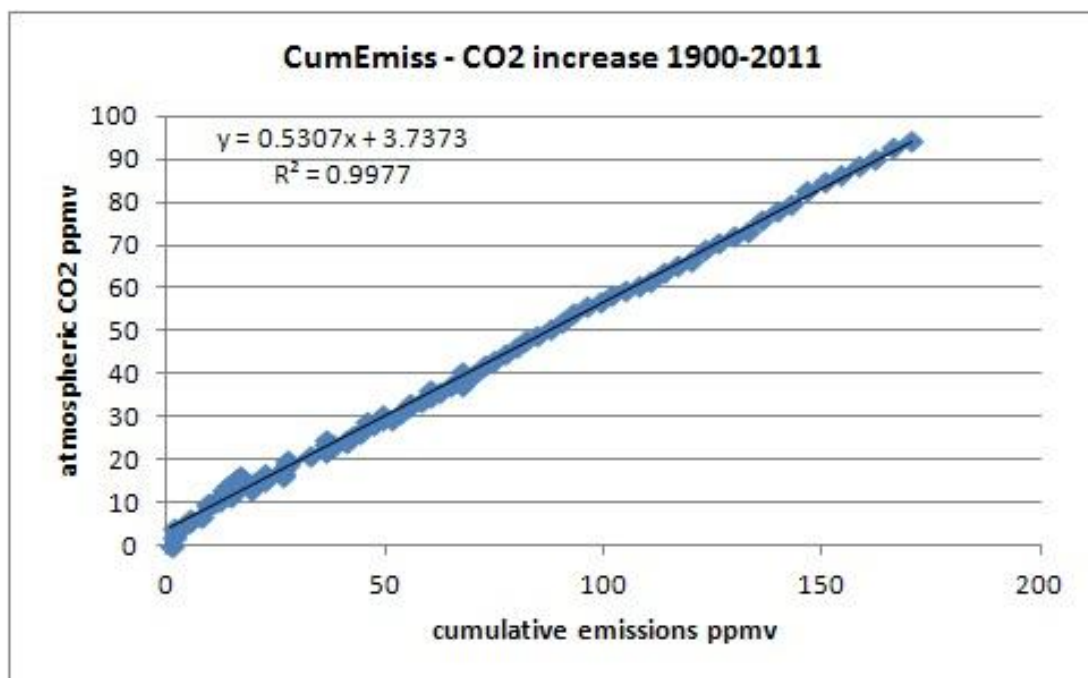


Figure 6. Total human emissions plotted against increase in the atmosphere. Data from [3] and [10]

Why should not the absorption rate change by further 2.5% or even more over the next hundred years

Good question... The IPCC follows the Bern model, which assumes a saturation of every compartment for CO₂ at a certain level. That is only true (and proven) for the ocean surface, not in the (far) foreseeable future for the deep oceans and certainly not true for vegetation...

Until now it is not possible to make a distinction between the multiple decay rates + limits of the Bern model and the single combined decay rate without limits, as both show similar decay curves...

5. Problems in the alternative accounting scheme

The more CO₂ molecules are available, the more they can be absorbed.

Seems rather in conflict with (more than) a few physical processes... Over at least the past 800,000 years, there was a dynamic equilibrium between the ocean surface and the atmosphere for CO₂ at ~16 ppmv/K: around 180 ppmv during glacial periods, around 300 ppmv during interglacials [9]. That is far from zero CO₂ as endpoint. Any deviation between the real CO₂ level in the atmosphere and the steady state is what drives more CO₂ into the atmosphere or reverse, not zero, or not even below 180 ppmv (as that means the end of all C3 plants).

Thus formula (10) is based on the decay rate for the total CO₂ in the atmosphere, while it should be only for the extra CO₂ above steady state...

It gets even worse in equation (11), as that violates the mass balance:

$$dCO_2/dt = (e_{(n)} + e_{(a)}) - 1/\tau * [CO_{2(atm)}] \quad (11)$$

At no moment in time $e_{(n)}$ is the sole contributor of natural CO₂ in the atmosphere, as oceans and vegetation fluxes are countercurrent with temperature and over the seasons, the biosphere wins the battle with less CO₂ in the atmosphere for higher temperatures, completely opposite to the long term trend. For near all months since 1958, the CO₂ levels in the atmosphere are negative for natural fluxes, which is the difference between $e_{(n)}$ and $s_{(n)}$, where $s_{(n)}$ is the sum of all natural sinks. Only during a few months in the strong El Niño's of the past, $e_{(n)}$ is larger than $s_{(n)}$. Using only the natural emissions in equation (11) without taking into account the natural sinks makes the whole formula invalid, as there is no observed increase in the atmosphere based on natural fluxes alone at all, only a decrease on seasonal (see Fig. 2) to decadal periods:

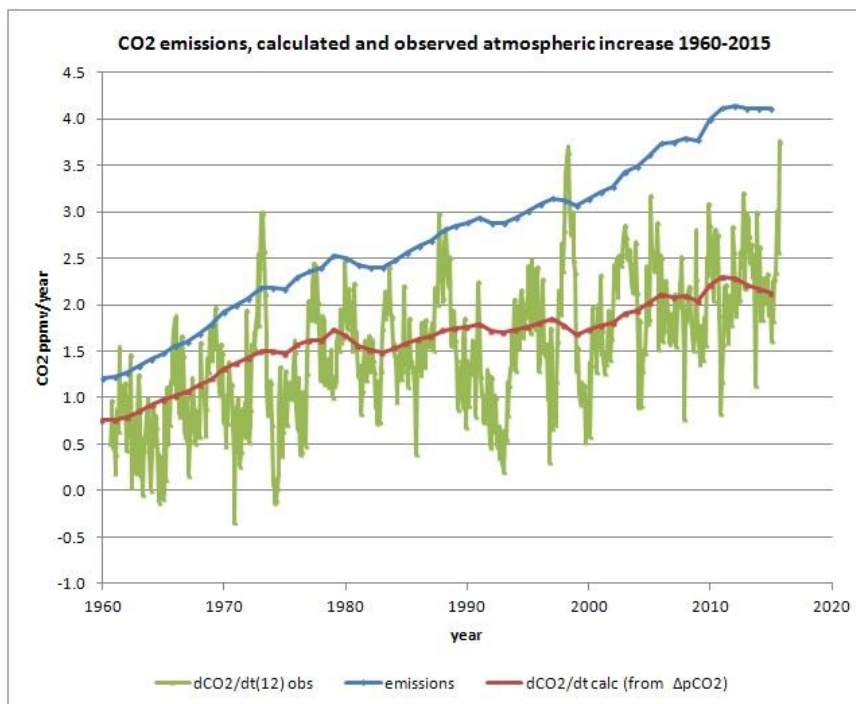


Figure 7. The difference between emissions rate of change and the observed rate of change is $e_{(n)} - s_{(n)}$. Data for observed dCO_2/dt , 12 month moving average, from [3]. Yearly emission data from [10].

The red line is the calculated trend taking into account the emissions and the net sink rate, based on the extra pressure in the atmosphere above steady state with the observed ~35 years half life time.

Further, formula (11) is a mix of temperature and pressure related processes, which are largely independent of each other, but are all lumped together: natural emissions have zero effect on the total mass in the atmosphere, as they are more than compensated by natural sinks, only the difference does, but that difference is almost always negative. Only if you increase (or decrease) $de pCO_2$ in the atmosphere above or below the steady state, there will be an extra uptake or release of CO₂.

Moreover, with the CO₂ concentration as base, one introduces the CO₂ pressure as driving force, while CO₂ pressure doesn't drive the large (seasonal) CO₂ cycles, which are all temperature dependent.

Because of that mix, the whole formula falls back to the residence time, which only moves lots of CO₂ in and out of the atmosphere but hardly changes the total amount of CO₂ in the atmosphere.

Just remove the term $e_{(a)}$ in formula (11) and see what happens: without human emissions there is an initial drop of over 2 ppmv/year reducing over time, but ultimately pulling remaining CO₂ down to zero ppmv in the atmosphere, which of course is impossible.

Formula (11) should be:

$$dCO_2/dt = e_{(a)} - [e_{(n)} - s_{(n)}] = e_{(a)} - 1/\tau^* [CO_{2(atm)} - CO_{2(eq)}] \quad (11)$$

Where $s_{(n)}$ are the natural sinks as only the difference (the net source/sink rate) plays a role in CO₂ absorption/release, not the absolute height of $e_{(n)}$ or $s_{(n)}$, even if these were 1,000 PgC/year each way... The real sink rate only depends of the pCO₂ difference between the observed CO₂ in the atmosphere and the equilibrium CO₂ level with the ocean surface. The latter depends of its temperature and moves with ~16 ppmv/K. τ is around 50 years over the past 57 years. The red line in Fig. 7 reflects the result of that formula.

That all makes that all conclusions and formulas (12-16) based on the short residence time have no value.

Further:

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 TE.

Initially that is true, but that doesn't last forever: after an initial increase of temperature there is an initial increase in natural emissions rate. For the deep oceans that increases the emissions at the equatorial upwelling zones and decreases the sink rates in the downwelling waters near the poles. That increases the pCO₂ in the atmosphere which reduces the initial pCO₂ difference between oceans and atmosphere, until at ~16 ppmv/K the original pCO₂ difference and thus the original CO₂ fluxes are restored. The new steady state only shifted with ~16 ppmv/K compared to the original steady state:

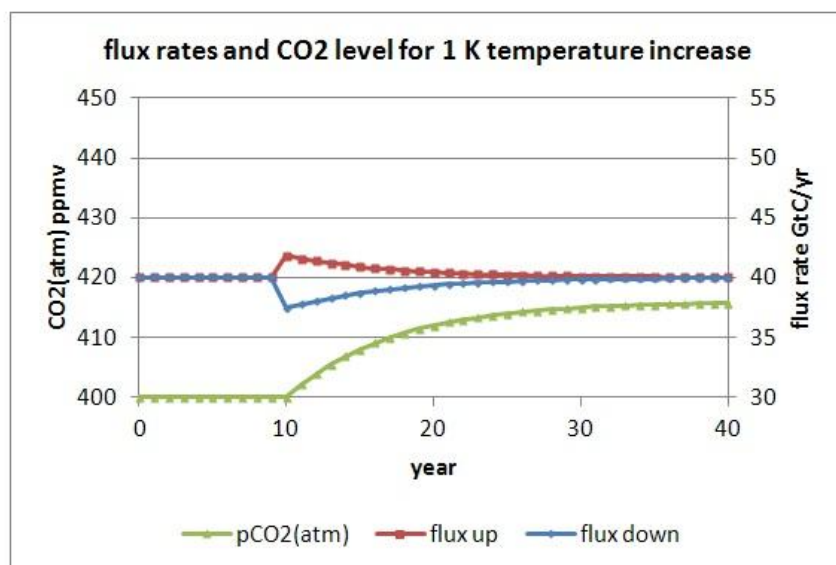


Figure 8. Reaction of CO₂ fluxes between ocean upwelling and atmosphere and back, and atmospheric CO₂ level for a sudden increase of 1 K in ocean surface temperature. Relaxation time arbitrarily.

For the ocean surface and vegetation, the main fluxes are seasonal, which show very little change over the decades for any increase in temperature:

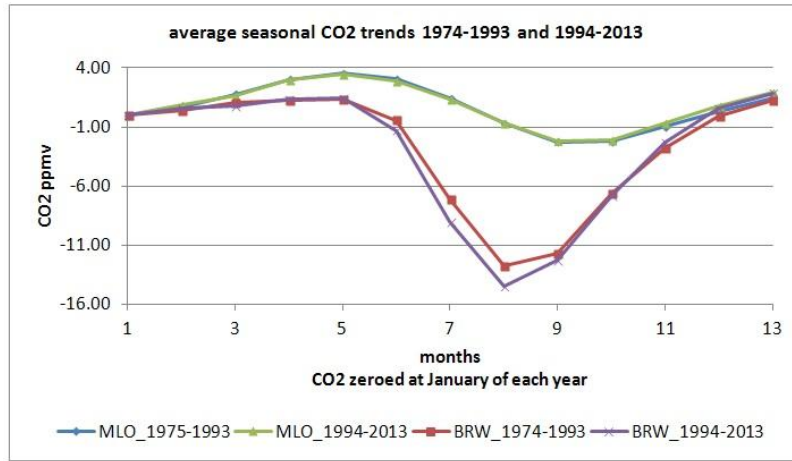


Figure 9. Changes in CO₂ amplitude over the seasons. The larger amplitude at Barrow may point to more local vegetation growth, but that is not measurable at NH (Mauna Loa) or global scale. Data from [2]

The only effect may be that more plants grow in colder areas and that influences the amplitude over the seasons, but not the residual CO₂ after a full seasonal cycle, which for plants is in fact negative: the earth is greening...[5]

The ocean surface reacts with a change of ~16 ppmv/K, thus for an increase of 0.7 K since 1958, that is a maximum of 11 ppmv, not the observed ~90 ppmv...

Neither the ocean surface, deep oceans or vegetation are the cause of most of the atmospheric increase.

Only one conclusion is left: any increase above ~16 ppmv/K is not natural.

So, in average ice core data show about 20–30 ppm lower concentrations than derived, e.g., from fossil stomata analyses

Stomata (index) data are proxies of CO₂ levels of plants growing on land, which has an inherent local CO₂ bias. They don't reflect "background" CO₂ data, but fluctuating local CO₂ levels as an average over the previous growing season. For that reason these are calibrated over the past century against ice core data and direct measurements. The main problem is that no one knows how the local bias changed over the centuries due to huge land (use) changes in the main wind direction, or even changes in the main wind direction itself (MWP to LIA and back).

Thus if there is a discrepancy in average CO₂ level between ice cores and stomata data over the period of resolution of ice core CO₂ data, one need to recalibrate the stomata data, not reverse.

The "error bars" around the ice core data don't reflect reality: multiple samples of the same ice core at the same depth show 1.2 ppmv variability (1 sigma). Different ice cores with extreme differences in temperature, accumulation rate and resolution show maximum 5 ppmv difference for the same average gas age:

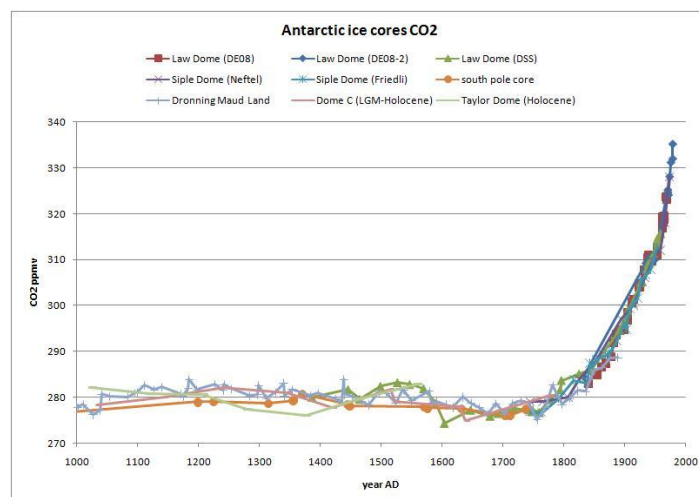


Figure 10. Ice cores CO₂ data from cores with extreme differences in temperature, accumulation rate and resolution.

There is even a 20 year overlap between ice core measurements at Law Dome and direct measurements at the South Pole:

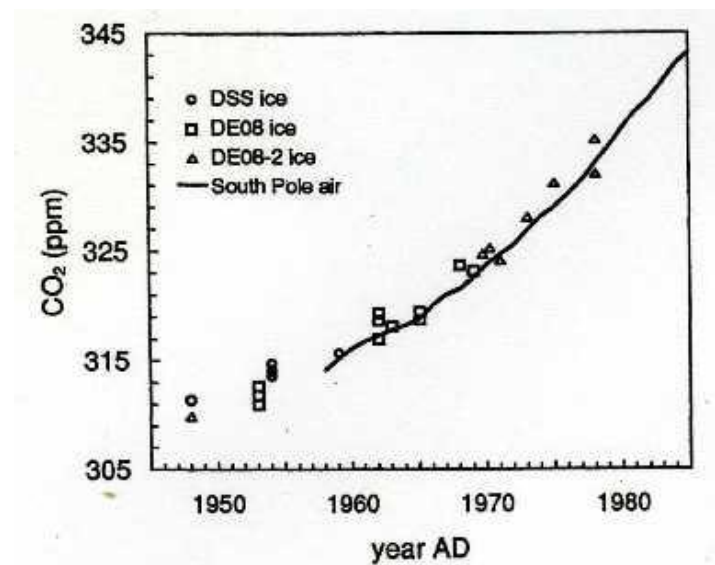


Figure 3. Comparison of CO₂ mixing ratios from the Law Dome DE08, DE08-2 and DSS ice cores and from the atmosphere at south pole. The ice core results have been corrected for average system enhancement and gravitational fractionation as described in the text. The south pole record is from the monthly means of Keeling [1991a], spline-smoothed to remove seasonality.

BTW, a change like the current 110 ppmv increase in 165 years would be visible in every ice core, even with the worst resolution, be it with a smaller peak.

Equations (17) and (18) look more like curve fitting than reflecting any physical process that can explain why the natural emissions would have increased with such a small change in temperature. The increase in human emissions was a fourfold since 1958, so did the increase in the atmosphere and the net sink rate. If the sinks react equally to any extra CO₂, no matter human or natural, then the total natural cycle should have increased a fourfold too. Or a decrease of a fourfold in residence time, while we see an increase...

Moreover, that theory doesn't fit the previous warm interval, the Eemian. Global temperatures were ~2 K warmer than today and in Alaska and Siberia even 5-10 K higher than today: trees were growing up to the Arctic Ocean on the North Slope. If there was an exponential dependency of CO₂ on a small temperature change, the CO₂ levels in the Eemian would have been much higher than today while they are much lower measured in ice cores (290 ppmv). Neither does it fit the first part of the Holocene, also with higher temperatures than today (the "Holocene Optimum") and other warm periods like the Roman times, the MWP,...

5. Conclusions

Dr. Harde makes three fundamental errors:

Using the residence time, or even the decay rate of the 14C bomb tests excess, doesn't say anything about the time needed to reduce an extra bulk CO₂ injection - whatever the source - above the temperature controlled steady state of the oceans with the atmosphere.

Using the total concentration of CO₂ in the atmosphere as base implies a steady state of zero CO₂ in the atmosphere, which is not realistic.

Using only natural emissions without taking into account the natural sinks violates the mass balance.

Besides that, the "temperature fits almost all" solution violates about every single observation in the atmosphere, oceans and vegetation, while the human cause fits them all. Like the mass balance, the decline of $\delta^{13}\text{C}$ level (in atmosphere, ocean surface and vegetation), the pre-1950 change in ^{14}C , the changes of pH and DIC in the ocean surface, the change in oxygen balance and last but not least Henry's law for the solubility of CO_2 in seawater [11].

References:

- [1] Amounts and fluxes from the graphic of AR5-Chap.6-Fig.6.1.
- [2] Carbon tracker of NOAA at <https://www.esrl.noaa.gov/gmd/dv/iadv/>
- [3] Wood for Trees different temperature and Mauna Loa CO_2 series at:
<http://www.woodfortrees.org/plot/>
- [4] Address of Pieter Tans at the 50th anniversary of Mauna Loa, from slide 11 on:
<https://esrl.noaa.gov/gmd/co2conference/pdfs/tans.pdf>
- [5] Global Carbon Sinks and Their Variability Inferred from Atmospheric O_2 and $\delta^{13}\text{C}$:
<http://science.sciencemag.org/content/287/5462/2467>
- [6] Eruptive and diffuse emissions of CO_2 from Mount Etna:
<http://www.nature.com/nature/journal/v351/n6325/abs/351387a0.html>
- [7] Compare the increase in DIC (total inorganic carbon) in the ocean surface of Bermuda with the increase of CO_2 in the atmosphere over the same period (1983-2012). See Fig. 5 in:
<http://www.biogeosciences.net/9/2509/2012/bg-9-2509-2012.pdf>
- [8] ^{14}C distribution in atmosphere and oceans in:
http://shadow.eas.gatech.edu/~kcobb/isochem/lectures/lecture10_14C.ppt
- [9] Data from ice cores temperature proxies, CO_2 levels and other gas/ice data at:
<https://www.ncdc.noaa.gov/paleo-search/>
- [10] Emissions data for fossil fuel combustion and cement production without land use changes:
Up to 2008: http://cdiac.ornl.gov/trends/emis/tre_glob.html
From 2009 on: <http://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm?tid=90&pid=44&aid=8>
- [11] For a comprehensive overview see:
http://www.ferdinand-engelbeen.be/klimaat/co2_origin.html