

On the CO₂ residence time and other confusions...

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The CO₂ residence time confusion...

Naturalists:

Realists:

Alarmists:

~4 years

~50 years

>>100 years

(“turnover time”)

(“adjustment time”)

(“lifetime”)

Molecule based

Mass based

Model based

Overview

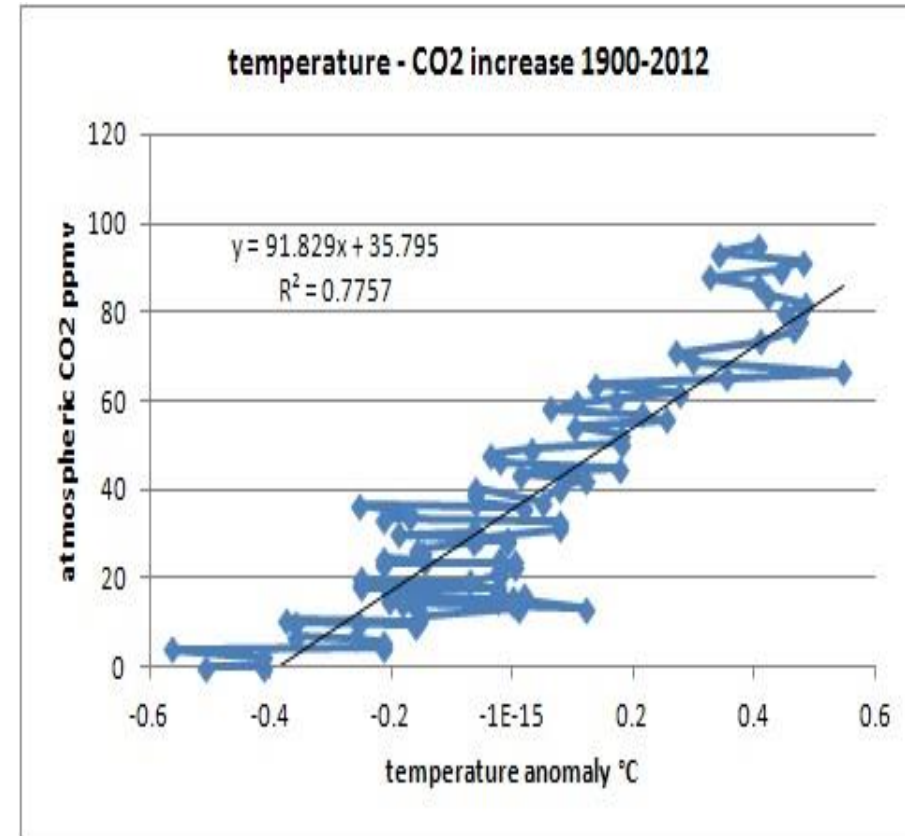
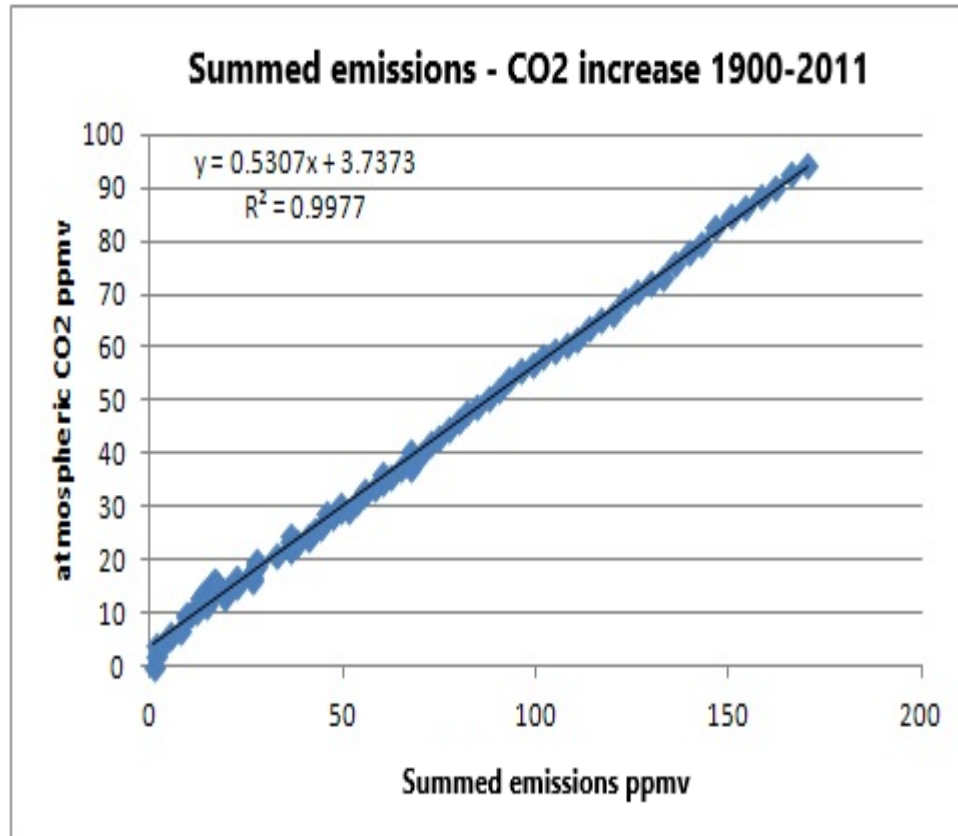
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2. The influence of temperature on CO₂ levels in the atmosphere.
3. The formulas for residence time and relaxation time.
4. Are the processes involved in CO₂ removal linear?
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INTRO (or what triggered my interest)

The different behavior of human emissions and temperature processes



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The influence of temperature on CO₂ levels - 1

Influence over the past 800,000 years in ice cores:

CO₂ in ice cores never exceeded 310 ppmv in 800,000 years.

CO₂ lags T with ~800 years during increase of T and several thousand years with decrease of T

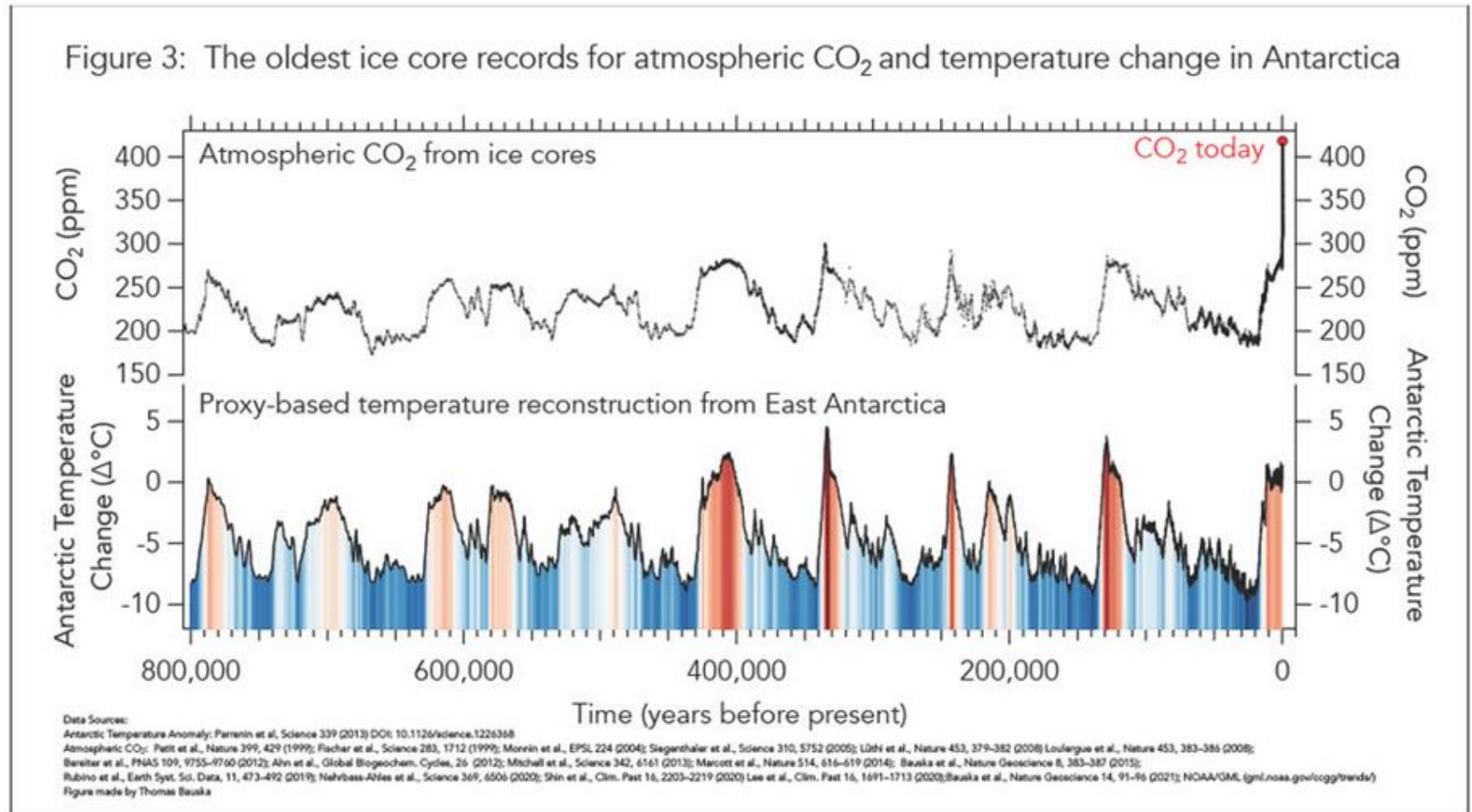
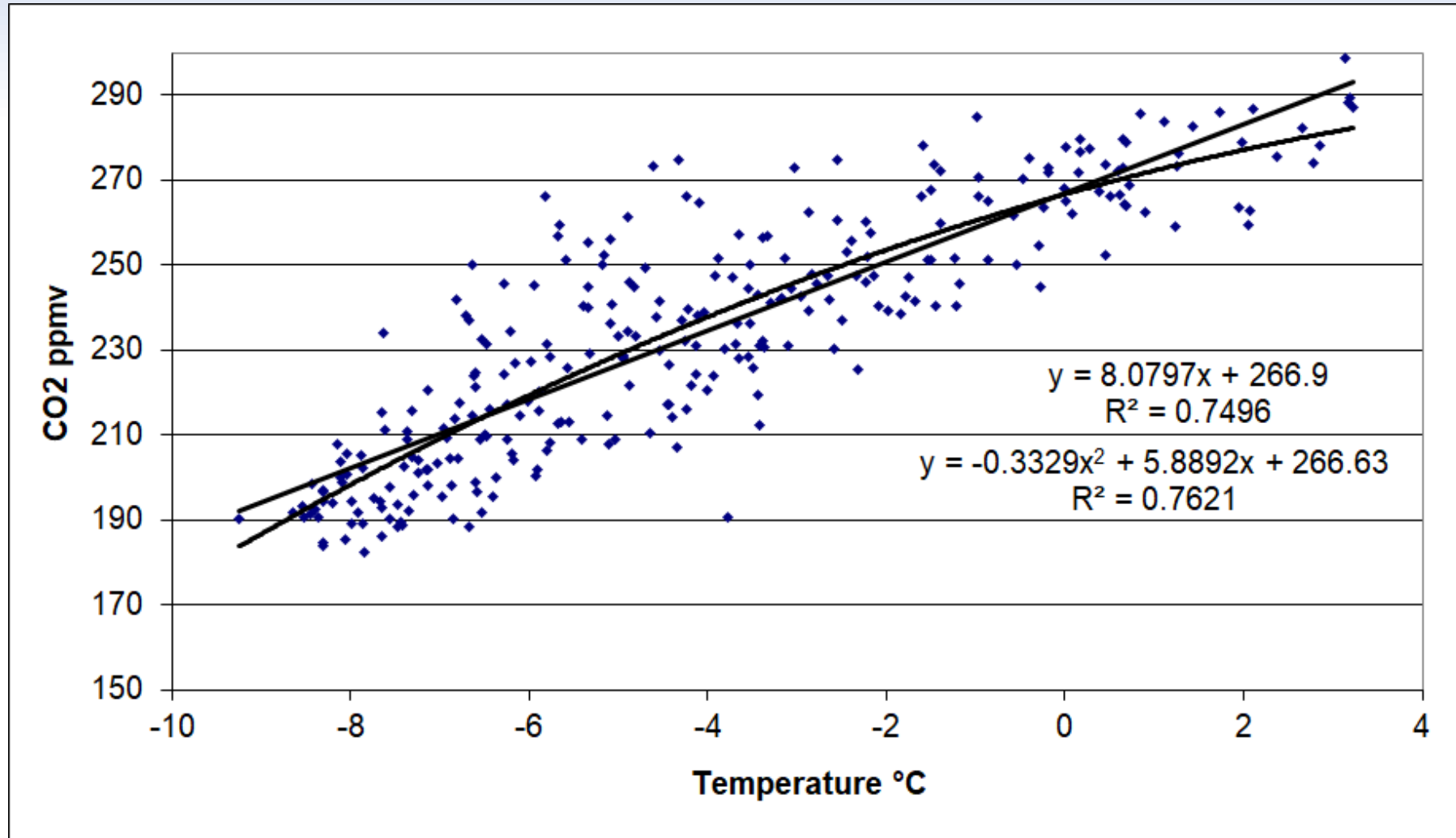


Figure from the
British Antarctic Survey

The Vostok ice core CO₂/T ratio



Vostok CO₂/T ratio. T based on δD and $\delta^{18}O$, without compensation for the lags of CO₂ after T.

The influence of temperature on CO₂ levels - 3

Vostok ice core CO₂/T ratio over 420,000 years with changes of around 100 ppmv for over 12°C difference gets some **8 ppmv/°C** for Antarctic temperatures mainly where the snow was formed. For global temperatures that may double to some **16 ppmv/°C**, due to polar amplification.

For modern CO₂/T changes, we have the formula of Takahashi, based on near one million seawater samples:

$$(pCO_2)_{\text{seawater @ } T_{\text{new}}} = (pCO_2)_{\text{seawater @ } T_{\text{old}}} \times \text{EXP}[0.0423 \times (T_{\text{new}} - T_{\text{old}})]$$

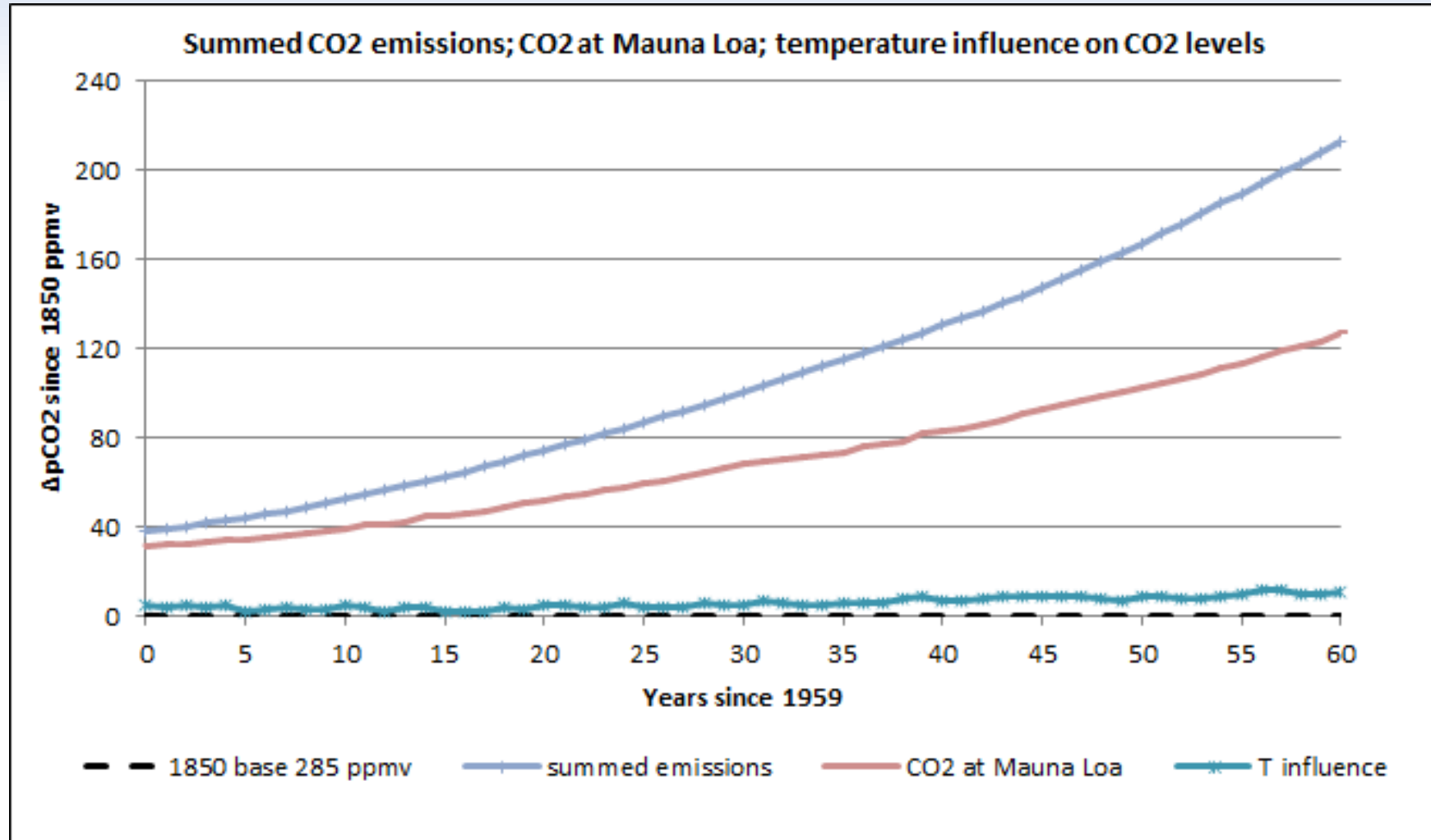
That gives some 4.3%/°C in/decrease or from the Little Ice Age to 1850:

$$275 \text{ ppmv} * \text{EXP}[0.0423 * 0.8^\circ\text{C}] = \mathbf{284 \text{ ppmv}}$$

Or from 1958 to 2024, if you don't trust ice core CO₂:

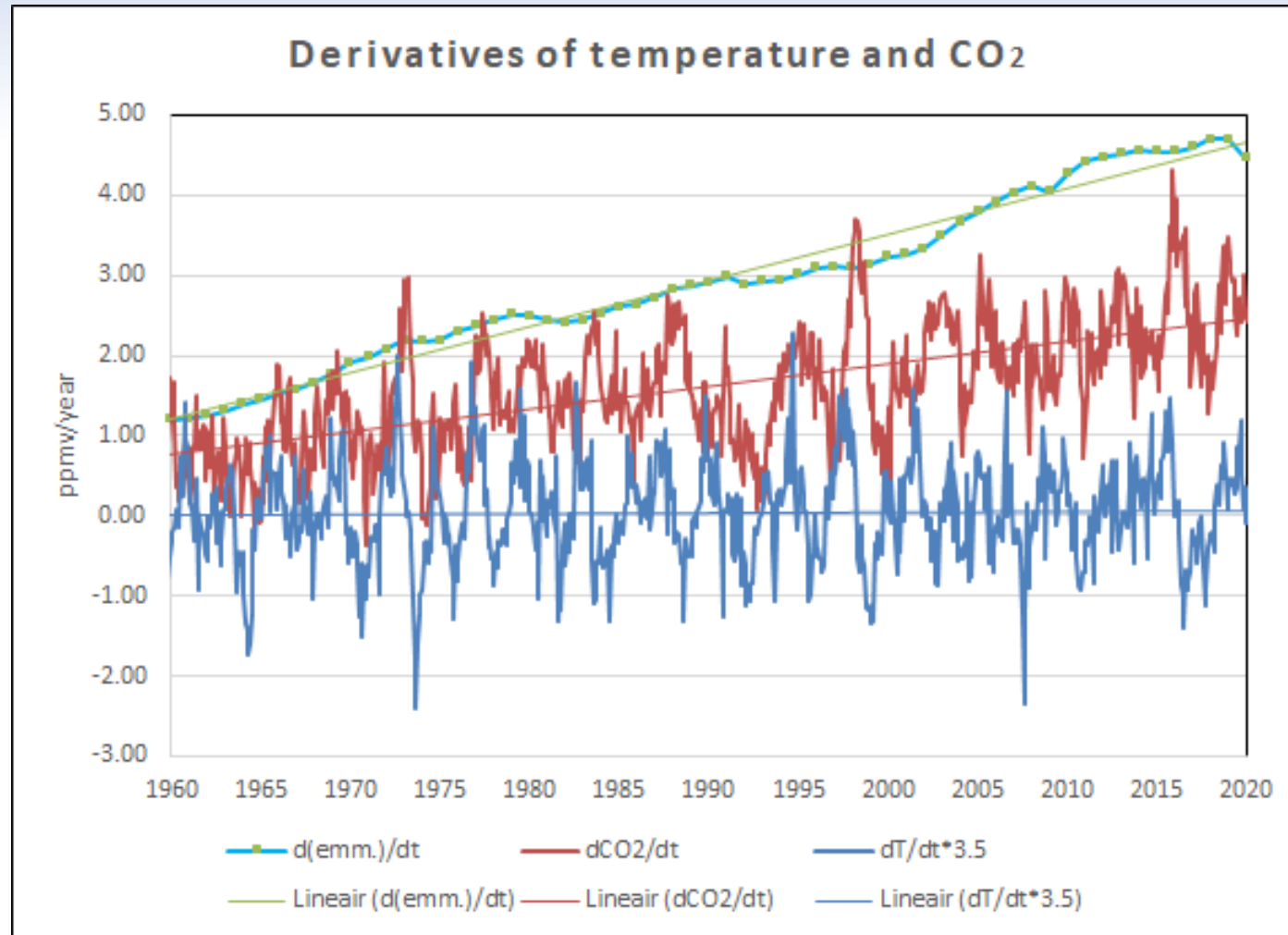
$$310 \text{ ppmv} * \text{EXP}[0.0423 * 0.6^\circ\text{C}] = \mathbf{318 \text{ ppmv}}$$

CO₂ increase over modern times



Influence of temperature and fossil emissions compared to Mauna Loa CO₂

Influence of T and emissions in the derivatives

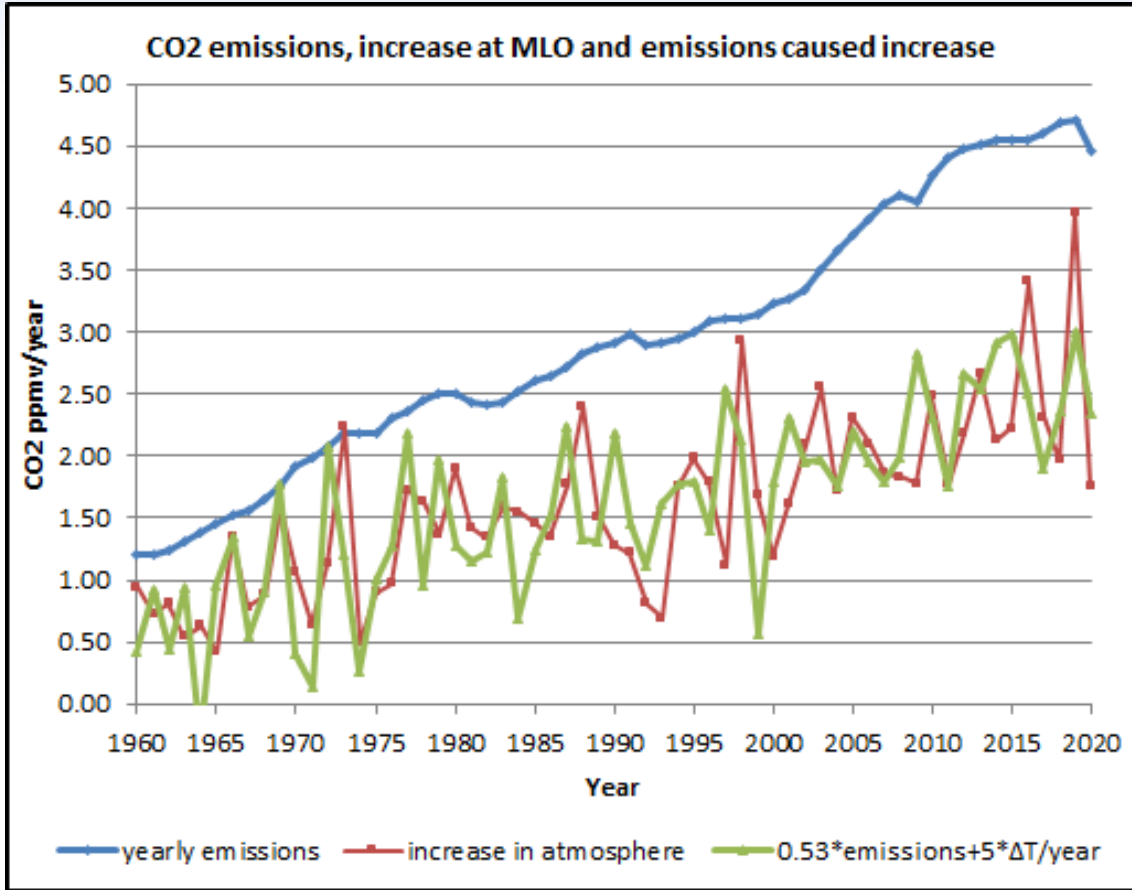


Derivatives of temperature and CO₂ increase in the atmosphere obtained from 12-month running average monthly values. Fossil emissions are yearly values. T influence used with a factor 3.5.

Influence of T and emissions in the derivatives - 2

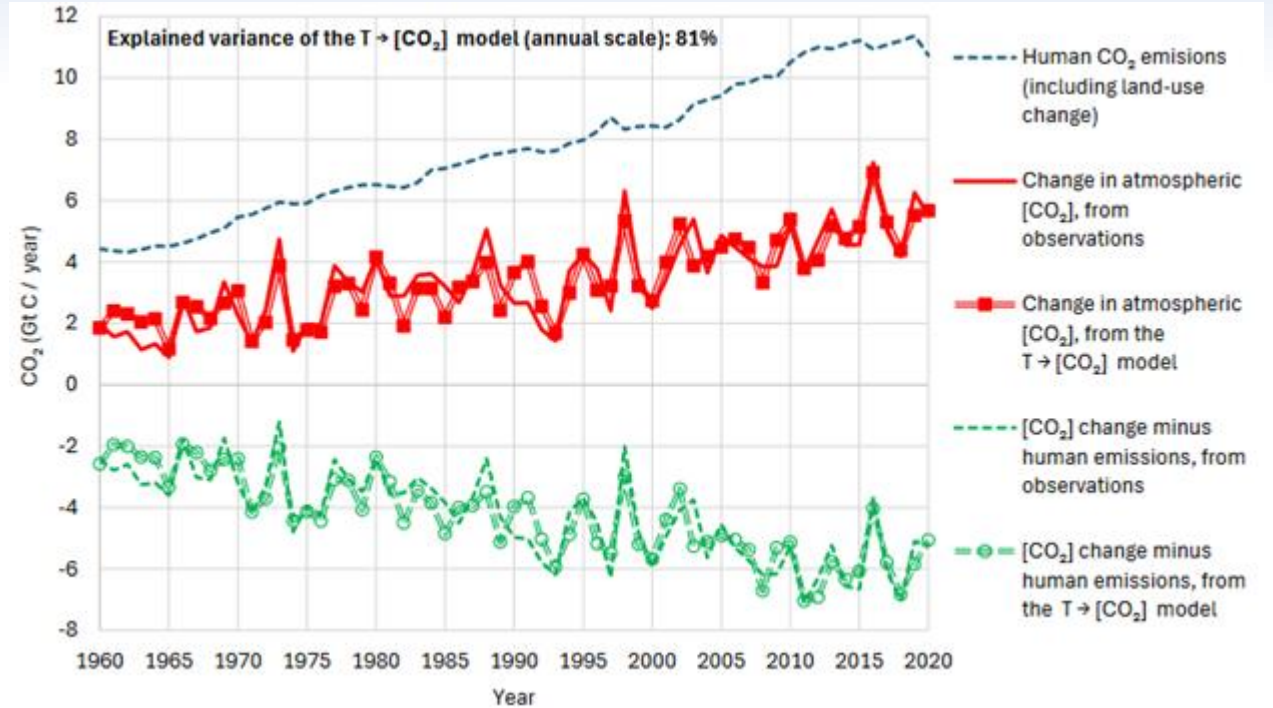
- Temperature rate-of-change variability is certainly the cause of variability of the CO₂ rate-of-change, with a short lag of about 6 months.
- Temperature rate-of-change has no slope, only a small offset from zero, thus is **not the cause** of the slope of the CO₂ rate-of-change in the atmosphere.
- Fossil emissions rate-of-change has twice the slope of the increase in rate-of-change in the atmosphere, thus is certainly the cause of the bulk of the increase in the atmosphere.
- Fossil emissions have practically no variability. ***Any method that uses variability or stochastic behavior for the attribution of cause and effect is doomed to fail...***

CO₂ increase: emissions or temperature?



Increase in the atmosphere fully caused by human emissions, variability caused by temperature variability.

$$\Delta[\text{CO}_2\text{atm}] = \Delta[\text{CO}_2\text{em}] * 0.53 + \Delta T * 5$$



Increase in the atmosphere fully caused by temperature.

$$\Delta[\text{CO}_2\text{atm}] = \Delta[\text{CO}_2\text{em}] * 0 + \int T(\text{anom})$$

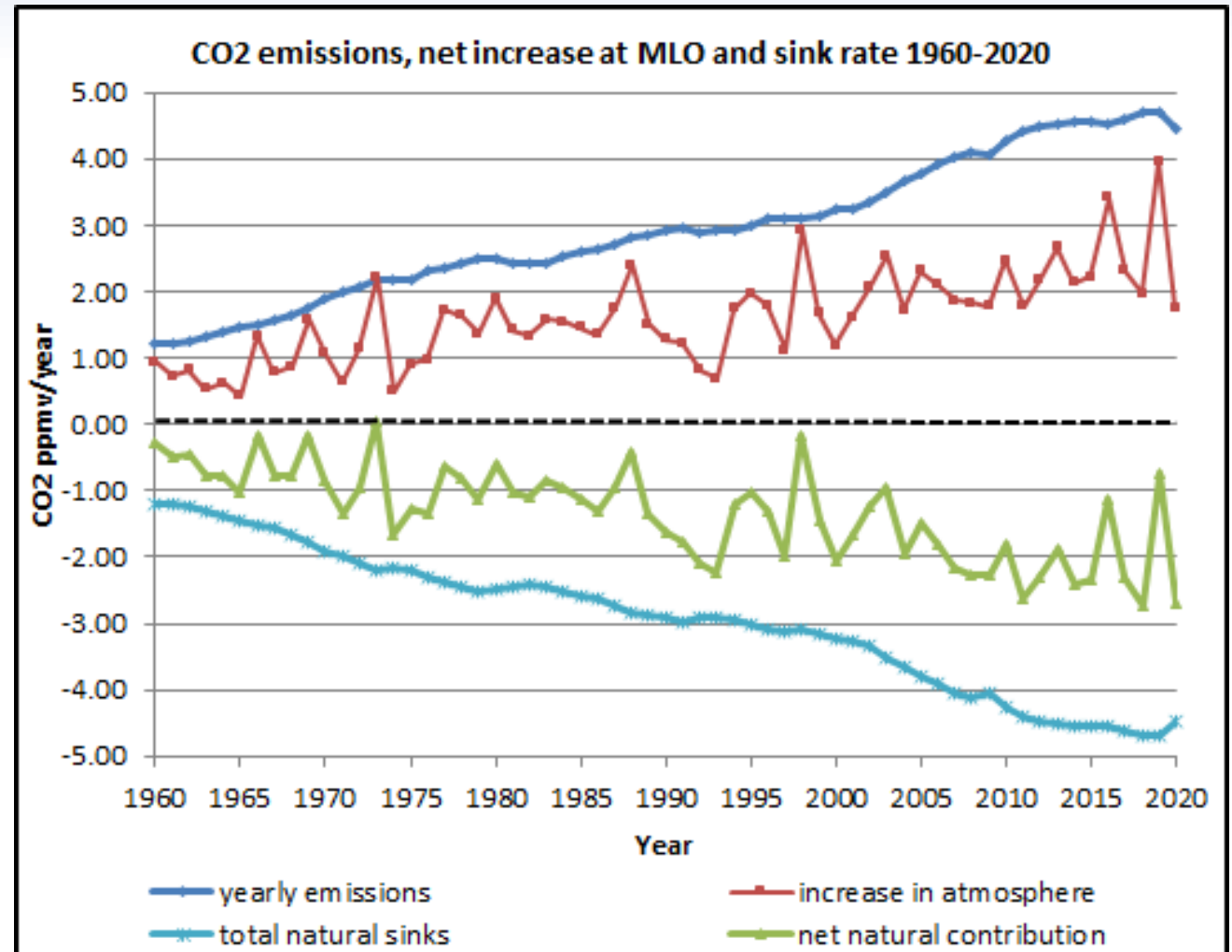
Koutsoyiannis, 2024.

Note: $T(\text{anom})$ is used, instead of ΔT .

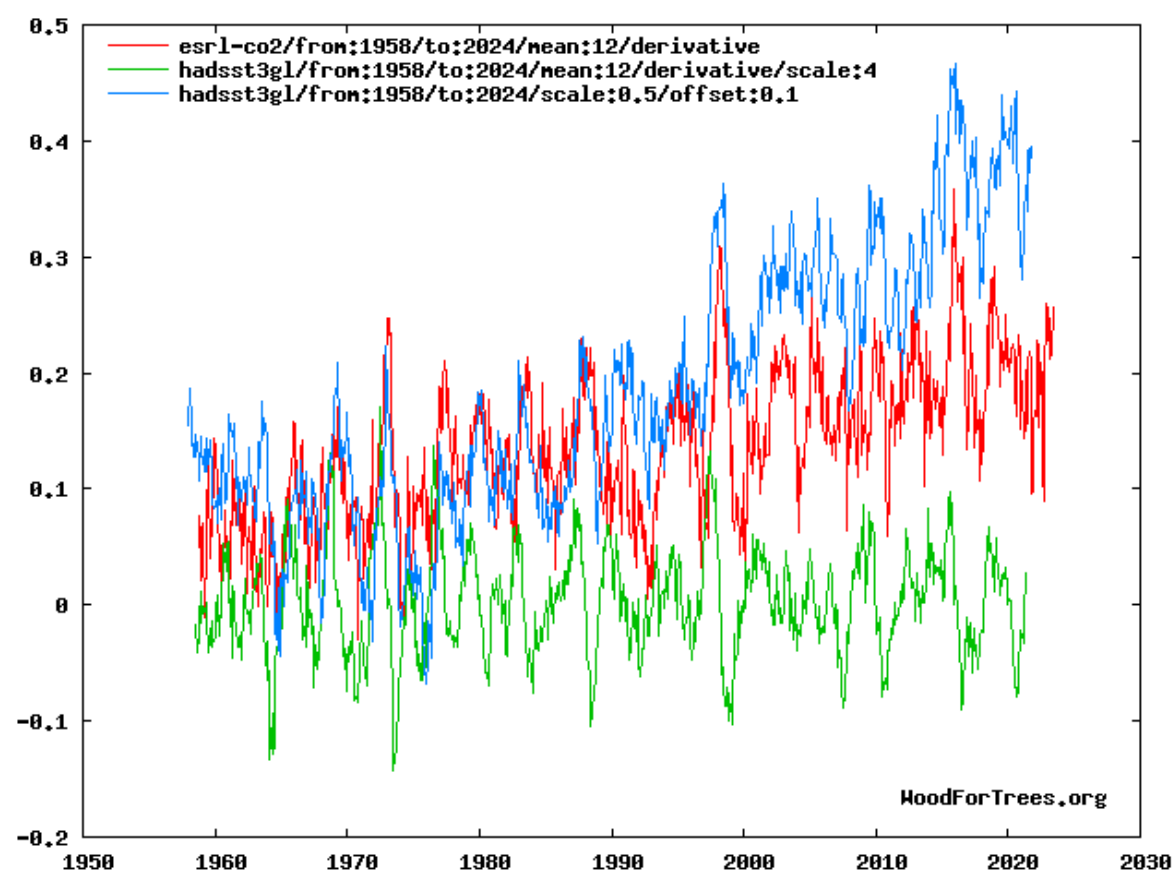
The mass balance for T as cause

If temperature is the only cause of the CO₂ increase in the atmosphere, then all CO₂ emissions from fossil fuel use (as mass, not the original molecules only) must be absorbed in natural sinks. All. 100%. Which is quite remarkable.

That means that natural sinks must be about twice the “natural” increase in the atmosphere to fulfill the carbon mass balance...



The use of T or dT/dt



Data obtained via WoodForTrees.org

T(anom) and dT/dt have very similar variability for the main disturbances (1991 Pinatubo, 1998/2016 El Niño).

While dT/dt has no slope, T(anom) has a slope with a $\pi/2$ shift in time for the variability, synchronising T(anom) variabilities with CO₂ variabilities...

Using variables of different order gives spurious results...

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The residence time is only 4 years

The turnover time or the main use of the word “residence” time is the time that a single CO₂ molecule, of whatever origin, in average “resides” or remains in the atmosphere.

- RT = mass / throughput
- RT = 890 PgC / 215 PgC/year = 4.14 year

Harde (2017): $RT = M(2012) / A(2012) = 4.1 \text{ yr}$ [8]

The adjustment time “can” be 4 years

The adjustment time is how long it takes to reduce an excess CO₂ mass, of whatever origin, above equilibrium to 1/e of the original disturbance.

If and only if unidirectional fluxes are involved and the removal is a ***linear process***, then the adjustment time and residence time are similar:

- $\tau = \text{disturbance} / \text{effect}$
- $\tau = 418 \mu\text{atm} / 101 \mu\text{atm}/\text{year} = 4.14 \text{ years}$

Where $1 \mu\text{atm} \approx 1 \text{ ppmv} = 2.129 \text{ PgC} = 2.129 \text{ GtC}$

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Are the decay processes linear?

The two main decay processes for any excess CO₂ in the atmosphere are linear processes:

Oceans:

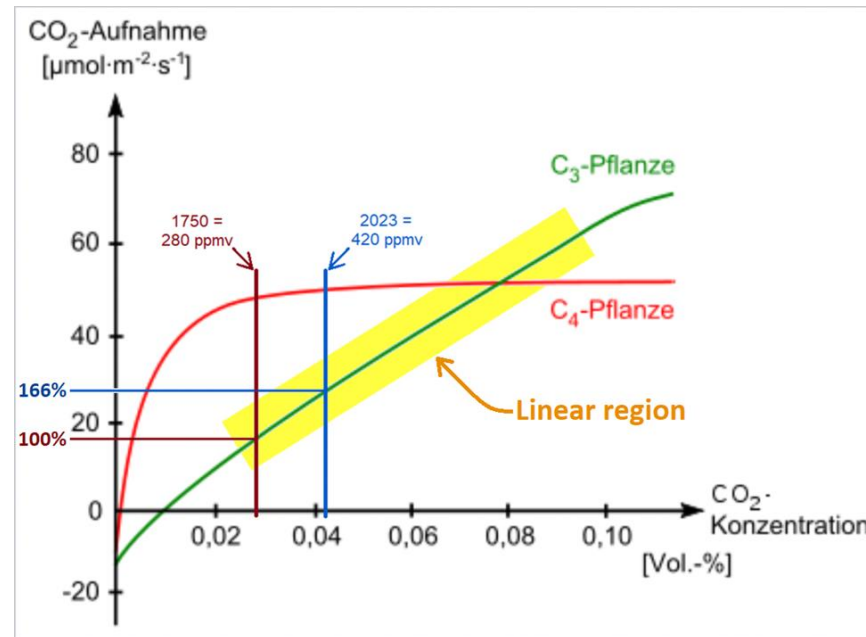
$$F = k \cdot s \cdot \Delta p \text{CO}_2$$

Where:

k = transfer coefficient (wind speed)
s = solubility parameter (composition)

Feely et al, 2001.

Biosphere:



Lütge, 2005.

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One-way theoretical world

One or more inputs unidirectional towards one or more outputs

$RT1 = \text{mass} / \text{throughput}$
 $RT1 = \text{mass} / \text{main inflow}$

$RT2 = \text{increased mass} /$
 $(\text{main inflow} + \text{disturbance})$

$RT1 = RT2$

Disturbance

Main inflow



Picture: Getty images

$F2 = f(h2)$

$F1 = f(h1)$

Outflow = $F1$ ($F2$)

$\text{Tau} = f(h2 - h1) / (F2 - F1) = RT1/2$

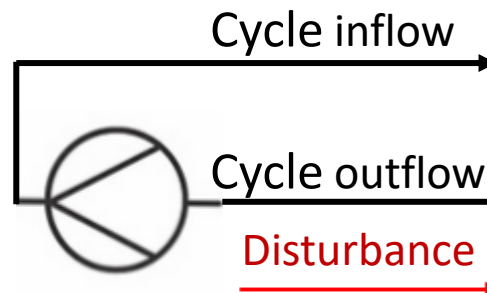
Extra: any “marker” in the disturbance (mud) down the lake and output can not exceed the ratio between the inputs

Two-way theoretical world

$RT1 = \text{mass} / \text{cycle inflow}$

$RT2 = \text{increased mass} / (\text{cycle inflow} + \text{disturbance})$

$RT1 \approx RT2$



$F2 = f(h2)$
Outflow = F2

Picture: Trevi fountain, Roma, Italy. Getty images

$\text{Tau} = \text{disturbance} / F2$

RT and Tau in this situation are completely decoupled!

Extra: any “marker” in the disturbance (green color) can asymptotically increase to 100% in the fountain water

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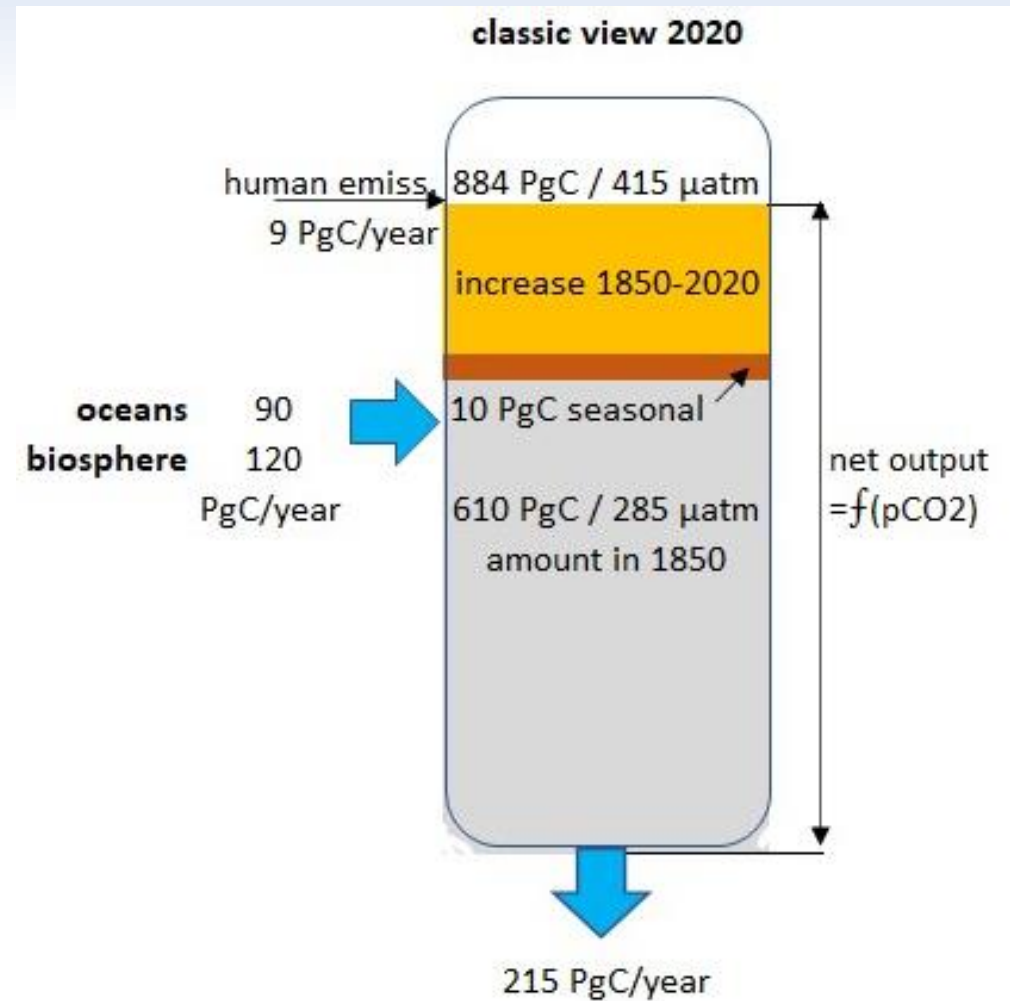
The “real” unidirectional world

This is the real world according to unidirectional processes only:

$$RT = 884 \text{ Pg} / 215 \text{ Pg/yr} = 3.8 \text{ yrs}$$

$\tau \leq RT$ (Stallinga)

One unidirectional process involved:
Inputs \rightarrow atm. pressure \rightarrow output(s)



$$RT = \text{mass} / \text{output} = 884 \text{ PgC} / 215 \text{ PgC/year} = 3.8 \text{ years}$$

$$\tau = RT$$

Problems with the unidirectional world

In spring/summer: T goes up, output into vegetation **increases** enormously while $p\text{CO}_2(\text{atm})$ goes down...

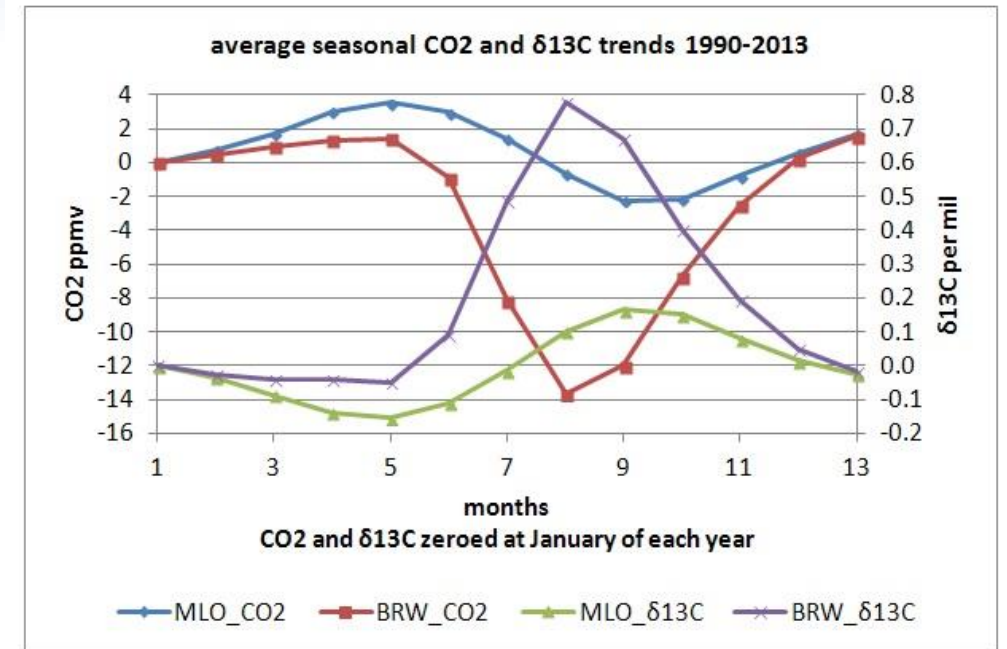
Ocean $p\text{CO}_2$ and outflux **increases** enormously, while DIC ($[\text{CO}_2]$ and (bi)carbonates) in surface waters drop.

Reverse for both in fall/winter.

Reverse for the hemispheres.

Near completely temperature controlled.

That are temperature/biology dependent processes, very limited in $p\text{CO}_2(\text{atm})$ dependency: Henry's law T dependency, photosynthesis, biological decay, feed/food digestion...



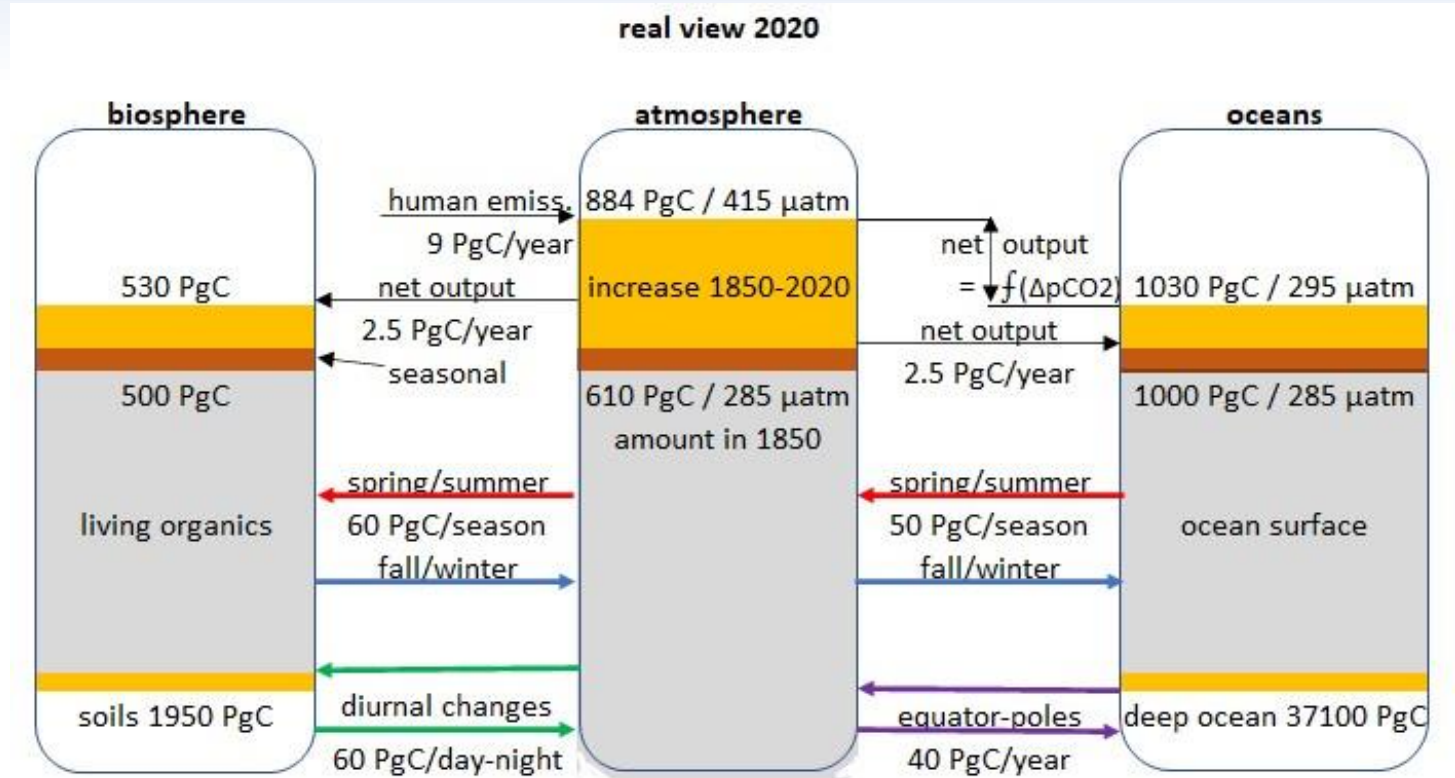
Markers of disturbance (fossil fuels $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$) in the atmosphere by far exceed the input ratio.

The real multidirectional world

The real world according to the observations.

RT is not influenced by the direction of the CO₂ fluxes and remains the same.

Tau is completely independent of the seasonal and other cycles and only influenced by the pCO₂ difference between atmosphere and ocean surface / plant alveoli



$$RT = \text{mass} / \text{throughput} = 884 \text{ PgC} / (60 + 60 + 40 + 50 + 5) \text{ PgC/year} = 884 / 215 = 3.8 \text{ years}$$

$$\text{Tau} = (415 - 295) \mu\text{atm} / 2.35 \mu\text{atm/year} = 51 \text{ years}$$

$$\text{Outflow} = f(\Delta pCO_2)$$

Multidirectional RT and Tau calculated

RT = mass / throughput

$$= 884 \text{ PgC} / (60 + 60 + 40 + 50 + 5) \text{ PgC/year} = 884 / 215 = 3.8 \text{ years.}$$

Tau = disturbance / effect

$$= (415 \text{ } \mu\text{atm} - 295 \text{ } \mu\text{atm}) / 2.35 \text{ } \mu\text{atm/year} = 51 \text{ years (*)}$$

Harde (2017): Tau = $[M(2012) - M(1850)] / \Delta A = 47.8 \text{ years [9] (**)}$

(*) $1 \text{ } \mu\text{atm CO}_2 \approx 1 \text{ ppmv CO}_2 = 2.129 \text{ PgC} = 2.129 \text{ GtC}$

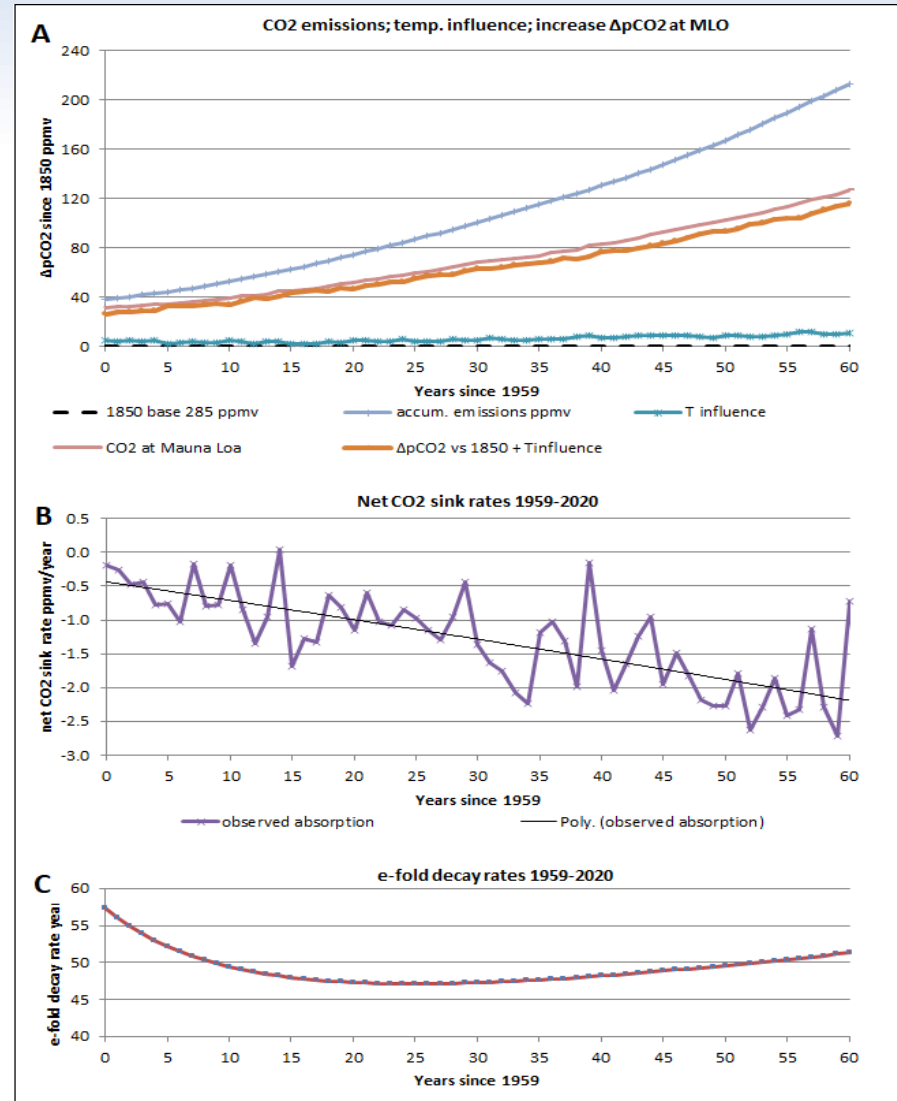
(**) Harde calculated the total decrease to zero, but as in a linear process $\Delta p\text{CO}_2$ gets reduced while taking away the excess CO_2 , Tau with the above formula is a reduction to $1/e$ (~37%) of the excess.

Multidirectional Tau since 1958

Figure A:
Human emissions, CO₂ in the atmosphere, T influence and effective $\Delta p\text{CO}_2$.

Figure B:
Calculated net CO₂ sinks in nature:
observed increase - calculated emissions
per year, with polynomial.

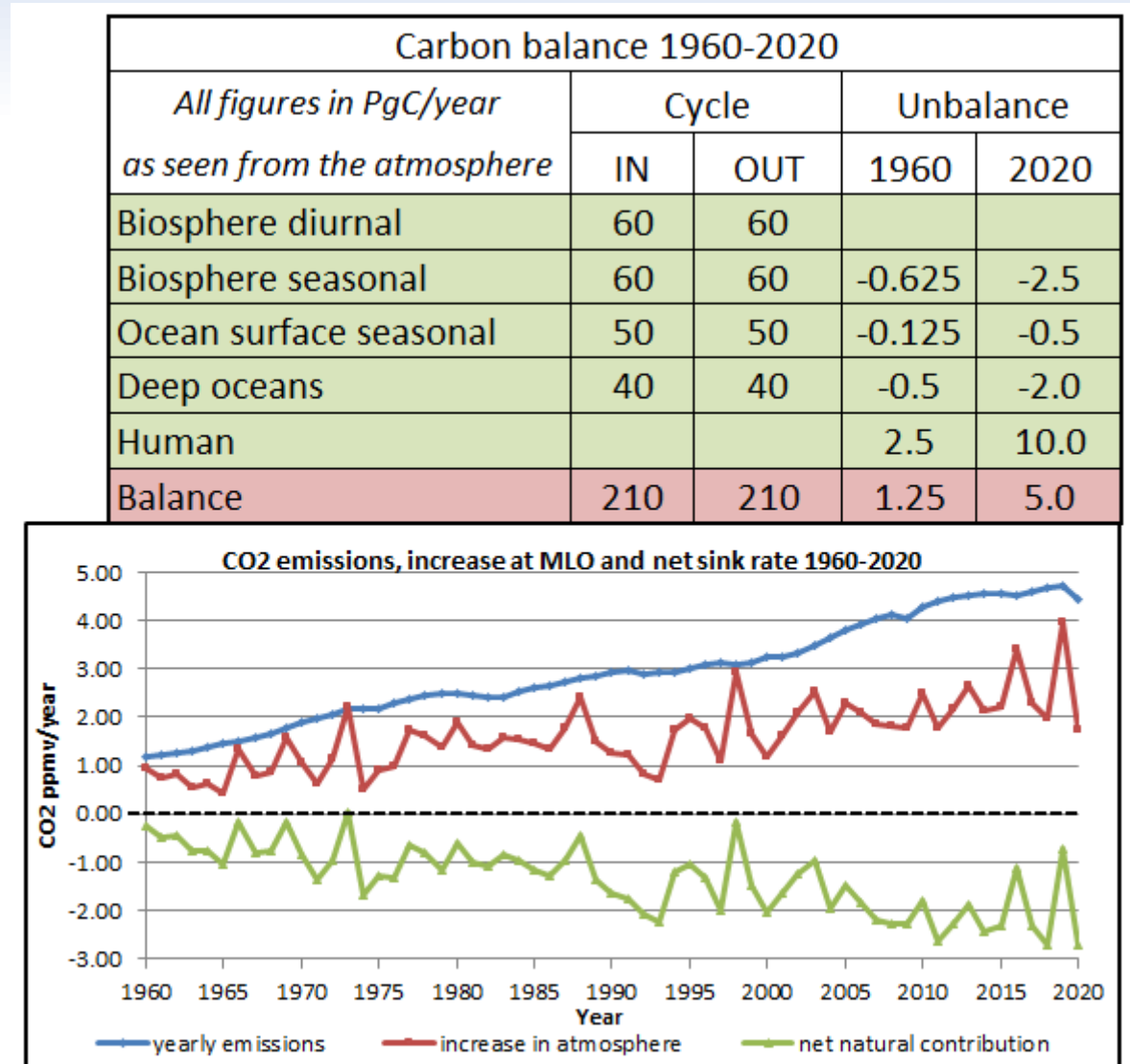
Figure C:
Calculated Tau based on the polynomial:
Around 50 years!



Mass balance checked

The mass balance is based on observations of the diurnal and seasonal CO₂/O₂/δ¹³C changes caused by the biosphere and pCO₂/pH/DIC changes of the ocean surface.

Deep oceans are supposed to absorb the remainder of the mass balance, confirmed by tracers into the deep oceans (δ¹³C, Δ¹⁴C, CFC's,...)



1 ppmv = 2.13 PgC = 2.13 GtC

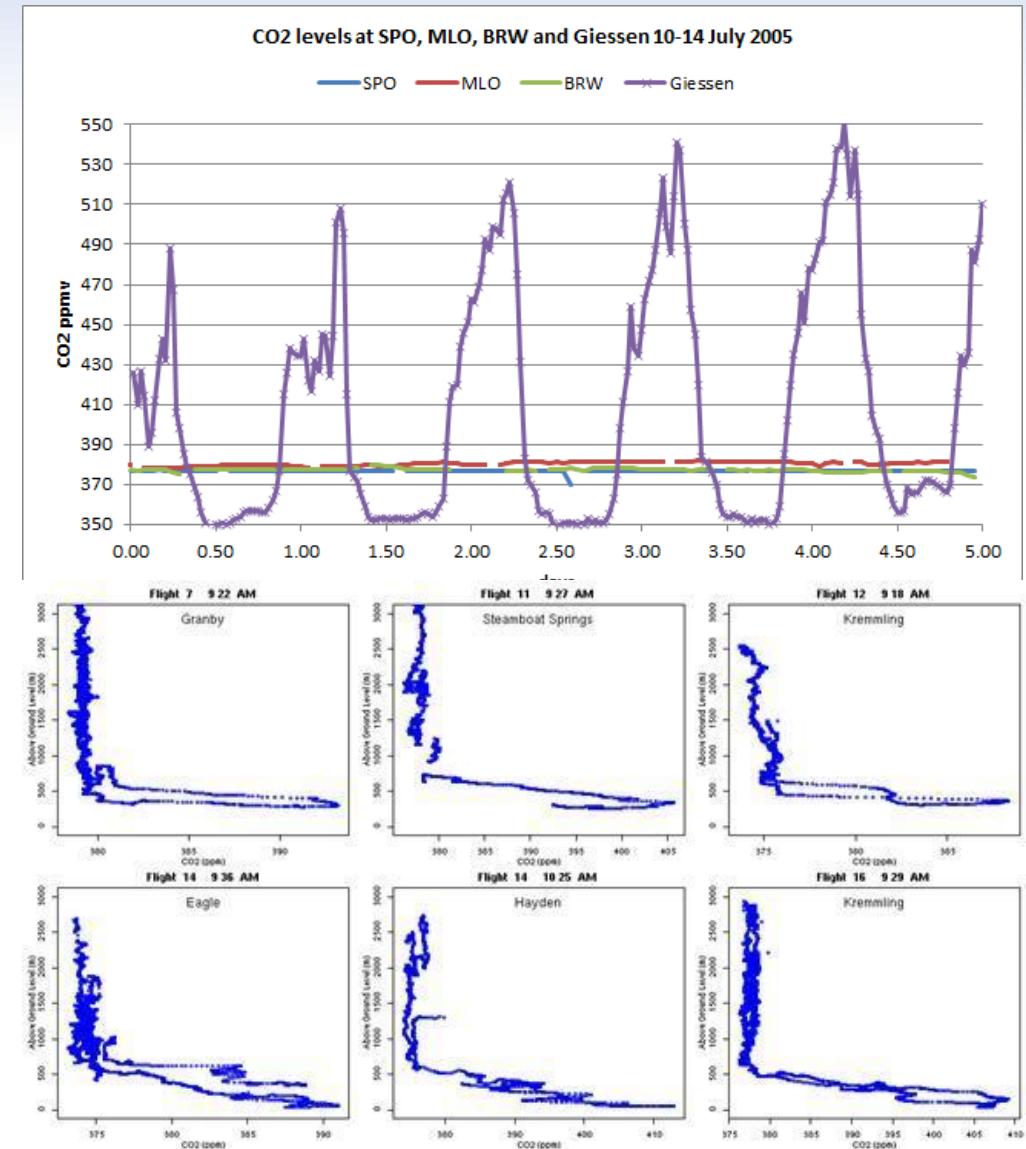
Diurnal changes caused by soil bacteria

Huge diurnal changes are caused by plant respiration at night and by soil bacteria, which mainly use sugars and other food near the roots that was prepared by photosynthesis during daylight.

Over some time period, never can exceed what was produced first.

Extreme changes near ground over a full day even doesn't reach the bulk of the atmosphere...

Here for flights over the Rocky Mountains



Markers checked

Fossil fuel emissions have two markers:

One unique marker: fossil fuels CO₂ doesn't contain any detectable amount of ¹⁴C, while all current living and recent death organisms and the oceans contain ¹⁴C.

That caused problems for radiocarbon dating from 1870 on, solved with correction tables.

That caused a faster decay rate for the excess $\Delta^{14}\text{C}$ from the nuclear bomb tests.

One not-unique marker: fossil fuels CO₂ has a much lower ¹³C/¹²C ratio (average -25 ‰ $\delta^{13}\text{C}$) than the atmosphere (-6.4 ‰ $\delta^{13}\text{C}$ before 1850).

Vegetation balance is ambiguous:

Vegetation decay CO₂ also is very low: average -24 ‰ $\delta^{13}\text{C}$.

Vegetation uptake of CO₂ leaves extra ¹³C in ratio behind in the atmosphere: +24 ‰ $\delta^{13}\text{C}$.

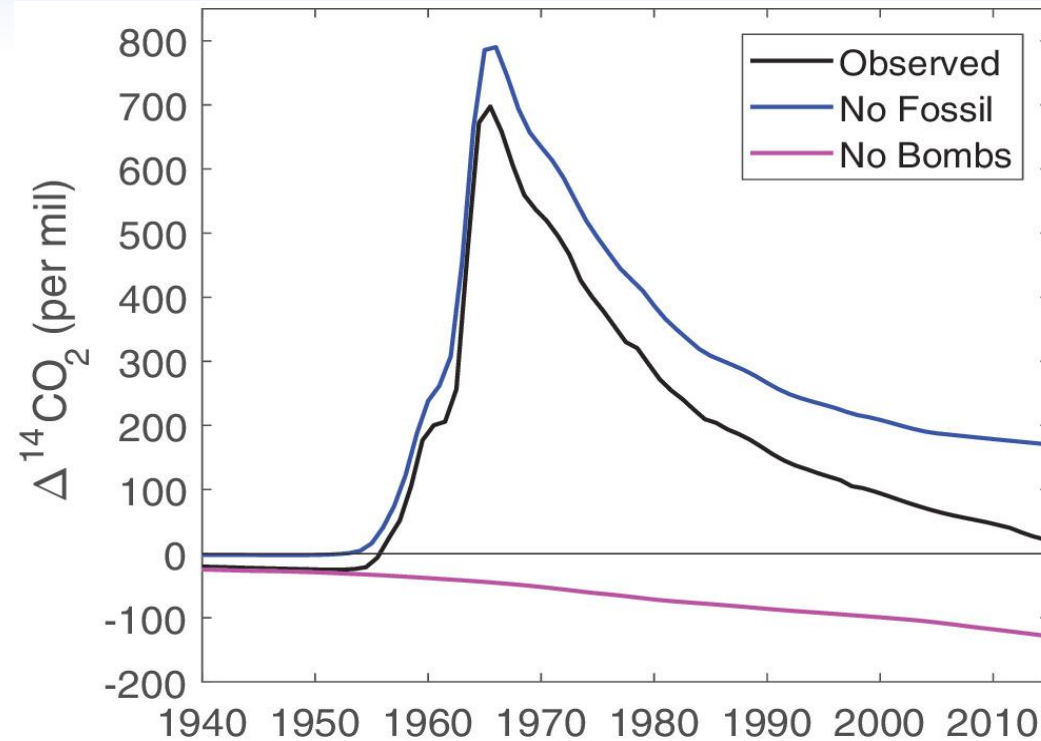
All inorganic C species (oceans, carbonate rock, volcanic vents,...) are around zero ‰ $\delta^{13}\text{C}$.

Ocean surface (at 1-5 ‰ $\delta^{13}\text{C}$) after equal bidirectional exchanges with the atmosphere maintains -6.4 ± 0.2 ‰ $\delta^{13}\text{C}$ in the atmosphere, due to physical fractionation at the water-air and air-water border.

$\Delta^{14}\text{C}$ marker in the atmosphere

Observed $\Delta^{14}\text{C}$ level in the atmosphere, calculated level without a bomb spike and calculated without ^{14}C -free fossil fuels.
Figure from Graven et al (2020).

Note: calculated no fossil level is on basis of the Bern model (which has its own problems).



Tau of $\Delta^{14}\text{C}$ marker calculated

Calculated Tau for the bomb spike without fossil fuels.

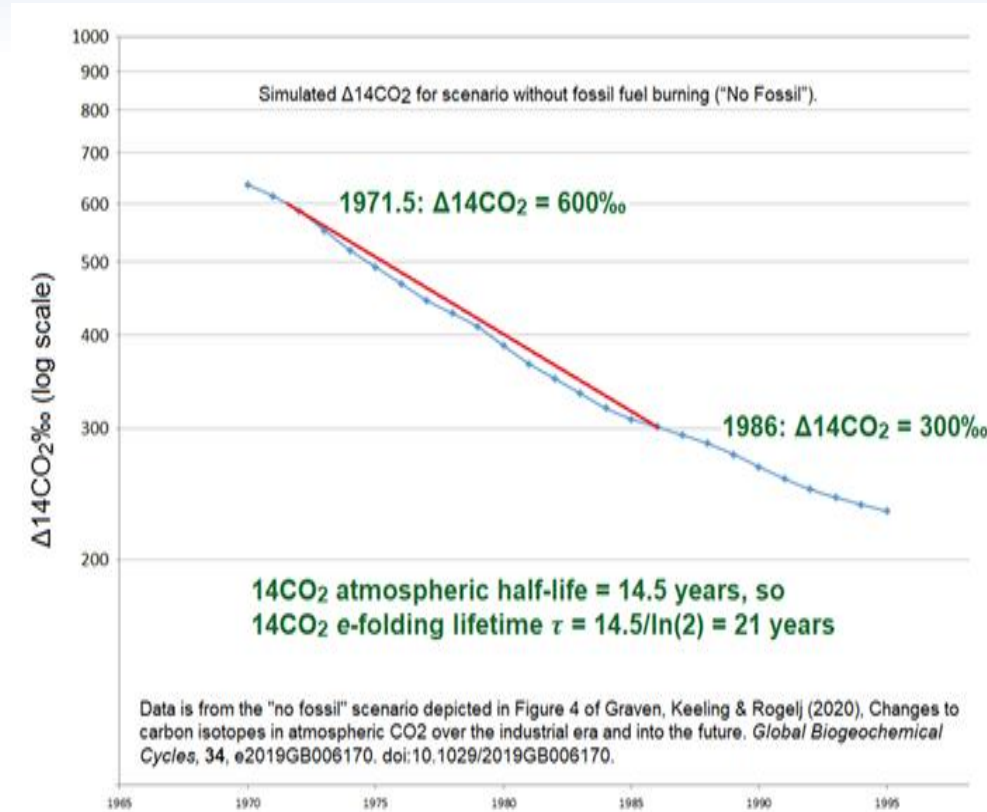
Figure calculated by David Burton (CO₂ Coalition member).

Tau = 21 years

Much larger than the ~4 years RT.

Smaller than the ~50 years for bulk CO₂, due to “thinning” of the marker by redistribution over multiple reservoirs and return of “old” low-¹⁴C from the deep oceans.

Single, unidirectional process rejected.



$\delta^{13}\text{C}$ in different media

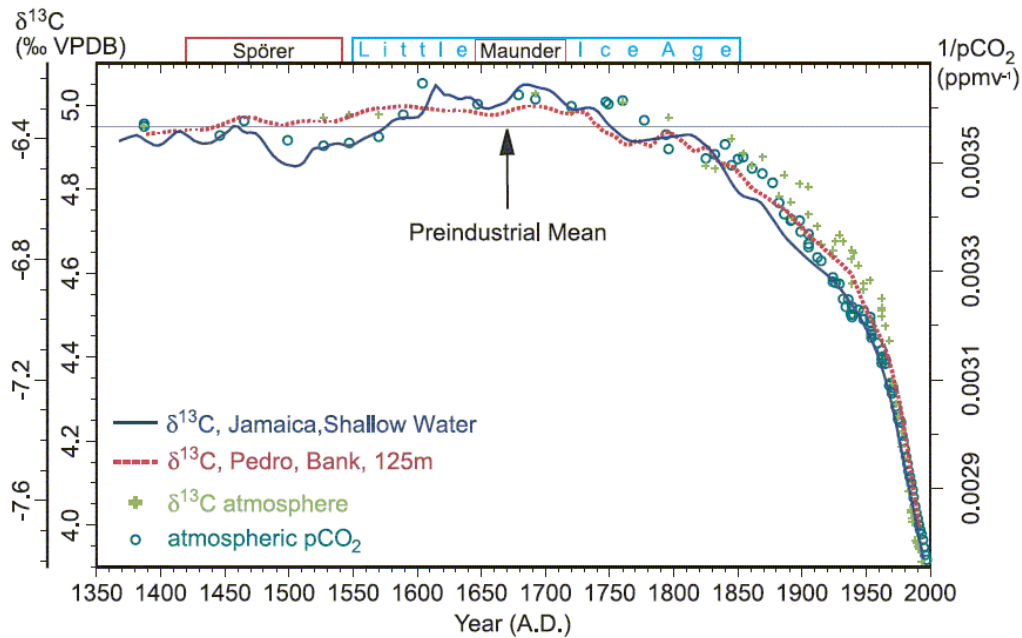
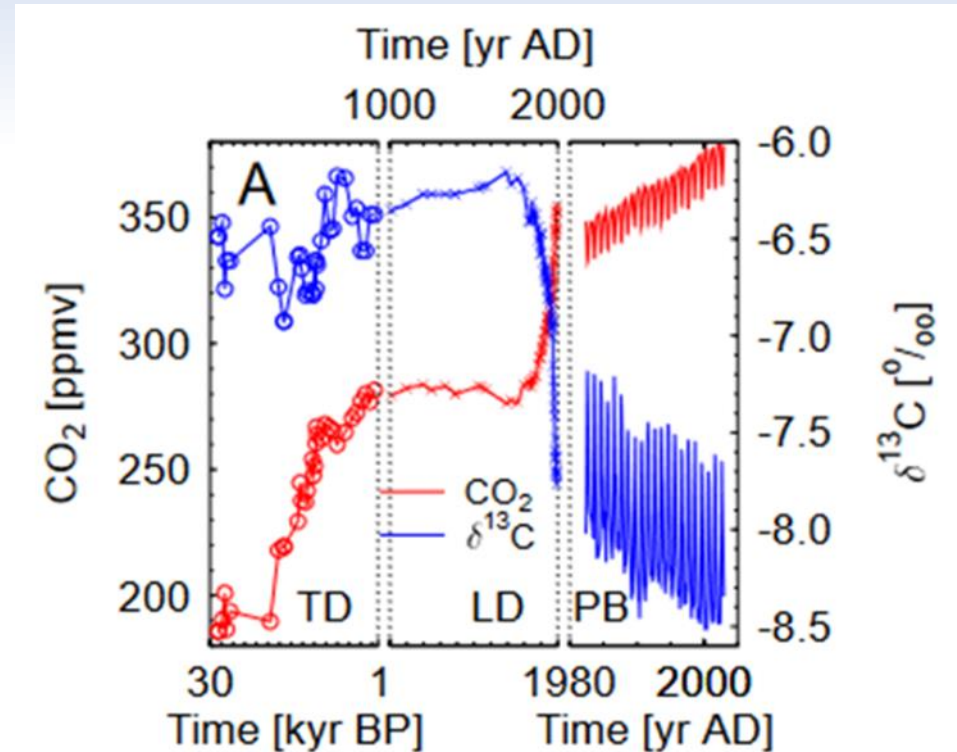


Figure 4. Comparison between Caribbean shallow (blue solid line) and deeper water (red dotted line) sponge $\delta^{13}\text{C}$ records (inner left y axis), $\delta^{13}\text{C}$ of atmospheric CO_2 (green crosses, outer left y axis) and atmospheric $p\text{CO}_2$ (circles, right y axis, reciprocal scale). Atmosphere data are derived from Antarctic ice core and firn air inclusions [Etheridge *et al.*, 1996; Francey *et al.*, 1999] and air measurements [Keeling and Whorf, 2001]. The atmospheric $\delta^{13}\text{C}$ record is scaled for its preindustrial mean and minimum values to fit the shallow water sponge record. The $\delta^{13}\text{C}$ curves are smoothed by locally weighted linear regressions (9% window). The horizontal line marks the preindustrial (1400–1850 A.D.) means (280.5 ppm, -6.37‰ , 4.95‰ VPDB, respectively). Slight offsets in the timing between atmosphere and sponge records can be artefacts of the dating methods. Blue bar at the top shows the approximate duration of the Little Ice Age [Grove, 1988]. Red bars mark the Spörer (ca. 1420–1540 A.D.) and Maunder (1645–1715 A.D.) sunspot minima.

$\delta^{13}\text{C}$ in ocean surface, ice cores, firn, atmosphere.

Figure from Böhm et al (2002).



$\delta^{13}\text{C}$ in ice cores, firn, atmosphere.

In ice cores: very little variability over the past 800,000 years ($\pm 0.4\text{‰}$ $\delta^{13}\text{C}$).

Since 1850 drop of more than 2 ‰ $\delta^{13}\text{C}$!

Figure from Köhler et al (2006).

$\delta^{13}\text{C}$ by the biosphere

Uptake/release of CO_2 by oceans and biosphere, based on the oxygen use of fossil fuel burning and oxygen balance of the biosphere.

The oxygen balance of the biosphere shows a net uptake of 1.0 ± 0.6 PgC/year of CO_2 over the period 1993-2002.

The biosphere is not the cause of the sharp $\delta^{13}\text{C}$ decline, it is opposing the decline. The earth is greening...

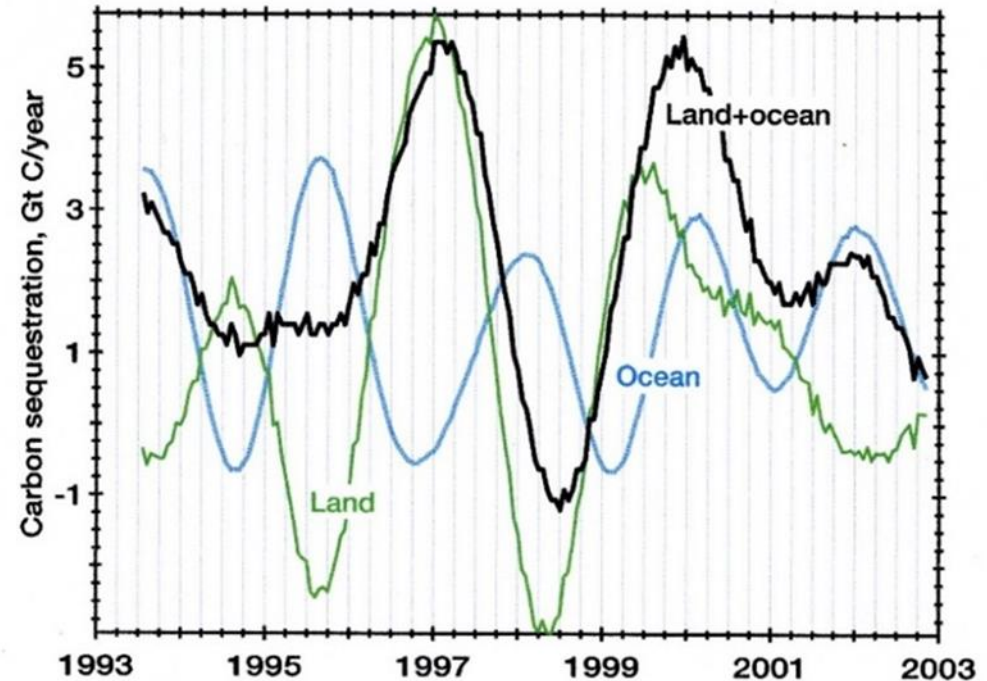


Figure from Bender et al (2005)

One-way only process rejected

- Tau of $\Delta^{14}\text{C}$ of the bomb tests \gg RT
- Tau of bulk CO_2 excess \gg RT
- “Fingerprint” of human $\delta^{13}\text{C}$ in atmosphere over 10%, zero in 1850, while input only 1.5% to 5% since 1958.
- “Fingerprint” of human $\delta^{13}\text{C}$ in ocean surface water over 6%, zero before 1850.

One-way only theory completely rejected.

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Problems with the IPCC's Bern model

The Bern model assumes that the ocean surface completely isolates the deep oceans from the atmosphere and saturation of both the ocean surface and biosphere.

Due to chemistry, changes in ocean inorganic carbon (DIC) $\sim 10\%$ of the change in the atmosphere. That is the Revelle/buffer factor.

No restriction for uptake into the biosphere up to 1,000 ppmv CO_2

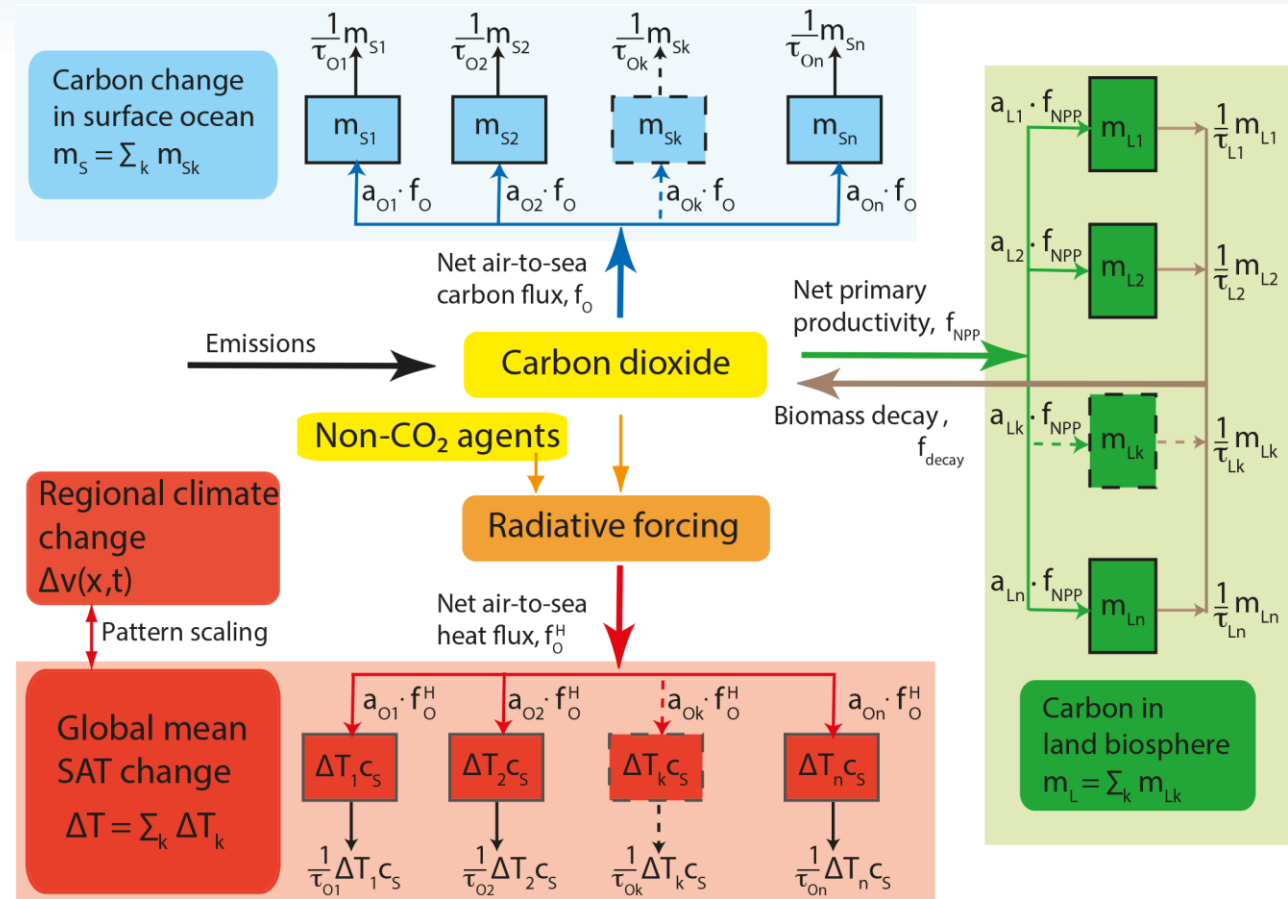


Figure from Copernicus (2018)

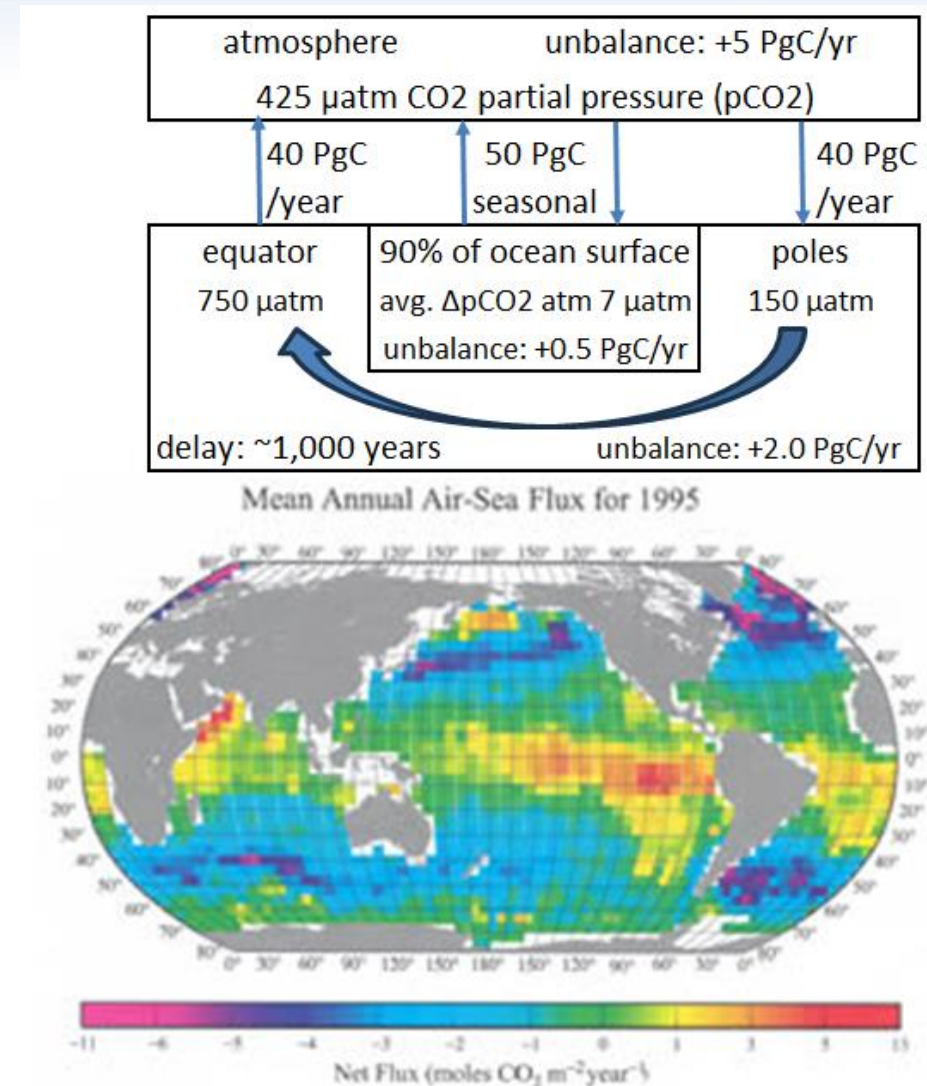
The problem with averages

The **average** $\Delta p\text{CO}_2$ between the atmosphere and the ocean surface is only $7 \mu\text{atm}$ and the ocean surface gets saturated at 10% of the change in the atmosphere. $\tau < 1$ year.

Direct atmosphere - deep ocean exchanges near the poles, returning after some 1,000 years near the equator, bypassing the surface restrictions. $\tau \sim 125$ years.

No saturation of the deep ocean exchanges expected into the far future...

$\Delta p\text{CO}_2$ figure from Feely (2001).



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