

The Human Contribution to Atmospheric Carbon Dioxide

How Human Emissions Are Restoring Vital Atmospheric CO₂



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ABSTRACT

Since the beginning of the Industrial Revolution in the late 1700s, the average concentration of Earth's atmospheric carbon dioxide (CO₂) has increased by about 140 parts per million by volume (ppmv) to the current amount of about 420 ppmv. This is much higher than concentrations of the past 800,000 years, which rarely exceeded 300 ppmv, according to ice core data. In this document, the CO₂ Coalition presents multiple lines of scientific evidence demonstrating conclusively that the modern increase in CO₂ is mainly due to anthropogenic emissions.

INTRODUCTION

While there have been significant industrial emissions of CO₂ for more than 200 years, only since 1958 has there been accurate measurement of atmospheric concentrations. This data is sufficiently precise to calculate year-to-year increases in CO₂ and compare them with human emissions of CO₂, which are derived from economic data. This “mass balance” calculation shows that atmospheric CO₂ has increased by less than the amount of CO₂ emitted by human activity every year since 1958, except arguably for the strong El Niño year of 1973. So, the net natural CO₂ fluxes have been negative in all the last 66 years but possibly one.

That is, nature is removing CO₂ from the atmosphere rather than adding to the total. Since nature is removing large amounts of the gas nearly every year, it follows that the rise in atmospheric CO₂ cannot be from natural causes.

Most scientists accept that human use of fossil fuels—first coal for steam engines, then oil and natural gas for wide application in industry and transportation—is the main cause of the recent increase in CO₂ concentrations in the atmosphere. That includes both scientists who believe the so-called “consensus opinion” that increasing atmospheric CO₂ is leading to dangerous warming and scientists who consider more CO₂ to be a net benefit.

Simply put, this publication documents that adding CO₂ to the atmosphere increases the atmospheric concentration of CO₂. Quantitatively, 7.8024 Gt of CO₂ (gigatonnes of carbon dioxide) contains 2.1294 PgC (petagrams of carbon). Adding that much CO₂ to the atmosphere increases its CO₂ concentration by 1.00 μmol/mol of dry atmosphere, which is nearly equal to “1.00 ppmv”.

Some recently published studies allege that most of or all the recent carbon dioxide increase is the result of natural causes rather than from human emissions. This study examines the scientific basis for determining the cause of the modern increase in atmospheric carbon dioxide.

We use multiple lines of scientific evidence to demonstrate that nearly all the increase in atmospheric CO₂ is from human emissions, most of which are from fossil fuel use. Each of these

lines of evidence confirms humans' role in the increase of atmospheric carbon dioxide. Together, they provide conclusive proof that the recent CO₂ increase is primarily due to human activity, not nature.

Oceans both release and absorb CO₂ from the atmosphere. However, the net sum of those fluxes is negative at currently elevated atmospheric levels, which means that the oceans are a net carbon sink. That fact is confirmed by an increase in the oceans' DIC (dissolved inorganic carbon: CO₂ + bicarbonates + carbonates) along with a slight decline in surface layer pH, which has an inverse relationship with seawater's absorption of CO₂.

A strong measured decrease in the ratio of the carbon 13 and carbon 12 isotopes in the atmosphere and ocean-surface waters also precludes a large net CO₂ contribution from the oceans. Since fossil fuels are sourced from organic matter, the ¹³C/¹²C isotope ratio is very low and similar for both fossil fuels and vegetation. Therefore, other indicators are needed to distinguish between their contributions to atmospheric CO₂, such as the ¹⁴C/C isotope ratio and changes in atmospheric oxygen.

Compared to the atmosphere, the ¹⁴C/C isotope ratio of vegetation is only very slightly changed. However, fossil fuels contain almost no ¹⁴C. This means that burning or rotting vegetation has little effect on the atmospheric ¹⁴C/C isotope ratio while the burning of fossil fuels lowers it. The reduction of the ¹⁴C/C isotope ratio currently observed in the atmosphere points to the burning of fossil fuels as the source of the additional CO₂.

Atmospheric oxygen (O₂) is also an indicator of whether vegetation is consuming or releasing CO₂. When the Earth is "greening," and vegetation is increasing, it is a CO₂ sink and a source of O₂ in the atmosphere. Careful measurements of atmospheric O₂ show that it is decreasing more slowly than would be expected from the amount of fossil fuels being burned. Therefore, additional O₂ is entering the atmosphere and vegetation is the only plausible source. That means vegetation is a net carbon sink rather than an overall contributor.

Other than the oceans and terrestrial biosphere, the processes of natural CO₂ sources and sinks are too slow to have much short-term effect on atmospheric CO₂ levels. Weathering of carbonate rock and volcanic eruptions and vents are important factors over geologic timespans, but they are much too gradual to have a significant effect over the last 250 years. Since the two major carbon reservoirs—oceans and terrestrial biosphere—are both currently carbon sinks, nature as a whole is a net sink for CO₂ and cannot be a net contributor.

The influence of temperature on CO₂ levels in the atmosphere was also examined. It has been shown that the increase in global temperature since the late 1700s could cause at most about a 13-ppmv increase in atmospheric CO₂, or just 10% of the observed rise.

After accounting for natural removal of CO₂ from the atmosphere, the increase of the gas closely tracks with accelerating emissions from human activity. Additionally, the strong decrease

in both $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/\text{C}$ isotope ratios, as well as atmospheric oxygen measurements, indicate that the burning of fossil fuels is the main source for the modern rise of CO_2 .

Note that the cause of rising CO_2 levels is just one of several common points of confusion about atmospheric CO_2 . For another example, the Intergovernmental Panel on Climate Change (IPCC) uses the Bern and similar models, which predict a saturation of natural CO_2 sinks and a consequent slowdown of natural CO_2 removals from the atmosphere. That leads to a prediction of a long atmospheric lifetime for CO_2 additions to the atmosphere and a “long tail” in the theoretical CO_2 decay curve should such additions cease. But saturation of CO_2 sinks is only true for the ocean surface. It is not correct for the vegetation sink while the atmospheric concentration is below 1,000 ppmv or so, nor for the deep oceans where both the biological pump and the direct sinks near the poles—e.g. the Atlantic Meridional Overturning Circulation (AMOC)—largely bypass the physicochemical restrictions of the ocean surface.

SCIENTIFIC DISCUSSION

1. EVIDENCE OF THE HUMAN INFLUENCE

In this chapter the evidence of the human cause for the recent CO₂ increase is established. The carbon mass balance is what definitely proves that humans are the main cause of the increase of CO₂ in the atmosphere: As long as the increase in the atmosphere is less than what humans emit per year, nature as a whole is a net sink and can't be the cause of the overall increase because that would violate the mass balance.

All other parts are additional evidence for the human contribution and/or exclude the specific natural reservoirs of the oceans and vegetation as cause for the increase. Any theoretical consideration that results in a natural cause for the CO₂ increase violates one or more of the following observations and therefore must be rejected.

1.1 The Carbon Mass Balance

The amount of “fossil CO₂” emitted by humans nowadays is nearly 10 PgC/yr. 1 ppmv CO₂ = 7.8024 Gt CO₂ = 2.1294 PgC, so 10 PgC is 4.70 ppmv. Yet the average annual increase in the amount of CO₂ in the atmosphere is only about half that (average +2.45 ppmv/year from 2012 to 2022 at Mauna Loa). That implies that there is little to no increase in the atmosphere due to other causes; otherwise, the increase of the amount of CO₂ in the atmosphere would be higher than the emissions, not lower.

Anthropogenic emissions of “fossil CO₂” are known with precision from economic data for the production figures of coal, oil, natural gas and cement because we know how much CO₂ is produced when a given amount of any of the common fossil fuels is burned. “Land use change effects” from clearing forests and draining swamps are typically estimated to add about 1 PgC/yr of non-fossil CO₂ to that total, but that figure is poorly understood (Global Carbon Project ongoing).

CO₂ is 27.29115% carbon by weight. So, for example, burning 1 tonne of 94% carbon anthracite coal produces $0.94 / 0.2729115 = 3.444$ tonnes of CO₂. Similarly, methane (CH₄) is 74.868±0.002% carbon, so burning 1 tonne of methane produces 2.743 tonnes of CO₂.

Precise measurements of atmospheric CO₂ concentrations began in 1958, at Mauna Loa, Hawaii. So, for every year since 1959, we have sufficient data to calculate the year-over-year change in the amount of CO₂ in the atmosphere. By comparing that data to fossil CO₂ production figures, we can see that anthropogenic emissions of fossil CO₂ were much larger than the measured increase in the amount of CO₂ in the atmosphere in almost every year. That means that the natural CO₂ sinks that remove CO₂ were nearly always much larger than natural CO₂ sources. Figure 1.1.1 shows this over the past 60 years.

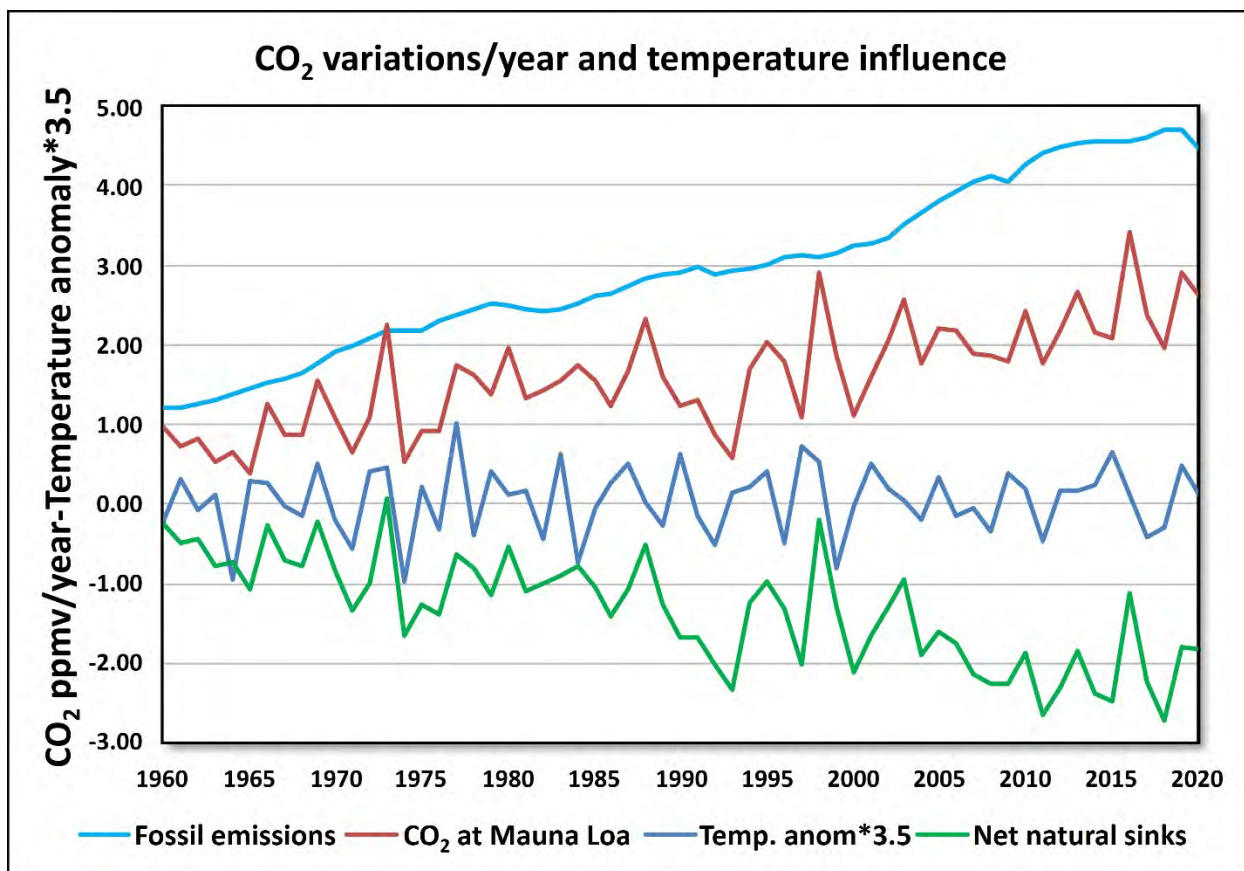


Figure 1.1.1: Fossil emissions, CO₂ increase in the atmosphere, net sinks and temperature influence. Emission data from the Global Carbon Project (ongoing), CO₂ increase from NOAA (ongoing) and temperature influence estimated as a factor 3.5 ppmv/°C for the changes in global ocean surface temperature (HadSST3gl ongoing).

The light blue trace shows CO₂ emissions per year from fossil fuel burning and cement manufacturing (The small drop in 2020 was due to the COVID-19 pandemic). The year-over-year increase measured in the atmosphere is shown in red. Net natural CO₂ sinks (mainly in vegetation and oceans) are the differences between human emissions and the increase in the atmosphere (green), shown as negative values for ease of comparison with the other traces.

Most of the year-to-year variability in rate of natural CO₂ uptake is explainable by temperature variations. The temperature variability (dark blue, in CO₂ equivalent) is enhanced with a factor 3.5 to show the same amplitude as for the CO₂ variability. That implies a temperature/CO₂ emission factor of about 3.5 ppmv/°C for short term temperature changes. Everything is expressed in ppmv/year (1 ppmv = 2.1294 PgC = 2.1294 GtC).

The graph is based on calculations of emissions, sampled from national inventories of fuel use and cement manufacturing (taxes!) and fuel burning efficiency (Global Carbon Project, ongoing). In the best case, these are quite accurate, in the worst case, the emissions are underestimated, due to the inclination to avoid taxes and because of the political reasons of

some countries. That doesn't make any difference for the net result of the balance, as an underestimate of emissions only implies that the net natural sinks must be even larger in order to produce the difference between the observed increase in the atmosphere and the larger amount of CO₂ released by human activity.

Inventories of CO₂ in the atmosphere are based on very accurate measurements of CO₂ at Mauna Loa (NOAA ongoing) and several other “background” stations. The difference between human CO₂ emissions and the CO₂ increase in the atmosphere is “net natural CO₂ sinks,” mainly what the oceans and vegetation absorb each year. Other processes, like rock weathering, have much smaller effects.

Interesting items in that graph:

- Nature was a net sink in all years except for a few borderline El Niño years.
- The net natural CO₂ sink has steadily increased as the CO₂ level in the atmosphere has risen. (In fact, there is a close linear relationship between those two quantities.)
- The trend of the CO₂ increase in the atmosphere is around 50% of human emissions.
- That proves that nature is a sink for the other 50%, not the cause of the increase.
- The annual temperature anomaly shows no trend at all, thus is not the cause of the ongoing increase of CO₂ in the atmosphere.
- Temperature variability is the main cause of the year-to-year variability in natural net CO₂ sinks.

The partitioning between vegetation and ocean as sinks can be calculated from the oxygen balance. That is not of interest for the total balance, as in nearly every year the sum of land plus oceans was more sink than source.

It is interesting to know how much CO₂ is absorbed by the terrestrial biosphere (plants and soil), and how much by the deep oceans. That was analyzed by Battle et al. (2000) and more recently by Bender et al. (2005), based on changes of $\delta^{13}\text{C}$ and oxygen content changes in the atmosphere over the last decade of the previous century. Figure 1.1.2 shows the detailed variability of the CO₂ sink/source level in 1994–2002 by oceans and vegetation, as measured from the O₂/N₂ balance by Bender et al. (2005).

Vegetation shows by far the largest variability in uptake and release of CO₂ as a result of temperature changes. Nonetheless, over the full period, on average vegetation was a net sink of around 0.5 ppmv/year (1 PgC/year) for an average release of about 3 ppmv/year in the period 1994–2002.

Precise measurements of atmospheric CO₂ began at Mauna Loa in March, 1958. From 1959 to 2023 the CO₂ level rose by 105 ppmv (224 PgC) to 421 ppmv. That is 74.5% of the total increase since the start of the Industrial Revolution (taken as 280 ppmv in 1780, determined from ice core data). It is based on measurements at places where “background” levels of CO₂ can be

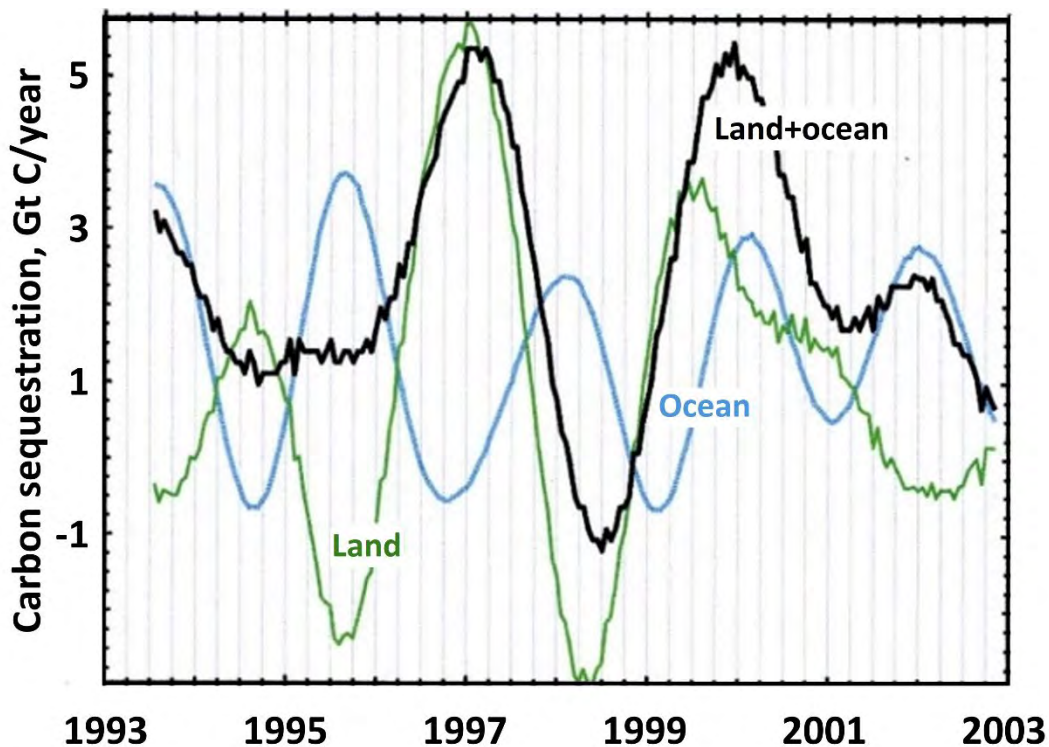


Figure 1.1.2: Vegetation and ocean CO₂ sources/sinks from Bender et al. (2005).

measured, with minimum interference from local CO₂ sinks and sources, and compared to ice core measurements for the period before 1958.

As Figure 1.1.1 shows, in nearly every year since 1959, human emissions of CO₂ have been much greater than the increase in the amount of CO₂ in the atmosphere. That means that, despite substantial variations in factors (like temperature) which affect natural sources and sinks, the sum of natural sources of CO₂ is exceeded by the sum of natural CO₂ sinks nearly every year.

The natural seasonal *exchange* between vegetation and oceans on one side, and the atmosphere on the other side, is estimated at around 210 PgC/yr (for details see chapter 1.6 about the process characteristics). That is not of interest for the total carbon *mass change* over a year, because no matter how large these natural sinks and sources are, only the *difference* between all the natural inputs together and all the natural outputs together influences the total amount of CO₂ in the atmosphere. This difference is exactly known because it is equal to the difference between human emissions and the increase in the atmosphere.

That is what is called the “mass balance.” The change in the amount of carbon in CO₂ in the atmosphere is equal to the difference between the amount added and the amount removed. According to the data, from 1959 through 2022, human emissions of fossil CO₂ totaled 405 PgC, yet the amount in the atmosphere increased by only 218 PgC. The combined effect of all other carbon fluxes was a 187-PgC sink.

No matter how high the natural seasonal turnover might be, in nearly all years over the last six decades, the natural CO₂ sinks were much larger than the natural CO₂ sources. Thus, it is physically impossible that natural sources could have been responsible for a substantial part of the increase of CO₂ in the past 60-plus years because that would violate the mass balance.

Mass Balance Conclusions

Anthropogenic emissions of fossil CO₂ are much larger than the measured increase in the amount of CO₂ in the atmosphere. Therefore, the natural CO₂ “sinks” are nearly always larger than natural CO₂ “sources.”

Any theory that leads to a substantial increase of CO₂ in the atmosphere due to natural factors violates the mass balance and thus cannot be correct.

1.2 The $^{13}\text{C}/^{12}\text{C}$ Ratio

The carbon of CO_2 is composed of different isotopes. Most is of the lighter type: ^{12}C (that has six protons and six neutrons in the nucleus). About 1.1% is heavier: ^{13}C (six protons and seven neutrons). There is also a very small amount of ^{14}C (six protons and eight neutrons), which is continuously formed in the stratosphere from the interactions of nitrogen with cosmic-ray particles. This type of carbon (also formed by above-ground nuclear bomb tests in the 1950s and early 1960s) is radioactive, with a half-life of $5,700 \pm 30$ years, so it can be used to determine the age of organic material and of fossils, which contain organic material, back to about 60,000 years (10 to 11 half-lives).

One can measure the $^{13}\text{C}/^{12}\text{C}$ ratio and compare it to a standard. In the past, the standard was a type of carbonate rock, called Pee Dee Belemnite (PDB). When the supply of the standard rock was exhausted, it was replaced by a zero definition in a Vienna conference, therefore the new standard is called the VPDB (Vienna PDB). The carbon in anything which contains it can be measured for its $^{13}\text{C}/^{12}\text{C}$ ratio. The comparison with the standard is expressed as ‰ (per mil) $\delta^{13}\text{C}$: (variously pronounced “delta C 13” or “delta 13 C”):

$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \right) \times 1000 \text{ ‰}$$

$$\text{Where: } (^{13}\text{C}/^{12}\text{C})_{\text{standard}} = 0.0112372$$

Thus, positive values have more ^{13}C and negative values have less ^{13}C . Now, the interesting point is that vegetation growth in general uses by preference ^{12}C , thus if you measure $\delta^{13}\text{C}$ in vegetation, you will see that it has quite low $\delta^{13}\text{C}$ values. As almost all fossil fuels were formed from vegetation (including zooplankton and algae), these have low $\delta^{13}\text{C}$ values, too. Most other carbon sources (oceans, carbonate rock wearing, volcanic outgassing) have higher $\delta^{13}\text{C}$ values. The NOAA (ongoing) website gives a good overview of the different carbon isotopes.

So we can determine whether CO_2 levels in the atmosphere (which are currently below -8‰ VPDB) were mainly influenced by vegetation decay or fossil fuel burning (both about -24‰) towards the negative side, or by ocean degassing (0 to +1 ‰ in general, but with fractionation at the water-air border) towards the positive side.

At different CO_2 base stations, both CO_2 and $\delta^{13}\text{C}$ are measured. There is a clear decreasing trend in $\delta^{13}\text{C}$ values, which indicates an extra source of low $\delta^{13}\text{C}$ in the atmosphere shown in Figure 1.2.1.

The large seasonal variability is due to the huge CO_2 transfer between atmosphere and deciduous forests in spring/summer and reverse in fall/winter, mainly in the Northern Hemisphere (NH), which is about 40% land, compared to only about 20% in the Southern Hemisphere (SH). The uptake of CO_2 in spring/summer also gives a shift in $^{13}\text{C}/^{12}\text{C}$ ratio, because

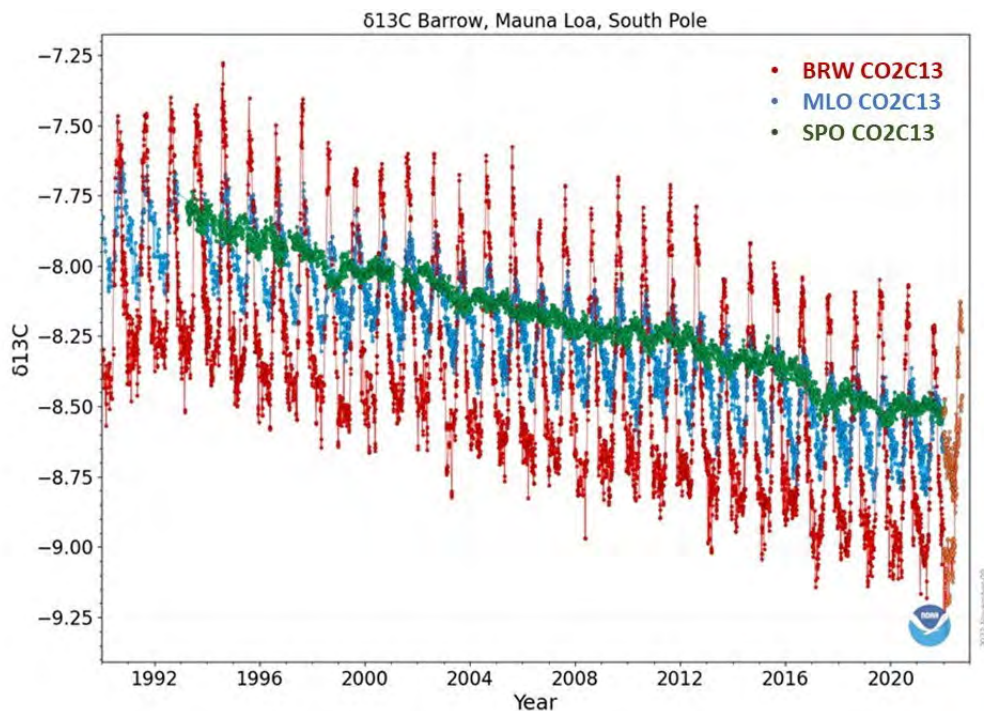


Figure 1.2.1: Trends in $\delta^{13}\text{C}$ from direct measurements of ambient air at three base stations. NOAA (ongoing) BRW=Barrow; MLO=Mauna Loa; SPO=South Pole.

of the preference of plants for $^{12}\text{CO}_2$ over $^{13}\text{CO}_2$. In fall/winter decaying leaves and other debris gives the opposite trends. In the Southern Hemisphere (SH), the amplitude is much smaller due to less land and more oceans.

The downward $\delta^{13}\text{C}$ trend in the SH lags the trend in the NH, which indicates that the source of low- $\delta^{13}\text{C}$ CO_2 is primarily in the northern hemisphere.

The question of whether the decrease is from vegetation decay (more present in the NH than in the SH) and/or from fossil-fuel burning (90% in the NH) is solved by the investigation of Battle et al. 2000, where it is shown that there is less oxygen used than can be calculated from fossil-fuel burning. Vegetation thus produces O_2 , by incorporating more CO_2 than is formed by decaying vegetation (which uses oxygen). This means that more ^{12}C is incorporated, and thus more ^{13}C is left behind in the atmosphere. As a result, vegetation is relatively depleting the atmosphere of ^{12}C , leaving relatively more ^{13}C behind and so not the cause of decreasing $^{13}\text{C}/^{12}\text{C}$ ratios.

There are several other, older measurements of $\delta^{13}\text{C}$ in the atmosphere, from ice core and firn. These align completely with the recent air measurements. There is a similar line of measurements from coralline sponges and sediments in the upper oceans. Coralline sponges grow in shallow waters and their skeleton is built from CO_2 in the upper ocean waters, without altering the $^{13}\text{C}/^{12}\text{C}$ ratio in seawater at the time of building. The combination of atmospheric/firn/ice and ocean measurements gives a nice history of $\delta^{13}\text{C}$ changes over the past 600 years (Figure 1.2.2).

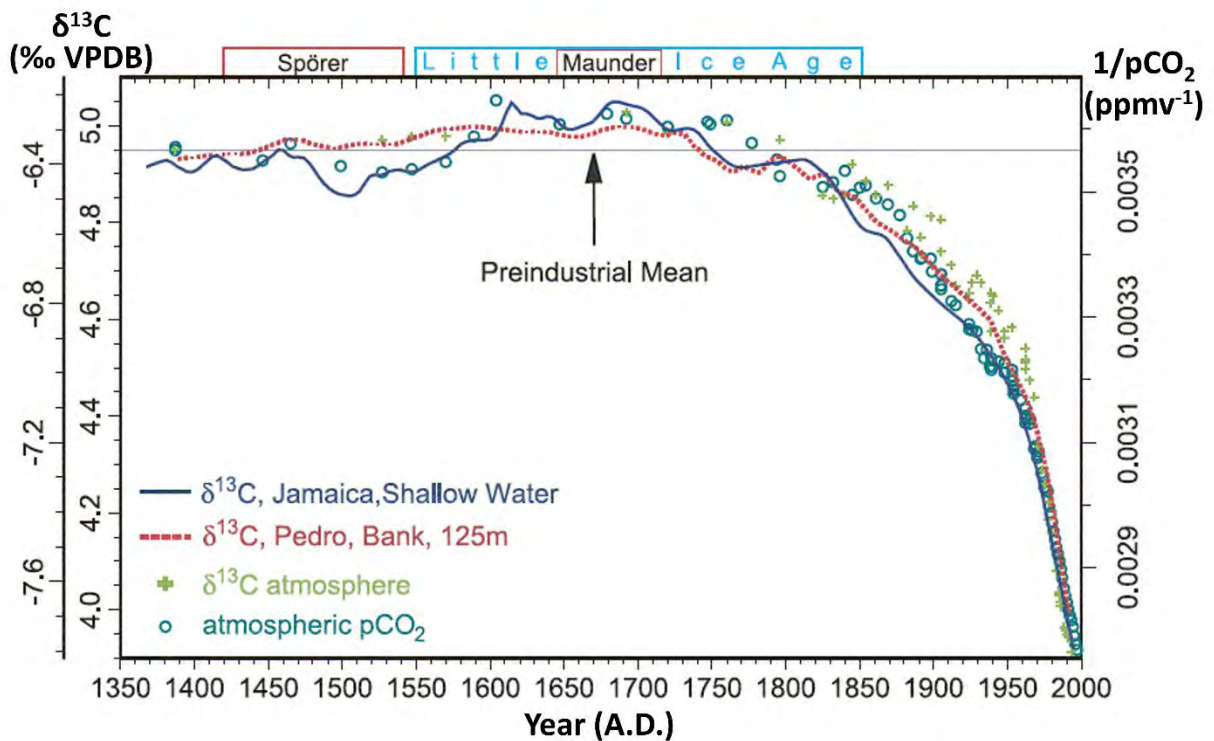


Figure 1.2.2: Böhm et al. (2002) gives a comparison of upper ocean water and atmospheric $\delta^{13}\text{C}$ changes.

We can see that the $\delta^{13}\text{C}$ levels in both the atmosphere and the upper oceans start to decrease from 1850 on, as the Industrial Revolution was getting fully underway. In the 400 years before, there was only a small variation, probably caused by the temperature drop in the Little Ice Age.

Longer term measurements of the $\delta^{13}\text{C}$ ratio in CO_2 from ice cores show that over the whole Holocene, prior to the industrial revolution, the variations were not more than $\pm 0.2\%$, as shown in Figure 1.2.3. Even the change from a glacial to an interglacial period did not give more than 0.2% $\delta^{13}\text{C}$ change. The largest variability was $\pm 0.4\%$ $\delta^{13}\text{C}$ around a small increase of about 0.2% . That points to the ocean CO_2 cycle as the dominant cycle, suppressing the large change in vegetation as more land was set free from ice covered to plant covered.

Over the whole Holocene there was a slight increase in $\delta^{13}\text{C}$, the attribution of which still is under investigation, but the variability in $\delta^{13}\text{C}$ in high-resolution ice cores was very small: $\pm 0.2\%$. That is visible in the atmosphere- and ocean-surface changes in Figure 1.2.2 over the last 600 years.

From about 1850 on, a very rapid drop occurs in $\delta^{13}\text{C}$, which is obviously from increasing fossil-fuel use. The trend is ongoing and accelerates with increasing use of fossil fuels.

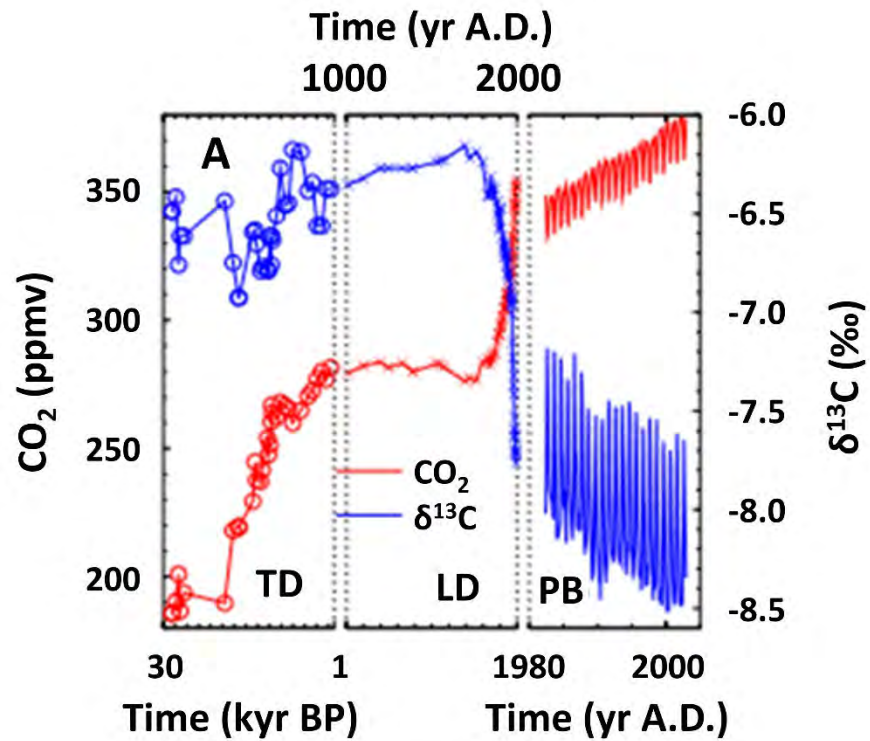


Figure 1.2.3: Köhler et al (2006): CO_2 and $\delta^{13}\text{C}$ as measured in ice cores and recently in the atmosphere over different time frames.

$^{13}\text{C}/^{12}\text{C}$ Conclusion

The strong decrease of the $^{13}\text{C}/^{12}\text{C}$ ratio in the atmosphere and ocean surface waters excludes any huge contribution of the (deep) oceans to the CO_2 increase in the atmosphere.

1.3 The $^{14}\text{C}/\text{C}$ Ratio

The carbon isotope ^{14}C (“radiocarbon”) is created in the atmosphere by the impact of cosmic rays. It is an unstable (radioactive) isotope and breaks down with a half-life time given as $5,730 \pm 40$ years (Godwin 1962) or $5,700 \pm 30$ years (Kutschera 2019). ^{14}C is used for radiocarbon dating of organic material up to a maximum age of about 60,000 years. The amount of ^{14}C in the atmosphere depends on the sun's activity, but despite that, it is considered a reasonable dating method (Oxford University date unknown).

The amounts of ^{14}C in the atmosphere and in vegetation are more or less in equilibrium, as is the case for ^{13}C , except for a slight depletion due to preferential uptake of ^{12}C by biological processes with a fast, seasonal cycle. About half of the ^{12}C returns to the atmosphere within a year by the decay of leaves and grasses. Most ^{12}C returns to the atmosphere within a few decades except for what resides in more permanent peat, lignite and coal.

$\Delta^{14}\text{C}$ is the fraction of atmospheric carbon which is (or was) in the form of the ^{14}C isotope, divided by a standard value for that fraction, and reported as ‰ (parts-per-thousand) relative to that standard (either positive or negative).

An additional complication is that two different “standard” (“Modern”) definitions are in use for $\Delta^{14}\text{C} = 0\text{‰}$, $^{14}\text{C}/\text{C} = 1.170\text{e-}12$ and $^{14}\text{C}/\text{C} = 1.176\text{e-}12$ (Orr 2017). Many authors unfortunately do not report which definition they’ve used.

For the oceans, the lag between ^{14}C sinking into the deep oceans (e.g., at the North Atlantic sink of the AMOC “conveyor belt”) and its release around the equator is 500–1,500 years, which causes a slight depletion of ^{14}C due to radioactive decay. E.g., after 1,000 years the carbon will have lost 11.45% of its ^{14}C , because $0.5^{(1000/5700)} = 88.55\%$.

In pre-industrial times, cosmogenic ^{14}C production and oceanic depletion were more or less in equilibrium.

When fossil fuels were formed—either from wood and peat for coal or plankton and organic sediments for oil and gas—they incorporated some ^{14}C , but as they are millions of years old, there is no measurable ^{14}C left anymore. Just as is the case for ^{13}C , the amount of CO_2 released from fossil-fuel burning dilutes the ^{14}C content of the atmosphere. This is called the “Suess Effect,” and it caused problems for radiocarbon dating from about 1890 on (Keeling 1979).

In the 1950's another human intervention caused complications for carbon dating: Above-ground nuclear-bomb testing released a lot of radiation, which nearly doubled the atmospheric ^{14}C content (i.e., $\Delta^{14}\text{C}$ reached nearly +1000 ‰). This is commonly called the ^{14}C “bomb spike” (Figure 1.3.1).

When the Limited Test Ban Treaty went into effect, in 1963, it prohibited atmospheric tests of nuclear weapons by the signatories (the U.S., USSR & U.K.), and the amount of ^{14}C in the

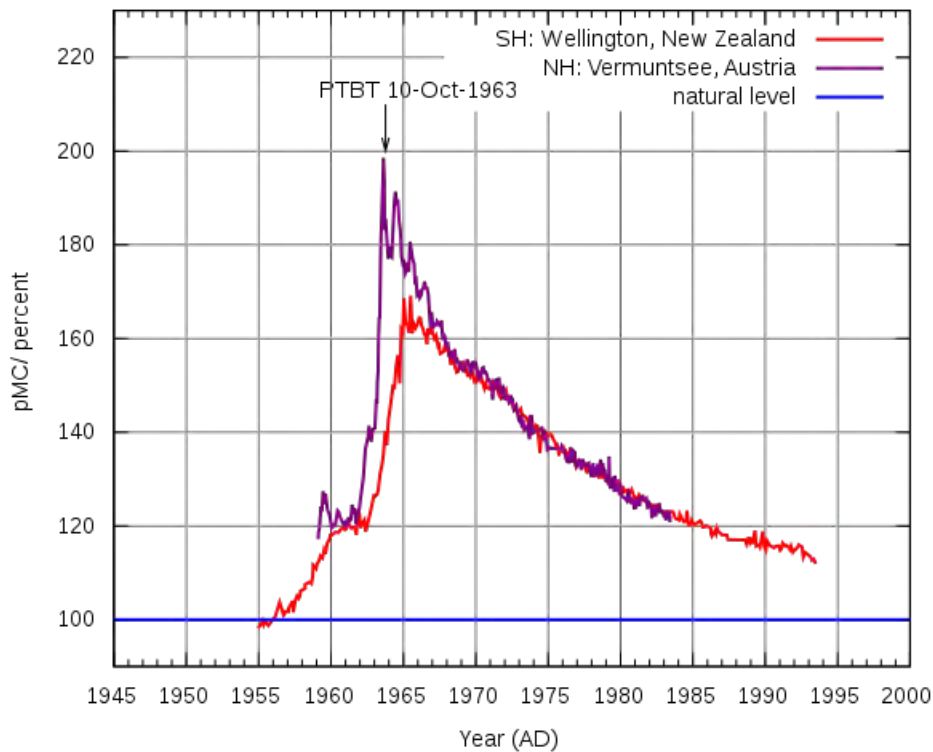


Figure 1.3.1: The ^{14}C spike from the atomic bomb tests in the NH resp. SH plotted by Wikipedia (2008). Data from Manning et al. (1994) and Levin et al. (1994).

atmosphere quickly declined as exchanges with the oceans and other carbon reservoirs replaced it with “normal” ^{14}C levels.

Additionally, the atmospheric CO_2 level was by then rising by nearly 1 ppmv/year due to additions of about 1.3 ppmv/yr from fossil fuel emissions, plus between 0.5 and 1.0 ppmv/yr from changes in land use, and less than 1 ppmv due to removals by natural carbon sinks. So Suess Effect dilution also lowered $\Delta^{14}\text{C}$.

As a result of the combined effects of those two processes, the $\Delta^{14}\text{C}$ bomb spike declined with a half-life of about 11 years. At first blush, that would appear to make the atmospheric lifetime $11/\ln(2) =$ about 16 years (Ubelaker & Buckholz 2005). However, the increase of CO_2 in the atmosphere from the burning of fossil fuels reduces $\Delta^{14}\text{C}$ without actually removing ^{14}C from the air, it only reduces the fraction of carbon which is in the form of ^{14}C . To calculate the actual average atmospheric lifetime of ^{14}C added to the atmosphere by the bomb spike, we need to consider, instead, what the $\Delta^{14}\text{C}$ decay rate would have been were it not for Suess Effect dilution from fossil-fuel use.

Graven (2020) conducted simulations with a simple carbon-cycle model, and reported a striking difference between the calculated $^{14}\text{CO}_2$ decay with and without fossil-fuel CO_2 supply, as shown in Figure 1.3.2 (their Figure 4).

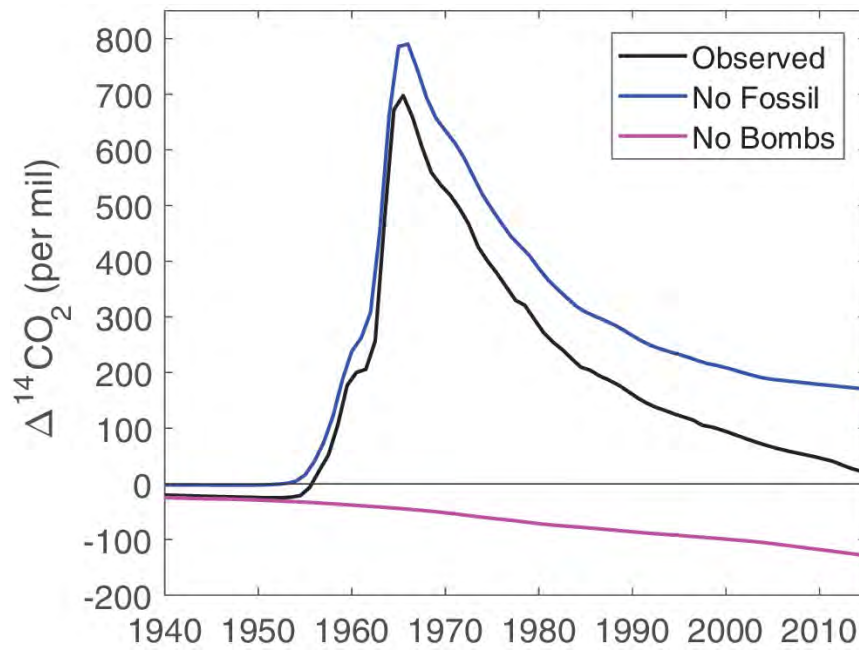


Figure 1.3.2: $^{14}\text{CO}_2$ decay as observed and as calculated if there was no human $^{14}\text{CO}_2$ -free fossil supply or if there was no bomb spike. From Graven (2020).

Dr. Graven graciously sent us their data, from which we constructed a log-linear plot, which is shown on Figure 1.3.3.

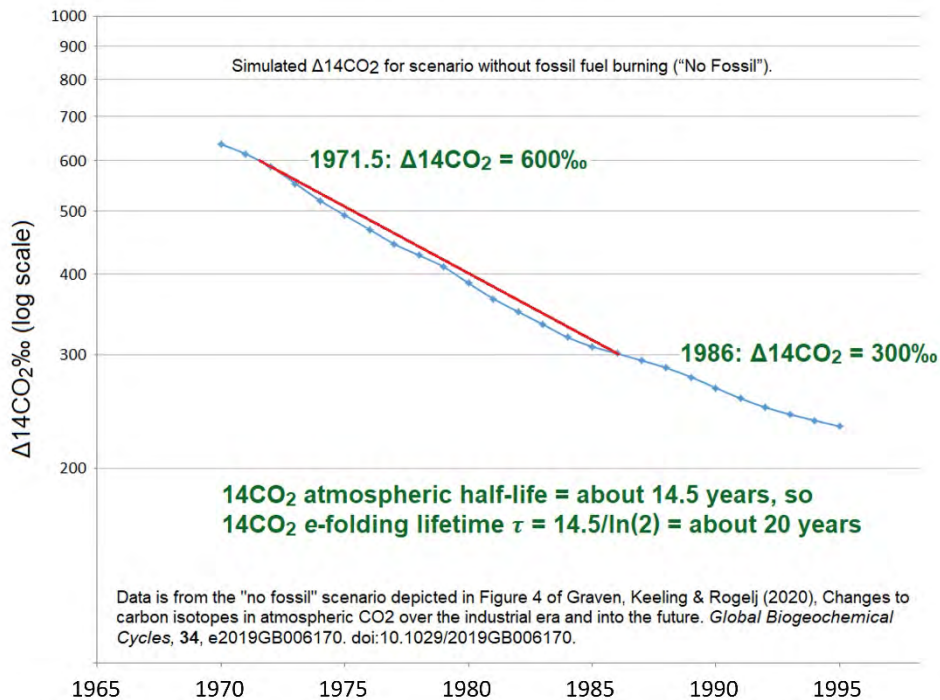


Figure 1.3.3: Log-linear plot of $^{14}\text{CO}_2$ decay without Suess Effect dilution from human fossil-carbon emissions, used to estimate bomb-spike radiocarbon lifetime. From simulation data provided by Graven (2020).

Based on their simulation, without Suess Effect dilution from fossil carbon emissions, the $\Delta^{14}\text{C}$ decay rate half-life would have been about 14.5 years, making the atmospheric lifetime of ^{14}C bomb spike radiocarbon $14.5/\ln(2) =$ about 20 years.

Note: Only the left side of the Fig. 1.3.3 log-linear plot is used for this purpose, because that is the part where most of the bomb-spike decay is due to transport of ^{14}C radiocarbon into other carbon reservoirs; which is what we're interested in quantifying. From 1970 to 1995 the transport of ^{14}C from the air to other carbon reservoirs slowed as the level of ^{14}C in the atmosphere fell, and simultaneously, fossil fuel emissions increased by 57%. So the right side of the plot is much more affected by carbon-cycle modeling and Suess Effect dilution than is the left side. The noticeable flattening of the right side of the simulated log-linear-decay plot is probably because Bern and similar models overestimate saturation of CO_2 sinks. Such saturation is realistic for the ocean-surface layer, but not for vegetation in the foreseeable future and not for the deep oceans.

Over the sixty years since the Partial Test Ban Treaty, most of the bomb spike ^{14}C has been removed from the atmosphere, and in recent years $\Delta^{14}\text{C}$ has turned negative, meaning that the ^{14}C level has fallen below the "Modern" historical ^{14}C levels, due to Suess Effect dilution from fossil carbon emissions. See Graven (2015).

The measurement-derived "adjustment time" (effective atmospheric lifetime) of CO_2 emissions is about 50 years (Spencer 2023, Engelbeen 2023, Burton 2024). The relatively short half-life of excess "bomb spike" $^{14}\text{CO}_2$ in the atmosphere is sometimes cited as evidence that the 50-year adjustment time can't be true. That is incorrect because the bomb spike decay is due, not only to removal of CO_2 from the atmosphere, but also due to exchanges of CO_2 between the atmosphere and other reservoirs (terrestrial biosphere, soil, and oceans). Those exchanges contribute to the fall of the bomb-spike radiocarbon level in the atmosphere without reducing the total amount of CO_2 in the atmosphere.

Additionally, in the case of exchanges with the ocean, the CO_2 returned to the atmosphere is, on average, considerably older than the CO_2 which enters the ocean from the atmosphere because of the approximately 1,000-year AMOC ("ocean conveyor") cycle time. After 1,000 years, about 11.45% of the radiocarbon will have decayed back into nitrogen.

$^{14}\text{C}/\text{C}$ Conclusion

The decrease of the $^{14}\text{C}/\text{C}$ ratio in the atmosphere supports the fact that fossil fuels are the cause of the CO_2 increase in the atmosphere.

1.4 The Oxygen Use

In order to burn fossil fuels, you need oxygen. As for every type of fuel the ratio of oxygen use to fuel use is known, so it is possible to calculate the total amount of oxygen that is used by burning fossil fuels.

On the other hand, the real amount of oxygen that was used can be measured in the atmosphere. This is quite a challenging problem, as the change in atmospheric O_2 from year to year is quite low, compared to the total amount of O_2 (a few ppmv in over 200,000 ppmv). Moreover, for oxygen as for CO_2 , there is the seasonal to year-by-year influence of vegetation growth and decay. The oxygen decrease and CO_2 increase are shown together in Figure 1.4.1 for two monitoring stations in different hemispheres.

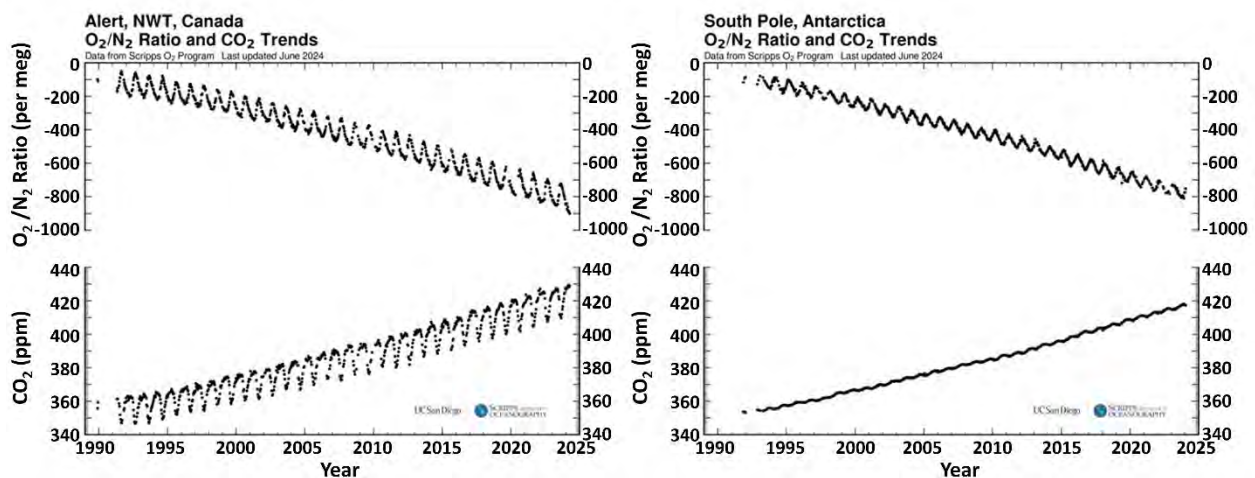


Figure 1.4.1: *Oxygen and CO_2 measurements at Alert and the South Pole, Scripps (ongoing). The difference in seasonal amplitude between the NH and SH stations is from the different ratio of land vegetation vs. ocean surface in each hemisphere.*

Only since the 1990s have oxygen measurements with sufficient resolution been available. These revealed that there was less oxygen used than was calculated from fossil fuel use. This points to vegetation growth as source of extra O_2 , thus vegetation is a sink of CO_2 , at least since 1990. The combination of O_2 and $\delta^{13}C$ measurements allowed Battle et al. (2000) to calculate how much CO_2 was absorbed by vegetation and how much by the oceans. That work was later extended by Bender et al. (2002).

The most visible consequence of increased CO_2 uptake by the terrestrial biosphere is “greening” of the Earth, which is measurable from satellites. (Zhu 2016, Piao 2020, Chen 2024.)

The trends of O_2 and CO_2 in the period 1990–2000 can be plotted in a nice diagram shown in Figure 1.4.2.

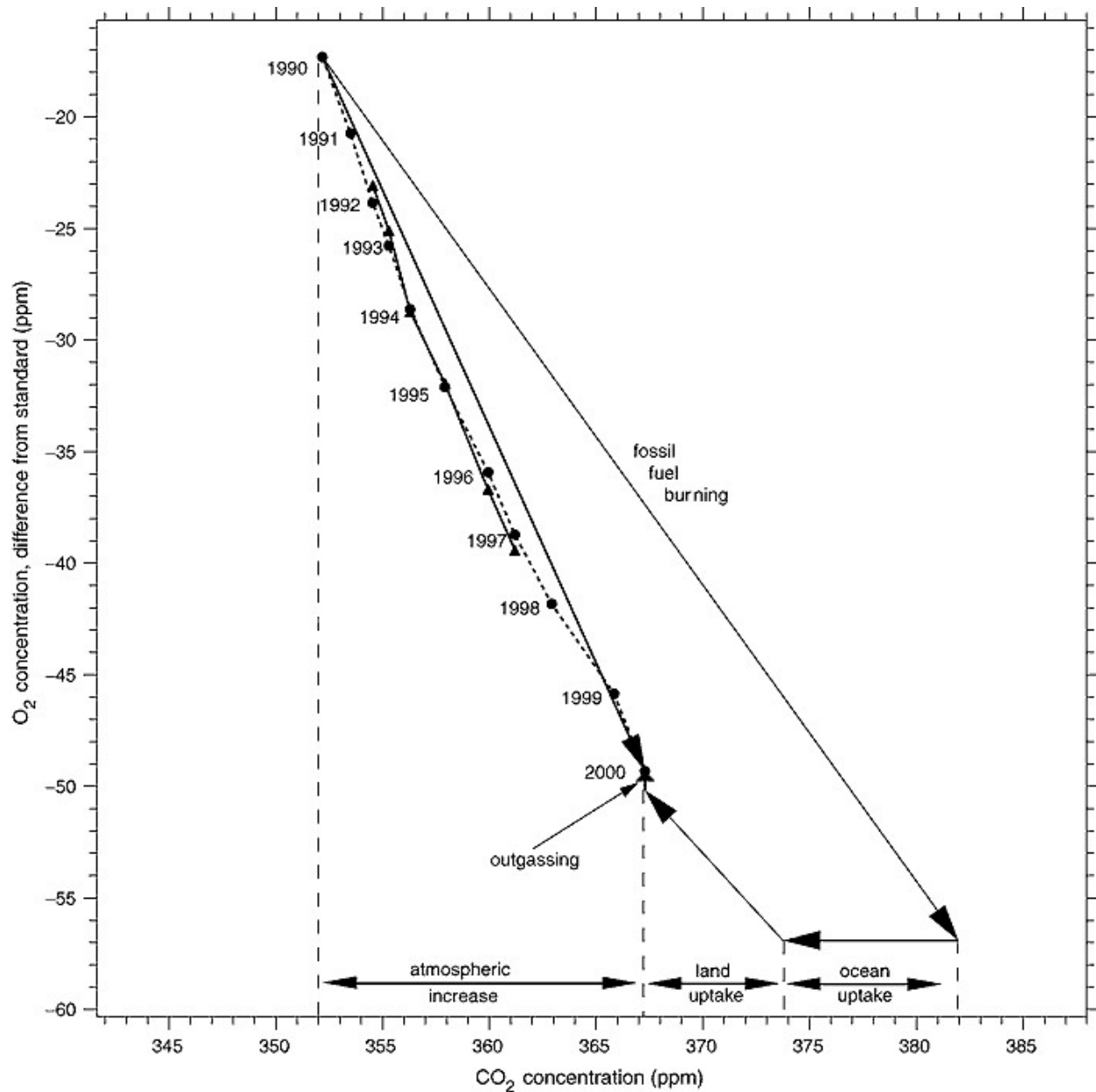


Figure 1.4.2: *O₂-CO₂ trends 1990–2000, figure from the IPCC TAR (2003).*

The main O₂ reduction in the atmosphere is from fossil fuel burning, but as less oxygen is used as calculated, vegetation is a net source of O₂ and thus a net sink for CO₂. O₂ is released by plants when they absorb CO₂, in exact 1:1 ratio to each other, and the reverse is the case when plants decay or are eaten by insects or animals.

Both the oceans and vegetation, which are the fastest and largest sinks and sources, show a net uptake. Other sources are much slower and/or smaller (such as rock weathering and volcanic outgassing).

Oxygen Conclusions

The production of extra O₂ in the atmosphere excludes a net contribution from the whole biosphere to the CO₂ increase in the atmosphere.

As both oceans and vegetation are net sinks for CO₂ and other sinks/sources (carbonate rock weathering, volcanic eruptions and vents) are much slower and/or smaller, this also means that nature as a whole is a net sink for CO₂, and thus cannot be a net source.

1.5 The Ocean's pH and pCO₂

Introduction

Since 1958, when accurate CO₂ measurements at Mauna Loa began, the amount of CO₂ in the atmosphere has been increasing at a rate that is only about 50–55% of the rate CO₂ is being emitted from the combustion of fossil fuels. All human emissions go straight into the atmosphere, so that means an amount of CO₂ equivalent to at least 45% of fossil fuel emissions is being removed from the atmosphere by natural “carbon sinks,” the main ones being vegetation (see chapter 1.4) and the oceans.

When CO₂ is absorbed by the oceans, this is partially in solution in its original form as dissolved CO₂ gas and as undissociated acid (H₂CO₃, both together only 1%), but most of it dissociates to form bicarbonates (90%) and carbonates (9%).

As a result, since the start of the Industrial Revolution, the average pH of the ocean surface has probably decreased by about 0.1 pH unit. An interesting Q&A can be found at the Woods Hole Oceanic Institution (WHOI unknown year).

Aside: The pH decrease is mostly confined to the surface layer, which is thereby made slightly less alkaline. However, the oceans remain alkaline everywhere, rather than acidic, and the surface layer is the most alkaline part. Moreover, pH differences with changes in depth over time, and even between ocean basins, dwarf the 0.1 pH unit reduction in surface-layer alkalinity.

The Ocean Surveys

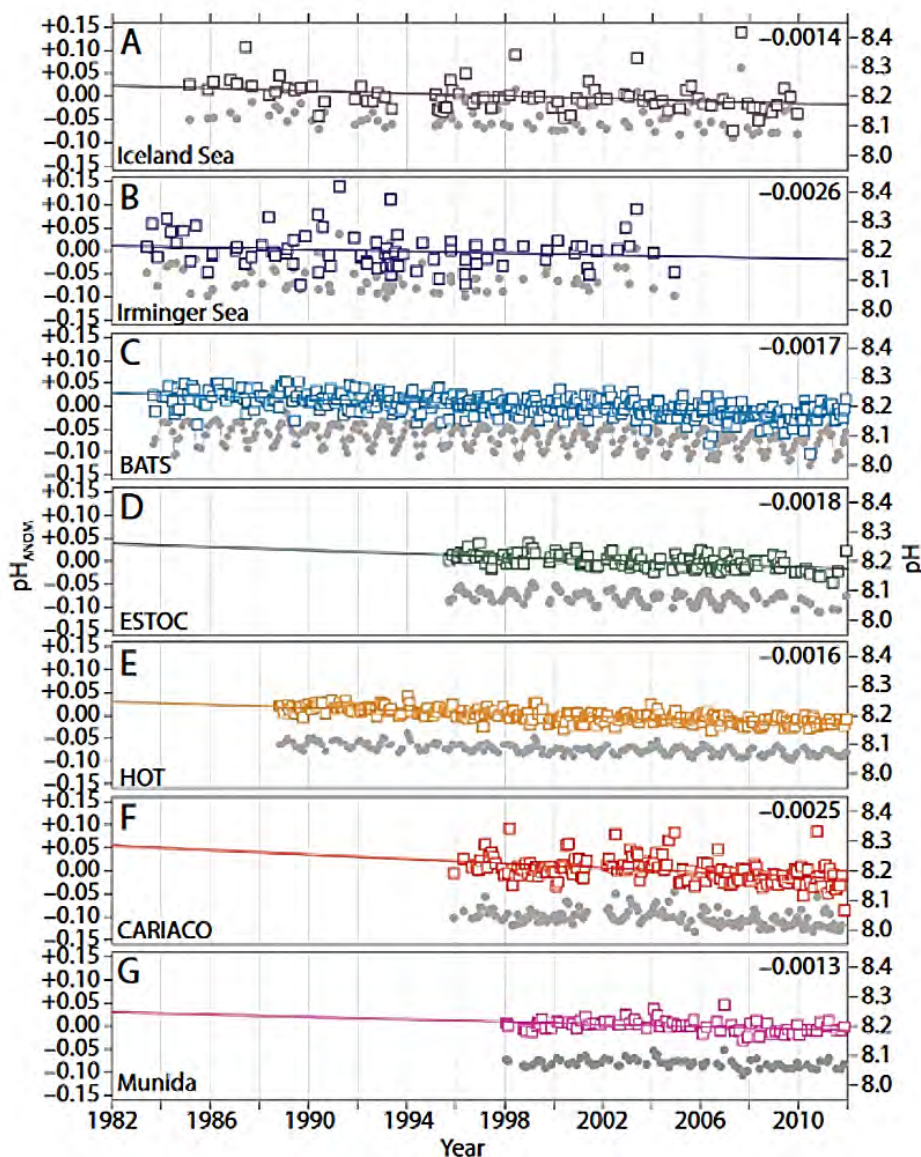
Over the years, many surveys have been conducted over the oceans, but quite sporadically. Also, over the last few decades, several fixed monitoring stations have been established that regularly take ocean water samples, and perform analyses of pH, pCO₂ and other variables.

***Note:** The pCO₂ of the ocean waters is the measured partial CO₂ pressure in the atmosphere above a seawater sample after equilibrium between water and atmosphere is reached. Expressed in μatm in air “as is”, thus including water vapor. Values are within a few percent of ppmv, which is similar, but expressed in dry air.*

The results of the pH change at these stations over the past decades are shown in Figure 1.5.1.

The Direction of CO₂ Transfer Between Oceans and Atmosphere

The ocean's pH can be impacted in another way. If the pH is reduced (e.g. by an undersea volcanic event with lots of SO₂), this leads to an important increase of pCO₂ (oceans), which may release a lot of oceanic CO₂ into the atmosphere.



Time series of surface seawater anomalies of pH (colored symbols) and observed pH (gray symbols; no units), with trends (yr^{-1}) reported in Table 2 shown in top right-hand corner of each panel. Seawater CO_2 -carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site.

Figure 1.5.1: *pH changes of the ocean surface waters at different monitoring stations over time (Bates et al. 2014).*

However, that is in contradiction with the observed change in ^{13}C . If CO_2 from the deep oceans were released to the surface and into the atmosphere, the $^{13}\text{C}/^{12}\text{C}$ ratio of both the upper oceans and the atmosphere should increase. However, we see the reverse trend happening. Moreover, the release of more CO_2 from the upper oceans due to a lower pH would reduce the total amount of carbon (DIC: dissolved inorganic carbon, that is CO_2 + bicarbonates + carbonates) in the ocean's surface layer. But we see the reverse trend as DIC is increasing over time. Thus, the increase of atmospheric CO_2 is going into the oceans, not reverse.

Figure 1.5.2 shows the dissolved inorganic carbon (DIC) trends at the same monitoring stations as for the pH measurements.

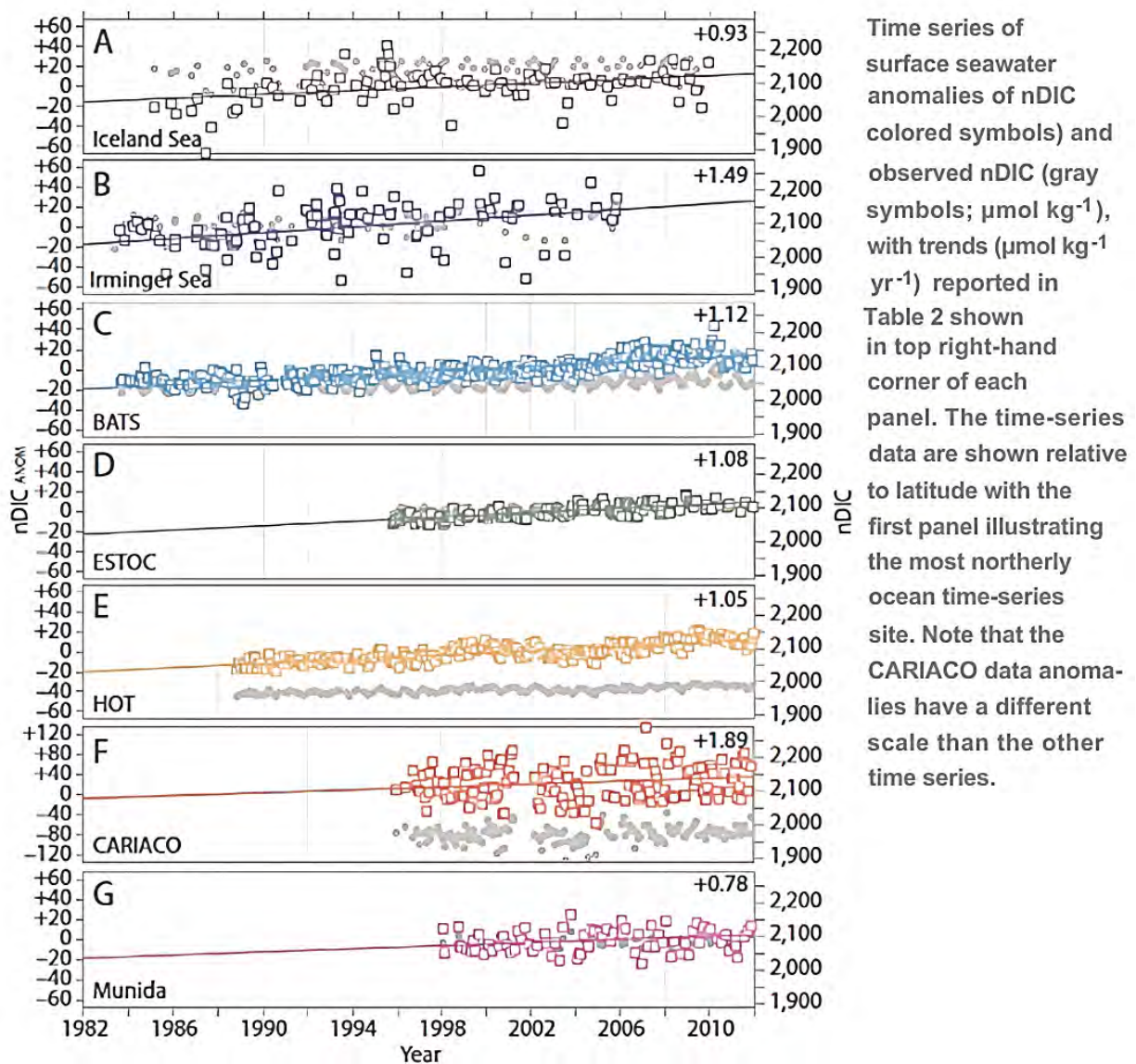
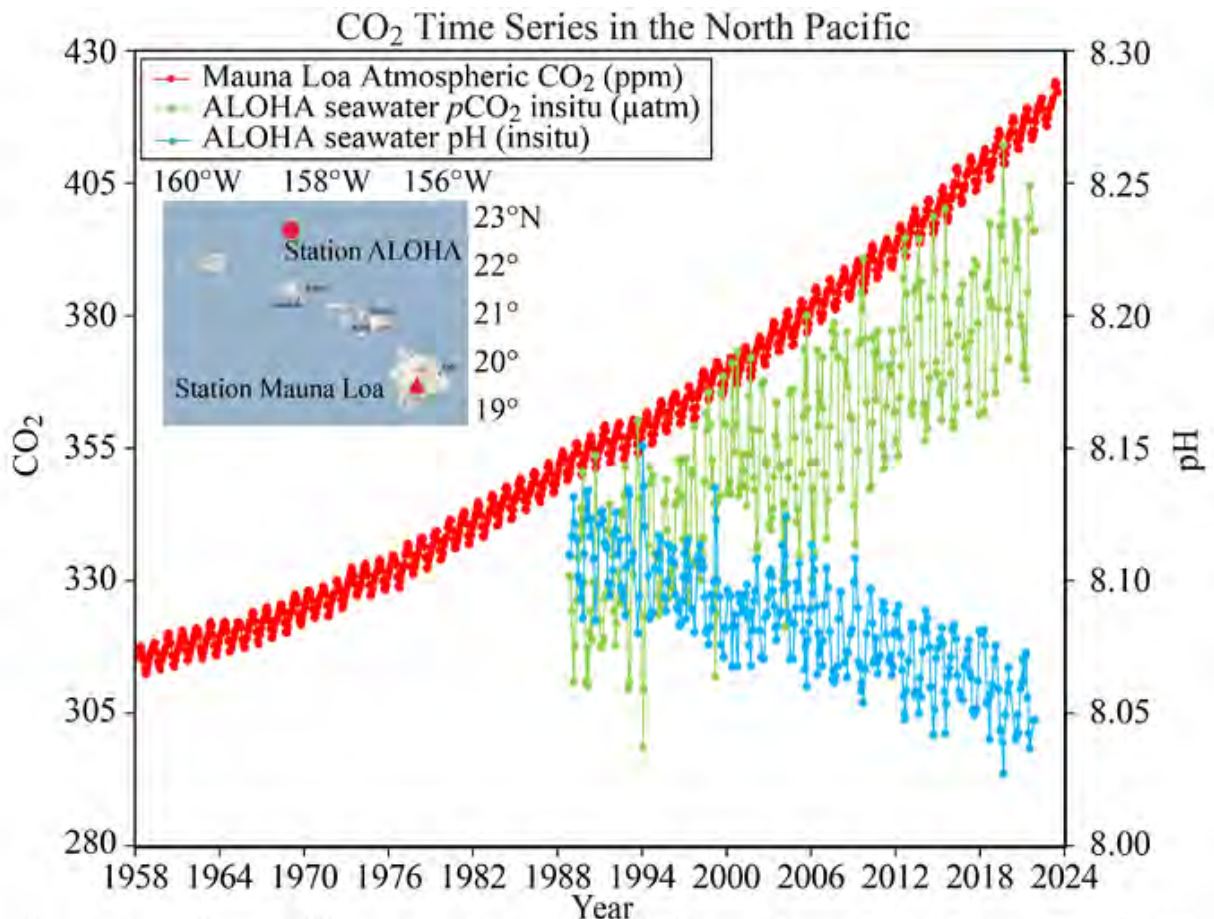


Figure 1.5.2: DIC (dissolved inorganic carbon) changes of the ocean surface waters at different monitoring stations over time (Bates et al. 2014).

Further, another part of the oceanic survey compares the $p\text{CO}_2$ of the atmosphere with that of the oceans at different latitudes in different oceans. This shows that there are huge differences in oceanic $p\text{CO}_2$ at different latitudes due to changes in temperature and DIC. This gives a continuous release of CO_2 in the tropics ($p\text{CO}_2$ of maximum $750 \mu\text{atm}$ in the upper oceans vs. about $410 \mu\text{atm}$ for the atmosphere) and a continuous sink of CO_2 in the polar oceans, especially in the North-East Atlantic (minimum $150 \mu\text{atm}$ vs. $410 \mu\text{atm}$), see Feely (2001). That gives a continuous CO_2 flux of about 40 PgC/year between the tropics and the poles through the atmosphere, where the polar waters with extra CO_2 sink and return some 1,000 years later near the equator.

The oceans at mid-latitudes are seasonal emitters/absorbers of CO₂, depending on the water temperature and sea life (plankton). The average yearly global difference of pCO₂ (atmosphere) minus pCO₂ (oceans) is about 7 ppmv. That means that on average more CO₂ is going from the atmosphere into the oceans than reverse (Feely 2001). Moreover, different surveys over time revealed that ocean parts which were net sources of CO₂ gradually changed into net absorbers.

For the HOT (Hawaii Ocean Time-series) station, the pCO₂ level of the ocean surface gradually increased over time in parallel with and slightly lower than the pCO₂ of the atmosphere shown in Figure 1.5.3. The increase in pCO₂ of the ocean results in a simultaneous decline in the pH of the ocean.



Data: Mauna Loa (https://gml.noaa.gov/webdata/ccgg/trends/co2/co2_mm_mlo.txt) ALOHA (https://hahana.soest.hawaii.edu/hot/notco2/HOT_surface_CO2.txt) ALOHA pH & pCO₂ are calculated at in-situ temperature from DIC & TA (measured from samples collected on Hawaii Ocean Times-series (HOT) cruises) using co2sys (Pelletier, v25b06) with constants: Lueker et al. 2000, KSO4: Dickson, Total boron: Lee et al. 2010, & KF: seacarb

Figure 1.5.3: pCO₂ levels from the atmosphere (Mauna Loa) and oceans at Hawaii (HOT) compared to the pH at the same place. NOAA PMEL data program (unknown).

Although the ocean pCO₂ data are scattered in time and location, the trends over the past 30 years are clear. They show that the average (increasing) flow of CO₂ is from the atmosphere into the oceans and not reverse.

Ocean pH and pCO₂ Conclusions

The increasing pCO₂ in the oceans and the accompanying slight reduction of ocean alkalinity indicates that the oceans are a CO₂ sink. Therefore, the oceans are not a source for the modern increase of CO₂ in the atmosphere.

This adds to the overall evidence that human emissions are the main cause of the increase of CO₂ in the atmosphere.

1.6 The Process Characteristics

Introduction

Each process, be it in chemistry, biology or any other kind of process, has its own characteristics. In the case of the modern CO₂ increase, the typical part is that there is a quite monotonic, slightly quadratic increase of CO₂ in the atmosphere at a near constant rate of 50–55% of human emissions. That is a unique characteristic, as many natural processes are rather chaotic.

The Trends of CO₂ Emissions and Increase in the Atmosphere Compared

Figure 1.6.1 is a graph of the global temperature trend, the summed human CO₂ emissions, and the calculated increase of CO₂ in the atmosphere (1960–2020) due to warming of the ocean surface.

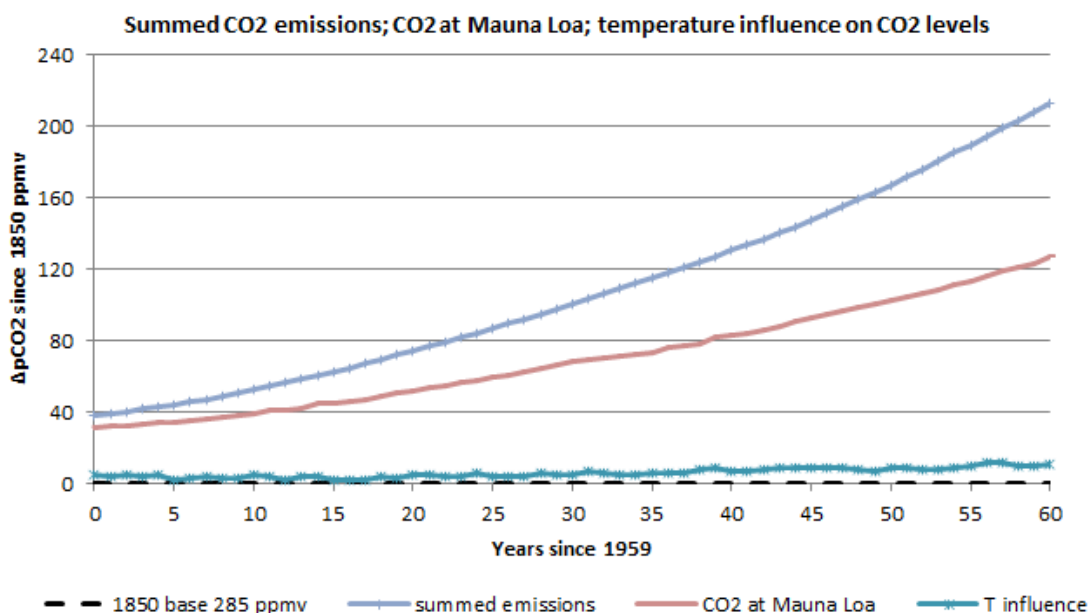


Figure 1.6.1: Evolution of summed human CO₂ emissions from fossil fuels, without and with land-use changes (LUC), increase in the atmosphere, and theoretical increase of CO₂ due to the increased ocean-surface temperature since 1850, at the main start of the industrial revolution. Data from the Global Carbon Project (GCP ongoing), Mauna Loa (NOAA ongoing) CO₂ increase above 1850 level and calculated ocean-surface-temperature influence on CO₂ levels (Takahashi 2000).

The temperature influence is based on the yearly averaged global (sea + land) temperature according to the Hadley Center in the U.K. (WoodForTrees plot ongoing), and the formula of Takahashi (Takahashi 1993) that calculates the influence of temperature on the increase/decrease of the ocean surface pCO₂. The baseline of the CO₂ level is taken as 285 ppmv (since 1850—at the start of the Industrial revolution).

As one can calculate, the correlation between temperature and CO₂ levels in the atmosphere is fair (corr.: 0.881; R²: 0.776), as shown in Figure 1.6.2. However, from the detailed T/CO₂ graph, a large temperature change in a certain year has little influence on CO₂ levels. If temperature were responsible for the CO₂ change over the whole period, the influence would be much larger, but that violates Henry's law for the solubility of CO₂ in seawater with temperature. Henry's law states that increased CO₂ partial pressure (pCO₂) in the atmosphere above the equilibrium pCO₂ of the ocean water causes more CO₂ to be absorbed in the ocean.

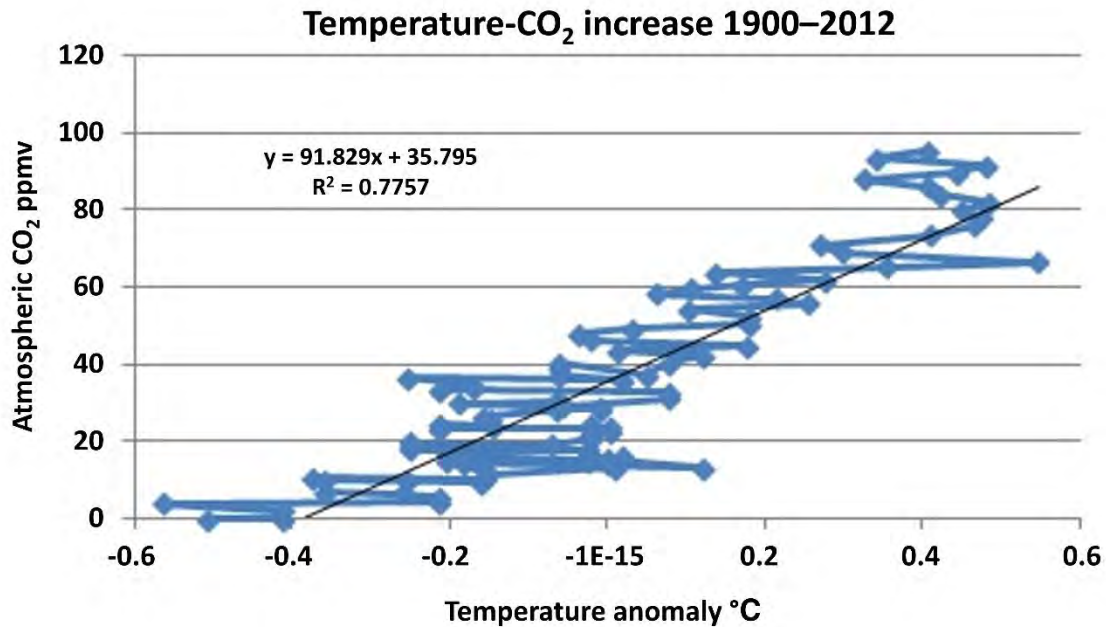


Figure 1.6.2: Comparison of temperature variability with the increase of CO₂ in the atmosphere. Data from HadCRUT4.0 via WoodForTrees (WFT ongoing), for atmospheric CO₂ from ice cores (Law Dome, NOAA ice ongoing) and from 1958 on of Mauna Loa (NOAA CO₂ ongoing).

This indicates that temperature is not the main cause of the overall increase, but only the cause of the variability (± 1.2 ppmv) around the total increase of over 100 ppmv since the measurements at Mauna Loa and other stations started.

Conversely, the correlation between summed CO₂ emissions and increase in the atmosphere is a near-fit (corr.: 0.999; R²: 0.998) over the whole period since 1900 shown, as shown in Figure 1.6.3.

The reason for that strong correlation is that human CO₂ emissions have steadily accelerated over the last 66 years, and that acceleration has more than kept pace with accelerating natural removals of CO₂.

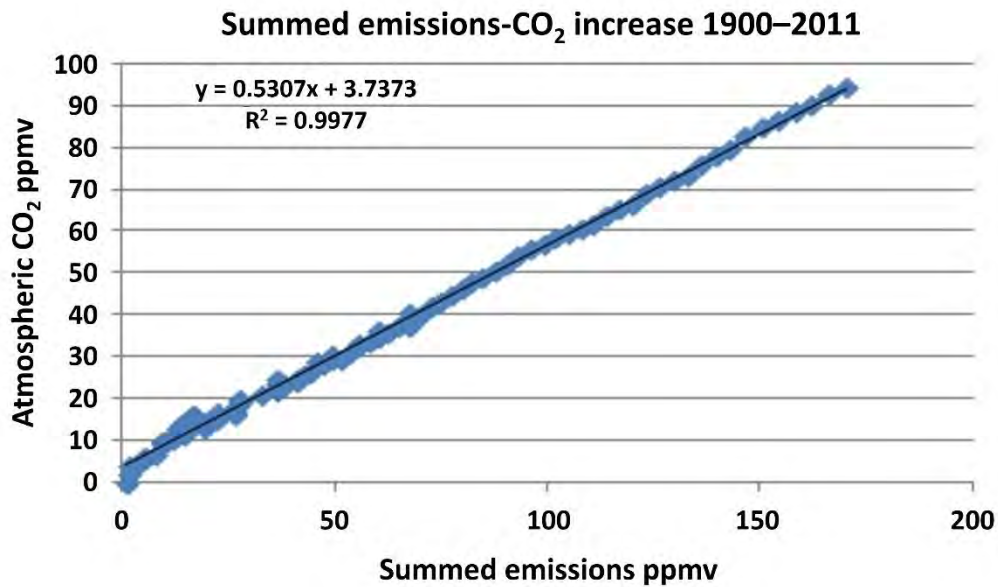


Figure 1.6.3: *Summed human CO₂ emissions, including land-use-changes human CO₂ emissions compared to the CO₂ increase in the atmosphere. Data for CO₂ emissions are from the Global Carbon Project (GCP, ongoing), for atmospheric CO₂ from ice cores (Law Dome NOAA ice ongoing) and from 1958 on of Mauna Loa (NOAA CO₂ ongoing).*

Although human emissions are the cause of the increase in atmospheric CO₂, that doesn't mean that all the original CO₂ molecules from human emissions are still in the atmosphere! In addition to the natural sinks which remove CO₂ from the air, continual exchanges of carbon between the atmosphere and other carbon reservoirs mean that the great majority of the original CO₂ molecules emitted by our factories and power plants are no longer in the air.

Net natural CO₂ sinks (mostly the oceans and terrestrial biosphere) accelerate by +1 ppmv/year for each approximately 40 to 50 ppmv increase in atmospheric CO₂. Human CO₂ emissions are currently outpacing natural CO₂ removals by about 2.5 ppmv/year. So if human CO₂ emissions were to plateau at the current rate, then the atmospheric CO₂ concentration could rise by only about $2.5 \times (40 \text{ to } 50) = 100 \text{ to } 125$ ppmv, before it, too, would plateau.

However, human CO₂ emissions have continued to accelerate, so the atmospheric CO₂ concentration has likewise continued to rise, causing the observed correlation.

This points to a simple linear first order process, in direct ratio to the partial pressure (pCO₂) difference between CO₂ in the atmosphere and the pCO₂ in the oceans (and vegetation). The higher the CO₂ content/pressure in the atmosphere, the higher the push to drive CO₂ into the oceans and vegetation. Currently, the average partial pressure difference between the atmosphere and the oceans is about 7 ppmv (Feely et al, 2001), based on ships' surveys and buoys. The increase of the pCO₂ difference causes more and more uptake of CO₂ by the oceans (and similarly in vegetation).

Again, this clear relationship points to a direct influence of the emissions on the increase in the atmosphere. As emissions accelerate, so the “plateau level” at which natural removals would balance those emissions must rise, and the atmospheric level will continue to rise as long as it remains below that rising plateau level. Thus the steadily rising CO₂ level is consistent with steadily rising emissions being the dominant cause, and inconsistent with the variability of the temperature curve, which has a limited short-term influence on CO₂ levels of 3–4 ppmv/°C and only a small influence on the equilibrium CO₂ level between ocean surface and atmosphere.

The Influence of Temperature on CO₂ Levels

Temperature and CO₂ levels are tightly coupled over very long periods, as can be seen in ice cores. There is a quite constant ratio between the temperature proxies (δD and $\delta^{18}O$) and the CO₂ level over the 420,000-years Vostok period, recently confirmed by the 800,000-years record of the Dome C ice core shown in Figure 1.6.4.

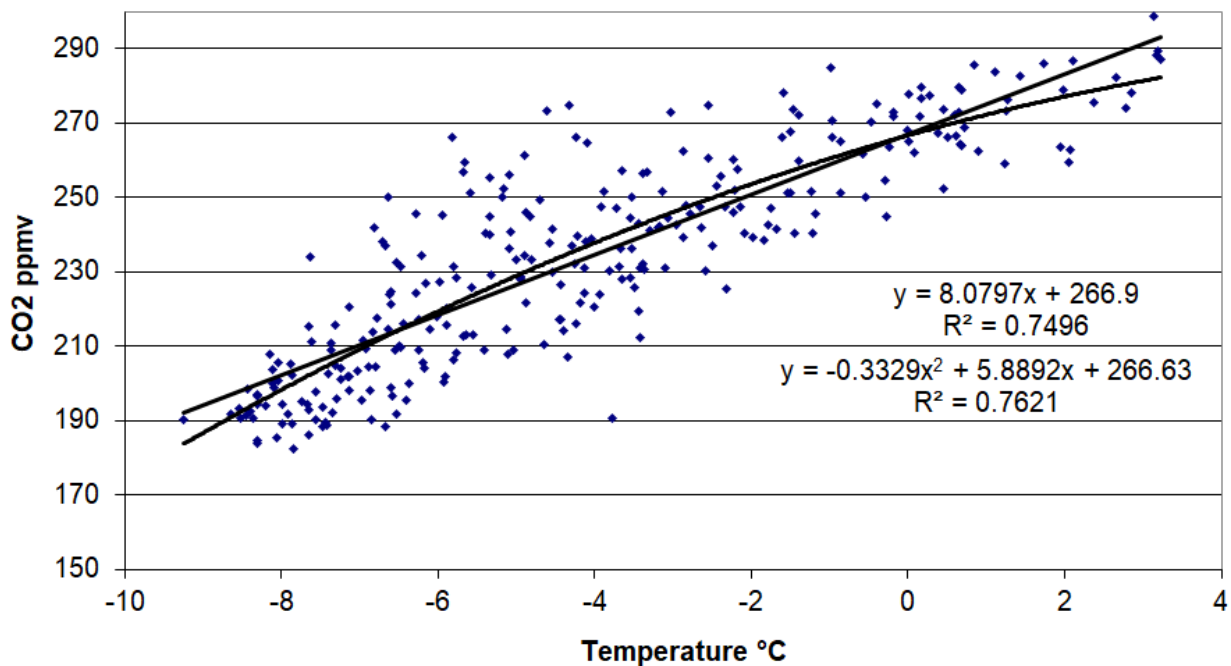


Figure 1.6.4: Vostok ice core ratio between CO₂ levels and calculated temperature from the $\delta^{18}O$ proxy (NOAA ice ongoing).

In general, the Antarctic ice cores show CO₂ trends and temperature-proxy trends well correlated over glaciation cycles, but with CO₂ trend reversals usually lagging temperature-trend reversals. That means the correlation we see in those records is due to temperature’s effects on CO₂ levels, not vice-versa. Most of the deviations in the Figure 1.6.4 plot are from the CO₂ lag after a temperature change, which is much larger during a cooling period than during a warming period. That gives the deviations at the high side of the trend lines. There was no compensation for the lags in the above plot.

The temperature proxies of Vostok and other inland ice cores are measured in ice: the heavier isotopes are increasing in ratio to the lighter isotopes with higher seawater temperatures at the area of water evaporation and (mainly) by the temperatures in the atmosphere where the snow is formed. As for many ice cores the latter is in Antarctica where “polar amplification” plays a role. When the global temperature increases, that hardly influences tropical temperatures. However, at the poles the temperature increases about twice as fast as global, thus the above 8 ppmv/K is about 16 ppmv/°C for global changes.

In any case, there is a clear relationship between temperature and CO₂ levels, where CO₂ lags about 800 years with ±600 years of uncertainty during a deglaciation. The lag is several thousands of years during a temperature decrease towards a new glaciation.

The same ratio can be seen in the medium resolution (~20 years averaging) Law Dome DSS ice core shown in Figure 1.6.5.

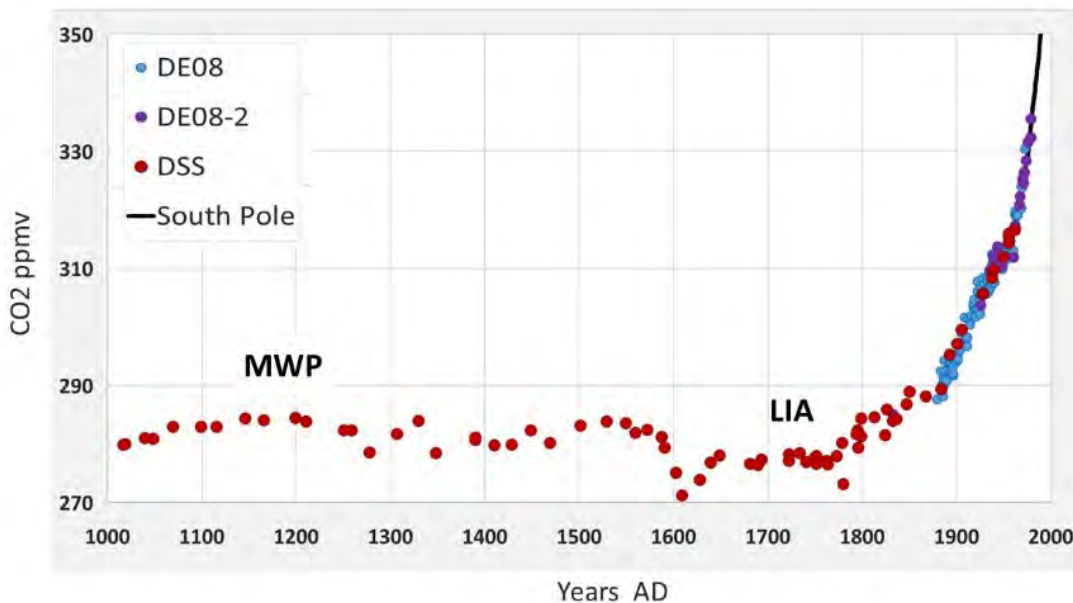


Figure 1.6.5: CO₂ from Law Dome DSS core 1,000 years, DE08 and DE08-2 cores over 150 years (Etheridge et al. 1996). There is a 20-year overlap (1958–1978) between the ice cores CO₂ and direct measurements at the South Pole.

If we assume the temperature difference between the MWP (Medieval Warm Period) around 1200 AD and the LIA (Little Ice Age) was about 0.8 °C (Moberg, Esper and several others); and the drop of CO₂ was 10 ppmv with a lag of ~50 years, then we are around 12.5 ppmv/°C for the CO₂-temperature ratio. That’s not far off of the 16 ppmv/°C for the very long-term changes over glacial/interglacial periods during much longer time frames.

During shorter periods there is a direct influence of a temperature-rate-of-change variability (mostly due to ENSO) on the CO₂-rate-of-change variability shown in Figure 1.6.6.

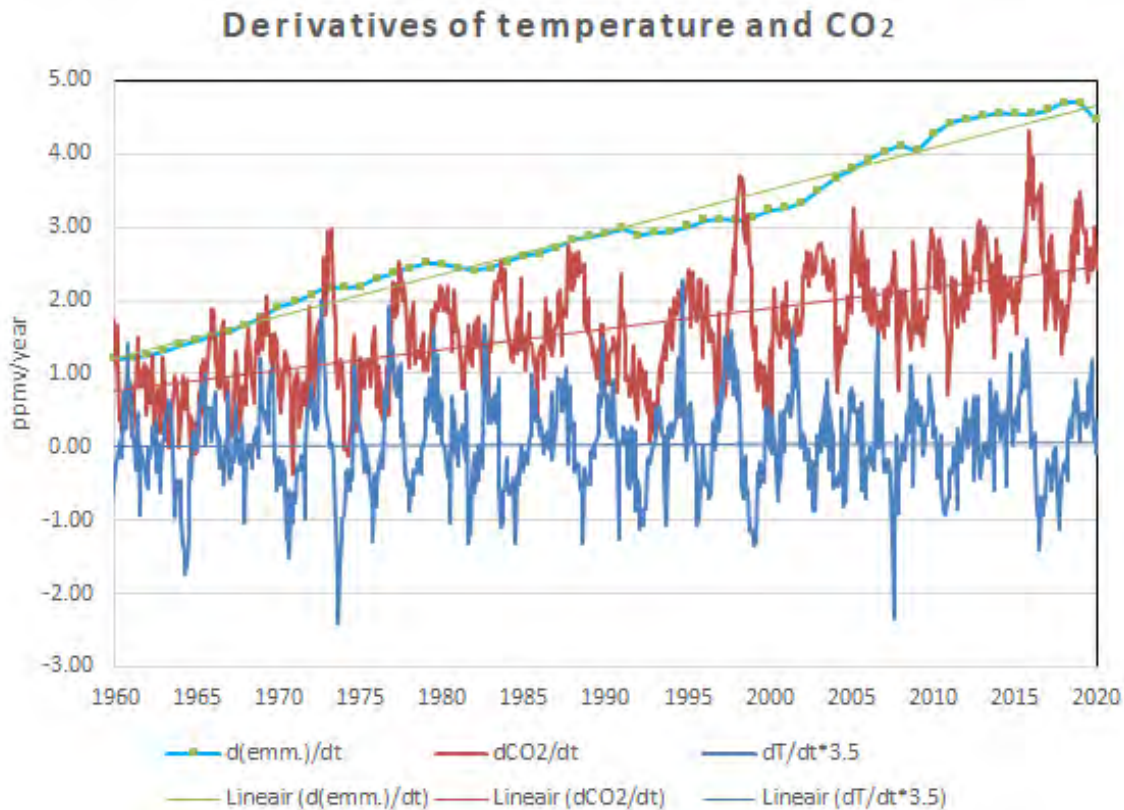


Figure 1.6.6: Twelve-month-moving-average temperature changes (HadCRUT4gl) scaled by a factor 3.5 and CO₂ changes in the atmosphere (Mauna Loa) both plotted by Wood for Trees tool (WFT, ongoing) plotted against fossil emissions (Global Caron Project, ongoing) since 1958.

A scaling factor of 3.5 for the temperature plot is used to make the amplitudes of the temperature and CO₂ rate of change similar. That means there is a 3.5 ppmv/°C ratio between short term (1–3 years) year-by-year temperature changes and year-by-year CO₂ changes with a small (about 6 months) CO₂ lag.

The fact that there is no trend in the derivative of the temperature, while there is a trend in the CO₂ rate of change shows that temperature is not the main cause of the increase. This is because the temperature increased more or less linearly, while both the CO₂ emissions and the CO₂ increase in the atmosphere are accelerating. The increase in the atmosphere pushes more CO₂ into the natural sinks (both vegetation everywhere and oceans mainly at the sink places) linearly with the extra CO₂ pressure in the atmosphere. As long as the total net sinks are less than human emissions, the CO₂ level in the atmosphere will increase further.

A similar factor can be derived for the CO₂ change and the temperature change over the seasons. A factor of 4–5 ppmv/°C between CO₂ and seasonal temperature variability exists in opposite direction. The seasonal temperature increase gives a drop of CO₂ in spring/summer and opposite in fall/winter as shown Figure 1.6.7, while the 1–3 years and longer temperature increase gives an increase of CO₂.

The seasonal CO₂ fluxes are huge. The flux estimates, based on O₂, δ¹³C changes for vegetation and Henry's law for the ocean fluxes show global fluxes of some 60 PgC/season in and out for vegetation and in the opposite direction some 50 PgC/season out and in for ocean fluxes. The net result is a global amplitude of some 10 PgC (~4–5 ppmv) over the seasons for a global temperature amplitude of 1°C, mainly visible in the NH, where most of the deciduous forests are situated, while the opposite far smaller amplitude is visible in the SH, where most of the oceans are situated.

While the seasonal fluxes, which are responsible for the short residence time of only four years, are huge, that is irrelevant to the long term increase of CO₂ in the atmosphere. The change of CO₂ in the atmosphere after a full seasonal cycle is the result of all CO₂ fluxes in and out together after a full year and is visible as the small change between one month and 13 months in Figure 1.6.7.

Note that while of the same order of magnitude, the seasonal and modern CO₂ changes caused by temperature variability are in opposite directions. As described above, the short-term year-by-year changes show increasing CO₂ with temperatures.

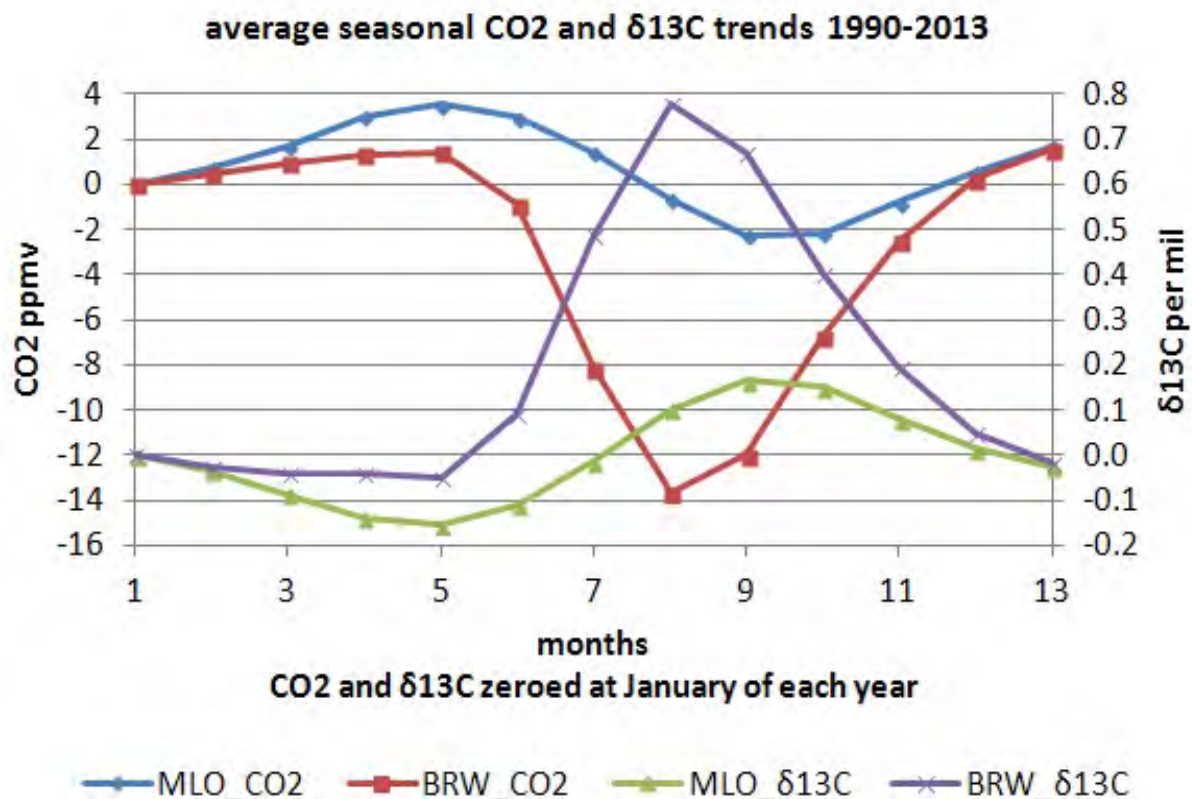


Figure 1.6.7: CO₂ and δ¹³C over the seasons for Barrow and Mauna Loa, each year the start data are fixed in January. Data from NOAA (NOAA CO₂ ongoing). The opposite CO₂ and ¹³C changes prove that vegetation is the dominant factor of the seasonal changes, specifically the deciduous forests, mainly in the NH.

The Influence of Temperature on the Total CO₂ Increase in the Atmosphere

In the above sections, we observed that the influence of temperature on CO₂ increases and decreases—even during long periods of time—is very modest and is at most 16 ppmv/K, as shown in Table 1.6.1.

The observations made above eliminate temperature as the main cause of the 130-ppmv CO₂ increase over the past 170 years. Also, the global warming since the “preindustrial” late Little Ice Age is generally estimated to be between 1.0 and 1.5 °C, which is a sufficient temperature increase to eventually cause at the very most a 24-ppmv CO₂ increase, or less than 20% of the measured CO₂ increase.

Table 1.6.1: summarizes the temperature influence on CO₂ concentrations:

Event	Time (years)	CO ₂ Lag (years)	Global (ppmv/°C)
Glacial/Interglacial	1000's	~600	16
MWP/LIA	100's	~50	12.5
Modern	1–3	~6 months	3.5
Seasonal	months	~2 months	(4–5)

The average temperature of the sea surface is the driving force for the pre-industrial CO₂ levels in the atmosphere. That is what is seen in the Vostok and Law Dome data up to about 1850. That is a dynamic equilibrium: warmer oceans emit CO₂, colder oceans absorb CO₂, which causes a lot of CO₂ flowing from warm parts to cold parts, where it sinks with the cold waters into the deep oceans, to return some 1,000 years later near the equator, where it is released. That total cycle is estimated at about 40 PgC/year.

In equilibrium, there is no difference between a static ocean with the same temperature all over the surface and a dynamic equilibrium of an ocean with a lot of exchange but with the same (area-weighted) average temperature.

Vegetation only follows with some lag in the opposite direction: higher temperatures = more vegetation = more permanent uptake by vegetation.

There is a formula to calculate the exact increase of CO₂ in the atmosphere with temperature: the formula of Takahashi, based on hundreds of thousands of seawater samples. No matter the composition or temperature of seawater at the initial conditions, any increase/decrease in temperature gives a change of pCO₂ of seawater according to following formula:

$\partial \ln p\text{CO}_2 / \partial T = 0.0423/\text{K}$ (Takahashi 2002)

or more readable:

$$(p\text{CO}_2)_{\text{oceans @ } T_{\text{new}}} = (p\text{CO}_2)_{\text{oceans @ } T_{\text{old}}} \times \text{EXP}[0.0423 \times (T_{\text{new}} - T_{\text{old}})]$$

This results in an approximate 4%/°C increase or decrease of pCO₂ in seawater, and consequently in the atmosphere, in (dynamic) equilibrium with each other.

This proves that, while temperature changes are responsible for the short term and pre-industrial (very) long term variability, temperature is not responsible for the current increase of CO₂ in the atmosphere.

Other Processes Involved in CO₂ Changes

There are a lot of other natural processes that influence CO₂ levels in the atmosphere, like volcanic vents and eruptions, carbonate rock dissolution, etc. These are much smaller in amounts-per-year and/or much slower in reaction speed than temperature changes or human emissions. Over the current period of interest, since the start of the Industrial Revolution, these have played a very minor role.

For example, the Mount Pinatubo event was one of the largest eruptions in modern history, emitting 42 million tonnes of CO₂ (Gerlach et al. 1996). According to the CDIAC, there were 23 billion tonnes of human CO₂ emitted in 1991, so the largest eruption in the last 70 years amounted to 0.2% of human CO₂ emissions in just that year.

Process Characteristics Conclusions

From the process characteristics, it is clear that the observed increase of CO₂ in the atmosphere follows the acceleration of human emissions. Temperature fluctuations can cause only very small deviations (1.2 ppmv for the extremes like the 1991 Pinatubo eruption or the 1998 El Niño) from the over-100-ppmv trend line since 1958.

There are two main processes that influence the CO₂ levels in the atmosphere beyond time frames of a few years: human emissions and temperature. The latter accounts for a maximum of 10%, or 13 ppmv, of the current increase since the start of the Industrial Revolution. The main cause of the observed 130-ppmv increase is the 210-ppmv one-way human addition.

2. HISTORICAL CO₂ LEVELS

Documentation of valid historic CO₂ levels during glacial advances and retreats during the past several hundred-thousand years is an important component to any discussion of the provenance of the modern 140-ppmv increase. If previous warm interglacial periods experienced concentrations similar to the modern levels, then that would be supportive evidence that natural sources may also be a major contributor to the recent increase. Contrarily, if modern concentrations are significantly higher than previous similar warm interglacials, that is strong confirmation that a new source such as fossil fuel combustion is a primary driver of modern CO₂ increases.

This chapter examines the utility and drawbacks of several measurement techniques utilized to determine historic CO₂ concentrations prior to direct measurement in the 1950s. Using proxy data, we also examine the effects that temperature changes and glaciation cycles had on atmospheric CO₂ levels before the Industrial Revolution began adding large amounts of “fossil CO₂” to the atmosphere. We will see that CO₂ measurements from before the Industrial Revolution show relatively small changes compared to the 125-ppmv increase since 1900.

Antarctic ice cores allow for the direct measurement of past CO₂ concentrations enclosed in air bubbles. For timescales in the millions of years, terrestrial and marine proxies are used to reconstruct past CO₂ concentrations when ice core data is not available. There are many types of proxies including, but not limited to, paleosols, plant stomata and phytoplankton, each with different assumptions and uncertainties. Proxy CO₂ estimates can be inconsistent with large error bars (see CenCO2PIP 2023 supplement). For example, the traditional paleosol CO₂ reconstructions have a significant uncertainty in unconstrained soil-respired CO₂ concentration which can be highly variable both spatially and temporally. The focus here is on ice core data over the past 800,000 years and on the frequently cited Holocene CO₂ reconstructions from the plant stomata proxy.

2.1 Ice Core CO₂ Concentrations in the Past

Introduction

As of 2024, the CO₂ level measured at Mauna Loa, Hawaii, has increased to more than 420 ppmv. In contrast, measurements from ice cores over the past 800,000 years show that CO₂ concentrations rarely exceeded 300 ppmv.

CO₂ and other gases as measured in ice cores are direct measurements of ancient air. They represent reliable measurements of these gases, although the ability to detect variations of gas concentrations within a time span depends on the rate of local snow accumulation and how quickly air inclusions are closed within the ice. Where snow accumulation is very rapid, the dates associated with trapped air bubbles are fairly precise, with as little 10–14 years uncertainty (“resolution”) for Law Dome cores. Usefully, the Law Dome data includes a 20-year

overlap (1958–1978) with direct CO₂ measurements at the South Pole. On the other hand, where snow accumulation rates are slow, the uncertainty of the dates associated with the trapped air bubbles is much greater, even as much as several centuries for the Vostok and Dome C ice cores.

If an increase in CO₂ concentration comparable to the current rise had occurred at any time in the past 800,000 years, it would be visible in even the lowest resolution ice core measurements as an unusual peak of several tens of ppmv, and as a sharp dip in the carbon isotope $\delta^{13}\text{C}$.

This section evaluates the robustness of CO₂ concentrations measured in air bubbles in ice cores, the repeatability of CO₂ data at various ice core sites, and the effects of extraction techniques. Also considered is the data's temporal resolution—its ability to retain accurate fluctuations of CO₂ concentrations within a span of time. It is widely accepted that CO₂ records from air bubbles in Antarctic ice cores are regarded as the gold standard for paleo-atmospheric global CO₂ concentrations, and we agree with that conclusion.

Ice cores from Antarctic glacial ice provide past temperature proxies from oxygen isotopes, as well as gas composition from small air bubbles trapped within the ice. As snow accumulates and compacts over time, it is transformed into firn; a granular intermediate stage between snow and ice. The firn eventually becomes dense enough that open pores begin to close, forming bubbles that trap atmospheric gases.

Figure 2.1.1 shows key Antarctic ice cores and global CO₂ concentrations over the past 800,000 years. In general, CO₂ concentrations rise to almost 300 ppmv during warm interglacial periods and decrease to as low as 180 ppmv during the cold glacial periods. The interglacial periods are noted using the marine isotope stage (MIS). There are numerous ice cores that cover our current interglacial (MIS 1), also known as the Holocene, and the preceding glacial period. There are only a few that extend over the previous interglacial period referred to as MIS 5, (also known as the Eemian) and only one that extends the entire 800,000 years, EPICA Dome C.

Notable differences exist between ice cores taken in high accumulation/warmer temperature sites versus low accumulation/colder temperature sites. The deeper, older ice cores tend to occur in low-snow-accumulation sites in Eastern Antarctica, and include EPICA Dome C, Vostok, and Dome Fuji. These cores tend to have a prolonged entrapment of gas within ice bubbles and more extensive gas mixing of CO₂ with the atmosphere, resulting in lower temporal resolution. The shallower ice cores are drilled in high-snow-accumulation sites and in the peripheral areas of the ice field. High-accumulation sites such as Law Dome and WAIS have rapid burial, less gas diffusion within the firn, and better temporal resolution; but shorter records.

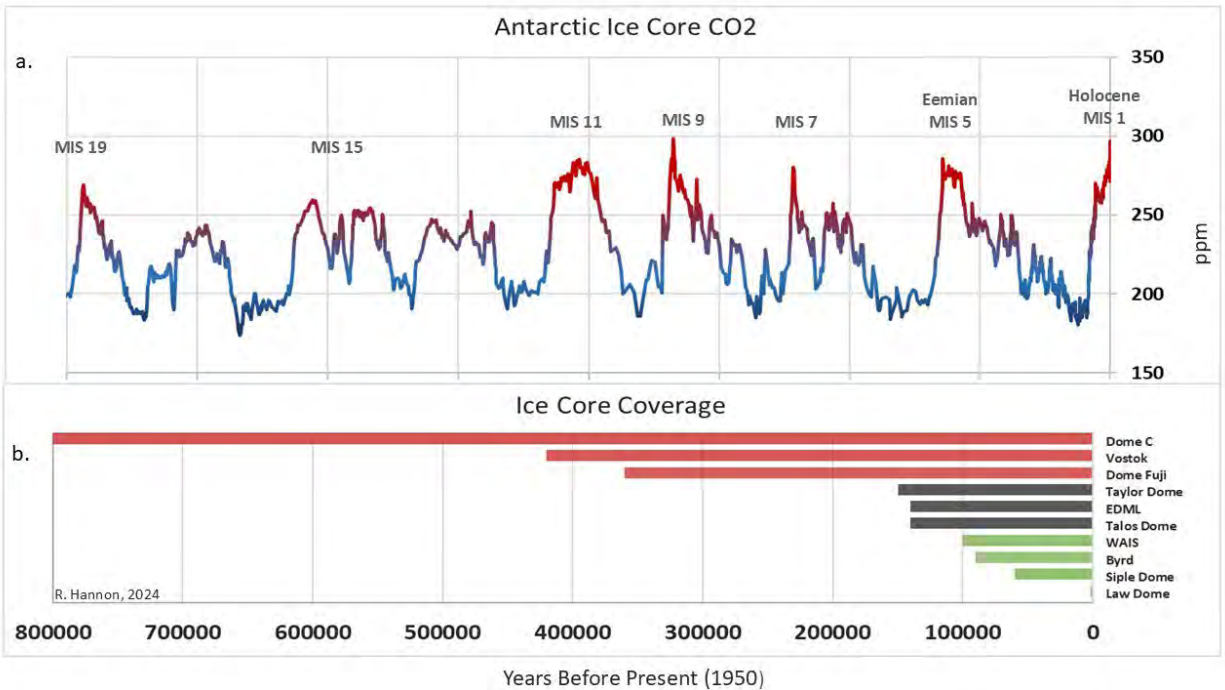


Figure 2.1.1: a. Global CO₂ concentrations from ice cores after Bereiter (2014) plotted over time. b. Key ice cores showing approximate cored interval length. Colors indicate CO₂ resolution, red is low, gray is intermediate, and green is high.

Ice-Age to Gas-Age Time Shift

Two key adjustments occur to atmospheric gases during the firm transition to ice prior to being trapped in ice bubbles. First, the peaks and valleys of atmospheric CO₂ concentrations are smoothed over time due to atmospheric mixing and gas diffusion within the firm. Second, the gas is believed to be younger than the age of the ice when it is eventually trapped within bubbles (Trudinger 2002, Schwander 1984). Once trapped within the bubbles, gas is assumed to age with the ice. This age difference is referred to as the ice-gas age delta. The delta ranges from 31 years in Law Dome to 835 years in the lower-snow-accumulation EDML ice core. Very low snow-accumulation sites such as Dome C and Vostok have a delta of thousands of years. In addition, the ice-gas age delta varies between interglacial and glacial periods due to varying snow-accumulation rates.

Figure 2.1.2 shows CO₂ concentrations versus the age of ice in which it is trapped for five ice cores in the Antarctic before adjustments. Atmospheric data from Cape Grim, Australia, and firn data are included on the plot for comparison. Noted are the delta differences in years, between the (younger) gas age and (older) ice age. Ice-gas age deltas have uncertainties of 10–15%, especially in low accumulation sites where the ice-gas age deltas are exceptionally large (Seigenthaler 2005). This plot is a profile rarely found in published literature.

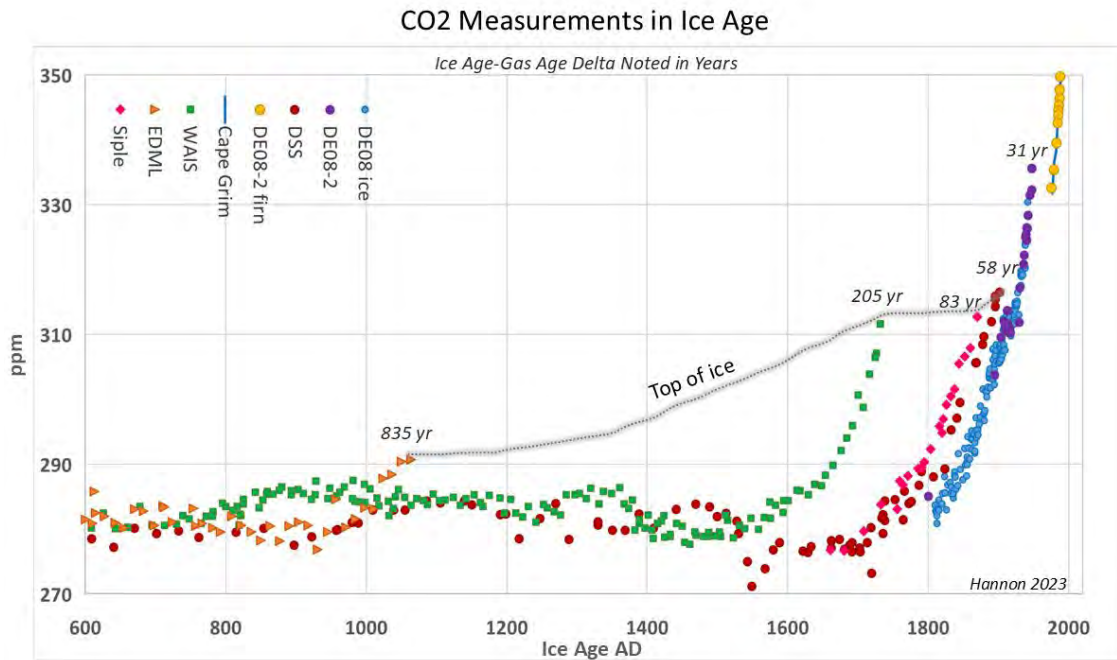


Figure 2.1.2: CO₂ concentrations measured in ice age. The numbers show the average ice-gas age difference in years. The gray line is the top of ice and approximate position of the base of the bubble zone. CO₂ data for Law Dome (DE08, DSS) is from Rubino (2019); WAIS is from Bauska (2015); Siple is from Neftel (1994); and EDML is from Siegenthaler (2005) compiled by Bereiter (2014).

Gas age is the age of CO₂ that is reported in most public datasets and graphs. Different CO₂ datasets overlap quite nicely, with few exceptions, when corrected to the appropriate gas age (Figure 2.1.3). Within multiple ice cores, these gas shifts appear reasonable as distinct CO₂ highs, such as the Medieval Warm Period CO₂ bulge (~1000 to 1500 AD), and lows, like the Little Ice Age (LIA~1500–1850 AD). Law Dome ice and firn CO₂ measurements closely overlap the modern CO₂ rise measured in southern hemisphere monitoring stations, which are recording 420 ppmv as of June, 2023.

Ice Core CO₂ Resolution

Variations in atmospheric CO₂ concentrations are smoothed over time due to atmospheric mixing and gas diffusion within firn. The gas-age distribution is modeled and represents the time it takes for gas to be trapped in bubbles and amount of gas mixing. Its temporal width is a representation of the resolution or smoothing of ice core gas in years. High-snow-accumulation sites at Law Dome have a CO₂ gas-age distribution of only 10–14 years. Low-accumulation sites, such as Dome C and Vostok, contain gas that is mixed with the atmosphere over hundreds of years. According to Monnin 2001, Dome C is smoothed over 200 years in the Holocene interglacial, and smoothing increases to 550 years during glacial periods. However, a more recent publication shows Dome C resolves CO₂ fluctuations as brief as 100 years during the MIS 9 and 11 interglacials (Nehrbass-Ahles 2020).

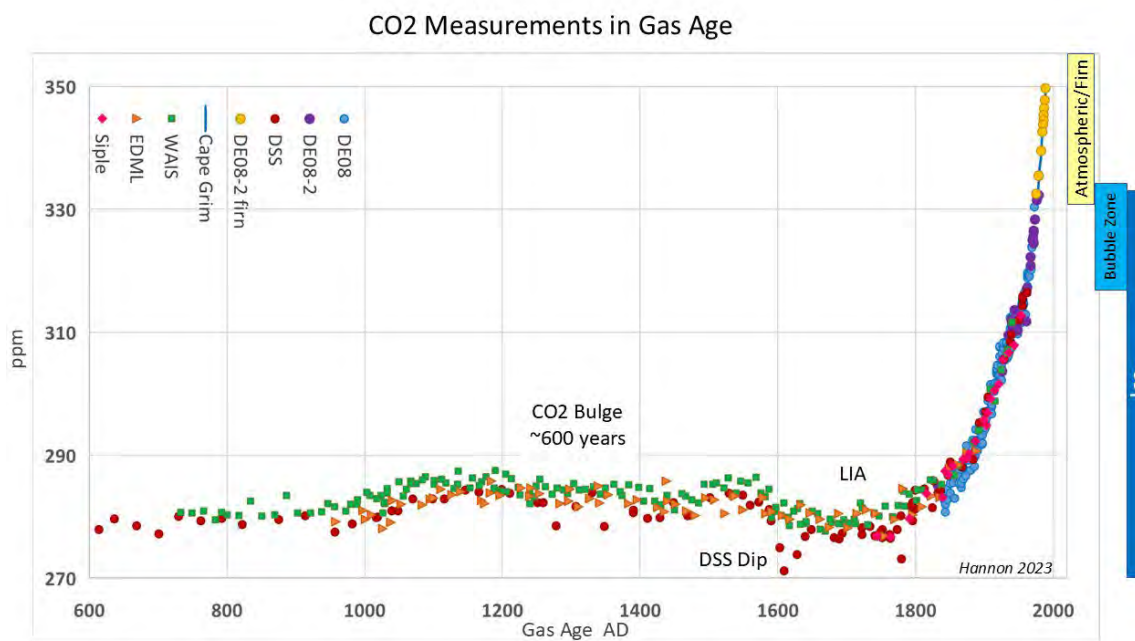


Figure 2.1.3: *CO₂ concentrations corrected to appropriate gas age. Boxes on the right side highlight different data medium and approximate location of the ice bubble zone. CO₂ data references noted in Figure 2.1.2.*

Even in ice cores with the least resolution, the current 120 ppmv increase of CO₂ over the past 800,000 years would be visible as an abnormal peak of several tens of ppmv and as a sharp dip in $\delta^{13}\text{C}$ in the ice core measurements.

Figure 2.1.4 shows CO₂ concentrations over the past 1,000 years in high resolution records from Law Dome and WAIS. Law Dome can identify CO₂ rises and dips as brief as 10 to 14 years. Ahn (2012), using synthetic age distributions and modeling, deduced that WAIS experiences about 30 years of smoothing due to gas diffusion within the firn.

Ice Core CO₂ Repeatability

At least six ice cores with high resolution cover the Holocene or MIS 1 and preceding deglaciation shown in Figures 2.1.5 and 2.1.1b. These data provide the opportunity to understand CO₂ fluctuations, as well as a comparison to lower resolution ice core data. All CO₂ values were measured using the dry-extraction technique to minimize ice core melt and potential chemical reactions. The precision of the individual measurements or analytical uncertainty is estimated to be 1.5 ppmv (Rubino 2019). Data points are rejected due to obvious contamination, fractures, or presence of meltlayers.

All records show that CO₂ reached a high of about 280 ppmv at the end of the deglaciation about 11,700 years B.P. (“Before Present,” which actually means before 1950). During the mid-Holocene, CO₂ concentrations decreased to a minimum of 260 ppmv around 8,000 years B.P. CO₂ concentrations gradually increased to 285 ppmv in the late Holocene, up to the time of the

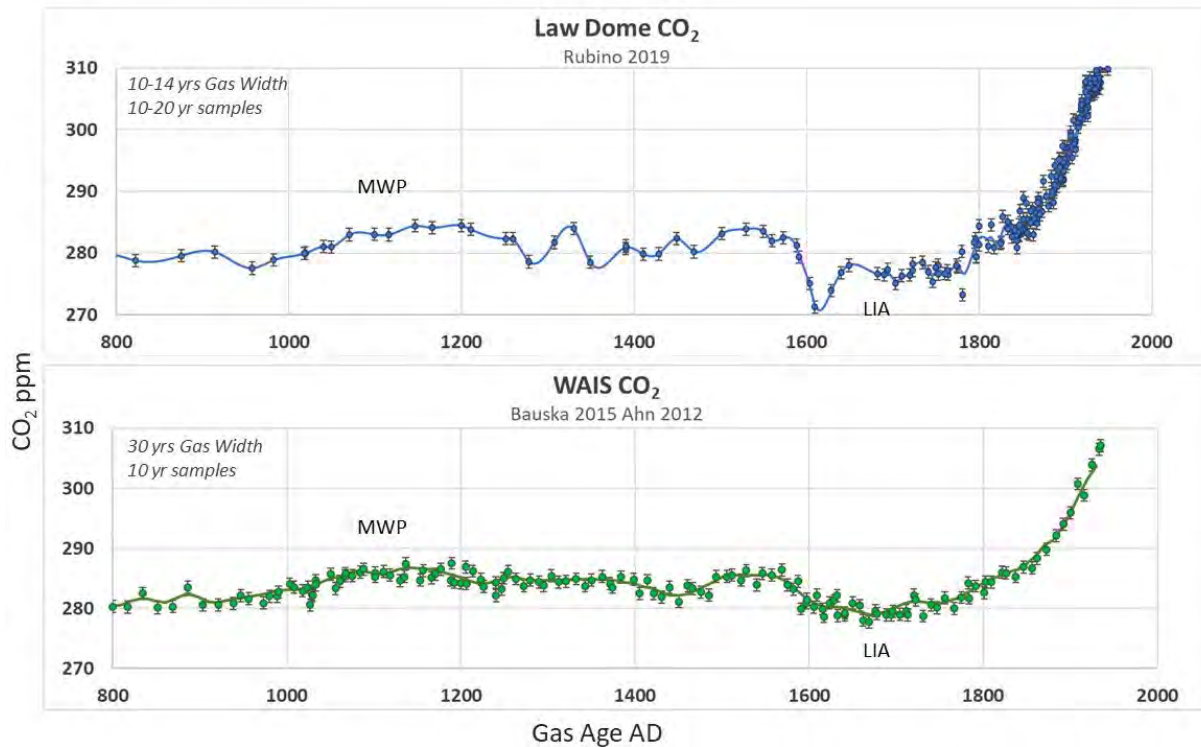


Figure 2.1.4: High-resolution Antarctic ice core CO₂ data during the past 1,000 years. Data points are plotted with 20-yr trend lines. Law Dome trend is the 20-year spline provided by Rubino (2019). Gas width due to firn-ice transition and sample-spacing resolution in years (yr) are noted in text box. Data references shown on plots.

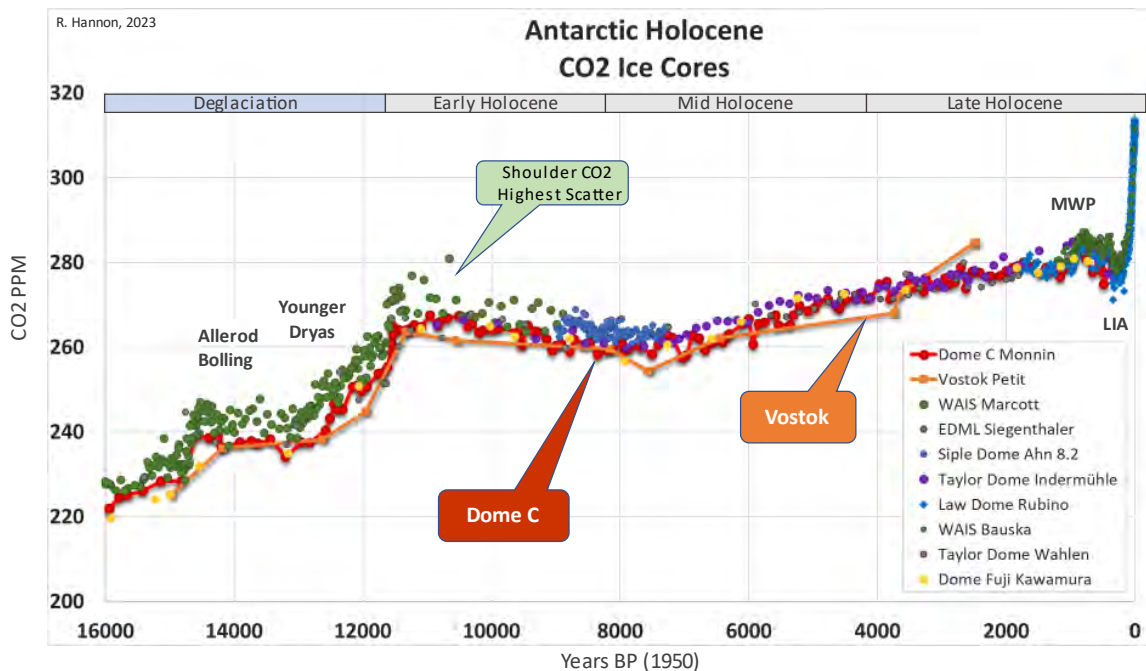


Figure 2.1.5: Antarctic ice core CO₂ datasets compiled over the Holocene. High-accumulation sites with higher resolution are shown in green and blues. Data references shown on graph.

Medieval Warm Period (MWP) about 1,000 years B.P. A distinct drop in CO₂ values to about 270 ppmv occurred during the Little Ice Age (LIA), followed by the modern increase in CO₂ past 400 ppmv and continuing to rise.

The repeatability and agreement between the ice core CO₂ records is quite impressive. There is less than a 4-ppmv difference over most of the Holocene, consisting of over 1,000 data points. Standard deviations of the samples average 1.5 ppmv. The largest amount of discrepancy appears at the end of deglaciation and on the shoulder of the Early Holocene interglacial from 10,500 to 11,500 years B.P., where the WAIS data shows CO₂ records of 10–15 ppmv higher than lower resolution Dome C and Vostok records.

Clathrates and Wet Extraction

Bubbles begin to transition into solid clathrates, or small crystals, at depths of between 500–1,200 meters (Stauffer and Tschumi 2000). This transition zone consists of both bubbles and clathrates. Below the transition zone, there are no more bubbles, and the entrapped air (including CO₂) is entirely in the form of clathrates.

It is frequently challenged that the dry-extraction method is inefficient for analyzing CO₂ concentration in ice samples containing both bubbles and clathrates. Air extracted from the transition zone using mechanical destruction preferentially extracts air from the bubbles, which are depleted in CO₂, resulting in lower CO₂ concentrations (Bereiter 2014). Gas within a clathrate may not be released. A newer technique of sublimation of ice in a high-vacuum apparatus has a 100% extraction efficiency. The downside is it takes a long time (45 minutes per sample). Released gas from all extraction methods is collected cryogenically and measured via gas chromatography or with a mass spectrometer.

Kawamura (2003) conducted a wet extraction technique that heats ice under vacuum on Dome Fuji that helps ensure that the extracted gas is free from being entrapped within the clathrates. A disadvantage of the wet-extraction technique is acid-carbonate reactions or oxidation of organic components in the ice may result in higher CO₂ readings. However, Antarctic ice cores have low concentrations of impurities or dust, so differences between the wet and dry extraction can be attributed mostly to hydrates.

Figure 2.1.6 shows the CO₂ concentrations from the Dome Fuji wet-extraction compared to the dry-extraction CO₂ values from Dome C and Vostok ice cores. In general, high CO₂ values occur during the interglacial periods and low values in the glacial periods, paralleling dry-extraction values from other Antarctic ice cores. The wet-extraction values range from 190 ppmv to 300 ppmv over the past 350,000 years. Standard deviations on the wet extraction were on average 0.7 ppmv.

There are a few notable differences between the wet and dry extraction from the various ice cores. The wet CO₂ values in the Last Glacial Maximum (LGM) and the glacial period preceding

MIS 5 are systematically higher by 10–20 ppmv than the records from dry extraction. There is also a notable increase of wet CO₂ values during the Eemian or MIS 5 interglacial by 10–20 ppmv. Kawamura believes that the wet CO₂ values are higher mostly due to incomplete extraction during the dry technique.

Kawamura states the wet extraction should be regarded as an upper-limit estimation of atmospheric CO₂ in the past. Note that even though the wet extraction yields higher CO₂ values than dry extraction values, the wet CO₂ values rarely exceed 300 ppmv over the past 800,000 years.

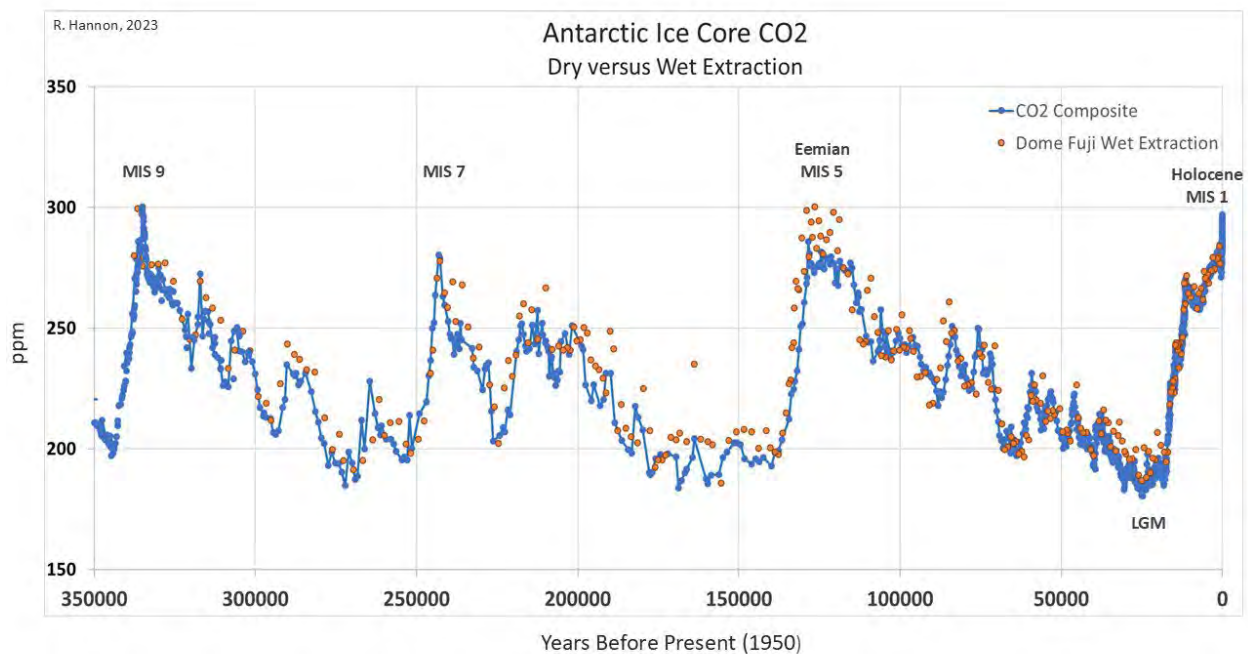


Figure 2.1.6: Comparison of CO₂ measurements from wet- and dry-extraction techniques. Wet data is from Dome Fuji after Kawamura, 2003, and dry data is from a composite of various cores from Bereiter (2014). LGM is Last Glacial Maximum.

Ice Core CO₂ Conclusions

Antarctic ice cores capture the highest quality measurement of CO₂ concentrations prior to the modern measurement record, which began in 1958. They provide a continuous global CO₂ record over the past 800,000 years. Ice core CO₂ data are accurate, repeatable and overlap well with modern CO₂ measurements representing well-mixed atmospheric global CO₂ levels. CO₂ measurements from ice cores show that CO₂ over the past 800,000 years rarely exceeded 300 ppmv, which is much lower than present day concentrations of about 420 ppmv.

2.2 Plant Stomata CO₂ Reconstructions over the Holocene

Introduction

Plant stomata CO₂ data have been used to attack the reliability of ice core data. While plant stomata data in general have a better resolution than ice core data over the same periods, they are proxy measurements while ice core gas data are direct measurements of enclosed ancient air. Plants grow on land, where there is always a local bias influenced by factors such as variations in local climate, land use, development of infrastructure and even changes in the direction of prevailing winds. This section evaluates seven different stomata studies to understand factors that influence stomata-proxy CO₂ values and stomata-proxy CO₂ repeatability, as well as key uncertainties.

Stomata in leaves are used as indirect measurements for paleo-atmospheric CO₂ reconstructions (Jessen 2005, Wagner 2004). Basically, CO₂ enters through a plant leaf's stomata or pores. When CO₂ in the atmosphere increases, plants have fewer stomata. When atmospheric CO₂ decreases, stomata in plants increase to compensate for low CO₂ levels. Therefore, an inverse relationship exists between stomata frequency and atmospheric CO₂ concentration. Scientists count the number of stomata on different plant species to determine what is known as the stomata density (number of stomata per area).

A more accurate measure is the stomatal index (number of stomata proportional to the sum of stomata and epidermal cells), which is used to minimize the influence of local environmental variables. The stomatal index (SI) is calibrated with modern training sets to calculate the sensitivity to atmospheric CO₂ levels.

Plant Stomata CO₂ Reconstructions

Atmospheric CO₂ reconstructions from seven different plant stomata studies have been compiled over the Holocene interglacial and preceding deglaciation, shown in Figure 2.2.1. The individual stomata studies cover continuous time intervals ranging from only 500 years to almost 2,000 years. Stomata CO₂ reconstructions show a range of 250 to 345 ppmv over the Holocene interglacial. In contrast, during the deglaciation, stomata CO₂ reconstructions are very erratic, and show ranges from 175 ppmv to almost 400 ppmv.

Different stomata CO₂ reconstructions during similar time periods are inconsistent with each other. Van Hoof's *Quercus* and Kouwenberg's *Tsuga* stomata CO₂ reconstructions during the late Holocene diverge by almost 25 ppmv. Kouwenberg's reconstruction is based in stomatal frequency, not stomatal index and is the lower quality dataset. McElwain's conifer and Wagner's *Betula* CO₂ reconstructions during the early Holocene also differ by about 25 ppmv.

During the Holocene, almost all stomata CO₂ reconstructions are on average 30 to 40 ppmv higher than ice core CO₂ concentrations, with higher amplitude variability. It is widely

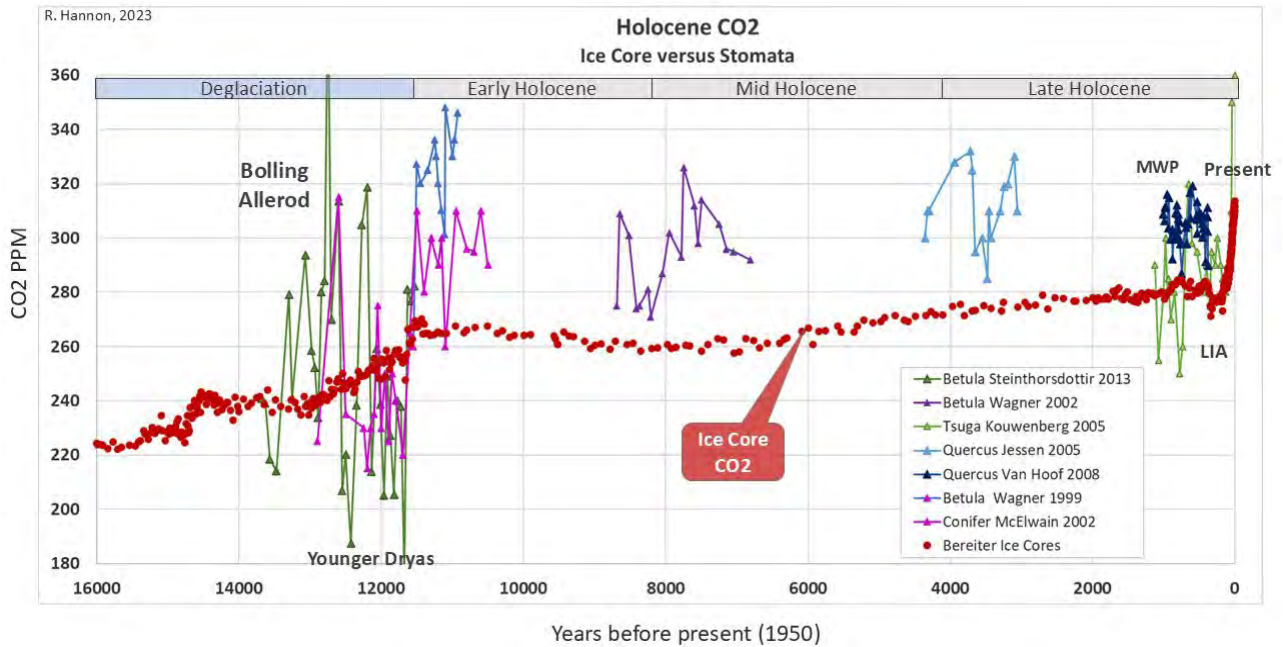


Figure 2.2.1: *CO₂ proxy reconstructions from plant stomata compared to CO₂ concentrations from ice cores (red dots). References are shown on the graph.*

recognized that the average of stomata CO₂ reconstructions are consistently higher than Antarctic ice core CO₂ values (Jessen 2006, Wagner 1999, Indermuhle 1999). In contrast, during the deglaciation, stomata CO₂ values are both lower and higher than ice core, with significant amplitude variability. McElwain states that CO₂ reconstructions from stomatal frequency data appear to consistently underestimate CO₂ levels during the stadials (ice advances) and overestimate them during interstadials (ice retreats), when compared to ice core direct measurements.

Normalized Plant Stomata CO₂ Reconstructions

Since stomata studies over the Holocene cover short age ranges, it is nearly impossible to establish a longer-term baseline trend in CO₂. A simple solution is to use the continuous ice core CO₂ records as the CO₂ baseline and normalize the stomata records to this baseline. Wagner (2004) adopted a similar approach, where he normalized different stomata records on the long-term average of each record for comparison. This normalization approach is also utilized when evaluating and establishing a database for vastly different proxy-temperature records (Kaufman 2020). Figure 2.2.2 shows stomata CO₂ reconstructions normalized to the ice core CO₂ baseline. This allows for the comparison of amplitude trends and temporal synchronicity of the records.

Once normalized to ice core records, one can examine stomata CO₂ amplitudes compared to ice core CO₂ amplitudes. Over the Holocene, normalized stomata values show amplitudes approximately ± 20 ppmv higher or lower than ice core CO₂ values. Ice core CO₂ values show

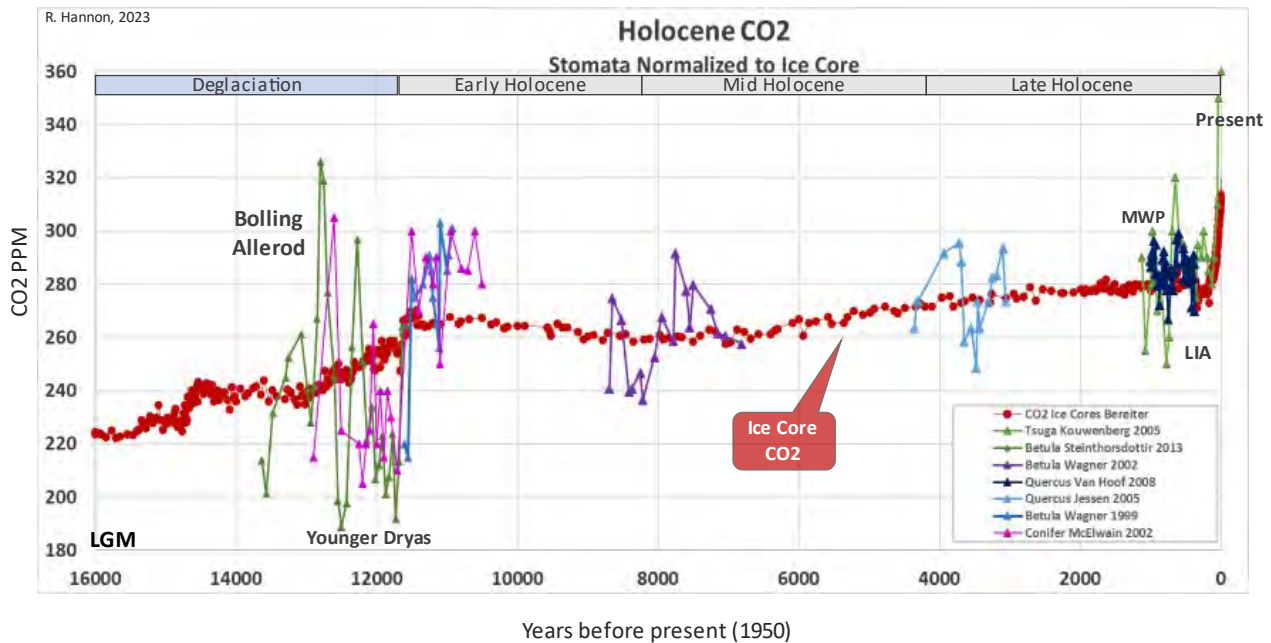


Figure 2.2.2: *CO₂ proxy data from plant stomata, with the mean normalized to CO₂ baseline from ice cores (red dots). A three-point average was applied to the Steinthorsdottir data.*

smaller increases and decreases of ± 5 ppmv. Stomata CO₂ reconstructions during deglaciation suggest much more instability and higher fluctuations. Also, note that normalized stomata CO₂ rarely exceeds 300 ppmv.

Plant Stomata Limitations

Many authors of stomata studies discuss the smoothing effects of gas diffusion within the firm and attribute to this the absence of the CO₂ fluctuations seen in stomata. However, the WAIS and Law Dome ice cores are from high-snow-accumulation sites that experience lower gas diffusion rates and have high temporal resolution. WAIS has a resolution of 30 years and is sampled at 10–20-year intervals over the past 1,000 years. Law Dome has a resolution of about 14 years and is sampled at 10-year intervals. Since these high-resolution ice cores do not record the high CO₂ variations seen in stomata over the same period, the temporal resolution difference is a questionable hypothesis.

There are several shortcomings associated with stomata CO₂ reconstructions, including improper calibration, plant evolution, and local or seasonal bias. Plant stomata CO₂ reconstructions are from an empirically derived relationship between the stomatal index and CO₂ concentration. A general model covering multiple genera is difficult due to highly individual reactions of the various genera (Wagner 2004). Different model regressions are developed for broad-leaved trees versus conifers. The SI-CO₂ model developed for *Betula* by Wagner has a strong correlation coefficient R^2 of 0.78. However, van Hoof's calibration for *Quercus* had an R^2 of only 0.52 with an RMSE of 10.2 ppmv.

Rapid CO₂ fluctuations seen in plant stomata may be the result of improper assembling and calibration of the modern training sets (Wagner 2004). Assuming that the physiological response of a modern modeled species is transferable to a fossil species is also problematic, according to Reichgelt (2019). Typically, the nearest living relative is used, and plants tend to evolve. Reichgelt states that CO₂ proxies that use the assimilation rates of modern species based on phylogenetic relatedness to the fossil species result in CO₂ estimates that are biased by a factor greater than 2.

In addition to phylogenetic errors, Royer (2019) states that published uncertainties associated with the stomatal density proxies are probably too small. They only reflect uncertainty in either the calibration or in the measured values of fossil stomatal density, but not both. When both error sources are considered, errors often exceed $\pm 30\%$ at 95% confidence.

Plant stomata may retain local signatures of conditions that may not be truly global in nature. There are a wide variety of plant species and habitat conditions, but most represent Northern Hemisphere atmospheric conditions. Rundgren (1999) states that CO₂ concentrations recorded by *Salix herbacea* leaves during bud-burst in spring may be 3–5 ppmv higher than ice cores due to the pronounced seasonal CO₂ variation in the northern hemisphere.

Arborescent tree species and herbaceous species experience different CO₂ environments. Herbaceous species grow near the forest floor where soil respiration can significantly raise the CO₂ concentration. If a species grows near a CO₂ source rather than a secluded forest it will have a higher CO₂ reading. Significant differences can occur between the stomatal frequency in sun and shade leaves of *Quercus*, and therefore Van Hoof restricted his analysis to sun morphotypes.

Stomata CO₂ Conclusions

CO₂ concentrations from plant stomata are indirect proxy measurements consisting of discontinuous records. The uncertainties and shortcomings associated with plant stomata CO₂ reconstructions mean that they are less reliable than Antarctic ice core measurements for determining paleo-atmospheric global CO₂ concentrations. The main value of such studies is to test and calibrate methodologies for application to earlier time periods, for which ice core data is unavailable.

2.3 Historical CO₂ Levels Using Chemical Methods

Introduction

This section examines historical CO₂ measurements with chemical methods during the 19th and early 20th centuries before C.D. Keeling started his more accurate infrared CO₂ readings at the South Pole and Mauna Loa. The chemical method data compilation shows a huge peak of around 70 ppmv in the past century. If that peak were real, then it would suggest that the current peak of 120 ppmv might not be unique. The evidence of the historical peak is evaluated.

In March, 1958, C.D. Keeling began what is now a 68-year-long continuous record of very accurate measurements of “background” CO₂ concentration, at Mauna Loa Observatory (MLO), on Mauna Loa Mountain in Hawaii. Additionally, accurate CO₂ measurements from the South Pole (SPO) began sporadically in 1957, and near-continuous measurements began there in 1961. Subsequently, accurate measurement records have been compiled from many different locations, giving us a clear, reliable understanding of atmospheric CO₂ trends, including seasonal variations, and slight hemispheric differences.

In addition, there were historical measurements of CO₂ taken in many places with chemical methods in the 19th and early 20th centuries, before Keeling began measuring CO₂ at MLO and SPO.

The late Ernst Beck compiled tens of thousands of historical CO₂ measurements between 1900 and 1958 (and reporting measurements as early as 1812). His work was first published in 2007 in *Energy and Environment* (Beck 2007) with comments from Harro Meijer (Meijer 2007) and Ralph Keeling (Keeling 2007), and a reply from the author on these comments (Beck’s reply 2007). Recently a postmortem, extended version was published in the on-line journal *Science of Climate Change* (Beck 2022).

Beck concluded that there was a 70 ppmv peak in CO₂ levels in the period 1935–1945, even though the ice cores and several proxies show no change, in addition to the gradual change caused by human emissions from burning fossil fuels.

Beck’s Herculean work to collect and compile tens of thousands of historical CO₂ measurements is admirable. But, unfortunately, many of those measurements were taken over land, near large sinks and sources, making them unsuitable for global CO₂ estimates. Those problems are comparable to the problems with stomata data, which are discussed in section 2.2. Further, Beck made several errors in his compilation and his criteria to include or exclude some of the measurement series are not very clear.

The following is a compilation of discussions with the late Ernst Beck in the years 2000–2010, until his untimely death in 2010. The more extended reaction on his postmortem work is published in *Science of Climate Change* (Engelbeen 2023).

The Accuracy of the Historical CO₂ Measurement Methods

Historical measurements of CO₂ in the atmosphere were based on chemical methods. The accuracy was quite good for many of the methods. These methods were accurate to 3% of the measurement, thus for data around 300 ppmv, that is an error of approximately ± 9 ppmv. For that time, that was good performance. Even so, it was not good enough to be certain of the seasonal variations in the atmosphere, and it was far inferior to the near-IR method—accurate to 0.2 ppmv—that C.D. Keeling started to use in the 1950s.

For many of the historical measurements, there is little description of methods used, sampling, sample handling, calibration, etc. Thus, while a certain method may have been sufficiently accurate, the sampling, handling or lack of calibration may cause inaccuracies in data.

The Compilation by the Late Ernst-Georg Beck

Figure 2.3.1 is the trend shown by Beck from his compilation of historical CO₂ measurements. A first point of interest is the “error range,” which is based on the error range of the instruments used (and even that is questionable), not the error range of measurements, which for most years extend from the bottom of the graph up to far beyond the ceiling.

The period around 1940 will be examined as there are more data available. The data compiled by Beck shows a CO₂ increase of about 70 ppmv. In contrast to the peak around 1942, the ice core CO₂ records show only a few ppmv of variability and an upward trend of some 10 ppmv over the period 1930–1950 shown in Figure 2.3.2.

Any real peak of some 70 ppmv over a period of nearly a decade would have been detected by the high-resolution (10–14 year) Law Dome ice cores, but it is not visible in the ice core record.

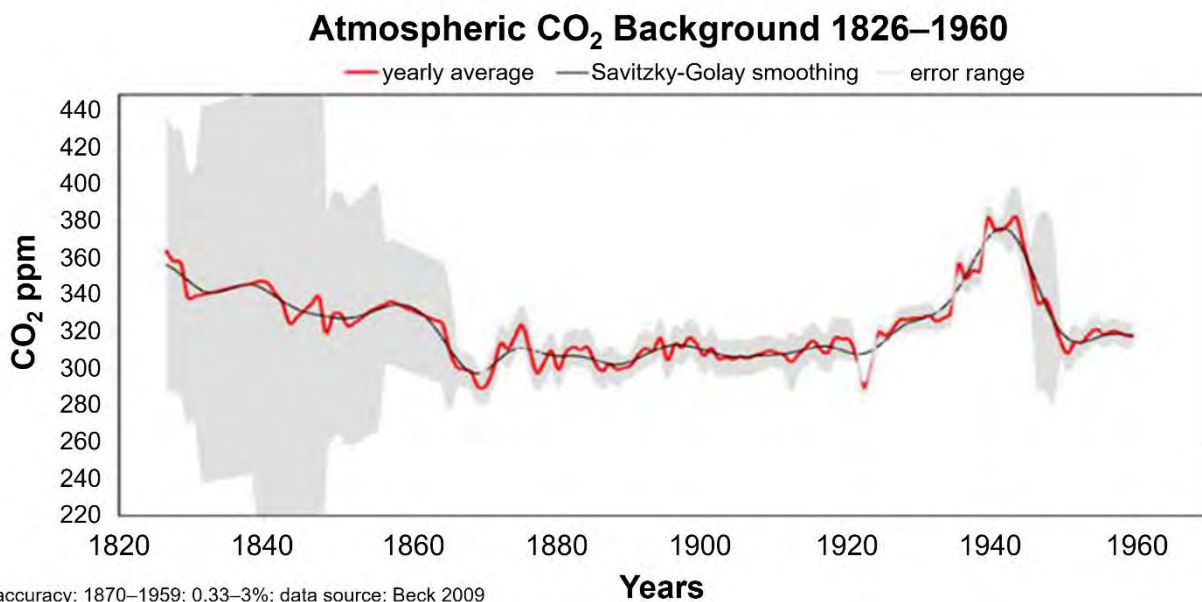


Figure 2.3.1: *Compilation of historical CO₂ data by Ernst-Georg Beck (Beck 2022).*

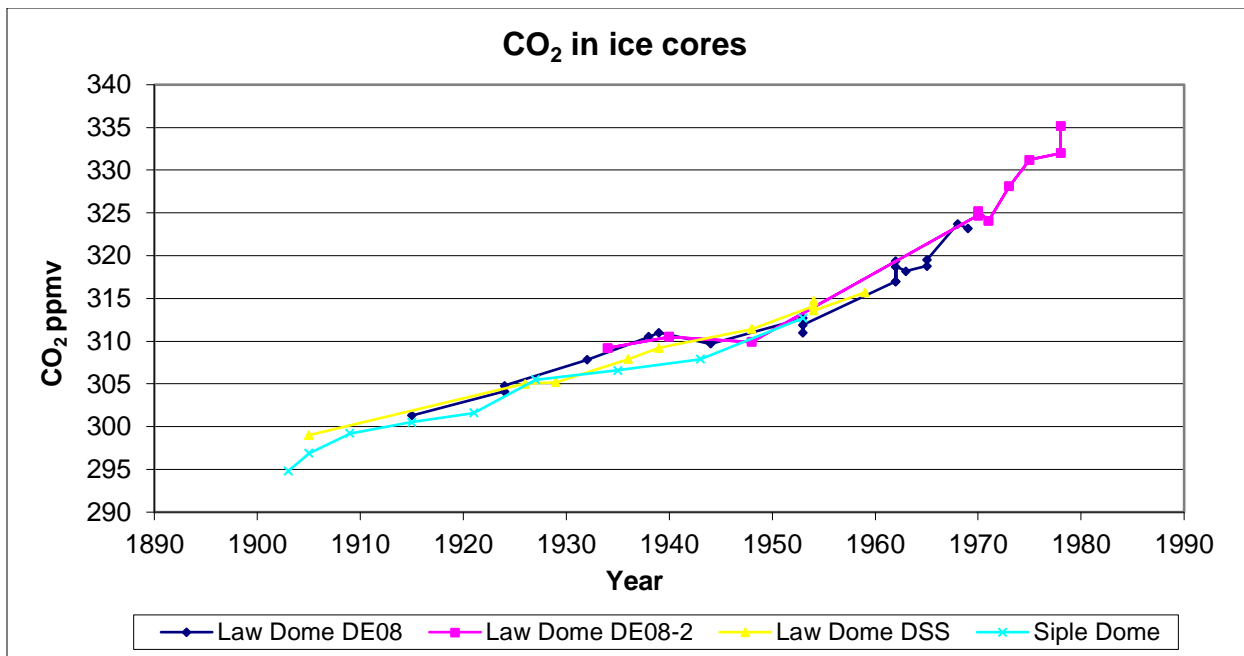


Figure 2.3.2: Ice core CO₂ in four ice cores, Law Dome DE08 and DE08-2 have a resolution of eight years and Law Dome DSS and Siple Dome a resolution of around 20 years. The Law Dome ice cores have an overlap with the South Pole CO₂ data (1958–1978) within a few ppmv of each other (NOAA ongoing).

That means that Beck’s “peak” is questionable and is probably an artifact of local biases in the historical CO₂ measurements.

The impacts of those biases are investigated by examining modern measurements discussed in the following section.

Modern Variations Due to Local Circumstances

For evaluating historical measurements, it is important to know where and how they were sampled and measured, including wind direction and surroundings. In this section, modern measurements over land are compared with the historical measurements and with background measurements.

Most of the historical CO₂ measurements came from sites on land: some in towns, some in rice fields, some in forests and grassland. In many cases, the measurement environment was effectively a mix of those types of sites and a mix of direction in the prevailing winds. Many of the measurements were taken near the ground, only up to a few meters high.

It is clear from modern measurements that the CO₂ levels measured at low height over land do not reflect the “background” level of CO₂. The influence of local sources and sinks is too high, mostly overstating CO₂ concentrations. This conclusion is based on modern measurements, including some made near the same places where the historical measurements were taken.

One example is Linden-Giessen, Germany, which had the longest continuous data series and largest number of samples, and comprises the main 1942 “peak” of the historical measurements. At Linden-Giessen, a modern continuous monitoring station measures CO₂ and other gases by gas chromatography, at half-hour intervals, (Source: HLNUG, ongoing). The station is only a few kilometers from the original station and in surroundings that are still semi-rural, though vehicle traffic has increased since 1942.

In Figure 2.3.3, the performance of the modern measurements at Linden/Giessen under an inversion layer, with little wind to mix the air, is compared to the real “background” stations at Barrow, Mauna Loa and the South Pole. Within a 24-hour period, CO₂ will fluctuate from 350 to over 500 ppm at the modern Linden/Giessen station.

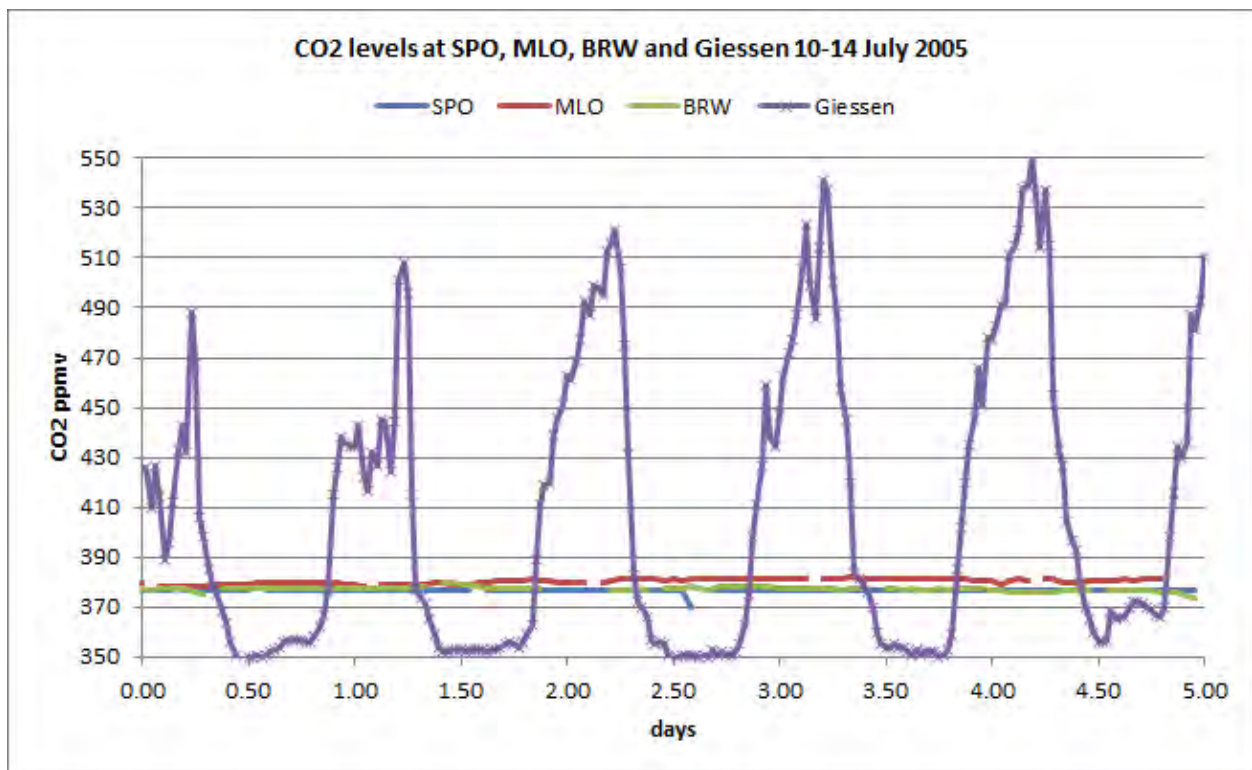


Figure 2.3.3: CO₂ levels as measured at Linden/Giessen under inversion (HLNUG, ongoing) compared to hourly averaged raw CO₂ data from Barrow, Mauna Loa and the South Pole for the same days, including all local outliers. Data from (NOAA ongoing).

Moreover, other than a few days of multiple sampling at 1.5-hour intervals, the historical data were taken only three times a day at 7 a.m., 2 p.m. and 9 p.m. That causes a problem under an inversion layer because CO₂ concentrations at ground level can vary dramatically over the course of a day, e.g., as photosynthesis draws down the CO₂ level during morning hours, shown in Figure 2.3.4. What’s more, those effects change drastically with changing daylight and temperature over the seasons.

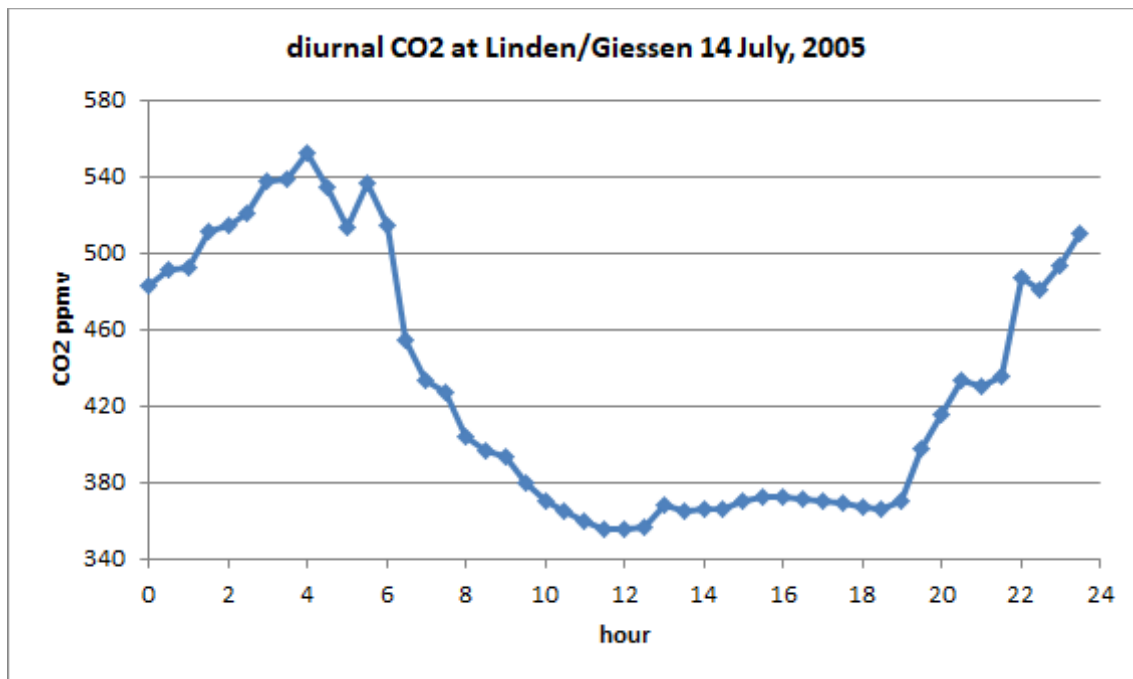


Figure 2.3.4: Diurnal CO₂ change at Linden/Giessen under inversion (HLNUG ongoing).

There is also a substantial local bias at Linden/Giessen compared to the background CO₂ levels measured at Mauna Loa and other stations. Figure 2.3.5 shows the monthly averages at Linden/Giessen for the period 1995–2008. There is clear positive bias averaging 30–40 ppmv in the Linden/Giessen data, which are quite variable even when averaged over a month.

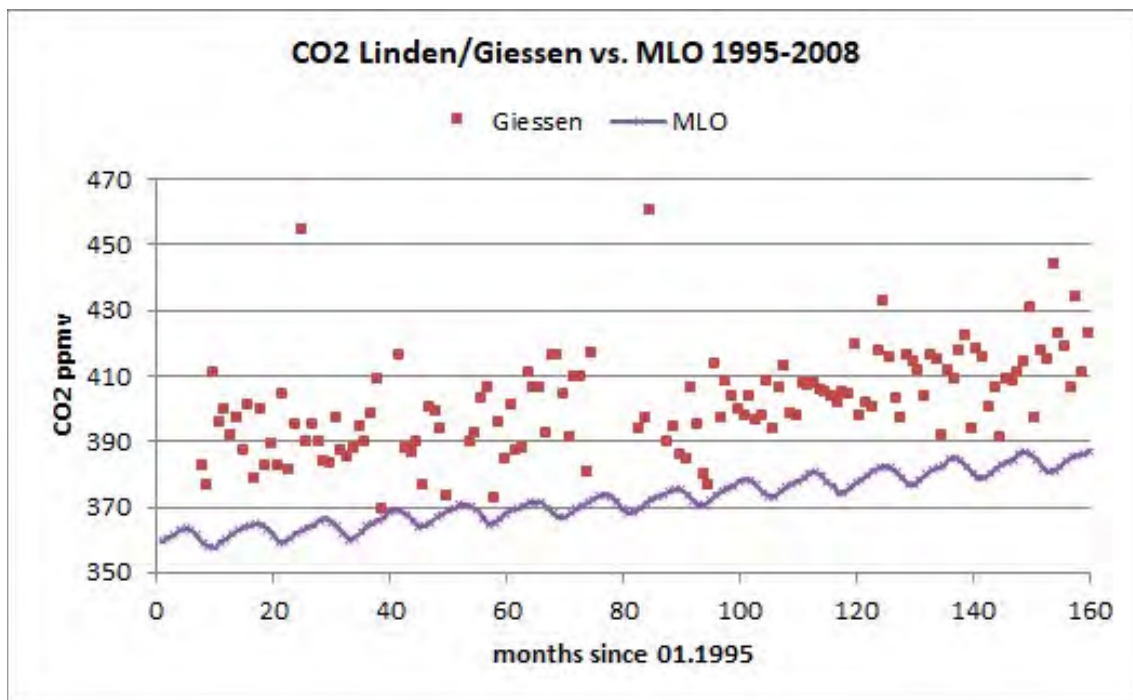


Figure 2.3.5: Monthly averages at Linden/Giessen compared to Mauna Loa data.

Comparison with the Historical Measurements

There are two long series in Beck's compilation which comprise the 1942 peak in his historical compilation.

The main series is data collected at Giessen in the period 1939–1940 at four heights and a frequency of three times a day. The second one was at Poonah, India, which only shows monthly CO₂ data over several years. Both show a huge variability over the measurements. Figure 2.3.6 and Table 2.3.1 show Giessen's CO₂ levels and standard deviations, respectively. Figure 2.3.7 shows CO₂ levels at Poonah.

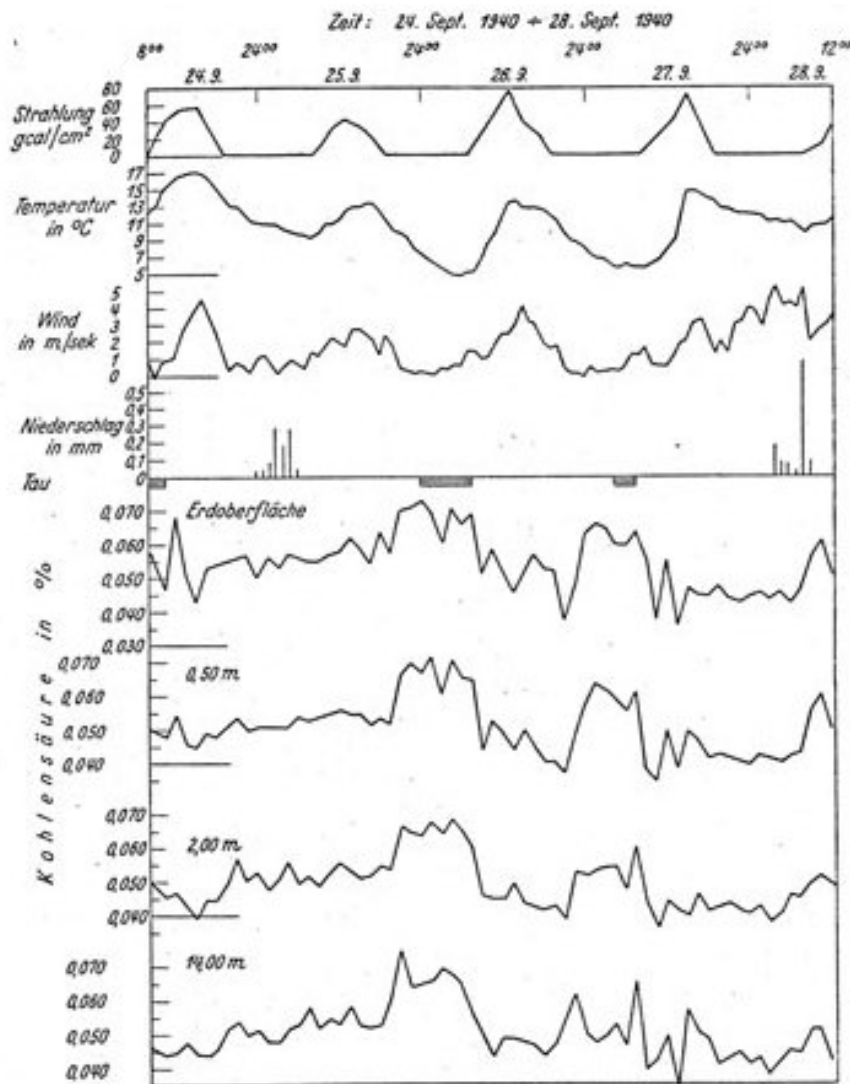


Abb. 1. Tagesverlauf der Kohlensäure und Witterungsfaktoren.

Figure 2.3.6: CO₂ levels at four heights were measured each 1.5 hour during four days at Giessen (24–28 September 1940), plus climate factors: light input, temperature, wind speed and precipitation. The scale of the CO₂ measurements is in percent: 0.04 % is 400 ppmv. Over the full period (August 1939–January 1940) only three samples per day were taken (Kreutz 1941).

Table 2.3.1: *Averages and mini/max + standard deviation (Streuung in German) of the historical data of Giessen. Data are expressed in thousandth of a percent or tens of a ppmv. For the data over 1940 at 14.0 meters, that gives a range of 240 to 680 ppmv with a standard deviation of 65.9 ppmv (Kreutz 1941).*

Tabelle 1 a und b.
Mittlere CO₂-Werte.
a) vom 1. August 1939 bis 31. Januar 1941.

	0 m	0,5 m	2,0 m	14,0 m	Mittel
Vormittag	42,8	41,7	40,5	43,2	42,1
Nachmittag	52,9	45,0	43,0	46,4	46,8
Abend	42,5	42,5	41,6	44,0	42,7
Tagesmittel	46,1	43,1	41,7	44,4	43,85

b) für das Jahr 1940

	0 m	0,5 m	2,0 m	14,0 m
Mittel	46,8	45,1	43,4	46,2
Maximum	64	62	62	68
Minimum	27	28	24	24
Streuung σ (abs.)	$\pm 6,42$	$\pm 6,11$	$\pm 6,12$	$\pm 6,59$
Streuung σ (%)	13,7	13,6	14,1	14,3

The very wide range of 240 to 680 ppmv at a height of 14.0 meters of the Giessen historical data, and standard deviation between 61.1 and 65.9 ppmv, are shown in Table 2.3.1. The bulk of the modern data have a smaller range of measurement about 330 to 380 ppmv for practically the same place—still semi-rural—even with far more traffic than in the 1940’s. This may indicate that the measurement method and/or procedures were too inaccurate to reliably determine the local CO₂ values of that time. Thus, they also may be far off the true background values.

The station at Poonah, India, collected a few ambient air CO₂ measurements, shown in Figure 2.3.7. Besides these measurements, they collected measurements under, in between and just above growing crops, monitoring the CO₂ use by these plants. The data gathered documents that surface and near-surface measurements have no connection with background or ambient CO₂ levels at all.

The extreme differences in CO₂ level (between 300 and 700 ppmv) within a year allow only one conclusion: these are highly contaminated data that do not reflect background CO₂ levels.

The Probability of a Huge CO₂ Peak Around 1942

The hypothesis of a 70-ppmv peak increase in the years 1920–1940 and dropping in 1945–1955, conflicts with physics, with CO₂ measurements in ice cores and with evidence from other proxies.

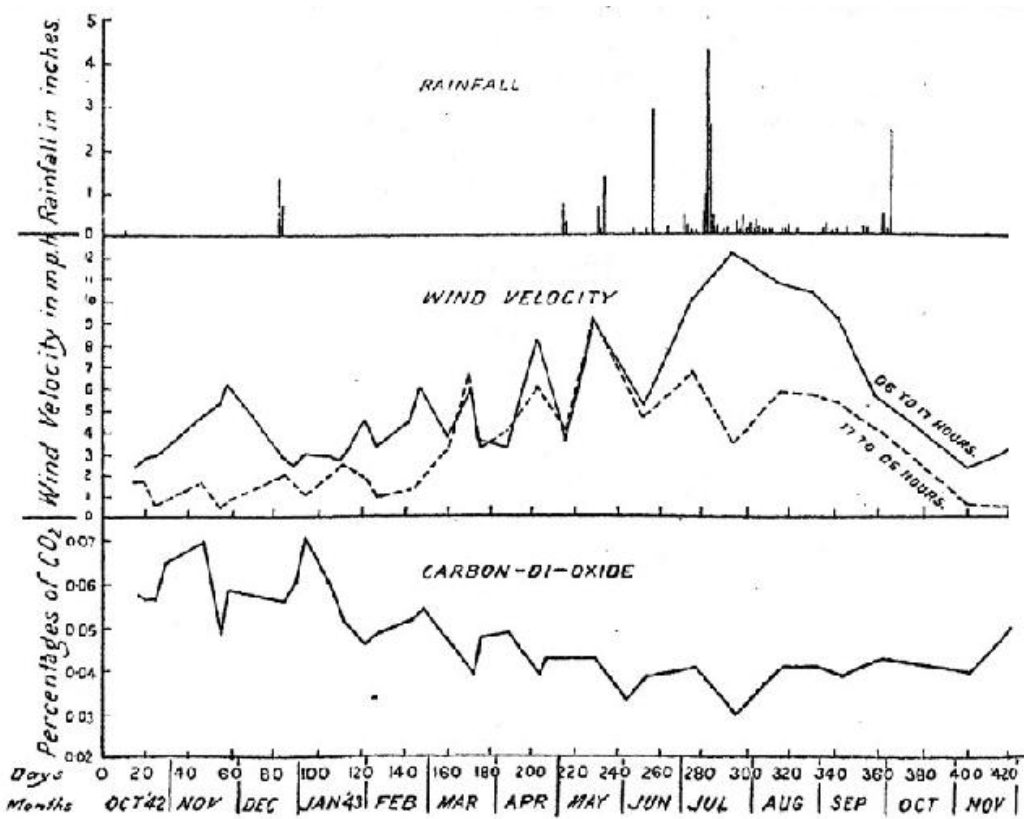


FIG. 2

Figure 2.3.7: CO₂ measurements at Poonah, India, a few times a month (1941–1943) including wind speed and rainfall at the moment of measurement.

A single ppmv of CO₂ contains 2.1294 Pg of carbon (PgC), so if vegetation were the main source of such a large swing, that would mean that about 150 PgC was released in 20 years and then recovered in only 10 years. Inasmuch as the total carbon content of all vegetation on Earth is estimated to be only 550 ±100 PgC (IPCC AR5), a 70-ppmv CO₂ increase would require burning 23–33% of all vegetation on Earth. That is physically impossible. Taking into account even the vast destruction of WWII, there’s no evidence of such a cataclysm.

The current net removal rate of CO₂ in vegetation and oceans together is only about 5 PgC/year, not including “land use change emissions,” or about 6 PgC/year if emissions from changes in land use are included (IPCC AR6 WG1 Table 5.1).

Further, the probability of a huge peak of CO₂ in 1942 conflicts with the CO₂ measurements from ice cores, which only show an increase of about 9 ppmv over the period 1930–1960, without any peak, and even a 1-ppmv dip around 1945 for the high resolution (10–14 year) Law Dome ice cores in Figure 2.3.2. There is also the stomata data over the past century shown in Figure 2.3.8.

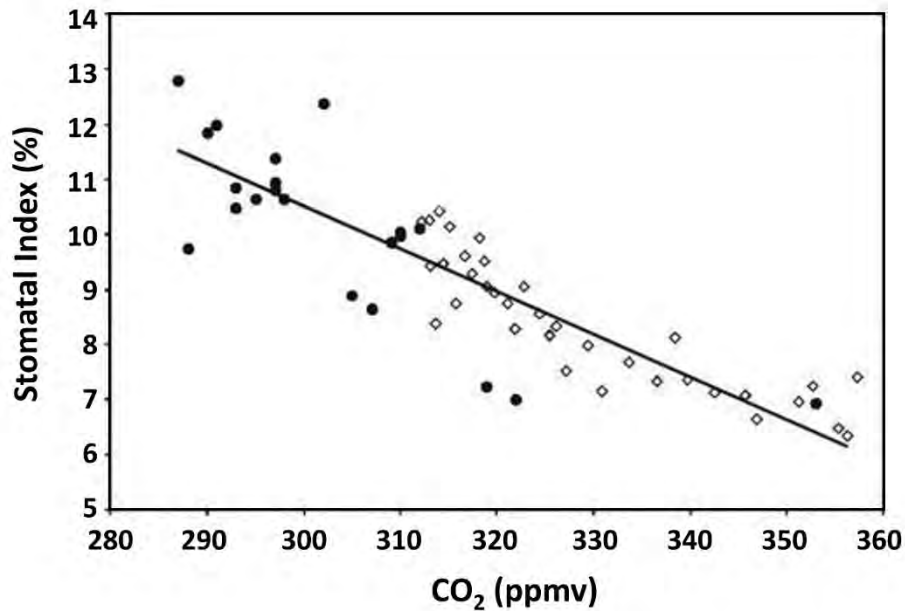


Figure 2.3.8: Calibration of the stomata data over the past century (1900–1990) against ice core CO_2 , firn and direct measurements, van Hoof (2004).

If there had been a peak of +70 ppmv around 1942 (when the ice cores show 310 ppmv), the stomatal index (SI) should have reacted with an extreme low value at the 310 ppmv point. But nothing special over the full period can be observed.

Lastly, carbon isotopes in coralline sponges do not indicate a dramatic change during the 1942 period, as shown in Figure 2.3.9.

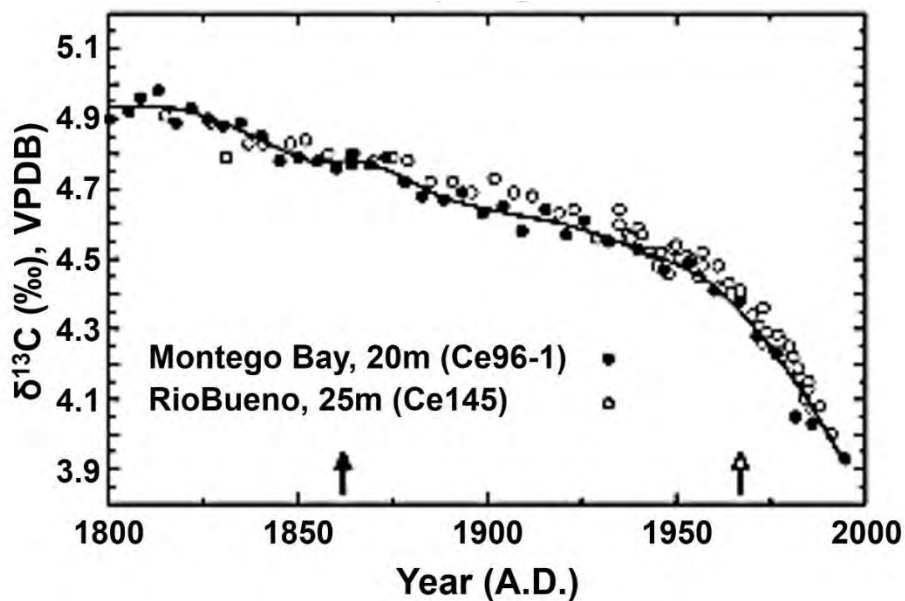


Figure 2.3.9: Evolution of $\delta^{13}\text{C}$ in coralline sponges, Böhm et al. (2002).

Coralline sponges grow in shallow waters in the tropics. The carbonates built into the sponges follow the isotopic composition ($^{13}\text{C}/^{12}\text{C}$ ratio expressed in $\delta^{13}\text{C}$) of CO_2 in the surrounding water, without modification. Shallow waters closely track the CO_2 in the atmosphere (half-life time less than a year) over the years since the start of the Industrial Revolution. If there had been a huge release of CO_2 in the atmosphere around 1942, it would be seen in the $\delta^{13}\text{C}$ ratio, as such a release from vegetation should give an enormous drop in $\delta^{13}\text{C}$ (about 4% decrease), while such a release from the deep oceans should give an important increase in $\delta^{13}\text{C}$ (about 1.6% increase). But there is no visible change in trend around that period.

Historical CO_2 Conclusions

A huge peak of +70 ppmv CO_2 (150 PgC) in the atmosphere around 1942 is physically impossible, and the claim is based on measurements at places contaminated by huge local CO_2 sources. It also conflicts with reliable high-resolution ice core CO_2 measurements, and with several proxies over the same period.

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He has a B.Sc. in process chemistry, Antwerp, Belgium, 1965. Most of his career was dedicated to process engineering, primarily in manufacturing of paints and inks and later in a large chlorine/VCM/PVC factory. He is a member of the CO₂ Coalition.

In retirement, he developed a deep understanding of the carbon cycle. Working independently, he derived the approximate effective residence time for CO₂ added to the atmosphere and he achieved about the same figure that Peter Dietze, Dick Lindzen, Roy Spencer and others had calculated (about fifty-years e-fold decay rate or 35-years half-life time).

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He is a member of the CO₂ Coalition and was previously a member of the North Carolina Sea Level Rise Impact Study Advisory Committee. He also created the sealevel.info website. He's also a two-time IPCC WG1 Expert Reviewer. He also wrote a simple computer simulation of CO₂ decay, based on historical CO₂ removal rates vs. atmospheric levels and found the same approximate adjustment time (effective residence time) for additional CO₂ that Engelbeen and others have reported (about 50 years).

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About the CO₂ Coalition

The CO₂ Coalition was established in 2015 as a non-partisan educational foundation operating under Section 501(c)(3) of the IRS code for the purpose of educating thought leaders, policy makers and the public about the important contribution made by carbon dioxide to our lives and the economy. The Coalition seeks to engage in an informed and dispassionate discussion of climate change, humans' role in the climate system, the limitations of climate models and the consequences of mandated reductions in CO₂ emissions. In carrying out our mission, we seek to strengthen the understanding of the role of science and the scientific process in addressing complex public policy issues like climate change. Science produces empirical, measurable, objective facts and provides a means for testing hypotheses that can be replicated and potentially disproven. Approaches to policy that do not adhere to the scientific process risk grave damage to the economy and to science.

The Coalition is comprised of nearly 200 of the top experts in the world who are skeptical of a theoretical link between increasing CO₂ and a pending climate crisis while embracing the positive aspects of modest warming and increasing CO₂. They include physicists, chemists, engineers, geologists, economists and more. More than 70% of the members hold doctorates or commensurate degrees and include three members of the National Academy of Sciences.