CO2 MEASUREMENTS

In climate sceptics circles, there is rather much confusion about historical/present CO2 measurements. This is in part based on the fact that rather accurate direct measurements of CO2 in the atmosphere show much higher values in certain periods of time (especially around 1942), than the around 280 ppmv which is measured in Antarctic ice cores. 280 ppmv is assumed to be the pre-industrial amount of CO2 in the atmosphere by the scientific community. This is quite important, as if there were (much) higher levels of CO2 in the recent past, that may indicate that current CO2 levels are not from the use of fossil fuels, but a natural fluctuation and hence its influence on temperature is subject to (huge) natural fluctuations too and the current warmer climate is not caused by the use of fossil fuels.

To be sure about my scepticism: I like to see and examine the arguments of both sides of the fence, and I make up my own mind, based on these arguments. I am pretty sure that current climate models underestimate the role of the sun in climate variability and overestimate the role of greenhouse gases and aerosols. But I am as sure that the increase of CO2 in the atmosphere since the start of the industrial revolution is mainly from the use of fossil fuels.

There are several reasons why the hypothesis of large non-human CO2 variations in recent history is wrong and that most of the recent increase in CO2 in the atmosphere indeed is mainly man-made, but that need a step-by-step explanation. Follow the steps:

1. Accuracy of modern CO2 measurements.
2. Variations due to local circumstances.
3. Variations of CO2 due to the seasons.
4. Where to measure? The concept of "background" CO2 levels.
5. Evidence of human influence on the increase of CO2 in the atmosphere.
   - The mass balance

1. Accuracy of modern CO2 measurements:

Historical measurements of CO2 in the atmosphere were based on chemical methods. The accuracy was quite good for several of the methods, including CO2 in air, but less appropriate for atmospheric CO2 measurements for other methods. This is especially the case for the micro-Schollander method, which was intended for exhaling air oxygen and CO2 (around 2%) measurements.
Charles D. Keeling wanted methods which needed a minimum of maintenance/chemicals for a maximum of near-continuous measurements, which he found in the NDIR (non-dispersive infrared) method.
According to his notes [1][2]:

> **The imprecision in measuring references gases approaches 0.1 ppmv and is rarely greater than 0.2 ppmv. However, agreement differences less than 0.5 ppmv between flask and analyzers or between different analyzers on a short-term basis are difficult to obtain. Monthly averages from May 1964 to January 1969 may be in error by as much as 1.0 ppmv; but since 1970, systematic error probably does not exceed 0.2 ppmv. The precision of monthly averages is approximately 0.5 ppmv. In summary, monthly and annual averages of the Mauna Loa data are statistically robust and serve as a precise, long-term record of atmospheric CO2 concentrations.**

Of course, there is the question of throwing out of "suspect" values when averaging the hourly data. Some data are "suspect", because they differ too much from the (expected) average of the previous (and following) data with more than a given (3 sigma) difference, or when mechanical/physical problems occur, or when there is wind from the wrong direction (land side in the case of coastal stations), etc. In many cases, the source of the deviation is known. All the data still are available in the hourly averages of 4 raw measurements, but are "flagged" and not used for daily, monthly and yearly averages. More on this in next items.

## 2. Variations due to local circumstances:

There are several local conditions which can interfere with the measurements. In some locations, this is the influence of nearby (local/regional) vegetation and/or combustion of fossil fuels. In other cases, volcanic outgassing may interfere. This is the case for Mauna Loa. From the same source [1]:

> *Possible ambient error sources at Mauna Loa include volcanic, vegetative, and man-made effects (e.g., vehicular traffic, and industry). Daily peaks in measured concentrations occur because of complex wind currents. Downslope winds often transport CO2 from distant volcanic vents causing elevations in measured CO2 concentrations. Upslope winds during afternoon hours are often low in CO2 because of photosynthetic depletion occurring in sugarcane fields and forests. Vehicular traffic problems (since corrected) caused exaggerated elevations in 1971. Despite these sources of error and contamination, considerable effort has been made to alleviate and detect these sources.*

The difference in including and excluding "flagged" data in the final result gives some differences in variability around the seasonal trend, this can be seen e.g. in the hourly averages of Mauna Loa, where the raw data (average from 4 samples within an hour) are given. Hourly averages of samples which have large variations within an hour, large variations from hour to hour, upwind conditions, etc. are "flagged". Flagged data aren't used for daily, monthly or yearly averages. The data can be downloaded from [3] where MLO = Mauna Loa, the explanation of the data and different flags used in [3] can be found in [4]:
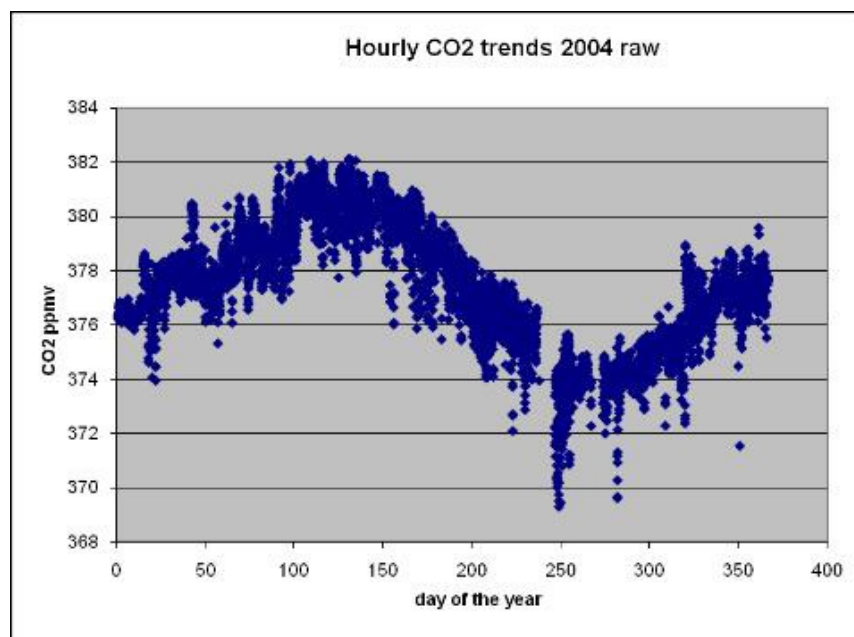
Mauna Loa raw hourly averages 2004.
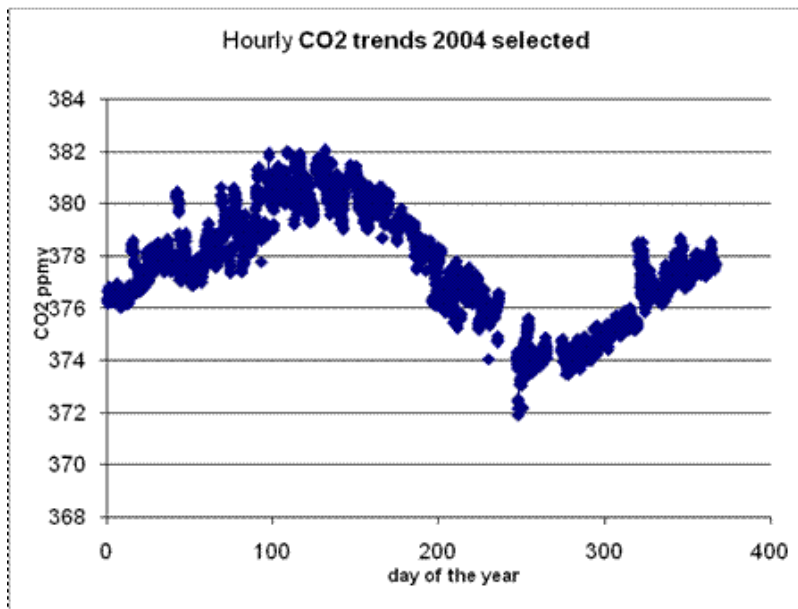
Mauna Loa selected (without "flagged") hourly averages 2004.

For 2004, 8784 hourly average data should have been sampled, but:
1102 have no data, due to instrumental errors (including several weeks in June).
1085 were flagged, due to upslope diurnal winds (which have lower values), not used in daily, monthly and yearly averages.
655 had large variability within one hour, were flagged, but still are used in the official averages.
866 had large hour-by-hour variability > 0.25 ppmv, were flagged and not used.

As one can see in the trends, despite the exclusion of (in the above second graph) all outliers, the difference in trend with or without flagged data is minimal, only the number of outliers around the seasonal trend is reduced and the overall increase in 2004 in both cases is about 1.5 ppmv.

That local production/uptake of CO2 has an influence can be seen in the detailed trend of Mauna Loa: with upslope winds, air comes from the valleys where agriculture and other vegetation reduces CO2 levels (with about 4 ppmv) during some parts of the day:
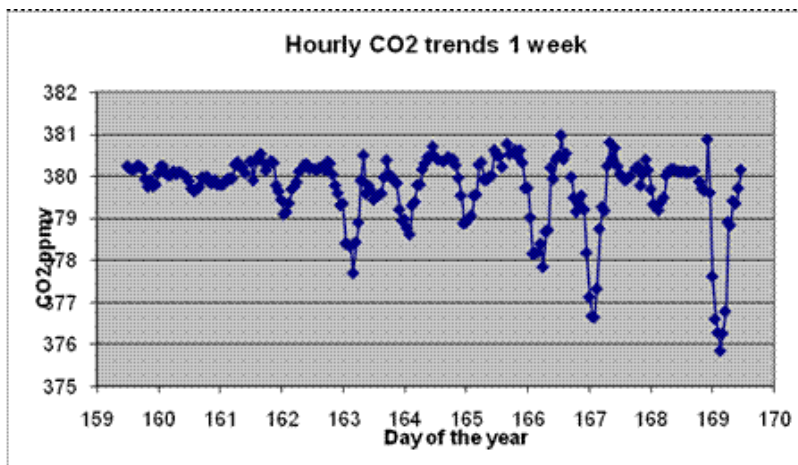
Mauna Loa hourly averages during 1.5 weeks

This shows that with upslope winds, the data is influenced by local CO2 depleted air. These data are rightfully discarded from the daily/monthly/yearly averages, as they don't reflect the background CO2 levels, which we are interested in.

Does discarding of "contaminated" data influence the trend over a year or several years? I have asked that question to Pieter Tans, responsible for dataprocessing of the Mauna Loa data. His answer:

The data selection method has been described in Thoning et al., J. Geophys. Research, (1989) vol. 94, 8549-8565. Different data selection methods are compared in that paper, including no selection. **The methods give annual means differing by a few tenths of 1 ppm***. I assume that you have read the README file* [4] *when downloading the data. The hourly means are NOT pre-processed, but they are flagged when the st.dev. of the minute averages is large.*

The good, the bad and the ugly stations.
Several stations are deemed "good", as these have minimal influence from local vegetation and/or human emissions (traffic, heating). These are stations in the middle of the oceans, sometimes at coastal points (as long as the wind is not blowing from land side) and/or above the inversion layer. These stations, after discarding outliers, differ from each other within 5 ppmv for yearly averages, of which most is from the delay between the NH and the SH, see next item. 10 of them, spanning the globe from near the North Pole (Alert, Canada) to the South Pole, are used as reference for daily, monthly and yearly averages and yearly trends. The graphs and the data can be found at [5].

Some inland stations, like Schauinsland only give reliable "background" CO2 levels, when the station (at 1200 m altitude) is above the inversion layer and with enough wind speed. This happens only about 10% of the time.

And last, but not least, many inland stations are practically unsuitable for background CO2 measurement, because of incomplete mixing with the higher air layers, partly due to too many local sources/sinks like vegetation and/or human use of fossil fuels, partly due to a shielded location. This is the case for e.g. Diekirch (Luxemburg) [6], where the station is in a valley with forests, urbanisation and traffic in the main upwind direction:
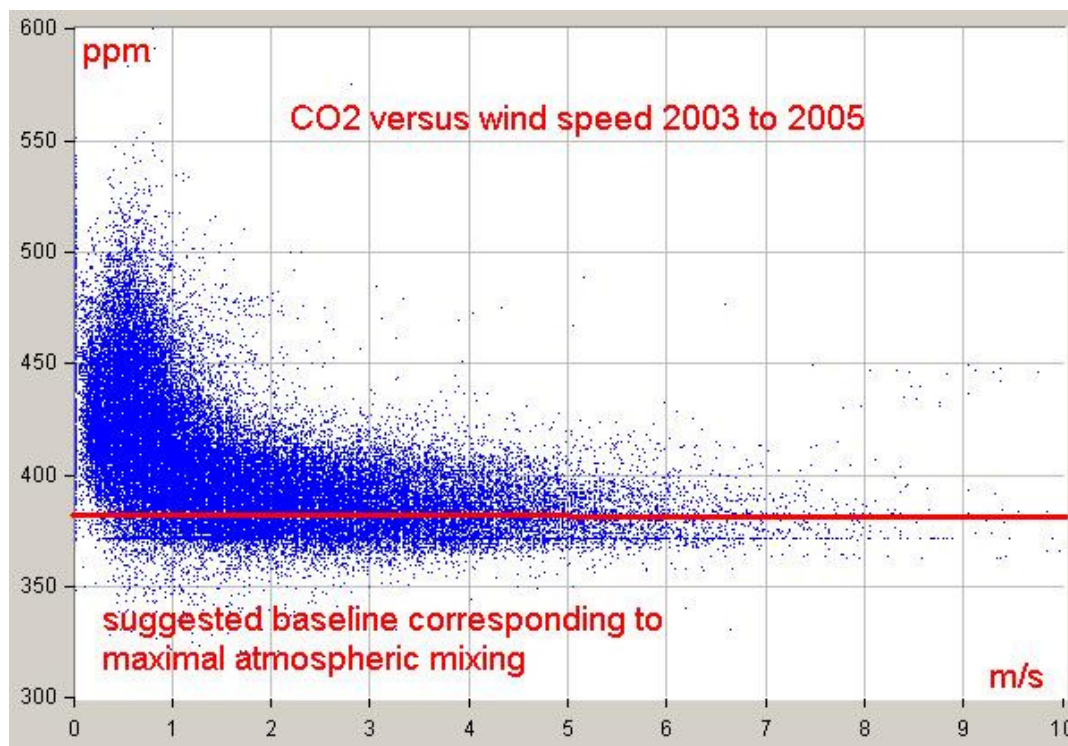
Diekirch (Luxemburg) CO2 measurements compared to wind speed
Graph from [6].

As can be seen, even at inconvenient places with lots of local sources/sinks, there is an inverse correlation between CO2 levels and wind speed. With higher wind speeds, CO2 levels are better mixed with higher air layers which have "background" CO2 content. This reduces the CO2 content at ground level. The assymptote of CO2 levels at high speed winds (as was seen during storm Franz, 11 January 2007) is about 385 ppmv, very close to the 382 ppmv level found at Mauna Loa in the same period. The same is true for diurnal variance: at daytime and with high enough wind speed (> 1 m/s), CO2 levels are lower and near background, while at night under the inversion layer, CO2 levels are up to 100 ppmv higher.

## 3. Variations of CO2 due to the seasons:

There are two main natural influences on the CO2 levels of the atmosphere: the temperature of the ocean's surface waters and the uptake of CO2 by plants in spring/summer and the release of CO2 by the decay of dead plant material in fall/winter. This is most clear in the NH (Northern Hemisphere), where most of vegetation on land is situated.
CO2 is continuously emitted by deep sea upwelling, especially in the tropics, where temperatures are high and the partial pressure of CO2 (pCO2) in the upper oceans is higher than in the atmosphere above it. CO2 is continuously absorbed in the upper ocean layers at higher latitudes, where the colder temperatures reduce the pCO2 of the oceans, lower than the pCO2 of the atmosphere. This is especially the case at the sink places of the THC (thermohaline circulation) in the Nordic Atlantic ocean. Colder water can retain more CO2 than warmer water, but in the case of CO2 there are also a lot of chemical and biological reactions which influence the solubility of CO2 and hence pCO2 at the surface of the oceans. For more details on this, Wiki has a quite good explanation.
The CO2 flow between the tropics and the colder places in the oceans is relatively constant (more about that later), and doesn't influence the seasonal variation that much. More variation is in the temperature (and thus pCO2) of the mid-latitudes, where there is absorption of CO2 in winter and release of CO2 in summer. The CO2 flow of vegetation (including algues in the upper oceans) is in opposite direction: more release in winter and more uptake in summer. The net effect in the NH is a variation of +/-4 ppmv in Mauna Loa (mid Pacific Ocean, middle troposphere) between summer and winter, up to +/-20 ppmv for Barrow (Alaska, USA, sea level, near tundra) or even 35 ppmv at Schauinsland (Germany, 1200 m high). The data of Schauinsland are heavily contaminated by the nearby fully inhabited and industrialised Rhine valley. And influenced by vegetation, in this case the Black Forest of SW Germany. Only at night, when separated from the valleys by an inversion layer, and with sufficient wind speed, the CO2 levels are better mixed with the rest of the troposphere and retained. This is the case for only 10% of the data.
Data series from the SH (Southern Hemisphere) show much less seasonal variation, because of the much smaller area of land/vegetation. The smallest influence of the seasons is found at the South Pole.

Here follows some comparison of the Mauna Loa (selected) monthly averages with these of other stations:
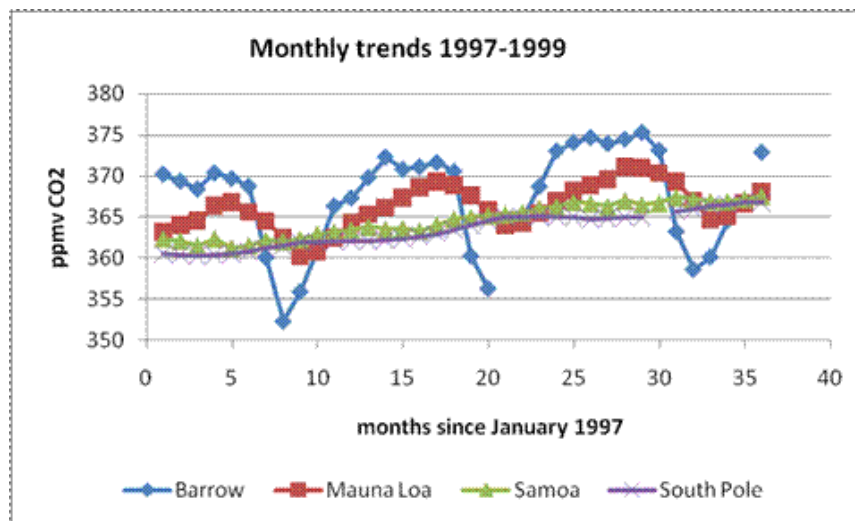
Monthly trends 1997-1999 of 2 NH stations (Barrow and Mauna Loa) and 2 SH stations (Samoa and South Pole)

As can be noticed, the variation at Mauna Loa is smaller than at Barrow and the SH stations have a much smaller seasonal influence than the NH stations. Also, although the trend of the SH stations is near the same, there is some lag between the NH and SH stations. This is the first indication that the source of the increase is situated in the NH, as the ITCZ (intertropical convergence zone) forms a barrier for the exchange of CO2 (and aerosols) between the NH and the SZ. This is even more clear in the longer term yearly trends:
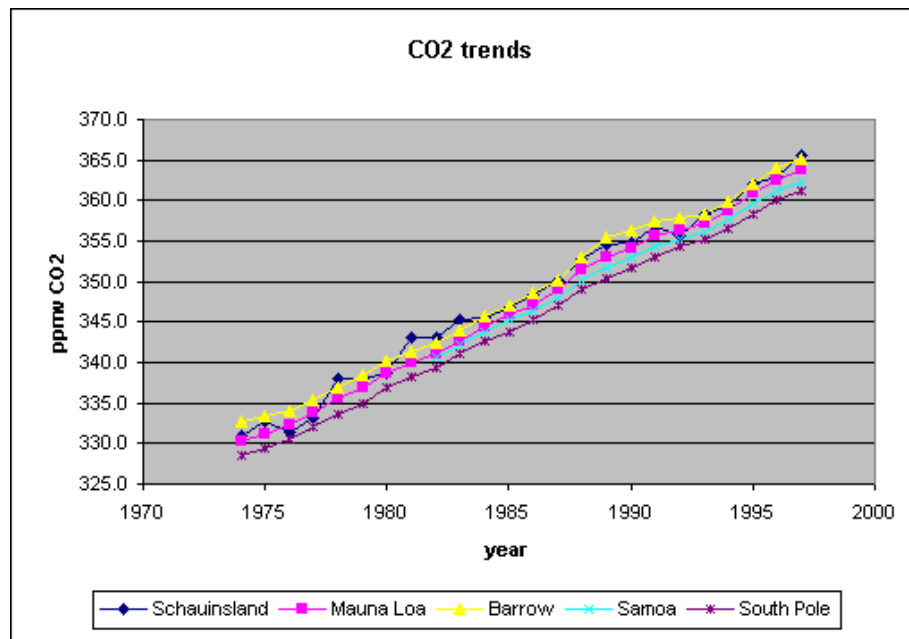
Trends in yearly averages of CO2 levels at different stations.

The trend of the SH stations has a growing delay of 6-12 months behind the NH trend. But all yearly average data of the "best" stations (and the average of least contaminated data from less suitable stations like Schauinsland) are within 5 ppmv for similar growth.

4. Where to measure? The concept of "background" CO2 levels.

The concept was launched by C.D. Keeling in the mid fifties, when he made several series of measurements in the USA. He found widely varying CO2 levels, sometimes in samples taken as short as 15 minutes from each other. He also noticed that values in widely different places, far away from each other, but taken in the afternoon, were much lower and much closer resembling each other. He thought that this was because in the afternoon, there was more turbulence and the production of CO2 by decaying vegetation and/or emissions was more readily mixed with the overlying air. Fortunately, from the first series on [2], he also measured 13C/12C ratios of the same samples, which did prove that the diurnal variation was from vegetation decay at night, while during the day photosynthesis at one side and turbulence at the other side increased the 13C/12C ratio back to maximum values.

Keeling's first series of samples, taken at Big Sur State Park, showing the diurnal CO2 and d13C cycle was published in [7], original data (of other series too) can be found in [8]:
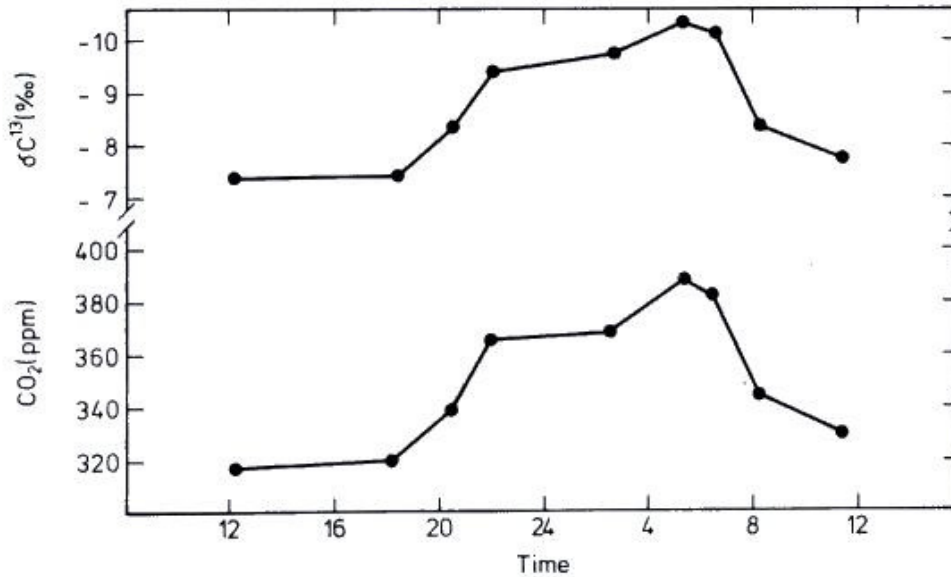
Figure 3.1 Diurnal variation in the concentration and carbon isotopic ratio of atmospheric CO_2 in a coastal redwood forest of California, 18-19 May 1955, Big Sur St. Pk. (Keeling, 1958. Reproduced by permission of Pergamon Press.)

Several others measured CO2 levels/d13C ratios of the their own samples too. This happened at several places in Germany (Heidelberg, Schauinsland, Nord Rhine Westphalia). This confirmed that local production was the origin of the high CO2 levels. The smallest CO2/d13C variations were found in mountain ranges, deserts and near the oceans. The largest in forests, urban neighbourhoods and non-urban, but heavily industrialised neighbourhoods. When the reciproke of CO2 levels were plotted against d13C ratios, this showed a clear relationship between the two. Again from [7]:
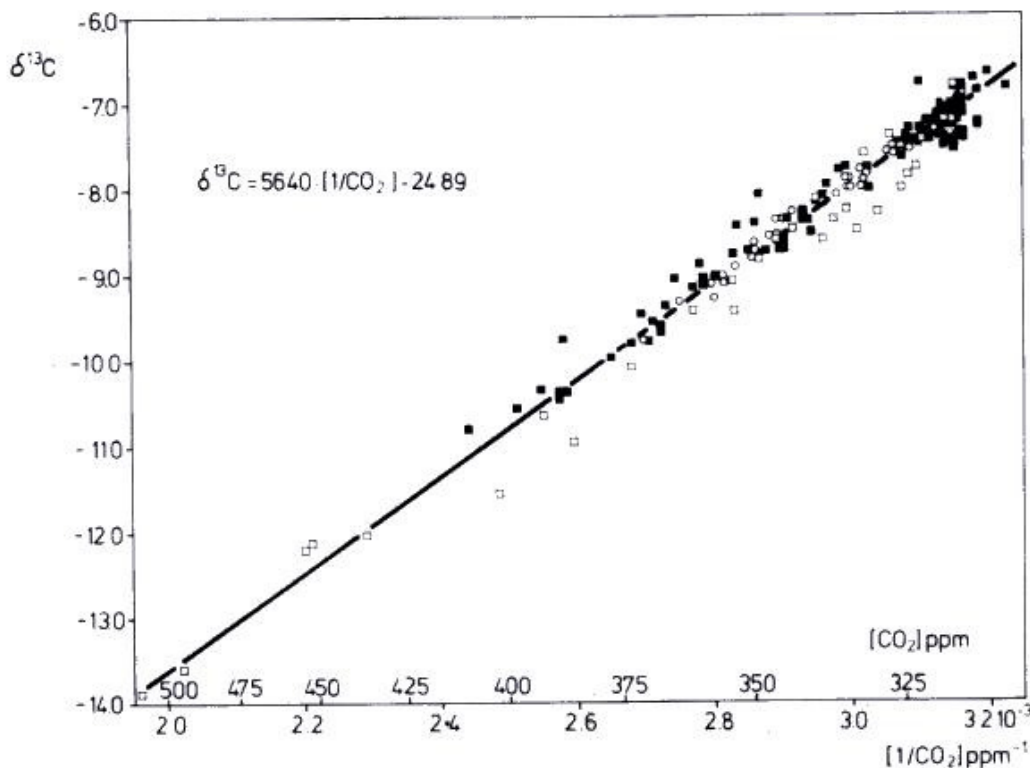

Figure 3.5 Relation between carbon isotope ratio and concentration of atmospheric CO_2 in different air types from measurements summarized in Table 3.4
(Keeling, 1958, 1961: full squares; Esser, 1975: open circles; Freyer and Wiesberg, 1975, Freyer, 1978c: open squares). All $\delta^{13}C$ measurements have not been corrected
for N_2O contamination (Craig and Keeling, 1963), which is at the most in the area of + 0.6‰

The search for background places.
Keeling then sought for places on earth not (or not much) influenced by local production/uptake, thus far from forests, agriculture and/or urbanisation. He had the opportunity to launch two continuous measurements: at Mauna Loa and at the South Pole. Later, other basic stations were added, all together 10 from near the North Pole (Alert, NWT, Canada) to the South Pole, most of them working continuous, some working with regular flask sampling.

We are interested in CO2 levels in a certain year all over the globe and the trends of the CO2 levels over the years. So, here we are at the definition of the "background" level:
Yearly average data taken from places minimal influenced by vegetation and human sources are deemed "background". For convenience, the yearly average data from Mauna Loa are used as reference. One could use any base station as reference or the average of the stations, but as all base stations (and a lot of other stations, even Schauinsland) are within 5 ppmv of Mauna Loa, with near identical trends, and that station has the longest CO2 record, Mauna Loa is the reference.

As the oceans represent about 70% of the earth's surface, and all oceanic stations show near the same yearly averages and trends, already 70% of the atmosphere shows background behaviour (within 5 ppmv). This can be extended to near the total earth for the part above the inversion layer.

Measurements above the inversion layer.
Above land, diurnal variations are only seen up to 150 m (according to [7]).
Seasonal changes reduce with altitude. This is based on years of flights (1963-1979) in Scandinavia [7] and between Scandinavia and California [9]. Further confirmed by old and modern [10] flights in the USA and Australia (Tasmania). In the SH, the seasonal variation is much smaller and there is a high-altitude to lower altitude gradient, where the high altitude is 1 ppmv richer in CO2 than the lower altitude. This may be caused by the supply of extra CO2 from the NH via the southern branch of the Hadley cell to the upper troposphere in the SH.
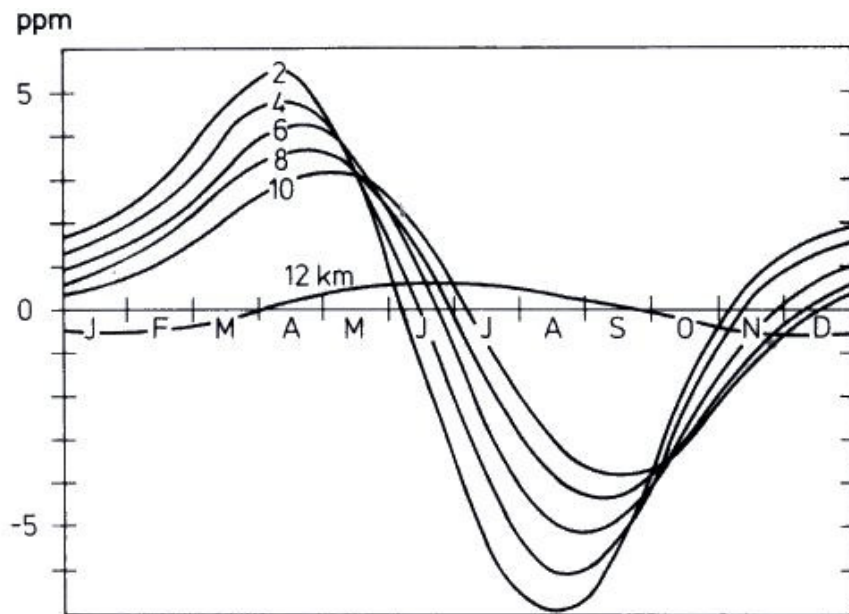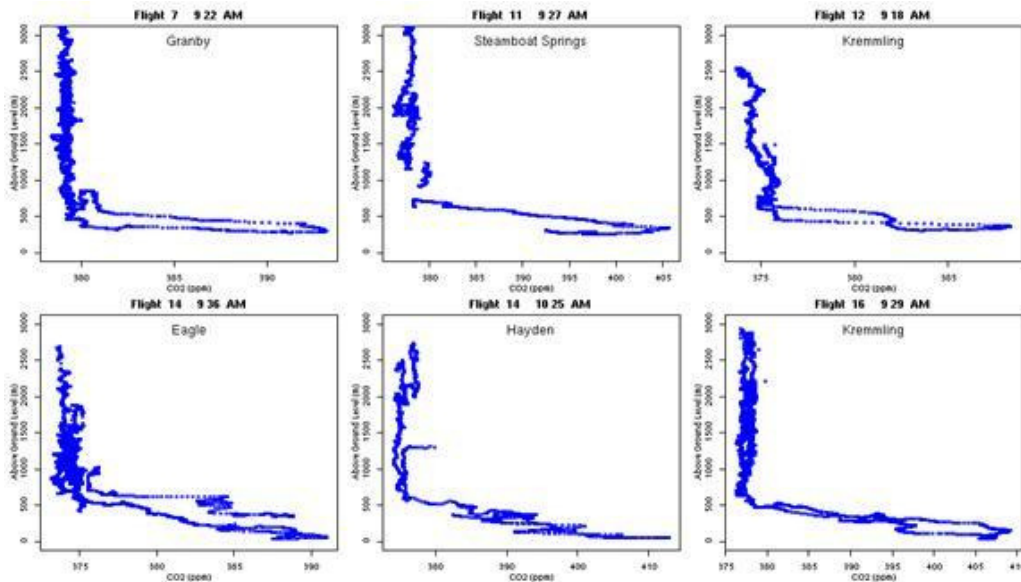
From [7], based on [9]:

Figure 3:2 Amplitude and phase shift of seasonal variations in atmospheric CO2
at different altitudes, calculated from direct observations by harmonic analysis
(Bolin and Bischof, 1970. Reproduced by permission of the Swedish Geophysical Society.)

From [10]:

Modern flight measurements in Colorado, CO2 levels below the inversion layer
in forested valleys and above the inversion layer at different altitudes

As one can see, again the values above the inversion layer are near straight and agree within a few ppmv with the Mauna Loa data. Below the inversion layer, the morning values are 15-35 ppmv higher, in the afternoon, these may sink to background again.

If we take the 1000 m as the average upper level for the influence of local disturbances, that represents about 10% of the atmospheric mass. Thus the "background" level can be found at 70% of the earth's air mass (oceans) + 90% of the remaining land surface (27%). That is in 97% of the global air mass. Only 3% of the global air mass contains not-well mixed amounts of CO2, which is only over land.

General conclusion:
Background CO2 levels can be found over all oceans and over land at 1000 m and higher altitudes (in high mountain ranges, this may be higher).

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5. Evidence of human influence on the increase of CO2 in the atmosphere.

The mass balance
The amount of CO2 emitted by humans nowadays is about 7 GtC/yr (CO2 counted as carbon). The increase in the atmosphere is about 4 GtC/yr. That implies that there is little to no increase in the atmosphere due to other causes, or the amount in the atmosphere in the case of a natural unbalance should be higher than the emissions, not lower. To show this for the past near 50 years [11]:
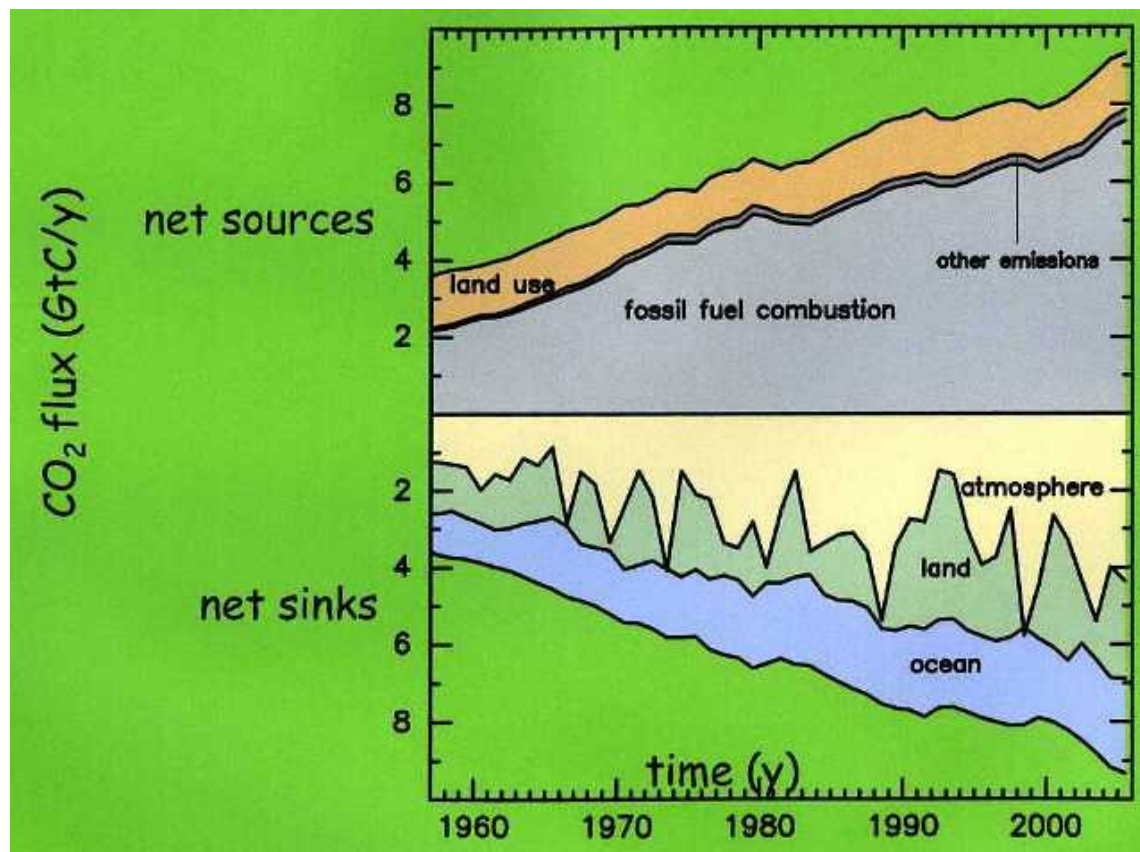
The graph shows the increase in CO2 from emissions, land use and others
vs. the increase found in the atmosphere, land and oceans, expressed in GtC/yr

The graph is based on calculations of emissions, sampled from national inventories of fuel use and land use change. In the best case, these are accurate, in the worst case, the emissions are underestimated (as probably is the case for China). Inventories of the atmosphere are based on very accurate measurements of CO2 at Mauna Loa. The difference between CO2 emissions (expressed in gigaton carbon per year - GtC/yr) and carbon increase in the atmosphere is what the oceans and/or vegetation absorb each year. The partitioning between land and ocean is less certain, but not of interest here, as in any case the sum of land+oceans is more sink than source.

As this graph shows, in any year of the past 40+ years, the emissions are larger than the increase in the atmosphere. That means that the total mass balance of all natural variables (temperature, ocean pH, vegetation) which influence CO2 levels, is always towards more sink than source over any year:

Csources + Cemissions = Csinks + dCair
where Cemissions = 2.5-6.5 GtC/yr
and dCair = 1-6 GtC/yr
and Csinks = Csources + 3 GtC +/- 2.5 GtC

The natural seasonal exchange between vegetation and oceans at one side and the atmosphere at the other side is estimated at about 150 GtC/yr. But that is not of interest for what the change is over a year, as most of the natural releases are absorbed within the same year. The difference after a year is not more than +/- 2.5 GtC, mainly caused by temperature changes (El Niño, Pinatubo eruption). Thus the natural variations over a year are smaller than the emissions. No matter how high the natural seasonal turnover might be, in all years over the previous near 50 years, the natural CO2 sinks were larger than the natural CO2 sources... Thus it is impossible that natural sources were responsible for (a substantial part of) the increase of CO2 in the past 50 years. The increase of CO2 in the atmosphere in the past near 50 years is about 70% of the increase since the start of the industrial revolution. This is based on accurate measurements at Mauna Loa and a lot of other places. The amount of CO2 in the atmosphere in pre-industrial times is based on ice cores, which of course are less certain and more smoothed.

This proves beyond doubt that human emissions are the main cause of the increase of CO2, at least over the past near

50 years. But there is even more proof of that...

References

[1] Carbon Dioxide Concentrations at Mauna Loa Observatory, Hawaii, 1958-1999, CDIAC NDP-001: http://ceos.
neonet.nl/metadata/dif/CDIAC_NDP1.xml

[2] Rewards and penalties of monitoring the earth, Charles D. Keeling, Ann. Rev. Energy. Envir. 1998.23.25-82:
http://scrippsco2.ucsd.edu/publications/keeling_autobiography.pdf
Fascinating autobiographic story from C.D.Keeling about the history of CO2 measurements and the struggle against the
administrations to get and continue funding for continuous measurements.
Of special interest:
- First measurements on 5 l flasks were done with enhanced barometric equipment, with an accuracy of better than 0.1
ppmv.
- The same barometric equipment was used to test calibration gases and NIR equipment. A change in calibration gases
(air/CO2 vs. N2/CO2) caused a jump in response of the NIR equipment. All previous collected data were corrected for this
change.

[3] Hourly average data of semi-continuous (4 samples + 2 calibrations per hour) CO2 measuremnets at different stations:
ftp://ftp.cmdl.noaa.gov/ccg/co2/in-situ/

[4] Explanation of the different data and flags used in the records of [3]: ftp://ftp.cmdl.noaa.gov/ccg/co2/in-situ/README

[5] Selected monthly average data and graphs of CO2 measurements of the 10 base stations:
http://cdiac.ornl.gov/trends/co2/sio-keel.htm

[6] Seasonal and Diurnal CO2 Patterns at Diekirch, LU: http://meteo.lcd.lu/papers/co2_patterns/co2_patterns.html

[7] Scope 13 - The global CO2 cycle, H.-D. Freyer, SCOPE Workshop on the Biogeochemical Cycling of Carbon held at
Ratzeburg, Federal Republic of Germany, 21-26 March 1977
http://www.icsu-scope.org/downloadpubs/scope13/chapter03.html
Although the data series are not up-to-date anymore (much more extended and much more is known nowadays), the
principles outlined and the original findings still are of interest.

[8] The concentration and isotopic abundance of carbon dioxyde in rural areas, C.D. Keeling, 1957. Can be found at the
web site of Ernst Beck (http://www.biokurs.de/treibhaus/180CO2_supp.htm).
His earlier work at Big Sur is here: http://www.biokurs.de/treibhaus/literatur/keeling/Keeling_1955.doc

[9] The CO2 Content of the Upper Polar Troposphere between 1963-1979, W. Bischof, (1980?):
http://globalecology.stanford.edu/DGE/SCOPE/SCOPE%2016/SCOPE_16_1.4.1_Bishoff_113-116.pdf
Data and trends are within 2 ppmv of Mauna Loa. Seasonal trend is +/- 4 ppmv

[10] The Airborne Carbon in the Mountains Experiment (ACME): Initial Modeling Results, Stephan F.J. De Wekker ea.
Powerpoint presentation (made around 2004).
swiki.ucar.edu/acme/uploads/28/vienna_poster_final.ppt (1.45 MB .ppt file).

[11] State of knowledge on the vulnerability of the oceanic CO2 sink, Powerpoint presentation by Corinne Le Quéré,
British Antarctic Survey and University of East Anglia.
lgmacweb.env.uea.ac.uk/lequere/presentations/ioccp07_lequere_public.ppt (2.52 MB .ppt file).

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To the climate change page

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