

meteoLCD Weblog

A weblog on climate, global change and climate measurements

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Climate trends at Diekirch, Luxembourg: part 2a (atmospheric CO2)

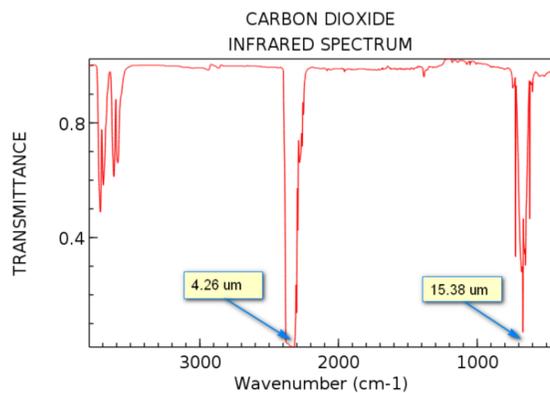
CO2, a gas that is essential to life, has become the villain par excellence during the last 20 years. Not because its undeniable positive effect on plant and crops, but because the "consensus" politicized climatology needed an easy to grasp culprit and enemy. CO2 which is after water vapour the second most important greenhouse gas has been chosen as the "climate killer" (what a horrible word!), even if the effect of its increasing atmospheric abundance still can not be quantified with precision and confidence. More than 20 years of lavishly financed climatology still has not delivered a steel-solid answer to the most often asked question: is the warming potential (i.e. the climate efficiency) of increasing mixing ratios?

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1. Measuring atmospheric CO2

CO2 is a very rare gas, with a relative abundance of about 0.04% in the atmosphere (or 400 ppmV, the unit most often used). Compare this to oxygen (20%) and nitrogen (nearly 80%), and you can imagine that measuring precisely such a small concentration (the correct expression would be "mixing ratio") is not very easy. Before Keeling started his CO2 measurement series at Mauna Lo in Hawaii, chemical methods were used, often with relative great precision. My coauthor, the late Ernst-Georg Beck, was a specialist of these historical measurements (see [here](#)), which often show wildly varying concentrations, mostly due to the fact that these measurements were done in locations where local effects were important (as for instance plant photosynthesis and human/industrial emissions). Keeling's admirable insight was to choose a location close to nearly always blowing ocean winds, far from vegetation cover and human activity. [Mauna Loa](#) was an ideal location, except for the fact that it is on an active volcano with heavy CO2 out-gassing from time to time; these periods have to be carefully monitored, and the CO2 measurements stopped during strong out-gassing events.

Keeling also was lucky to have a new class of gas sensors available: the NDIR (= non-dispersive infrared) sensors. Many molecules absorb infrared radiation, and that absorption is proportional to the concentration of the absorbing gas. CO2 for instance absorbs IR radiation in the two wavelength regions of 4 and 15 μm (the boxes added by me show the absorption at these wavelengths):



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Keeling used an SIO infrared CO2 analyzer built by the Applied Physics Company (see [here](#)). Later instruments were built by Siemens and many other companies. These IR analyzers killed the chemical methods, as they were much easier to do, more precise and could be added without problems to automatic measurement systems. But as with all measurements, there remain problems.

2. Problems when measuring CO2

A first and obvious difficulty when measuring atmospheric CO2 is to be sure that the air sample to be measured does not contain other gases absorbing IR radiation at the same wavelength as CO2 does. As water vapour is the most important gas with overlapping absorption regions, the air sample must be dry. Expressing the measurement as a "mixing ratio" in ppmV makes adjustments to standard temperature and pressure conditions superfluous; this would not be the case if CO2 concentration would be given as a mass per unit volume (as $\text{xx } \mu\text{g}/\text{m}^3$). All measurement systems have problems with stability. One solution to avoid drifts is to make correlation measurements: all sample measurement is followed by a dry clean air measurement (to give a zero level) and by a measure of an air sample containing a precisely known amount of CO2. These zero and reference samples may be held in capsules mounted on a rotating disk which lies in the path of the IR radiation. As the CO2 concentration in ambient air is usually so low, the IR rays should make a very long path through that sample. This means that the IR rays make many paths between two mirrors mounted at the end of the sample chamber. The quality and cleanliness of these mirrors (often gold coated) is essential for proper operation.

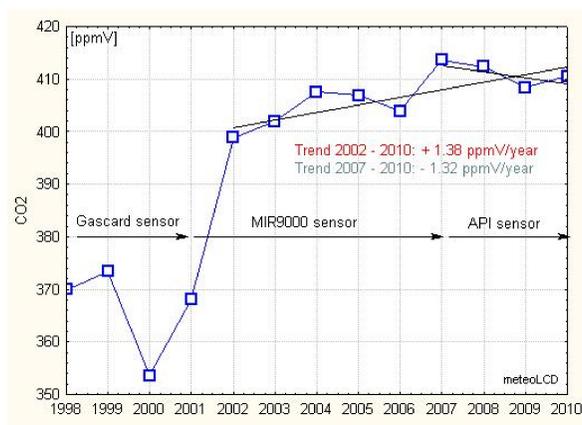
On top of these continuous zero/span measurements, zero and span measurements using real gas samples filling the measuring chambers must be made at certain intervals. At meteoLCD we (i.e. Raoul Tholl and myself) do these calibration checks about every three weeks.

Making zero air is not too difficult: we use either a Sonimix zero air generator from the Swiss company LNI or a chemical drying/absorber column. Sample air with a given CO2 concentration is difficult to obtain when the concentration has to be known with great precision. Keeling's son (Charles Keeling) long time had a near monopoly for delivering precise CO2 sample gas. At meteoLCD the best we can afford if a "primary standard" gas from PRAXAIR where the concentration is known to 1%. As we use bottles with about 600 ppmV CO2, this means that our uncertainty to the real concentration lies between 594 and 606 ppmV, a not negligible 12 ppmV amount! A bottle of such a gas costs close to 1000 Euro, including the location of the metallic container itself. It does not last much more than a year.

3. The instruments used at meteoLCD

Over the year, we used three different CO2 sensors, with only the last two being good enough for precise measurements and trend detection. From 1998 to 2001 we used a [Gascard](#) sensor made by Edinburgh Instruments (UK); from 2002 to 2007 an expensive [MIR9000](#) from the French company Environnement SA was in action. Finally from 2008 on an E600 instrument from the US company [Api-Teledyne](#) is measuring atmospheric CO2. The MIR9000 was replaced because its mirrors started degrading. In an ideal world, one everlasting non-degrading sensor would have made us happy. Alas, reality bites hard when it comes to long-time precise measurements. These are never easy to do, and one can not but warn of the often naive and extreme confidence that the public (and even many scientists!) has on many climate related measurements. As the German say "wer misst, misst Mist!".

The last figures shows the yearly mean CO2 mixing ratios measured with these three instruments:



The Gascard sensor clearly can not be relied upon for a correct investigation into increasing atmospheric CO2 concentrations.

(to be continued)

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