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Challenges in Estimating Atmospheric CO_2

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Abstract

Atmospheric CO_2 concentrations have been measured since the beginning of the 18^{th} century by chemical analysis with remarkable precision. Since then, methods have changed, and higher precision is achieved. The first observers discovered daily and yearly variations related to plant growth, distance from sea, elevation, and meteorological conditions. In 1938 an infrared gas analyzer was invented, and the first continuous monitoring physical device, later called NDIR was introduced. With this technique continuous observations were started at Mauna Loa volcanic peak at Hawaii around 1960.

To create a continuous curve which followed the history of anthropogenic emission, the chemical observations were heavily manipulated, and a bandy-stick type curve was created. From ice-core drillings it was believed to be possible to measure the CO_2 content in bubbles in the ice far back in time. Surprisingly they showed higher level in 1890'ies, than recorded at Mauna Loa in 1960. This led to the idea that the ice bubbles were open for CO_2 about 80 years later than the age of the bubble, and the bandy stick curve was restored. A peak of nearly 0.04 % CO_2 in about 1940 in the chemical observations was edited away by C. Keeling who started the Mauna Loa observations.

Keywords: Atmospheric CO_2; direct chemical methods; ice-core measurements; comparison of methods

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1. Introduction

My field of research is astrophysics. I started with theoretical work in cosmology in 1960 and finished in 2010 with a review of interacting binary white dwarf stars, a special group of variable stars I had worked on during more than 25 years. As retired, I started to investigate the relation between the Sun and our Climate.

In August 2009 I was visited by Professor Harald Yndestad, who had found a strong correlation between the lunar nodal period and sea level, temperature, and salinity in the North Atlantic and Barents Sea (Yndestad et al. 2008). He asked if there could be other periods involved, and I told him about the solar cycles.

Soon afterwards I got a huge manuscript written by Ernst-Georg Beck in Freiburg. This was about historic atmospheric CO_2 levels reconstructed from direct measurements by chemical methods. It was written in English translated from German, very detailed, and difficult to read by a non-expert, but it was clear that this was a monumental work, that should be published. Beck had been in contact with Yndestad and reported the same lunar nodal periods in the CO_2 data as Yndestad had determined. Beck also found a one-year delay in CO_2 peaks related to sea surface temperature peaks, indicating that sea temperature controls the CO_2 level.

Beck had already published a paper on his analysis of more than 200 000 historic chemical observations (Beck 2007). He also compared wet-chemical measurements with Mauna Loa measurements (Beck 2008). In the revised and larger paper (Beck 2010) the data for selected locations were analyzed together with meteorological observations, and methods were developed to find situations where the ground observations were almost the same as for higher altitudes as Mauna Loa (Massen 2022). The revised paper was submitted to the Journal of Climate in August 2010 but was rejected because it showed CO_2 variations not corresponding to what was estimated from ice core data from Antarctica. However, before the rejection came in November 2010, Beck had died from cancer, and it was not possible to resubmit the paper (Yndestad 2022a).

When Beck died, Professor Yndestad got the permission from his family to publish his work, this became possible in this journal in 2022. We did not find his final edited manuscript, but as Editor of SCC, I worked with a version from February 2010, and this was finally published in our volume 2.2 (Beck 2022).

At the Stockholm climate conference in 2016 Professor Anders Lindroth gave a talk about the Integrated Carbon Observation System (ICOS) European Network. He also invited the delegates to visit one of the stations situated in a boreal forest at Nordunda, north of Uppsala after the conference. Measurements from a 100 m tall tower, is shown in the conference report (Solheim 2022, Figure 3). We invited professor Lindroth to this conference, but he could not come.

In the following I will give a summary of the historic measurements collected by Beck and show the discrepancy with the ice core estimates used by IPCC, which erased the warm period in the 1940'ies and earlier peaks in CO_2 in the 19th Century.

2. Wet-chemical measurements of CO_2

When it was discovered in the beginning of the 19^{th} century that a tiny amount of the gas CO_2 was present in the atmosphere, the invention of accurate gas analyzers made it possible to measure the atmospheric content with increasing precision. Variations during the day, the season, local environment, distance from sea, elevation, flora etc. were reported in a large number of publications during the 19^{th} and 20^{th} century. According to Beck (2007, 2008) about 200 000 samples of air have been collected and analyzed. He found about 100 000 of these had enough information about the environment and local weather to be included in his selection of historical data for estimating the historic level of CO_2. The measuring sites are shown in Figure 1, below.

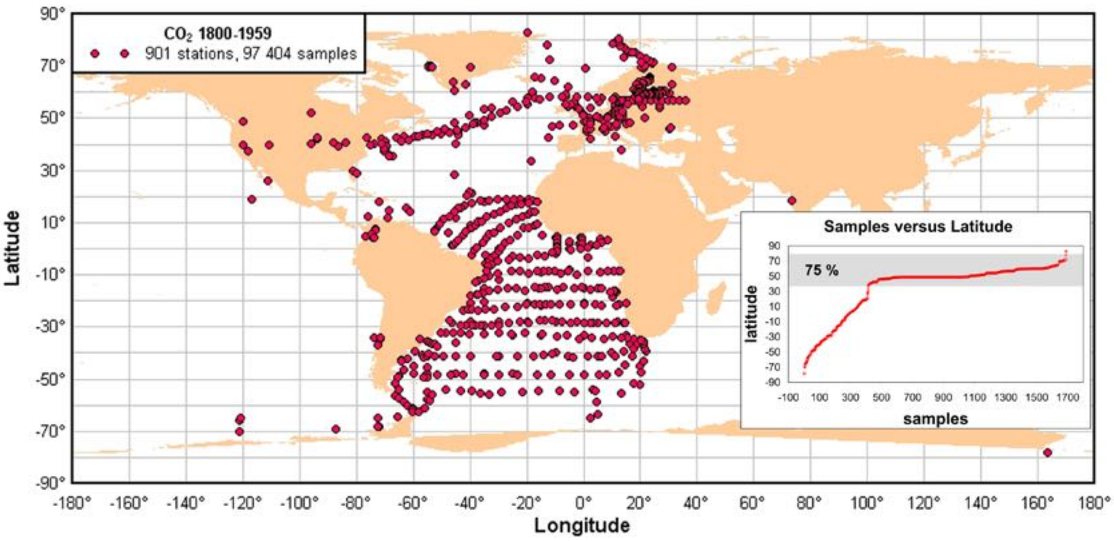

Figure 1: 97 404 samples from 901 stations included in Beck's analysis (Beck 2022, Figure 2a).

3. The Callendar, Keeling and the Siple bandy-stick curve

Guy Calendar, a British railroad engineer, published already in 1938, a CO_2 graph showing increasing CO_2 by using a special selection of historical measurements. He interpreted the rising CO_2 level as a result of combustion of fossil fuels. He can be titled as the inventor of the Anthropogenic Global Warming (AGW) hypothesis. In 1958 he repeated his investigation, and selected data only ±10 % from his predefined «Fuel line». The figure below shows his accepted values in black, compared with other observations collected by Beck (2007) in red.

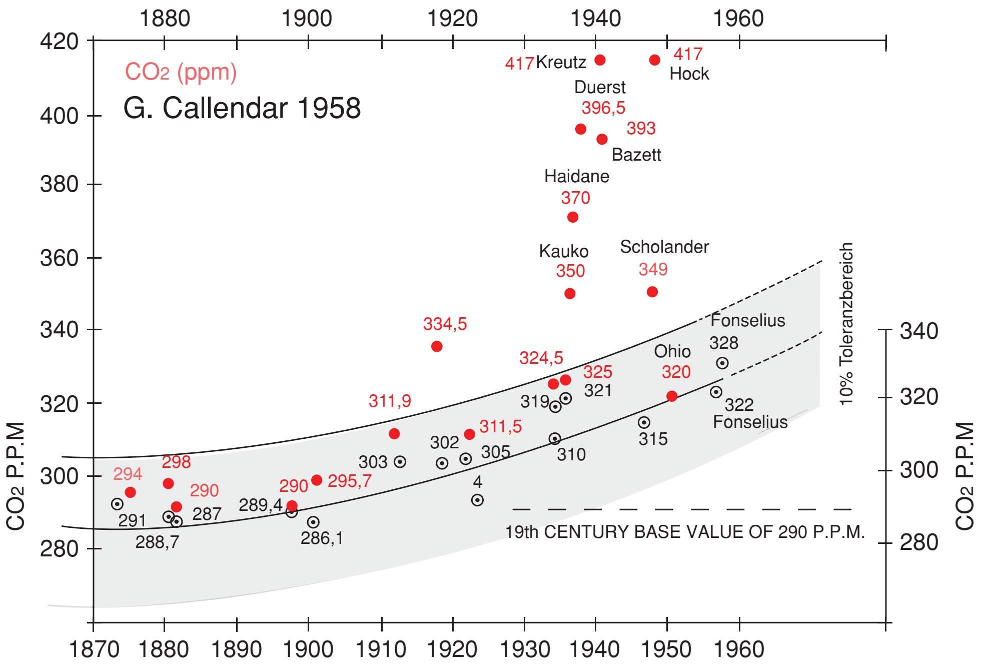

Figure 2: Callendar's "Fuel Line" published in 1958 was based on 30 historical measurements (gray). The gray area represents the ±10% level of tolerance for accepted CO2 data. In red are recalculated values and other important CO_2 observations (Beck 2008, Figure 6)

At the same time another important person entered the scene. A young chemist Charles Keeling started measurements of CO_2 in coastal forests of western USA in 1955, using a self-made manometer. This was a primitive device, needing 90 minutes to obtain a value, compared with existing high precision gas analyzers which could measure accurate values down to 0.33% within minutes. Keeling noticed that the level of CO_2 was rising, and convinced Roger Revelle, the former director of Scripps Institute of Oceanography at La Jolla, California, to start CO_2 measurement series on the largest volcano on the Earth, Mauna Loa on Hawaii, 4000 m above sea level. Keeling convinced Revelle to purchase an expensive gas analyzer which was used until Keeling's death in 2005. A simplified NDIR (non-dispersive infrared) method was developed, and measuring devices with this technique is now used all over the world. These devices are all calibrated by standard flasks delivered by the laboratory of Charles Keeling who owns the global monopoly of calibration of all CO_2 measurements (WMO 2001/2003). The picture below shows a NDIR handheld CO_2 measuring device calibrated with Keeling flasks.

Figure 3: A handheld NDIR CO_2 measuring device calibrated with Keeling flasks. It shows a deviation of +10 ppm from the calibration source.

3.1 The Siple problem

Analyzing air bubbles in ice-core drillings has given temperature and CO_2 values far back in time. Time is determined from layers in the ice, calibrated by ashes or Sulphur from known volcanic eruptions. The resolution diminish as one goes deeper in the ice. It is a question how reliable the time stamps are.

The researchers were surprises when they discovered that the Siple ice cores drillings from Antarctica showed values for 1890 which were considerably higher than what was measured at Mauna Loa in 1960. This is shown the left panel in the figure below.

To restore the CO_2 bandy-curve, the Siple curve was simply shifted 83 years - making the CO_2 in the bubbles 83 year younger than the ice where the bubble was found at a dept of 68 meters. The bandy-curve was saved, but nobody has been able to confirm that a bubble in the ice stays open for the air above the snow or ice layer of 63 m thickness for 83 years.

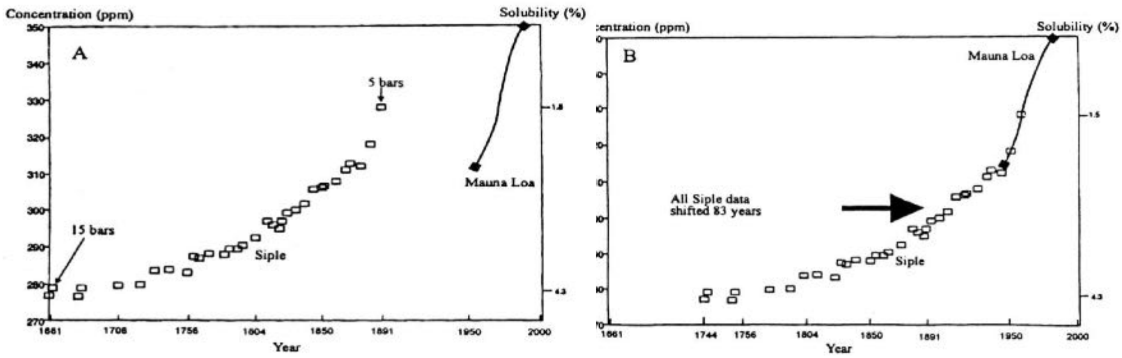

Figure 4: The CO_2 bandy-stick curve restored by making the observed values 83 years younger (Jaworowski 2008, Figure 16).

The timing of CO_2 in ice bubbles, relies on the assumption that the ice bubble is sealed from the outside environment. There should be no leaks or contaminations. But ice under pressure, develop small cracks and big cracks. Water sieves in - bubbles of water or even lakes are found deep inside the ice. More than 20 physical and chemo-physical processes, mostly related to the presence of liquid water, contribute to the alteration of the original air in gas clathrates (gas hydrates) which are solid crystals formed at high pressure by interaction of gas with water. This happens for CO_2 at about 5 bars. Due to this process, CO_2 starts to leave air bubbles at a dept of 200 m and the air bubbles disappear completely at about 1000 m (Jaworowski et al.1992). Making samples younger became a habit, and the lower values of CO_2 observed, bolstered the preconceived idea from Callendar that *the CO_2 level had grown because of humans*.

2.2 The CO_2 bandy-stick accepted by IPCC

IPCC accepted the Siple corrections procedure (Keeling is a co-author of the IPCC reports) and wrote in 2001 (AR3):

> *Before the Industrial Era, circa 1750, atmospheric carbon dioxide (CO_2) concentration was 280 ±10 ppm for several thousand years. It has risen continuously since then, reaching 367 ppm in 1999. The present atmospheric CO_2 concentration has not been exceeded during the past 420,000 years, and likely not during the past 20 million years. The rate of increase over the past century is unprecedented, at least during the past 20,000 years.*

This is still the IPCC mantra. Determination of CO_2 level from stomata-openings in leaves, show higher levels of CO_2 in the 1850'ies and 1940'ies, but this is overlooked by the IPCC.

4. Can Ernst-Georg Beck break the bandy-stick curve?

Ernst-Georg Beck's monumental work was finally published in our journal SCC in 2022 (Beck 2022). Below is his main result, based on 90 000 observations (red), compared with the Law Dome ice core determinations and some stomata values.

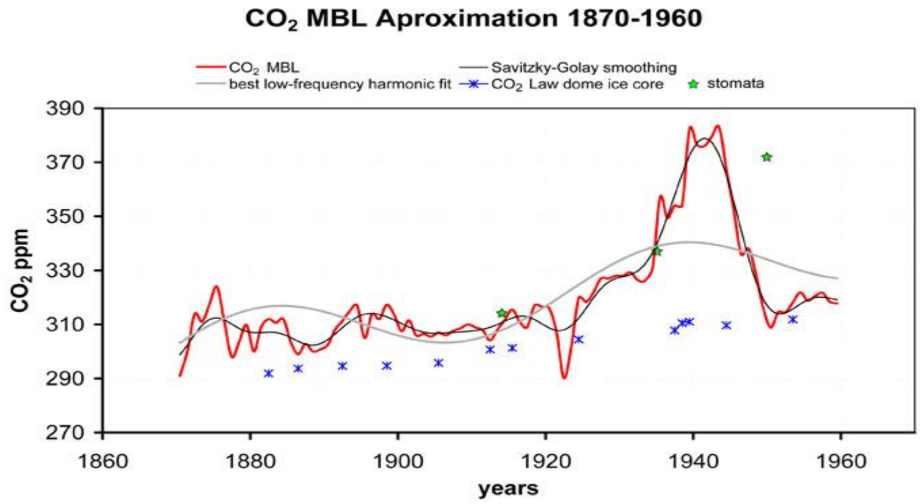

Figure 5: Atmospheric CO_2 background level 1870-1960: black line smoothed by a Savitzky-Golay filter; grey line= estimated best low-frequency harmonic fit (55,17 years = 18,39 x 3); blue stars= CO_2 law dome ice core; green stars=stomata; 1922: phase reversal (Beck 2022, Figure 25).

The most remarkable conclusion from Beck's data is that the CO_2 level between 1930 and 1950 was almost the same as it became in 2010 (380 ppm). This peak breaks the IPCC bandy-stick.

4.1 Comparison between Beck and Mauna Loa Data

When chemical and NDIR measurements of CO_2 were compared 1940 -1970 as shown in Figure 6, one finds that the chemical observations were more precise than the modern NDIR measurements in the period of overlap around 1960. Observations in Vienna, reported by Massen (2002) showed a 10 ppm difference covering the same period in 1958.

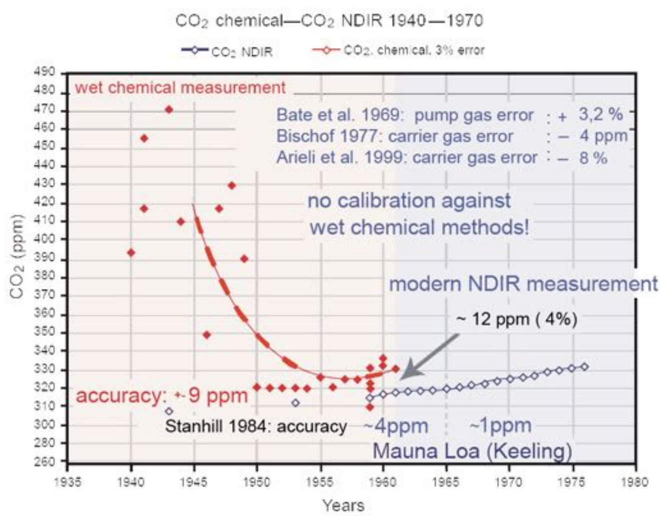

Figure 6: Known calibration and other errors documented in the early measurements of C. Keeling compared to the chemical standards (red). Systematic errors of NDIR also shown (Beck 2008, Figure 7).

5. Conclusions

Beck's CO_2-estimates were supported by a wavelet analysis by Yndestad (2022b), which showed that Beck's data for Atlantic CO_2 growth variability 1870-1960 coincides with Mauna Loa CO_2 growth variability from 1960 as well as global sea surface temperature variability. Harde (2023) was able to model the CO_2 peak observed in the 1940'ies mainly in terms of increased soil respirations resulting from higher land temperatures. SCC also received criticism from Engelbeen (2023) against Beck's 1940 CO_2 peak.

As editor of SCC, I found this discussion healthy for science and welcome more debate on the important question of the origin of the observed rise of CO_2 in the atmosphere. Is it chiefly natural or man-made?

Guest-Editor: Stein Storlie Bergsmark; Reviewers: anonymous.

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