# 50 YEARS OF CONTINUOUS MEASUREMENT OF CO2 ON MAUNA LOA

*by*

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# 50 YEARS OF CONTINUOUS MEASUREMENT OF $CO_2$ ON MAUNA LOA

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## 1. A SHORT HISTORY OF THE MAUNA LOA CURVE

When the young chemist Charles Keeling measured the atmospheric $CO_2$ concentration in the coastal forests of western USA in 1955, using a self-made manometer, he would have been astonished about the importance attributed to his data today.

The Mauna Loa Curve that measures the $CO_2$ concentration of air on the active volcano Mauna Loa, Hawaii (see fig.1), since 1958, is today regarded as the fever curve of the world. It stands for man-made climate change; a predicted change mankind is currently fighting with billions of dollars and growing business involvement.

The Keeling Curve represents the life's work of Prof. Dr. C. Keeling. He was awarded the National Medal of Science by president Bush in 2002. A building at the Mauna Loa Observatory bears his name today, showing a plaque with the curve engraved (see fig.1). C. Keeling died in 2005. His son Ralph Keeling is also a member of the Scripps Research Institute in California as his father in former days and is working on atmospheric oxygen measurements.

Roger Revelle, the former director of the Scripps Institute of Oceanography at La Jolla, California, U.S.A. agreed in 1956 to investigate the atmospheric $CO_2$ concentrations. This enabled C. Keeling to start his measurement series on the largest volcano of the world, Mauna Loa in 1958. Keeling succeeded in convincing Revelle to buy an Ultramat 3 gas analyser made by Siemens, which was very expensive at that time [2, 3]. Only after the death of Keeling in 2005 this equipment was exchanged for a modern version.

Most interesting is the stimulation Keeling received from Gustav Arrhenius, a grandchild of the 1903 winner of the Nobel Prize in chemistry, Svante Arrhenius. Gustav Arrhenius was also a member of the Scripps Institute at that time. In 1896 his grandfather had tried for the first time to make a physical connection between the temperatures of the ice ages and the $CO_2$ concentration of the air. But he did it in another way, as we know from the laws of nature. From Henry's law of dissolution in water we know that carbon dioxide is voluntarily dissolving in water by setting free energy. And we know from the oxidation process as a fundamental energy supplying chemical reaction that $CO_2$ is the final product in burning of organic matter accompanied by setting free heat. Arrhenius calculated that carbon dioxide as a low energy levelled product itself will produce heat by its emission. In fact the oceans as the largest store of $CO_2$ need heat to set free carbon dioxide.

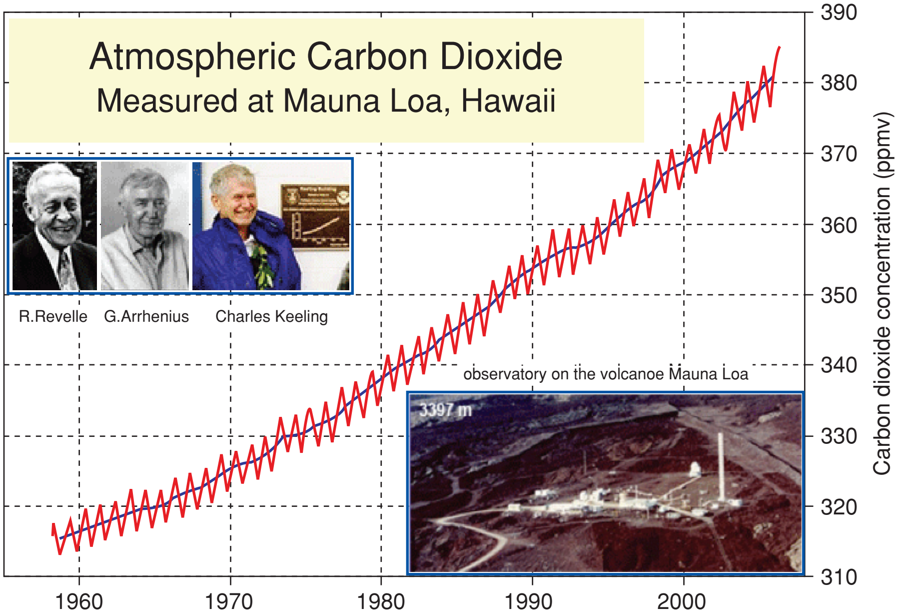

Abb. 1: The Keeling Curve, above on the left: Roger Revelle, Gustav Arrhenius and Charles Keeling. On the right the Mauna Loa Observatory at the elevation of 3397 m in an aerial view of the volcano Mauna Loa [1, 2, 3, and 4].

He had done the first investigation of the climatic influence of $CO_2$. S. Arrhenius calculated the radiative forcing of a doubling of $CO_2$ as a temperature increase of + 4 °C. But this value was too high by at least the factor 10 when doing a recalculation with modern data. In fact Arrhenius had used invalid spectra, as shown in 2003 [5]. Yet Arrhenius' erroneous figures are still cited by modern climate scientists [6].

## 2. THE $CO_2$ BACKGROUND HYPOTHESIS

Charles Keeling soon noticed a rise of atmospheric carbon dioxide concentration. From his measurements in the 50s and 60s on the Pacific coast in USA, on Mauna Loa and the Antarctica, he concluded that he had measured a constant worldwide background concentration of $CO_2$. The $CO_2$ background should be the $CO_2$ concentration around the world, free from local sources which had increased from 315 ppm in 1958 to 380 ppm in 2008 mainly by burning of fossil fuels.

According to the IPCC this is the main cause of global climate change [10].

Keeling also was the first to introduce carbon isotopes ($^{13}C$) to the investigation of the carbon cycle and the origin of the carbon source [17]. This lead to the assumption that $CO_2$ from fossil sources enrich in the atmosphere while natural photosynthesis and animal respiration compensate each other and can therefore be ignored. Consequently man-made $CO_2$ was firmly recognized as the polluter of the atmosphere, i.e. the worldwide rise of the $CO_2$ concentration. In fact $CO_2$ from burning fossil fuels and phytoplankton from the oceans—which cover the globe to 71%—have about the same $^{13}$ C value. Roy Spencer

1955: The invention of the background level out of 50 samples

Geochlmica of Cosmochimica Acts, 1958, Vol, 13, pp. 322 to 334. Pergarnon Press Ltd., London

The concentration and isotopic abundances of atmospheric
carbon dioxide in rural areas

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(Received 6 June 1957)

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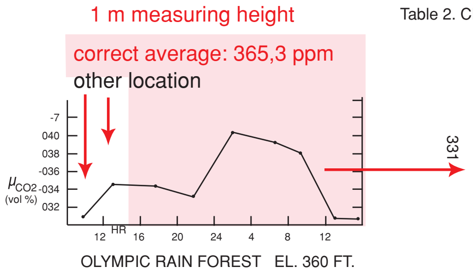


Fig. 5. Diurnal variation in the concontration and isotopo ration of atmospheric carbon dioxide in a rain forest of the Olympic Peninsula of Washington.

average : lowest values

Table 2. Characteristic composition of atmospheric carbon dioxid

| Station | Month of 1955 | Minimum $\mu_{CO2}$ (p.p.m.) |
|---|---|---|
| Forest or Grassland | | |
| Big Sur State Park | May | 316 |
| Yosemite National Park | June | 313 |
| Hart s Pass | August | 307 |
| Olympic National Park | September | 309 |
| Rock Lake | September | 309 |
| Barren Ground | | |
| Yosemite National Park | June | 314 |
| Inyo mountains | July | 312 |
| Olympic National Park | September | 309 |

Concentration variation too small to extablish value.

309 ppm

explanation: in the afternoon best mixing if air without plant + soil influence

missing: check of soil degassing, check of weather (humidity, precipitation..)!!

Figure 2: C. Keeling's first attempts to measure the $CO_2$ background concentration (Keeling 1958) using the lowest $CO_2$ concentration in the afternoon. On the top the head of the paper by C. Keeling 1958; below the graph of the diurnal variation of $CO_2$ at the Olympic Forest in the state of Washington. In red additional information on the measurement conditions and the type of calculation of a daily average C. Keeling had used. In blue missing measurements to get the right conclusion.

of the University of Alabama in Huntsville [21] therefore asks whether the IPCC assumption concerning these data can be realistic.

The data suggested that an outgassing of the oceans by warming is today the more likely the cause for the rising $CO_2$.

Figure 2 shows the birth of the idea of a $CO_2$ background concentration 1955. At that time C. Keeling had measured $CO_2$ in summer, using a home-made manometer. He needed about 90 minutes to obtain each value [17]. He conceded in 1993 that he had not read any technical literature [16], so he probably did not know that by using the existing high precision gas analysers designed by Haldane, Petterson, Schuftan or Kauko, he could have obtained readings within minutes, getting a far more accurate value down to 0.33%. This means an accuracy of about +/-1 ppm using 309 ppm in 1955.

Considering the measured diurnal $CO_2$ variation in the forest we notice a much higher $CO_2$ content in the air at night than during the day, caused by the absorption of some of the carbon dioxide by the photosynthesis. The correct average would have been 365.3 ppm, which is typical for such a location in summer. In fact Keeling used only the lowest measured values made in the afternoon on the grounds and that there is a compensation of soil respiration by soil organisms and photosynthesis. Soil respiration produces about the same amount $CO_2$ as the respiration of animals on the ground. But plants do respire too especially at night. Keeling did not measure the soil

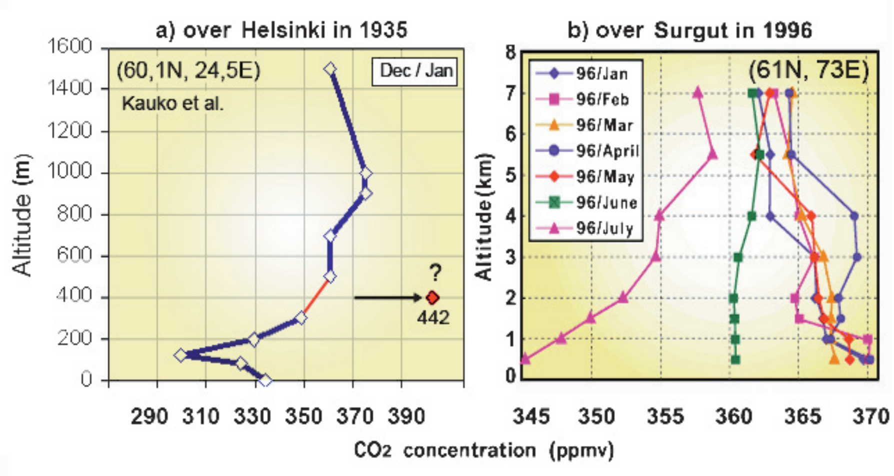


Figure 3: a) Vertical $CO_2$ profile over Helsinki 1935 and b) Surgut, Siberia 1996 [23, 24, 25].

respiration and the possibility of geological soil degassing by rock weathering remains. This procedure of ignoring natural $CO_2$ sources that may make a large contribution to the atmospheric concentration is maintained until today.

Today we know from measurements of the vertical $CO_2$ profiles up to the stratosphere that large variations are most prominent in the lower 5 km while in the higher troposphere the $CO_2$-concentration is nearly constant and variations much smaller. The larger variations near ground have been documented by the historical data presented in figure 5.

Presumably Keeling expected these difficulties of strongly varying concentrations near ground and hence decided to take measurement on a high mountain (Mauna Loa). As figure 3 shows, the average yearly variation has the same background value when carefully measured in time and space near ground.

## 3. $CO_2$ MEASUREMENTS OF THE BACKGROUND BEFORE 1958

This tropospheric $CO_2$ concentration from about 5 km height is the $CO_2$ background postulated by Keeling and the IPCC as stable in nature and rising since industrial time by burning of fossil fuels.

The Mauna Loa measurements initiated by Keeling show a rise of the background since 1958 until today. In fact the $CO_2$ concentration has been measured in the upper troposphere since the end of the 19th century by dozens of balloon flights and after the World War II by rockets. A literature research revealed [23] 63 single values since 1894 –1973, from which 18 yearly averages can be calculated for heights of 1 –50 Km (stratosphere). The resulting graph is shown in figure 4. In most cases cryogen condensation had been used to separate $CO_2$ from air using absorption in alkaline solution, by IR spectroscopy afterwards. A pronounced peak during the 30s of the 20th century is noticeable. The modern $CO_2$ concentration is therefore not unique for thousands of years, as is stated repeatedly. This confirms the analysis by chemical methods near ground since 1812, which also show a maximum during 1930–1945 [19].

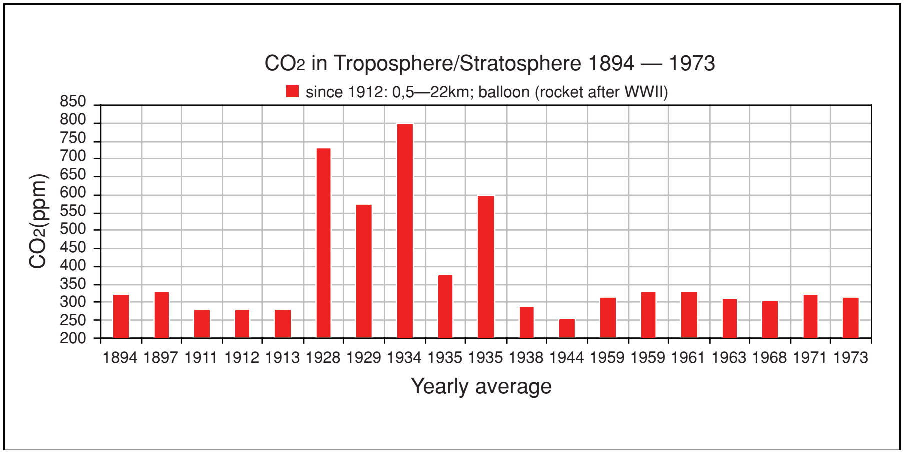


Figure 4: $CO_2$ measurements in the troposphere and stratosphere (0.5-22 km since 1897 –1973 during balloon, aeroplane and rocket flights [23].

A strong variation in the atmospheric $CO_2$ concentration since about 1800 is shown in figure 5 showing three maxima around 1825, 1857 and 1942. This is in severe contrast to the publications by the IPCC and the ice core reconstructions. The pre-Keeling $CO_2$ data show, the $CO_2$ curve lags temperature by about five years. A 19th century average of 321 ppm can be calculated from these data. Combining the

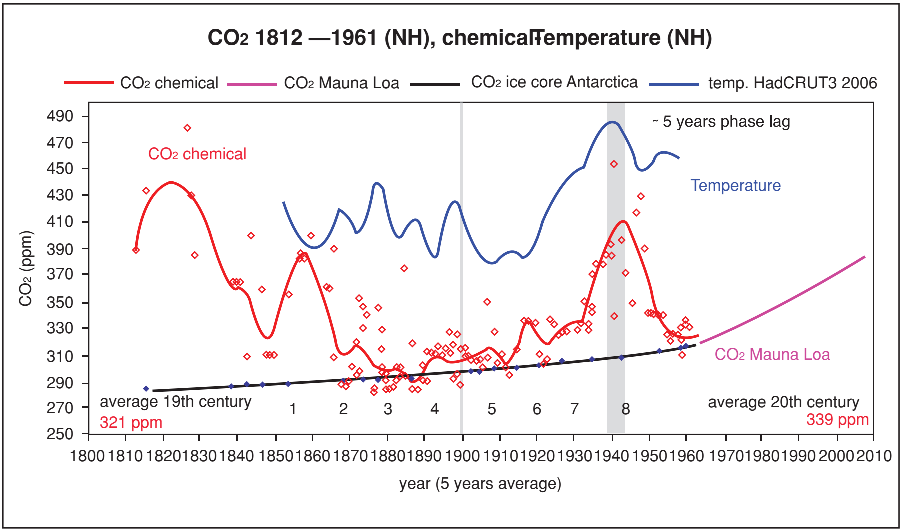


Figure 5: The atmospheric $CO_2$ concentrations of the northern hemisphere compared to the average northern hemispherical temperature and reconstructed $CO_2$ from ice core records of Antarctica. Data prepared from the historical measurements since 1812–1961 as a 5 years average (red line) out of 138 yearly averages [19] (red dots), the Keeling Curve in violet, the temperature of the northern hemisphere according to CRU 2006 in blue, the $CO_2$ concentration of Antarctica from ice core records after Neftel et al. 1984 [27]

chemical and modern measured $CO_2$ data a 20th century average of 339 ppm can be calculated, representing an increase of about 5 % within 200 years.

The IPCC ignored these directly measured $CO_2$ data prior to Keeling and published an increase of about 30% increase of atmospheric $CO_2$ since pre-industrial time. The evaluation of the chemical methods [Beck 2007] that have been used to measure $CO_2$ in air reveals an accuracy of +- 3% since 1857. Until 2007 [19] a careful evaluation of available literature and the investigation of the methods used prior to the Mauna Loa measurements cannot be found in literature. The WMO and the IPCC adopted these omissions without testing [19].

## 4. $CO_2$ FROM MAUNA LOA COMPARED TO OTHER LOCATIONS

Mauna Loa does not represent the typical atmospheric $CO_2$ on different global locations but is typical only for this volcano at a maritime location in about 4000 m altitude at that latitude.

To produce a $CO_2$ contour similar to Mauna Loa at continental locations extensive statistical filtering is necessary by elimination parts of the data range [30]. WMO therefore reduced the international network of measuring stations to mostly marine locations. Analysing the historical pre-Keeling $CO_2$ measurements at coasts and continents we can see a difference of about 20 ppm lower values at sea, representing the absorption by water [23]. The $CO_2$ concentration in air is also strongly influenced by fog, fine rain, and snow. We can also see a slightly higher $CO_2$ value in air during full moon [19, 23]. I cannot find any comments on these natural influences in modern papers concerning $CO_2$, e.g. by Keeling. Instead the Keeling curve was combined with ice core records to give an exponentially rising global contour for $CO_2$ since pre-industrial times. This graph is the basis of all climate reports of the IPCC 1990, 1995, 2001 and 2007.

Ice cores are recognized as ideal climate archives, the procedures for analysing the air bubbles in the ice was developed in the 1980s. In fact gas, bubbles only exist above about 200 m, below that depth so called clathrates will form (one $CO_2$ molecule in cage of water molecules). Therefore and through the losses and influence by drilling, the decompression of the cores and the metabolism of psychrophilic bacteria that live in the ice for thousands of years [28], the analysed $CO_2$ content is lower than in the past atmosphere above the ice. Furthermore the uncertainty by the difference of gas age and ice age of about 30 years in period of 200 years is very large so that small variations of some years cannot be resolved. This is what Z. Jaworowski had indicated for years [18].

The laboratory of Charles Keeling owns the global monopoly of calibration of all $CO_2$ measurements (WMO 2001/2003). The IPCC has accepted this procedure (Keeling is a co-author of the IPCC reports) and stated in 2001 [10]:

*"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.*

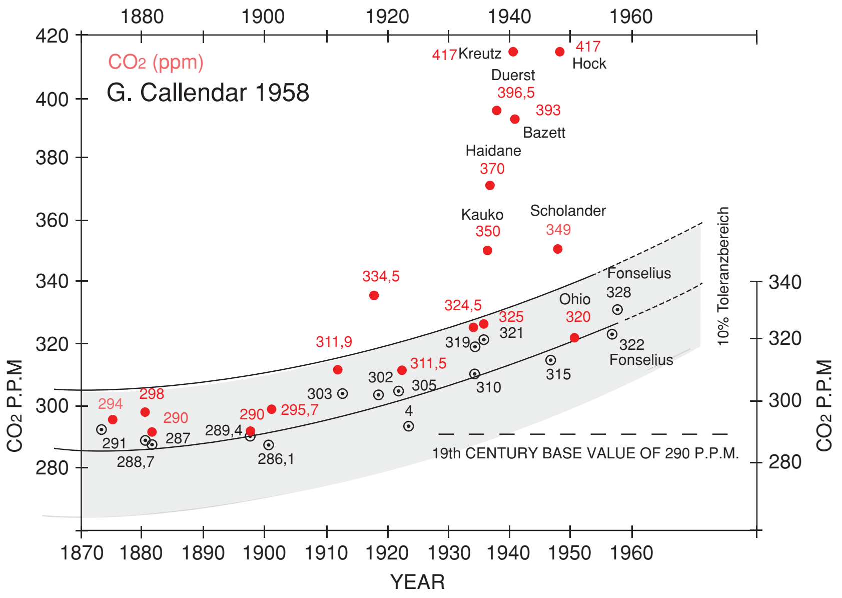
*The present atmospheric $CO_2$ increase is caused by anthropogenic emissions of $CO_2$. About three-quarters of these emissions are due to fossil fuel burning."*

## 5. KEELING, CALLENDAR AND HISTORICAL MEASUREMENTS

In Keeling's view the results of the analyses of ice cores concerning $CO_2$ are the logical supplement to his Mauna Loa measurements of background concentration because the reconstructed $CO_2$ from ice cores prior to Keeling fits perfectly to the Mauna Loa measurements since 1958. Jaworowski criticized this as an artificial fit because ice core data do represent older atmospheric concentrations because of the ice age /gas age difference.

Comprehensive data sets documented in more than 390 papers were ignored despite prominent scientists like Robert Bunsen, Konrad Roentgen, or the Nobel Prize winners August Krogh and Otto Warburg had measured the $CO_2$ content of air with high precision [19]. Their results are the basics of modern natural science lectured round the world. In fact there is one single publication in 1986 [20] Keeling discussed 18 historic measurement series of about 400 [20] and rejected the 20th century data prior to 1958 without having investigated them. So he missed that in 1936 the Finnish chemist Y. Kauko achieved a measuring accuracy of 0.33%, which means about ±1 ppm and Kauko had also measured a vertical $CO_2$ profile for the first time [23], (see fig.3 a).

One reason may have been the intention to 'prove' that the increase of the atmospheric $CO_2$ was due to fossil fuel burning, an idea that was strongly influenced by the work of the English steam engineer Guy Callendar.



G.S. Callendar, On the Amount of Carbon Dioxide in the Atmosphere. Tellus 10:243—48, 1958.

Figure 6: Callendar's "Fuel Line" in 1958 compiled from 30 historical measurement series. In grey the +-10% level of tolerance of accepted $CO_2$ data. In red, the recalculated values [Beck 2007] and other important $CO_2$ data [25].

In 1938 Callendar had published a paper and tried to get evidence for rising $CO_2$ levels since the late 19th century by a cursorily analysis of 13 historical measurements. His explanation was the enhanced burning of fossil fuels. Callendar can therefore be seen as the inventor of the AGW (Anthropogenic Global Warming) hypothesis that has its 70th anniversary 2008. In 1958 Callendar republished this analysis with 30 historical sources, thereby rejecting all data lying outside a +/- 10% long-time average and that did not fit the assumed rise. He named this rising contour “fuel line”.

Callendar failed to investigate the chemical methods used for these measurements. Hence he did not notice the systematic errors associated mainly with the French measurement series. Charles Keeling´s papers show that he embraced the arguments and data of Callendar’s. In his paper 1986 he rejected all but three of 18 historical measurement series of the $19^{th}$ century. Most of these had been presented by Callendar before and Keeling obviously did no research on the old data. Two of the three data sets Keeling denoted as most accurate; and one, conducted by the French chemist Reiset since 1872 and 1880, he praised as the most accurate from the late 19th century fitting exactly with the ice core records. (Neftel. et al. 1984).

But Keeling too—he was chemist—had not evaluated the methods Reiset had used. He was impressed by the lowest values and discussed the air masses Reiset had analysed. The average of 294 ppm fits with Keeling´s impression of a pre-industrial $CO_2$ at that time. In 2007 a detailed analysis of the historical wet chemical methods revealed that Reiset had used sulphuric acid to dry the air before analysing. Because sulphuric acid absorbs part of the $CO_2$ the results of Reiset are too low by about 20 ppm. This was known since 1848 and tested quantitatively by the Belgian chemist W. Spring in1883. The correct average in the end of the $19^{th}$ century was 312 ppm. Hence Keeling was wrong in 1986 [19].

As a consequence of his rejection of the old chemical methods there is no comparative measurement against the old measuring standards known by Keeling. But this is not standard practice in a period introducing a new technology. Figure 7 displays the directly measured $CO_2$ data of the northern hemisphere in the transition period 1940–1975 [25]. In red we see the historical measurements prior to Keeling using the wet chemical procedures. A sharp drop up to 1950 can be seen. The blue line represents the continuous data from Mauna Loa with the modern physical method.

There exist measurements in parallel with the old chemical and new physical NDIR method, even though C. Keeling argued that the old wet chemical $CO_2$ measurements in the $20^{th}$ century are all erroneous. In 1957/58 in Vienna, Ferdinand Steinhauser made $CO_2$ measurements in parallel to Mauna Loa using the gas analyser according to A. Krogh and in 1967 we have measurements on a ship with the modern NDIR method travelling the same route which the famous oceanographer K. Buch had chosen in 1935, crossing the Atlantic Ocean from Helsinki to New York. Buch also used the gas analyser according to Krogh. Both measurements show identical results for the old and new method within error range. Fig. 7 shows the transition time for the old and new method of gas analysis as yearly averages [25]. During time after the 1942 $CO_2$ peak the $CO_2$ concentration dropped down in the 50s to values around 320 ppm. Keeling’s values measured on Mauna Loa are roughly lower by 12 ppm as the corresponding data measured with the old chemical method without using latitude and other error

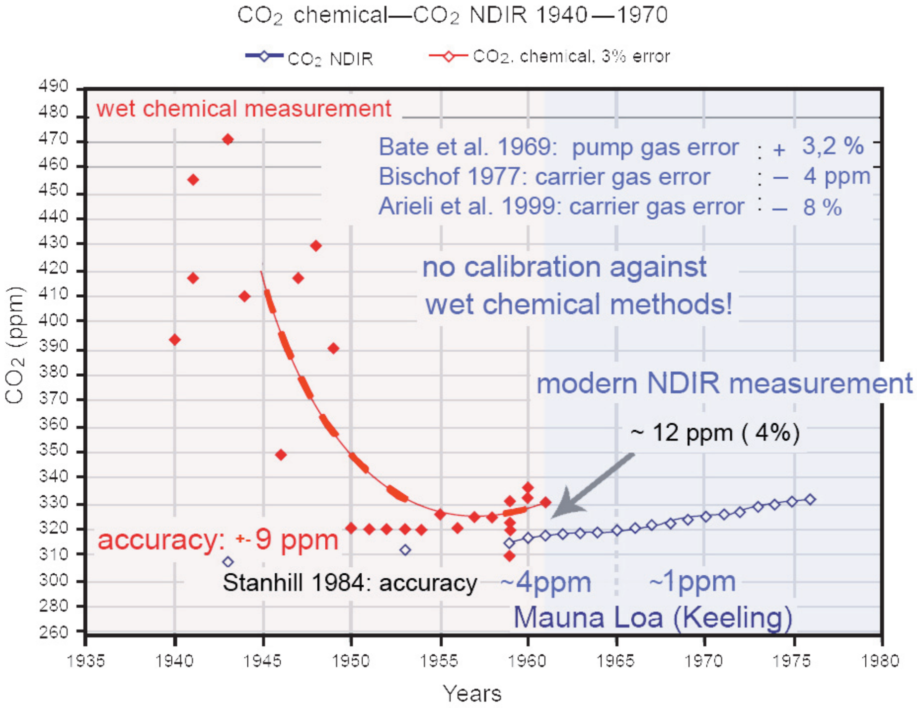


Figure 7: Known calibrating and other errors documented in the early measurements of C. Keeling compared to the chemical standard (in red). The historical measurements prior to Mauna Loa in red (dashed line show average counter), the Mauna Loa data in blue. Additional known systematic errors of the NDIR gas analyser are indicated.

correction. This is within the error range of both methods but also shows the lower concentration on Mauna Loa at a height of 3400 m, compared to the continental concentration.

Today the accuracy in modern laboratories is about 0.1 ppm in analysing air concerning $CO_2$ (WMO-Report 148 2003) [9]. The modern NDIR spectroscopic procedure is a relative method using calibrated reference gases and an absolute calibration with e.g. a manometric system used in the Scripps Institute until 2005.

The early NDIR analysers had produced several systematic errors mostly due to calibration gases [19, 23, and 25]. When Keeling started on Mauna Loa in 1958 a systematic error of 4 ppm has been documented [12, 33]. Up to about 1964 the accuracy was not as good as the best old analyses before the World War II using the chemical method.

## 6. SUMMARY AND PERSPECTIVE

The scientific community still ignore the above-cited critics. The concept of carbon dioxide producing the greenhouse effect continues to be promoted. Charles Keeling was one of the essential suppliers of data for this political trend today. What would he have replied to those questioning the anthropogenic greenhouse effect given falling temperatures since 1998 with further rises in $CO_2$? This eye catching discrepancy has led to a letter to the IPCC in April 2008 by 4 scientists including a Nobel Prize winner, where they challenged the climate action of $CO_2$ [26]. Also Fred Singer has compiled The NIPCC as a contradiction to the IPCC assumptions [32].

Despite current controversy, the pioneering efforts of C. Keeling will stand for he has developed a high precision analytical method and introduced carbon isotopes to find the origin of the carbon source. This remains the prevailing standard and has led to a much improved understanding of the carbon cycle. Nevertheless, many unknown variables remain to be explored, such as volcanic and non-volcanic degassing. During recent years several active sub-ice volcanoes had been detected in Greenland and Antarctica, which contribute to melting processes.

Despite of all this, the IPCC continues to argue that we have a full enough understanding of the carbon cycle to enable computer scenarios resulting in a 90 % confidence for a heated climate future of the world!

Yet Russian experts in particular predict a new little ice age up to 2030 deducted from astrophysical cycles [29]. Consequently the $CO_2$ curve would have to drop down to values similar to those at colder periods.

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