THE HISTORICAL DATA THE IPCC IGNORED

180 Years of Atmospheric CO$_2$ Measurement By Chemical Methods

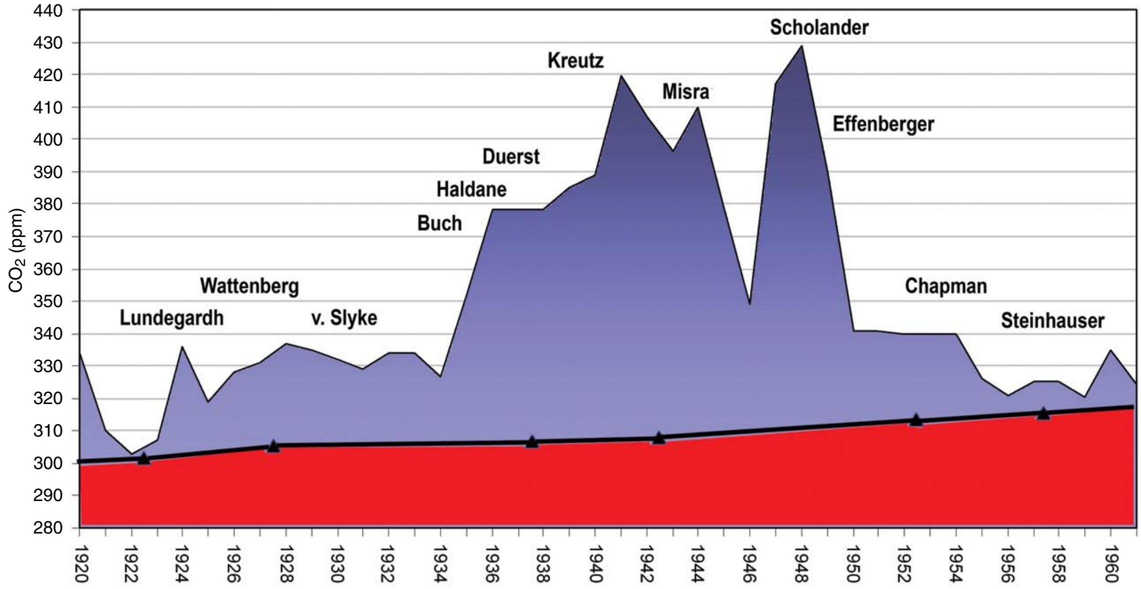
by Ernst-Georg Beck

The view of the Intergovernmental Panel on Climate Change (IPCC)—a United Nations body that is responsible for advising governments on climate change—follows closely the views of three influential scientists, Svante Arrhenius, G.S. Callendar, and Charles Keeling, on the importance of CO$_2$ as the major driver of climate change.

The linchpin in the IPCC argument is the assumption that prior to the industrial revolution, the level of atmospheric CO$_2$ was in an equilibrium state of about 280 parts per million (ppm), around which little or no variation occurred. This presumption of constancy and equilibrium is based upon a selective review of the older literature on atmospheric CO$_2$ content by Callendar, and later Keeling, of the University of California at San Diego, which essentially discounted all data not conforming to their preconceived notions of historical CO$_2$ levels. (See Figure 1.)

The truth is that between 1800 and 1961, more than 380 tech-

Figure 1
REAL CO$_2$ MEASUREMENTS VS. GLOBAL WARMERS' FABRICATION (1920-1961) NORTHERN HEMISPHERE



Actual historical CO$_2$ measurements (upper line) and the IPCC values concocted from ice cores—a fable designed to convince you that atmospheric CO$_2$ levels are rising because of industrial activity. The chemical measurements are yearly averages of data from 48 measuring series at different locations (±3% accuracy).

Thousands of direct chemical measurements of CO$_2$ concentration in the atmosphere since the mid-19th Century show that the current claim of human-induced CO$_2$ increase is a willful fraud.

Table 1
BIBLIOGRAPHIES AND NUMBER OF DATA-CONTAINING PAPERS THEY CITE

Cited authors and papers with data

Year	Authors	Total	19th Century	20th Century	Notes
1900	Letts and Blake [14]	252	252	-	Only 19th Century
1912	Benedict [15]	137	137	-	Only 19th Century, focus on O_2-determination
1940	**Callendar [16]**	**13**	**7**	**6**	**Cited Letts and Blake, Benedict**
1951	Effenberger [17]	56	32	24	Cited Duerst[1], Misra[1] and Kreutz[1]
1952	Stepanova [18]	229	130	99	Citation same as Effenberger
1956	Slocum [19]	33	22	11	Cited Duerst and Kreutz
1958	**Callendar [20]**	**30**	**18**	**12**	**No citing of Duerst, Kreutz, and Misra**
1958	Bray [21]	49	20	19	Cited most important through the centuries
1986	Fraser [22]	6	6	-	Only 19th Century, same as Callendar
1986	**Keeling [23]**	**18**	**18**	**-**	**Only 19th Century, same as Callendar**
2006	Beck [this study]	156	82	74	Only chemical determination until 1961

Note

1. See References

Between 1800 and 1961, there were more than 380 technical papers published on air gas analysis with data on atmospheric CO_2, but these have been rejected by the global warming promoters.

nical papers were published on air gas analysis containing data on atmospheric CO_2 concentrations. Callendar [16, 20, 24], Keeling, and the IPCC did not provide a thorough evaluation of these papers and the standard chemical methods that they employed. Rather, they discredited these techniques and data, rejecting most as faulty or highly inaccurate [20, 22, 23, 25-27]. (See Table 1.)

Although Callendar and Keeling acknowledge the concept of an "unpolluted background level" for CO_2, these authors examined only about 10 percent of the available literature, asserting from that, that only 1 percent of all previous data could be viewed as accurate, specifically that of Münz [28-30], Reiset [31], and Buch [32].

During my own review of the literature, I observed that the evaluation of the work of Reiset and Münz by Callendar and Keeling was erroneous. This spurred me to investigate carefully the criteria used by these and other authors to accept, or to reject, such historical data.

The stated intent of these authors was to identify CO_2 determinations that were made using pure, unpolluted air in order to assess the true background level of CO_2[1] however, Callendar set out the actual criteria that he used to judge whether older determinations were "allowable" in his 1958 paper [20]. There, Callendar presented only data that fell within 10 percent of a longer yearly average estimate for the region. He rejected all measurements, however accurate, that were "measurements intended for special purposes, such as biological, soil, air, atmospheric pollution." Callendar also rejected nearly all data before 1870, because of what he erroneously described as "relatively crude instrumentation." He reported only 12 suitable data sets for the 20th Century as known to him [20], out of 99 made available by Stepanova in 1952 [18].

Keeling, in 1986 [23], commented on the 19th Century CO_2 data:

> Our original goal was to find, if possible, a seasonal cycle in the nineteenth century atmospheric CO_2 data in agreement with modern observations by applying the air mass criteria of Callendar [16] to screen out contaminated data. This goal we have demonstrated to be unachievable. We find, after screening out suspicious data on the basis of air mass, that none of the five data sets of Callendar show the seasonal cycle which Callendar found in combination.

And then Keeling concluded:

> In conclusion, the measurements of atmospheric carbon dioxide carried out by Reiset (1882) from 1872 to 1880 on the coast of northern France appear to be valid. They indicate a mean annual concentration, with respect to dry air, of 292.4 ±1.2 ppm. Comparisons with other possibly valid contemporary data suggest that these data are not biased by more than 10 ppm. It is thus unlikely that the CO_2 concentration was less than 282

---

[1] CO_2 measuring stations are distributed across the globe. Most, however, are located in coastal or island areas in order to obtain air without contamination from vegetation, organisms, and industrial activity: that is, to establish the so-called background level of CO_2. In considering such measurements, account should be taken of the established fact that land-derived air flowing seaward loses about 10 ppm of its carbon dioxide to dissolution in the oceans—even more in colder waters—by Henry's Law.

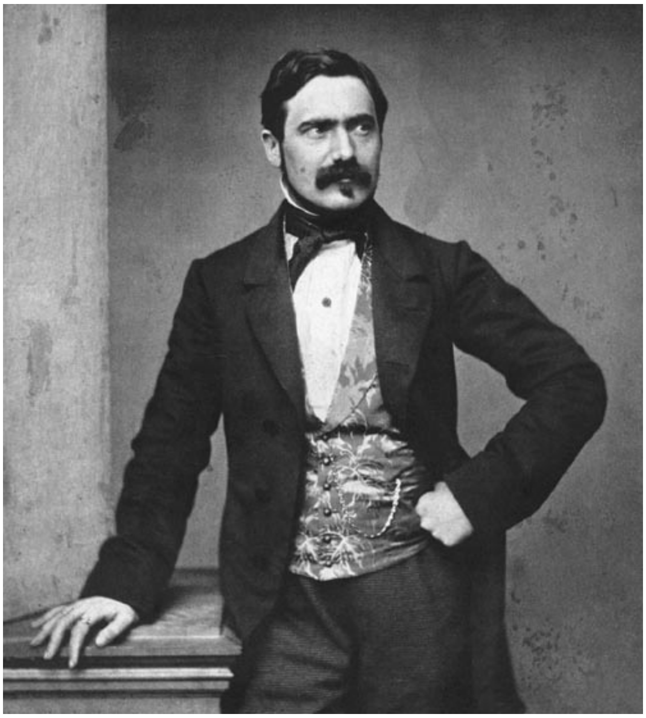
> ppm in the late nineteenth century, and was probably close to 292 ppm.

In other words, the historical CO_2 data acceptable to Callendar and Keeling had to be sufficiently low to be consistent with the greenhouse hypothesis that climate change is controlled by rising CO_2 emissions from fossil fuel burning. There was no verification or falsification of results and methods used by many other authors, especially those published in the 20th Century (for example, Lundegardh [35, 36], Duerst [37], Kreutz [38], Misra [39], Scholander [40])—with exception of the 1935 data of Buch [32], lying on the "fuel line" (Callendar 1958 [20]).

According to Callendar, Keeling, and the IPCC, CO_2 variations observable in air were due to diurnal and seasonal cycles (see Figure 2), or to glacial/interglacial fluctuations. Natural concentrations are assumed to have been in equilibrium until mankind disturbed the natural situation. Therefore, any long-term observations that might display decadal to centennial natural variations in atmospheric CO_2 are ruled out *a priori* by Callendar and Keeling.

As I discuss below, these criticisms by Callendar and Keeling, and the selective way in which they discarded historical data, are not justifiable. Their most egregious error was perhaps the dismissal of all data which varied significantly from their presupposed average. That said, it is of course the case that some of the older data must be viewed as less reliable for technical, analytical reasons, as also indicated below.

In 1958, Keeling introduced a new direct technique for the accurate measurement of atmospheric CO_2. He used cryogenic condensation of air samples, followed by non-dispersive infrared (NDIR) spectroscopic analysis against a reference gas, using manometric calibration. Subsequently, this technique was adopted as an analytical standard for CO_2 determination throughout the world, including by the World Meteorological Organization (WMO) [3-13].



Max Joseph von Pettenkofer (1818-1901), German chemist and medical doctor, was a student of Justus Liebig. Pettenkofer, who devised what became the standard method of measuring CO_2, was also known as a pioneer in epidemiology and public health.

Early Chemical Methods of CO_2 Gas Analysis

I have assembled here a 138-year-long record of atmospheric CO_2 levels, extracted from more then 180 technical papers pub-

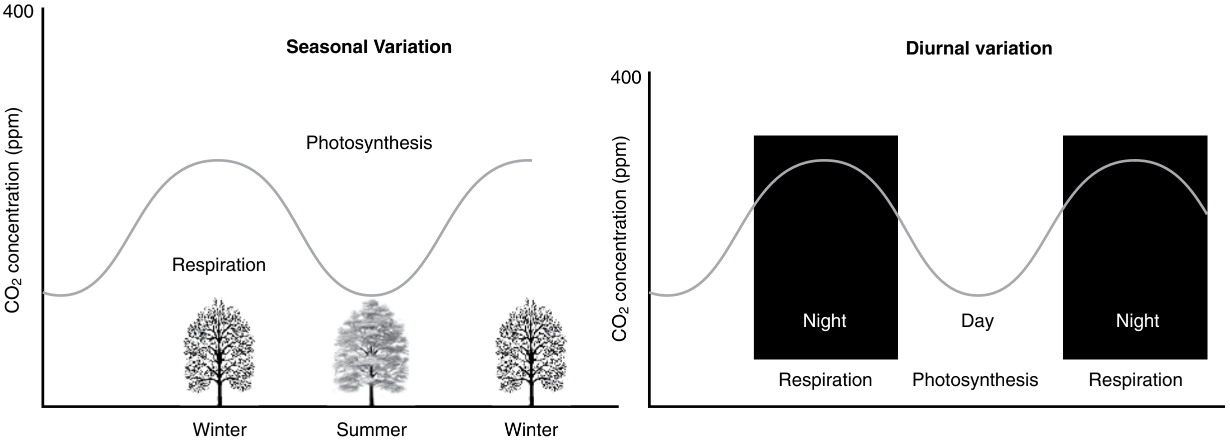


Figure 2
SEASONAL AND DIURNAL VARIATIONS IN CO_2
Carbon dioxide levels vary greatly by season and diurnally.

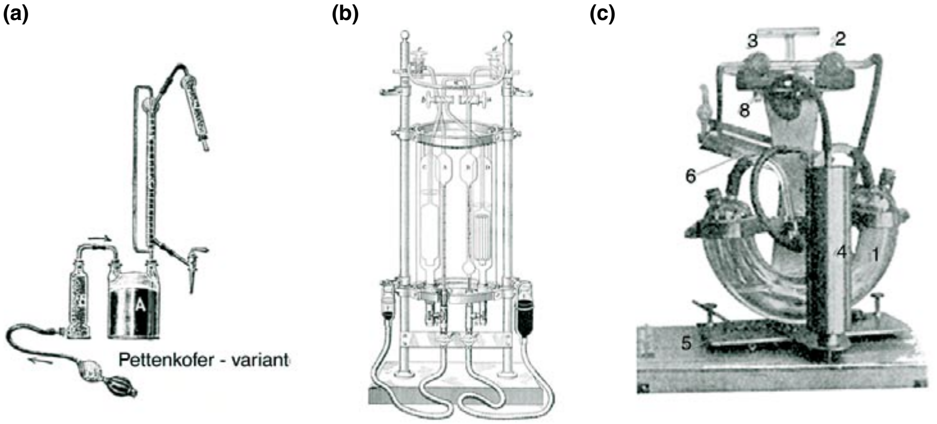


Figure 3
THREE PRINCIPAL CHEMICAL TECHNIQUES FOR MEASURING CO_2
(a) A type of Pettenkofer titrimetric apparatus (1920)
(b) Petterson/Sonden volumetric apparatus (1912)
(c) Riedel/Schuftan volumetric apparatus (1933)

Table 2
SERIES OF CO_2 MEASUREMENTS SINCE 1855 LASTING MORE THAN ONE YEAR (USING TITRIMETRIC PETTENKOFER PROCESS)

	Year	Author	Locality	No. of determinations
1.	Since 1855	v. Pettenkofer [46]	Munich	Many
2.	1856 (6 months)[1]	v. Gilm[1] [50]	Innsbruck[1]	19
3.	1863-1864	Schulze[2] [51]	Rostock,	426
4.	1864-1865	Smith [52]	London, Manchester, Scotland	246
5.	1868-1871	Schulze[2] [51]	Rostock,	1,600
6.	1872-1873	Reiset [53]	Dieppe, France (Northsea)	92
7.	1873	Truchot [54]	Clermont Ferrand	60
8.	1874-1875	Farsky[2] [55]	Tabor, Böhmen, (Czech)	295
9.	1874-1875	Hässelbarth[2] [56]	Dahme	347
10.	1879-1880	Reiset [31]	Dieppe	118
11.	1883	Spring[2] [57]	Liège	266
12.	1886-1887	Uffelmann [58]	Rostock	420
13.	1889-1891	Petermann [59]	Gembloux	525
14.	1897-1898	Letts and Blake [14]	near Belfast	64
15.	1898-1901	Brown and Escombe [60]	Kew Gardens	92
16.	1917-1918	A. Krogh [61, 62]	Copenhagen	Many
17.	1920-1926	Lundegardh [35]	Southern Sweden, Kattegat	>3,000
18.	1928	Krogh/Rehberg [62]	Copenhagen	Many
19.	1932-1935	Buch [32]	North Atlantic Ocean, Finland	176
20.	1936-1939	Duerst [37]	Bern	>1,000
21.	1941-1943	Misra [39]	Poona, India	>250
22.	1950	Effenberger [17]	Hamburg	>40
23.	1954	Chapman et al. [63]	Ames, Iowa	>100
24.	1957	Steinhauser [64]	Vienna	>500
25.	1955-1960	Fonselius et al.[65], Bischof [66]	Scandinavia	>3,400

Notes

1. v. Gilm: Used similar process as Pettenkofer, first calibrated.
2. Used identical variant of Pettenkofer process, sampling by tube through opening in window.

Table 3
VOLUMETRIC AND MANOMETRIC MEASUREMENTS

Year		Author	Notes	
1.	1875 (Marx)	Tissandier [67]	Paris, in balloon, volumetric	>10
2.	1880-1912	Müntz & Aubin [28, 29, 30]	Near Paris, Pyrenees, Carribean, etc. (F) volumetric	81+
3.	1910-1912	Benedict [15]	Washington (USA), volumetric	>264
4.	1920-1930	Rheinau [68]	Locations in Germany, Davos, Switzerland (volumetric)	
6.	1912-1936	Haldane [70]	Worldwide, manometric	Many
7.	**1939-1941**	**Kreutz [38]**	**Germany, (volumetric)**	**64,000**
8.	1946-1970	Scholander [40, 41]	Worldwide, (volumetric)	>1000

lished between 1812 and 1961, the year which marked the end of the era of classical chemical analysis.

The compilation of data was selective. Nearly all of the air sample measurements used were originally obtained from rural areas or the periphery of towns, under comparable conditions—a height of approximately 2 meters above ground, at a site distant from potential industrial or military contamination. Evaluation of the chemical methods used reveals systematically high accuracy, with a maximum 3 percent error, reducing to 1 percent for the 1920-1926 data of Henrik Lundegardh (1888-1969), a pioneer of plant physiology and ecology [34-36].

Three principal chemical techniques have evolved since 1812 for measuring the CO_2 content of air: gravimetric, titrimetric, and volumetric or manometric (Figure 3a-c). The Pettenkofer titrimetric method—being simple, fast, and well-understood—was the optimal standard method for more than 100 years after 1857 [45-48]. (See Table 2.) Various scientists routinely calibrated their methods against each other, and against a standard gas of known CO_2 content.

The Pettenkofer process (Figures 3a, 4) and all its variants involved the absorption of a known volume of air in an alkaline solution ($Ba(OH)_2$, KOH, NaOH) and subsequent titration of the produced carbonate with an acid (oxalic, sulfuric, hydrochloric). Basic accuracy is ±0.0006 volume percent [34, 45] optimized to ±0.0003 vol percent by Lundegardh [35], who provides measurements comparable to the other techniques (see Table 3).

Measurements made prior to the 1857 introduction of the Pettenkofer method, mostly by renowned French chemists (Boussingault [14], Brunner [14], Regnault [14, 75]), systematically understated the amount of CO_2 in the atmosphere, because of factors that include CO_2 absorption into the lengths of natural latex tubing used for connections, use of sulfuric acid for drying air, and lack of temperature management. There being no calibration against Pettenkofer, or modern volumetric/manometric equipment, I cannot quantify accurately the range of error. Well-known absorption errors are in the order of 30 ppm. Among these authors, only de Saussure, during 1826-1830 [76] measured a realistic picture of the seasonal CO_2 cycle.

Early volumetric CO_2 measurement techniques also systematically understated CO_2 levels. Those used before Haldane [70] and Benedict/Sonden/Petterson in 1900 [15, 44]—including gas analyzers used by the French researchers Regnault, Müntz, Tissandier, and others—were open systems which lacked efficient control of reaction temperature (see Schuftan [43]), leading to less reliable data. Furthermore, French researchers such as Müntz, Tissandier, and Reiset (Pettenkofer process) used sulfuric acid for drying air (or releasing CO_2, Müntz [28-30]) before determination of CO_2 content. Because of the absorption of a considerable fraction of CO_2 in the sulfuric acid, their values are too low. The Bunsen absorption coefficient for sulfuric acid (H_2SO_4 at 25°C is 0.96, while for H_2O at 25°C it is only 0.759 [72].

These systematic errors had been known since 1848. Hlasiwetz [73] in 1856, and Spring [57] in 1885, determined these absorption losses of CO_2 in sulfuric acid to be 7-10 percent, or about 20 ppm.

Neither Callendar or Keeling, nor the IPCC mentioned these systematic errors which resulted in overly low CO_2 values. Yet

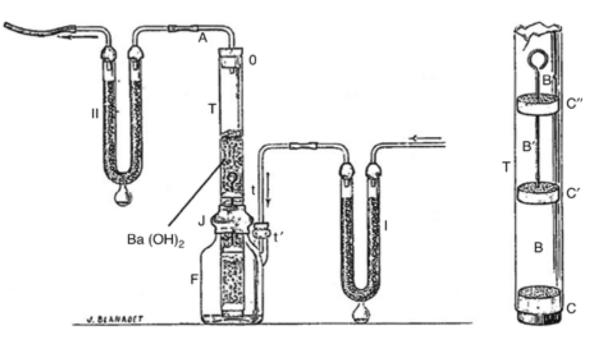
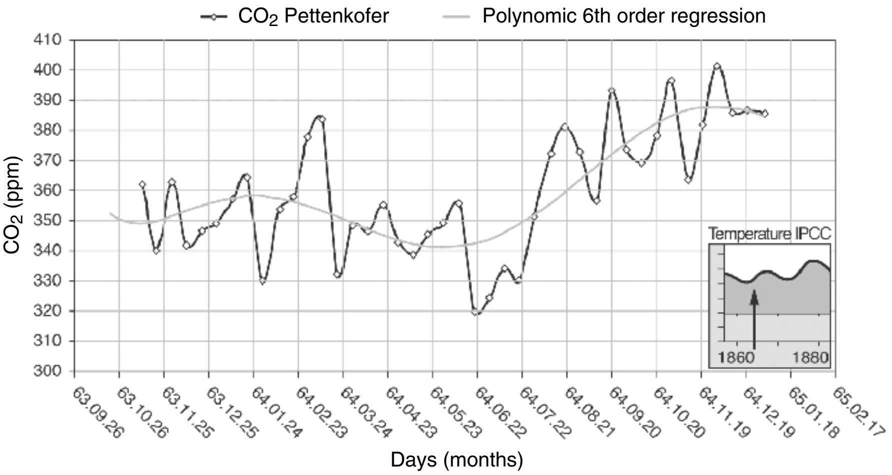


Figure 4
A TYPICAL TITRATION APPARATUS
The Pettenkofer titrimetric process, the standard method for CO_2 measurement since 1857, used the absorption of a known volume of air into an alkaline solution, barium hydroxide, $Ba(OH)_2$, for example. The carbon dioxide dissolved in the solution reacts with the $Ba(OH)_2$ to form the insoluble salt $BaCO_3$. The amount of acid required to neutralize the remaining $Ba(OH)_2$ vs. the original quantity determined the amount of CO_2 absorbed.

This is part of the equipment used by Reiset at Dieppe in 1872-1880 with sulfuric acid for drying air [31]. Sufuric acid is in the U-shaped tube at right.

Figure 5
SCHULZE'S MEASUREMENTS OF MONTHLY AND SEASONAL CO_2 VARIATION AT ROSTOCK, GERMANY (1863-1864)
Schulze and other 19th Century studies show CO_2 levels of 350 ppm or higher, when IRC ice core interpretations claim only 290 ppm.



Reiset and Müntz were singled out for special praise by Keeling and the IPCC as the sources of the best available data of that time [22, 23, 25-27, 74].

Even discounting such unsatisfactory data, in every decade since 1857, we can still identify several measurement series that contain hundreds of precise, continuous data (Table 2).

The highest density of data was achieved by Wilhelm Kreutz at the state-of-the-art meteorological station in Giessen, Germany [38], using a closed, volumetric, automatic system designed by Paul Schuftan, the father of modern gas chromatography [43, 78]. Kreutz compiled more than 64,000 single measurements using this equipment in an 18-month period during 1939-1941 (see below).

The longest single time series was carried out at the Montsouris laboratory in Paris, and comprised 12,000 measurements over the 30 years from 1876 until 1910 [79].

Historical Resolution of Short-term CO_2 Cycles

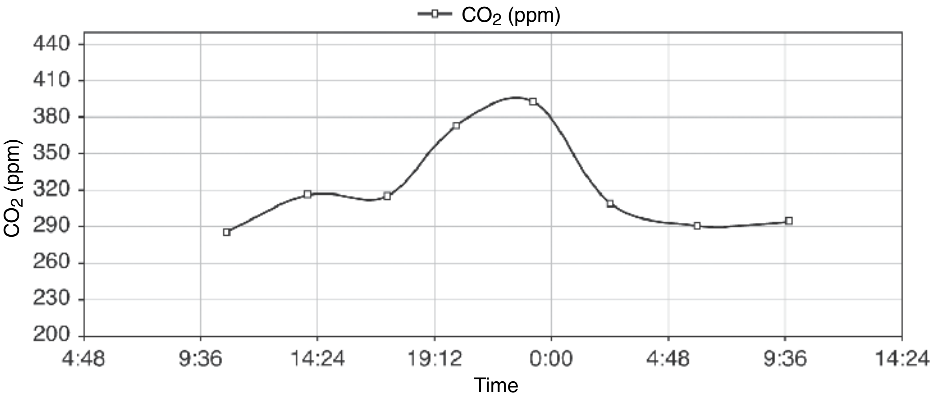
I first investigated short-term fluctuations in CO_2 concentration, stimulated by Callendar and Keeling's assertion that the historical data are unreliable because they reflect measurements made within an unresolved diurnal or seasonal cycle. Certainly, some observations deserve such criticism. But many others do not, as shown below.

Out of dozens of high quality data sets since 1857 that are available for analysis, I cite three 19th Century studies, in order to show the precision exhibited by historical gas analysis in detecting seasonal and diurnal variation of CO_2 levels. The three studies are by F. Schulze during 1863-1871 [51] at Rostock, Germany; P. Hässelbarth at Dahme, Prussia, in 1876 [56]; and W. Spring in 1883-1884 [57] at Liège, Belgium. (See Figures 5-7.)

The conditions of data acquisition, description of methods, prevailing weather conditions, and information about the precise location can be gathered from the appropriate papers. In general, these three sets of observations share levels of CO_2 as high as 350 ppm or more, at a time when data interpreted from ice cores indicate a level of around 290 ppm.

W. Spring, a chemist at the University of Liège in Belgium, analyzed 266 air samples during 1883-1885, resulting in an average CO_2 concentration of 355 ppm. His data clearly resolve the seasonal CO_2 cycling characteristic of temperate regions.

Figure 6
HÄSSELBARTH'S MEASUREMENTS OF DIURNAL CO_2 VARIATION AT DAHME, PRUSSIA (July 24-25, 1876)
CO_2 was measured with a Pettenkofer apparatus, taking 34 liters of air, every 3 hours, on a 1-meter-high table in a garden, with no wind and no clouds.



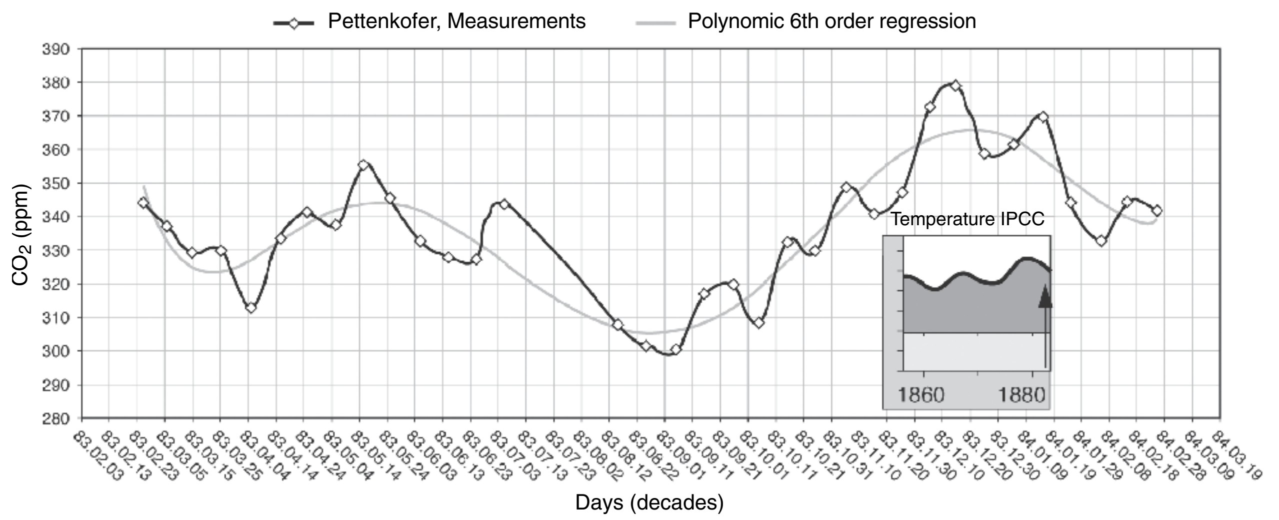


Figure 7

SPRING AND ROLAND'S MEASUREMENTS OF SEASONAL CO_2 VARIATIONS AT LIEGE, BELGIUM (1883-1884)

CO_2 was measured every 10 days with a Pettenkofer apparatus at the height of 5 meters. An average of 266 samples were 335 ppm, with a variation of 70 ppm. T he IPCC claims a CO_2 level of around 290 ppm for this same time period.

He carefully tested and calibrated his equipment, quantified local CO_2 sources from soil and industry (see Figure 8), and systematic CO_2 losses by drying air in sulfuric acid. He also discussed the influence of weather and the results of other scientists.

CO_2 Studies at Giessen, 1939-1941

Equipped with the best available hardware at that time [80, 81], W. Kreutz installed four measuring sites for parallel data acquisition beween 1939 to 1941, measuring all weather parameters including radiation, temperature, pressure, humidity, wind, and so on. Over an 18-month period, he analyzed more than 64,000 single CO_2 values at a rate of 120 samples per day, using a volumetric gas analyzer designed by Riedel & Co. of Essen, Germany [77]) and Paul Schuftan (Linde & Co), the famous expert in gas analysis, [43, 71, 78]. Kreutz's results [38] delineate well both the seasonal cycle and weather events around the city of Giessen, and confirm strikingly the persistence of CO_2 levels above 400 ppm over most of a period of two years (Figure 9).

The overall average CO_2 level for the 25,000 values plotted from Giessen is 438.5 ppm. This figure needs to be adjusted downwards to take account of anthropogenic sources of CO_2 from the nearby city, an influence that has been estimated as lying between 10 and 70 ppm (average 30 ppm) by different authors [61, 57, 82, 83].

Even after making this adjustment, the Giessen results strongly contradict recent IPCC estimates of carbon dioxide levels during the 1940s. These results of Kreutz were neither cited nor evaluated by Callendar and Keeling. Others who have mentioned Kreutz's work, such as Slocum [19], Effen-

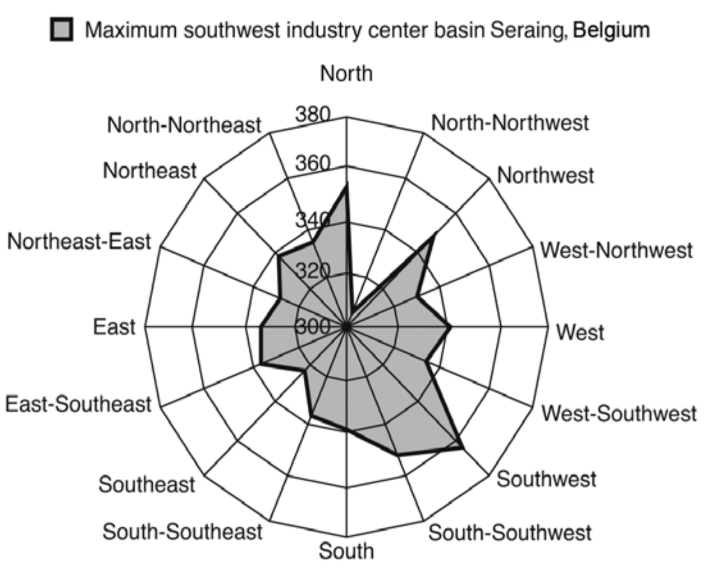


Figure 8

SPRING'S CALIBRATION OF CO_2 MEASUREMENTS FOR WINDS FROM INDUSTRIAL CENTER IN LIÈGE, BELGIUM (1883)

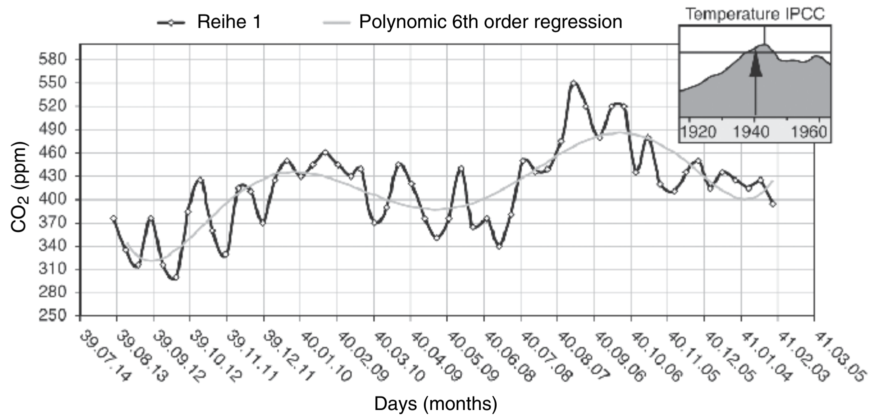


Figure 9
KREUTZ'S MEASUREMENTS OF CO_2 AT GIESSEN, GERMANY (1939-1941)
Kreutz installed four measuring sites for parallel data acquisition, measuring all weather parameters. Over an 18-month period, he acquired more than 64,000 readings, confirming the persistence of CO_2 levels above 400 ppm over most of two years.

berger [17], and Bray [21], invariably give faulty citation of the details.

The Historical CO_2 Data Compiled

In this section I present the analytical data over a 150-year period for air gas analysis determined by classical chemical techniques, as published in 138 scientific papers. The data presented have been retained unmodified. They mostly comprise measurements made on samples collected at a height of approximately 2 meters above ground, from stations located throughout the Northern Hemisphere, from Alaska, through Europe, to Pune, India.

Figure 10 gives an overview of the period 1812-1961 with 11-year smoothing to remove the short-term CO_2 fluctuations.

Figure 11 compares the 11-year-averaged CO_2 curve and the 2001 IPCC annually averaged temperature record between 1860 and 2000. Short-term fluctuations in CO_2 are suppressed by the filtering, but at this broad level there is a close match between the 1942 CO_2 and temperature peaks.

Figure 12 compares the yearly CO_2 averages over the period 1920-1961 to ice core CO_2 records compiled by Neftel et al. [33].

Notice in Figures 11 and 12 that the peak CO_2 concentration in the atmosphere and peak temperature coincide in 1942, an observation which will be given more attention below. The overall validity of the pattern of CO_2 fluctuations over this period is supported by the following considerations:

- Broad geographic coverage, with measuring stations spread throughout middle and northern Europe, the United States, the Atlantic Ocean, Alaska, India, and Antarctica.

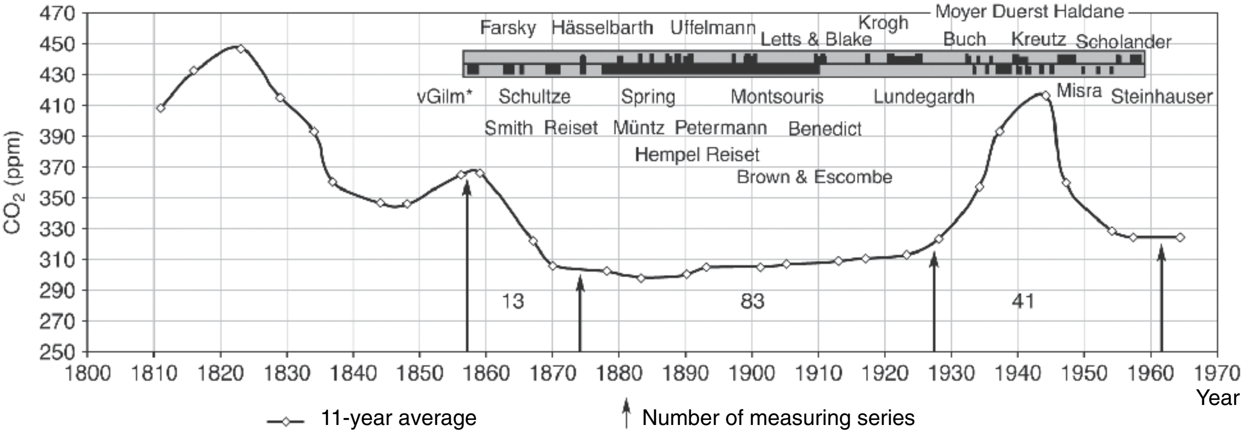


Figure 10
11-YEAR AVERAGED CO_2 MEASUREMENTS IN NORTHERN HEMISHPHERE (1812-1961)
For most of the 19th and 20th centuries, atmospheric CO_2 measured above 300 ppm, and sometimes above 400 ppm, despite claims to the contrary by Keeling and the IPCC. This 11-year averaging of data has eliminated short-term daily and seasonal variations. The researchers who compiled the data are noted by name, roughly on a time line; the bar diagram shows the periods of data coverage; and the number of measuring series for each period is given between the arrows.

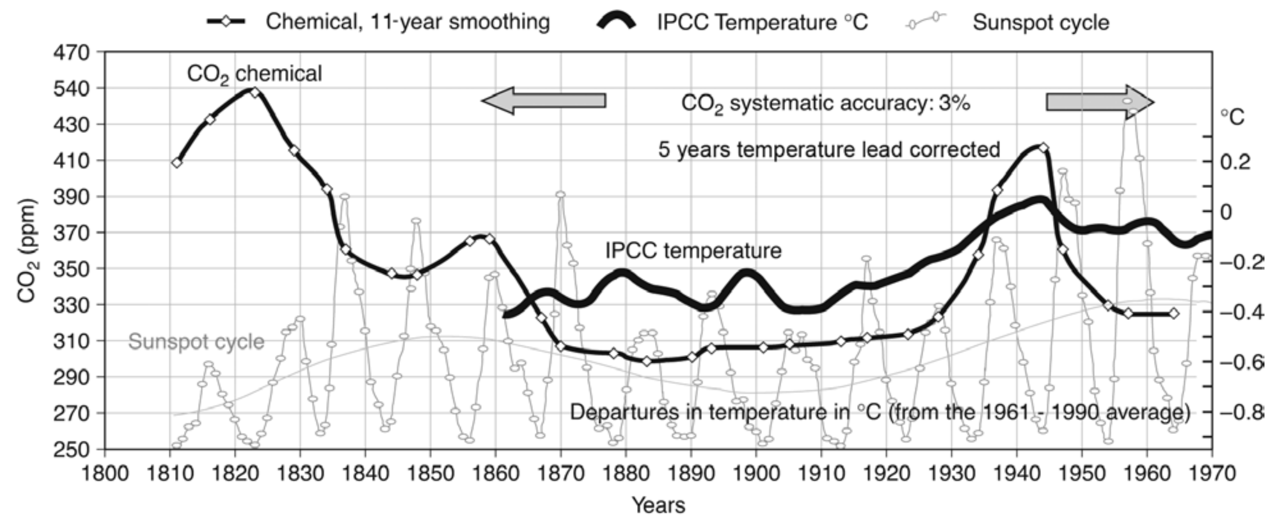


Figure 11

11-YEAR AVERAGED CO_2 CURVE OF ACTUALLY MEASURED CO_2 LEVELS, COMPARED TO 2001 IPCC TEMPERATURE RECORD (1860-1970)

Note the close match between the 1942 peaks in CO_2 and temperature—a vindication of the accuracy of chemical methods of CO_2 measurement, but not proof of the global warming conjecture. The CO_2 fluctuation peaks about five years after the temperature peaks. For more on this phase lag, see www.biokurs.de/treibhaus/180CO2_supp.htm .

- High data density: The 41 CO_2 series used include about 70,000 discrete measurements, with the highest data density in the peak between 1939 and 1942.
- Comparable CO_2 data were acquired using several different chemical techniques with accuracy of 2-3 percent, as designed by Krogh, Schuftan, van Slyke, Haldane, and Scholander.
- Measurements were made by several highly competent experts in air gas analysis: Buch [32], Haldane [70], Duerst [37], Kreutz [38], Scholander [40], Lockhart [84].
- There were verified suitable locations of the measuring stations: No contamination is known from human or natural sources; for example, conurbation, war, soil degassing, or volcanic emissions.
- World War II cannot be responsible for the high values, because a rise in CO_2 is exhibited from 1925 and culminating in 1942, and the second part of the maximum was recorded at places with no war activity (Alaska, India).

If the same CO_2 data are plotted as a five-year average (Figure 13), then the shorter-term CO_2 fluctuations reassert themselves. This plot shows that all eight temperature maxima during the 100 years from 1850 to 1950 correspond with CO_2 maxima. Ice core CO_2 data are included for comparison. Note that the ice core re-

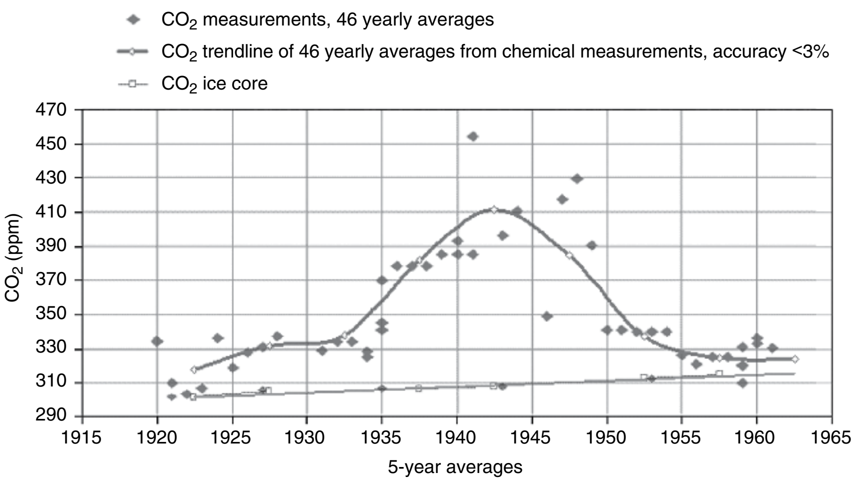


Figure 12

YEARLY CO_2 AVERAGES FROM CHEMICAL MEASUREMENT, COMPARED TO ICE CORE RECONSTRUCTIONS (1920-1961)

Direct chemical measurement (diamond symbols) showed considerable variation in atmospheric CO_2 content over the period from 1921 to 1961, compared to the almost flat curve (square symbols) produced by methodologically questionable means from gaseous inclusions in ice cores. The top line of direct chemical measurements has a standard error of less than 3 percent.

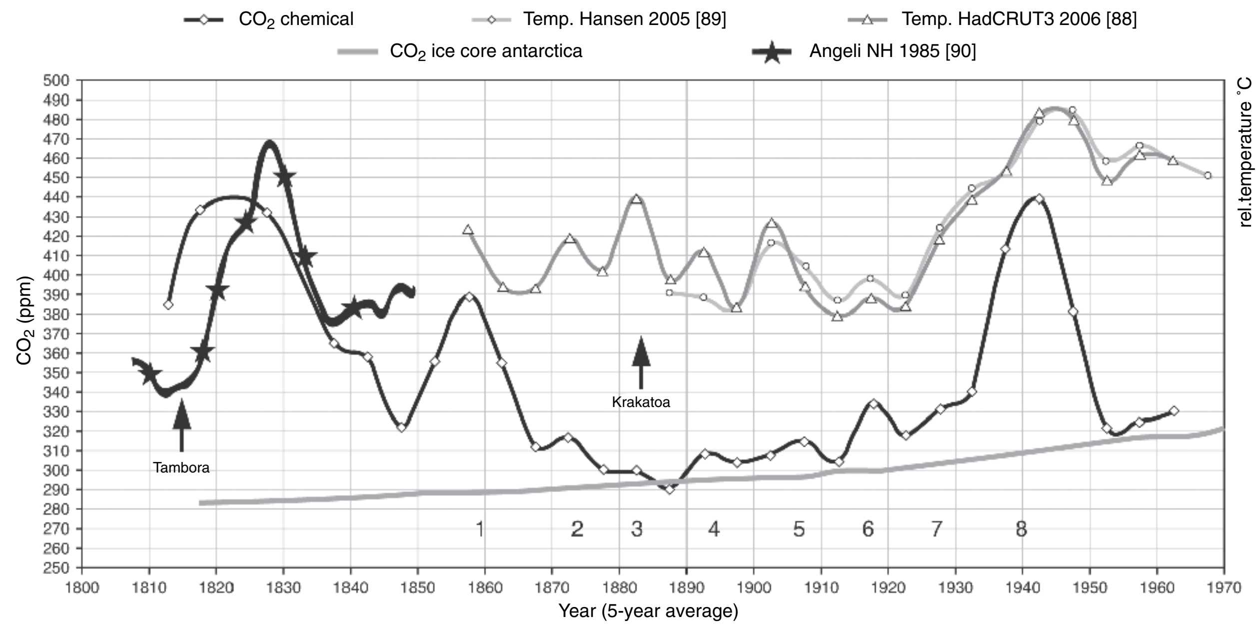


Figure 13
5-YEAR AVERAGED CO_2 MEASUREMENTS, COMPARED TO TEMPERATURE RECORD AND ICE CORE RECONSTRUCTIONS (1812-1970)
Plotted on a 5-year average, the shorter-term CO_2 fluctuations reassert themselves, showing a close correlation with temperature and suggesting that temperature is driving the level of CO_2, not the other way around.

sults do not contain decadal frequency fluctuations.[2] The unreliability of ice core reconstructions was indicated by Jaworowski [86].

The close relationship between temperature change and CO_2 level exhibited by these results is consistent with a cause-effect relationship, but does not in itself indicate which of the two parameters is the cause and which the effect. The greenhouse hypothesis of the IPCC argues for CO_2 being the cause (through radiative feedback) of the temperature rise. My results are equally, if not more consistent with the hypothesis that temperature drives the level of CO_2 in the atmospheric system. In support of this latter hypothesis, ice-core data consistently show that over climatic time scales, changes in temperature precede parallel changes in carbon dioxide by several hundred to more than a thousand years [91].

Historical Data Must Be Included

During the late 20th Century, the hypothesis that the ongoing rise of CO_2 concentration in the atmosphere is a result of fossil fuel burning became the dominant paradigm. To establish this paradigm, and increasingly since then, historical measurements indicating fluctuating CO_2 levels between 300 ppm and more than 400 ppm have been ignored. A re-evaluation has been undertaken of the historical literature on atmospheric CO_2 levels since the introduction of reliable chemical-measuring techniques in the early to mid-19th Century. More than 90,000 individual determinations of CO_2 levels are reported between 1812 and 1961. The great majority of these determinations were made by skilled investigators using well-established laboratory analytical techniques. Data from 138 sources and locations have been combined to produce a yearly average atmospheric CO_2 curve for the Northern Hemisphere.

The historical data that I have considered to be reliable can, of course, be challenged on the grounds that they represent local measurements only, and are therefore not representative on a global scale. Strong evidence that this is not the case, and that the composite historical CO_2 curve is globally meaningful, comes from the correspondence between the curve and other global phenomena, including sunspot cycles and Moon phases —the latter presented here for perhaps the first time in the literature (Figure 14)—and the average global temperature.

---

[2] Most of the historical chemical measurements were accomplished on samples collected from the boreal regions of the Northern Hemisphere. In these regions the diurnal and seasonal variation in atmospheric CO_2 displays a much higher amplitude than for oceanic areas, where smoothing influences result in a diminution of CO_2 levels by 10 ppm or more. An imbalance of photosynthesis, respiration, and soil respiration in and near to forests may lead to periodic emissions of large quantities of CO_2 [83, 92]. Substantial differences in amplitude of parts of the carbon cycle are well known in the Northern Hemisphere (for example, methane [93]; Luxembourg, [94]). Such effects may explain the various smaller fluctuations in CO_2 content through the historical chemical record, which are not imaged by ice cores or at ocean stations.

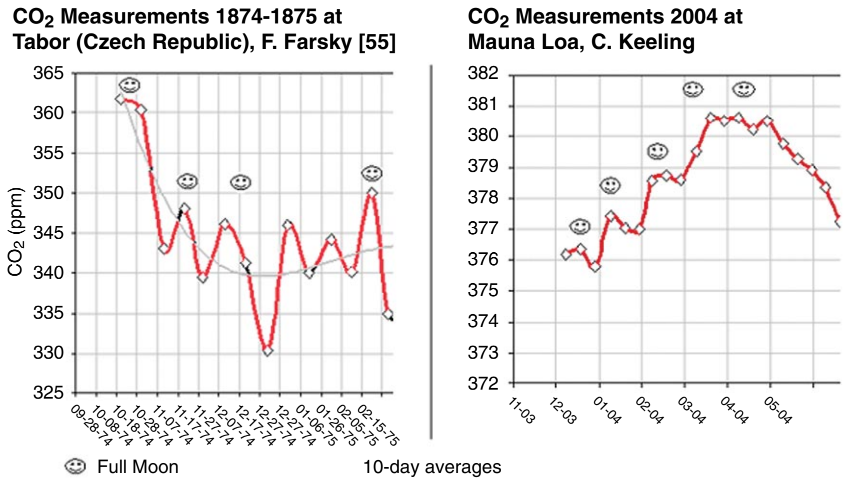


Figure 14

DATA INDICATING CO_2 PEAKS AT FULL MOON

Strong evidence that the direct chemical measurements are meaningful comes from the correspondence between the historical curve and other global phenomena, including sunspot cycles, and Moon phases (here noted for the first time).

Furthermore, that the historical data are reliable in themselves is supported by the credible seasonal, monthly, and daily variations that they display, the pattern of which corresponds with modern measurements. It is indeed surprising that the quality and accuracy of these historic CO_2 measurements have escaped the attention of other researchers.

Ernst-Georg Beck, Dipl. Biol., is a Biology and Bio-Technology Professor at the Merian-Schule, in Freiburg, Germany. An earlier version of this paper has appeared in the journal Energy & Environment, *(Vol. 18, No. 2, 2007). The author can be reached at egbeck@biokurs.de. His website (http://www.biokurs.de/treibhaus/180CO2_supp.htm) supplies links to the historical data for this article, and includes links to commentaries on his work.*

References

1. C.D. Keeling, "The Influence of Mauna Loa Observatory on the Development of Atmospheric CO_2 Research," Scripps Institution of Oceanography, University of California at San Diego, 1978: http://www.mlo.noaa.gov/ .
2. *IPCC Third Assessment Report: Climate Change 2001: The Scientific Basis,* Eds. J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, and D. Xiaosu (Cambridge, U.K.: Cambridge University Press), p. 944: http://www.grida.no/climate/ipcc_tar/wg1/index.htm .
3. A.G. Dickson, *Reference Materials for Oceanic CO_2 Measurements*, (Scripps Institution of Oceanography University of California, San Diego, La Jolla, Calif., Unesco, 1991).
4. G.C. Bate, A. D'Aoust, and D.T. Canvin, "Calibration of Infra-red CO_2 Gas Analyzers," Department of Biology, Queen's University, Kingston, Ontario, Canada, 1969: www.pubmedcentral.gov/articlerender.fcgi?artid=396226 .
5. AEROCARB Research Station Italy, Mt. Cimone, ISAC National Research Council: http://.aerocarb.lsce.ipsl.fr/ .
6. C.L. Zhao, P.P. Tans, and K.W. Thoning, "A High Precision Manometric System for Absolute Calibrations of CO_2 in Dry Air," *Journal of Geophysical Research,* Vol. 102(D 5), p. 5885, 1997.
7. "Scriptum Meereschemische Analytik," WS 2002/2003; Körtzinger, Arne, University of Kiel, Germany.
8. "A High Precision Manometric System for Absolute Calibrations of CO_2 Reference Gases," NOAA/ESRL Global Monitoring Division, Boulder, Colo. http://www.esrl.noaa.gov/gmd/ccgg/refgases/manometer.html .
9. "Charles David Keeling: Climate Science Pioneer: 1928-2005," Scripps Institution of Oceanography, University of California at San Diego: http://sio.ucsd.edu/keeling/ .
10. C.D. Keeling, "The Concentration and Isotopic Abundance of Carbon Dioxide in the Atmosphere," *Tellus*, Vol. 12 pp. 200-203, 1960.
11. C.D. Keeling, "The Influence of Mauna Loa Observatory on The Development of Atmospheric CO_2 Research," Scripps Institution of Oceanography, University of California at San Diego, 1978: http://www.mlo.noaa.gov/ .
12. C.D. Keeling and T.P. Whorf, 2005. "Atmospheric CO_2 records from sites in the SIO air sampling network," *In Trends: A Compendium of Data on Global Change,* Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn.: http://cdiac.ornl.gov/trends/co2/sio-mlo.htm .
13. "Global Atmosphere Watch Measurements Guide," *World Meteorological Organization Global Atmosphere Watch* Nos. 143 (2001) and 148 (2003): http://www.wmo.ch/pages/prog/arep/gaw/documents/gaw143.pdf, http://www.wmo.ch/pages/prog/arep/gaw/documents/gaw148.pdf.
14. E. Letts, R. Blake, "The Carbonic Anhydride of the Atmosphere," *Scientific Proceedings of the Royal Dublin Society,* Vol. 9, 1899-1902.
15. F.G. Benedict, "The Composition of the Atmosphere," *Carnegie Publication*, No. 166, Washington, D.C., 1912.
16. G.P. Callendar, "Variations of the Amount of Carbon Dioxide in Different Air Currents," *Quarterly Journal of the Royal Meteorological Society*, Vol. 66, No. 287, pp. 395-400, Oct. 1940.
17. E. Effenberger, "Messmethoden zur Bestimmung des C02-Gehaltes der Atmosphare und die Bedeutung derartiger Messungen für die Biometeorologie und Meteorologie," *Annalen der Meteorologie, Vierter Jahrgang*, Vol. 10, No. 12, pp. 417-427, 1951.
18. Nina A. Stepanova, "A Selective Annotated Bibliography of Carbon Dioxide in the Atmosphere," *Meteorological Abstracts*, Vol. 3, pp. 137-170, 1952.
19. G. Slocum, "Has the Amount of Carbon Dioxide in the Atmosphere Changed Significantly Since the Beginning of the Twentieth Century," *Monthly Weather Review*, Vol. 83, No. 10, pp. 225-231, 1955.
20. G.P. Callendar, "On the Amount of Carbon Dioxide in the Atmosphere," *Tellus X*, pp. 243-48, 1958.
21. J. Bray, "An Analysis of the Possible Recent Change in Atmospheric Carbon Dioxide Concentration," *Tellus XI*, Vol. 2, p. 220, 1959.
22. Fraser et al., in *The Changing Carbon Cycle*, Springer Verlag (1986), p. 66.
23. C.D. Keeling, "Reassessment of Late 19th-Century Atmospheric Carbon Dioxide Variations," *Tellus*, Vol. 38B, pp. 87-105, 1986.
24. G.P. Callendar, "The Artificial Production of Carbon Dioxide and Its Influence on Climate," *Quarterly J. Royal Meteorological Society*, Vol. 64, pp. 223-40, 1938.
25. T. Wigley, "The Preindustrial Carbon Dioxide Level," *Climate Change*, Vol. 5, pp. 315-320, 1983.
26. "The Pre-1958 Atmospheric Concentration of Carbon Dioxide," EOS Meeting, June 26, 1984, p. 415.
27. WPC-53, WMO: "Report of the Meeting in the CO_2-Concentrations from Preindustrial Times," I.G.Y, 1983.
28. A. Müntz and E. Aubin, "Recherches sur les Proportions d'acide carbonique contenues dans l'air," *Ann. Chim. Phyp, Serie 5*, Vol. 26, p. 222, 1882.
29. A. Müntz and E. Aubin, "Recherches sur les Proportions d'acide carbonique contenues dans l'air," *Ann. Chim. Phyp., Serie 5*, Vol. 26, p. 222, 1882.
30. A. Müntz and E. Aubin, "L'acide carbonique de l'air," *La Nature* (Paris), Vol. 2, p. 385, 1882: http://cnum.cnam.fr/CGI/page.cgi?4KY28.18/399/ .
31. J. Reiset, "Recherches sur la proportion de l'acide carbonique dans l'air," *Annales de Chimie,* No. 5, Vol. 26, p. 144, 1882.
32. E. Buch, "Der Kohlendioxydgehalt der Luft als Indikator der Meteorologisch-

en Luftqualitat,” *Geophysica*, Vol. 3, pp. 63-79, 1948.

33. A. Neftel et al. “Ice Core Sample Measurements Give Atmospheric CO_2 Content During the Past 40,000 Yr.,” *Nature* Vol. 295, pp. 220-223, 1982.
34. H. Lundegardh, “Neue Apparate zur Analyze des Kohlensäuregehalts der Luft,” *Biochem. Zeitschr.*, Vol. 131, p. 109, 1922.
35. H. Lundegardh, *Der Kreislauf der Kohlensäure in der Natur.*, Fischer, Jena (680), 1924).
36. A. Larkum, “Contributions of Henrik Lundegardh,” *Photosynthesis Research*, Vol. 76, pp. 105-110, 2003; Biography of H. Lundegardh: http://www.life.uiuc.edu/govindjee/Part2/09_Larkum.pdf .
37. U. Duerst, “Neue Forschungen über Verteilung und Analytische Bestimmung der wichtigsten Luftgase als Grundlage für deren hygienische und tierzüchterische Wertung,” *Schweizer Archiv für Tierheilkunde*, Vol. 81, No. 7/8, pp. 305-317, Aug. 1939.
38. W. Kreutz, “Kohlensäure Gehalt der unteren Luftschichten in Abhangigkeit von Witterungsfaktoren,” *Angewandte Botanik*, Vol. 2, pp. 89-117, 1941.
39. R.K. Misra , “Studies on the Carbon Dioxide Factor in the Air and Soil Layers near the Ground,” *Indian Journal of Meteorology and Geophysics*, Vol. 1, No. 4, p. 127, 1950
40. P.F. Scholander, “Analyzer for Accurate Estimation of Respiratory Gases in One-half Cubic Centimeter Samples,” *J. Biol. Chem.*, Vol. 167, pp. 235-250, 1947: http://www.jbc.org/cgi/reprint/167/1/235 .
41. R. Hock et al., “Composition of the Ground-level Atmosphere at Point Barrow,” *Journal of Meteorology*, Vol. 9, p. 441, 1952.
42. E. Abderhalden, *Handbuch der biochemischen Arbeitesmethoden,* (Berlin 1919), p. 480; and F.P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie, II. Band* (Vienna, 1949), p. 511.
43. P. Schuftan, *Chem. Fabrik*, Vol. 51, p. 513, 1933.
44. O. Pettersson and K. Sonden, *Skand. Arch. Physiol.*, Vol. 6, p. 16, 1895.
45. Y. Kauko and V. Mantere, “Eine genaue Methode zur Bestimmung des CO_2-Gehaltes der Luft,” *Zeitschrift für anorganische und allgemeine Chemie.*, Vol. 223 No. 1, pp. 33-44, 1935.
46. M. Pettenkofer, “Über eine Methode die Kohlensäure in der atmosphärischen Luft zu bestimmen,” *Chem. Soc. Journ. Tranp.*, Vol. 10, p. 292, 1858; and *Journ. Prakt. Chem.*, Vol. 85, p. 165, 1862.
47. M. Pettenkofer and C. Voit, *Zeitschrift für Biologie,* Vol. 2, p. 459, 1866.
48. M. Pettenkofer, *Ann. Chem. Pharm.*, Suppl. Bd. 2, I, 1862.
49. “The respiration apparatus by M. Pettenkofer,” Letter exchange by Dr. Eugen Freih. von Gorup-Besanez: http://gorup.heim.at/Briefe/Pettenkofer.htm .
50. H. v. Gilm, “Über die Kholensäurebestimmung der Luft Sitzungsberichte d. kaiserl.” *Akademie d. Wissenschaften*, Vol. 24, 1857.
51. F. Schulze, *Landw. Versuchsstationen*, Vol. 9, p. 217, 1867; Vol. 10, p. 515, 1868; Vol. 12, p. 1, 1875; Vol. 14, p. 366, 1871.
52. S. Smith, “On the Composition of the Atmosphere,” *Manchester Lit. Phil. Soc. Proc.*, Vol. 4, p. 30, 1865.
53. J.A. Reiset, *Compt. Rend.*, T. 88, p. 1007; T. 90, pp. 1144-1457, 1879-1880.
54. P. Truchot, “Sur la proportion d’acide carbonique existent dans l’air atmospherique,” *Compt. Rend.*, Vol. 77, p. 675, 1873.
55. F. Farsky, “Bestimungen der atmosphärischen Kohlensäure in den Jahren 1874-1875 zu Tabor in Böhmen, Wien,” *Akadem. Sitzungsberichte*, Vol. 74, No. 2, p. 67, 1877.
56. P. Hässelbarth and J. Fittbogen, “Beobachtungen über lokale Schwankungen im Kohlensäuregehalt der atmosphärischen Luft,” *Landw. Jahrbücher*, Vol. 8, p. 669, 1879.
57. W. Spring and L. Roland, “Untersuchungen uber den Kohlensäuregehalt der Luft; Chemisches Centralblatt No. 6, Oct. 2, 1886, 3. Folge 17. *Jahrgang and Mámoires couronnás par l’Academie Royal de Belgique,* Vol. 37, p. 3, 1885.]
58. J. Uffelmann, “Luftuntersuchungen,” *Archiv f. Hygiene*, p. 262, 1888
59. A. Petermann, “Acide carbonique contenu dans l’air atmospherique,” *Brux. Mem. Cour.*, Vol. 47, No. 2, p. 5, 1892-1893.
60. H. Brown and F. Escombe, “On the Variation in the Amount of Carbon Dioxide in the Air of Kew during the Years 1898-1901,” *Proc. Roy. Soc.*, B., Vol. 76, p. 118, 1905.
61. A. Krogh, “A Gas Analysis Apparatus Accurate to 0.001 Percent Dainly Designed for Respiratory Exchange Work,” *Biochem J.*, Vol. 14, Nos. 3-4, pp. 267-281, July 1920.
62. A. Krogh and P. Rehberg, “CO_2-Bestimmung in der atmospährischen Luft durch Mikrotitration,” *Biochemische Zeitschrift*, Vol. 205, p. 265, 1929.
63. H. Chapman et al., “The Carbon Dioxide Content of Field Air,” *Plant Physiology*, Vol. 29, p. 500, 1956.
64. F. Steinhauser, “Der Kohlendioxidgehalt der Luft in Wien und seine Abhängigkeit von verschiedenen Faktoren,” *Berichte des deutschen Wetterdienstes*, Vol. 51, p. 54, 1958.
65. S. Fonselius, “Microdetermination of CO_2 in the Air, with Current Data for Scandinavia,” *Tellus*, Vol. 7, pp. 259-265, 1955.
66. W. Bischof, “Periodical Variations of the Atmospheric CO_2 Content in Scandinavia,” *Tellus*, Vol. 12, pp. 216-226, 1960.
67. G. Tissandier, “Dosage de l’acide carbonique, de l’air a bord du ballon le Zenith,” *Comt. Rend.*, Vol. 80, p. 976, 1875.
68. E. Rheinau, *Praktische Kohlensäuredüngung in Gärtnerei und Landwirtschaft* (Berlin: Springer Verlag, 1927).
69. D.D. Van Slyke et al., “Manometric Analysis of Gas Mixtures,” I, II, *Biol. Chem.*, Vol. 95, No. 2, pp. 509, 531, 1932: http://www.jbc.org/cgi/reprint/95/2/531.
70. J.P. Haldane, *Methods of Air Analysis*, (London: Charles Griffin and Co., 1912).
71. P. Schuftan, *Gasanalyze in der Technik* (Leipzig: P. Hirzel Verlag, 1931.
72. IUPAC NIST Solubility Database: http://srdata.nist.gov/solubility/sol_detail.aspx?sysID=62_79.
73. W. Hlasiwetz, “Über die Kohlensäurebestimmung der atmosphärischen Luft,” *Wien akad. Sitzungsberichte,* Vol. 20, p. 18, 1856.
74. C.D. Keeling, “Atmospheric Carbon Dioxide in the 19th Century,” *Science*, Vol. 202, p. 1109, 1978.
75. V. Regnault and J. Reiset, *Ann. Chim. (Phyp.)*, Vol. 26, No. 3, p. 299, 1849.
76. T. de Saussure, “Sur la variation de l’acide de carbonique atmospherique,” *Annales de Chimie et Physique*, Vol. 44, p. 5, 1830.
77. F. Riedel, German Patent No. 605333, Oct. 18, 1934, Gasuntersuchungsapparat.
78. G. Arnold, V.G. Berezkin, L.S. Ettre, “Paul Schuftan and the Early Development of Gas-adsorption Chromatography,” *Journal of High Resolution Chromatography*, Vol. 8, No. 10, pp. 651-658, 1985.
79. G. Stanhill, “The Montsouris Series of Carbon Dioxide Concentration Measurements, 1877-1910,” *Climatic Change*, Vol. 4, pp. 221-237, 1982.
80. W. Kreutz, “Spezialinstrumente und Einrichtungen der agrarmeteorologischen Forschungsstelle,” *Biokl. Beibl.* H2, 1939.
81. A. Vaupel, Coworker of W. Kreutz, Deutscher Wetterdienst, personal notes, 2006.
82. S. Henninger and W. Kuttler, “Mobile Measurements of Carbon Dioxide within the Urban Canopy Layer of Essen, Germany,” *Proc. Fifth Symposium of the Urban Environment*, August 23-26, 2004, Vancouver, Canada, American Meteorological Society, p. J 12.3.
83. D. Schindler et al., “CO_2 Fluxes of a Scots Pine Forest Growing in the Warm and Dry Southern Upper Rhine Plain, SW Germany”, *Eur. J Forest Res*, Vol. 125, pp. 201-212, 2006.
84. E. Lockhart and A. Court, “Oxygen Deficiency in Antarctic Air, *Monthly Weather Report*, Vol. 70, No. 5, 1942.
85. M. Rogers et al., “Long-term Variability in the Length of the Solar Cycle,” *Penn. State Tech. Reports*, 2005: www.stat.psu.edu/reports/2005/tr0504.pdf .
86. Z. Jaworowski, “Ancient Atmosphere—Validity of Ice Records,” *Environ. Sci. & Pollut. Res.*, Vol. 1, No. 3, pp. 161-171, 1994.
87. National Geographic Data Center (NGDC] 2006: http://www.ngdc.noaa.gov/stp/SOLAR/ ftpsunspotnumber.html .
88. Jones et al., Climatic Research Unit 2006: http://www.cru.uea.ac.uk/cru/data/temperature/ .
89. J.E. Hansen et al, “NASA GISS Surface Temperature Analysis”: http://cdiac.ornl.gov/trends/ temp/hansen/hansen.html .
90. J. Angell et al., “Surface Temperature Changes Following the Six Major Volcanic Episodes between 1780 and 1980,” *Journal. of Climate and Appl. Meteorology*, Vol. 24, p. 937, 1985.
91. M. Mudelsee, “The Phase Relations among Atmospheric CO_2 Content, Temperature and Global Ice Volume over the Past 420 ka.,” *Quaternary Science Reviews*, Vol. 20, pp. 583-589, 2001.
92. John Hom et al., “Studies on Carbon Flux and Carbon Dioxide Concentrations in a Forested Region in Suburban Baltimore,” 2001, USDA Forest Service, Northeast Research Station, Indiana University, Bloomington, Ind.: http://www.beslter.org/products/posters/johntower_2003.pdf.
93. NOAA, Global Distribution of Atmospheric Methane: http://www.cmdl.noaa.gov/ccgg .
94. Meteorological station at Diekirch, Luxembourg: http://meteo.lcd.lu
95. C.D. Keeling, “A Brief History of Atmospheric CO_2 Measurements and Their Impact on Thoughts about Environmental Change,” Acceptance Speech as Winner of the Second Blue Planet Prize, 1993: http://www.af-info.or.jp/eng/honor/bppcl_e/e1993keeling.txt.