180 Years accurate CO_2 - Gasanalysis of Air by Chemical Methods (Short version)

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1. Short summary on the knowledge about the CO_2 air gas analysis (2006)

The context of carbon dioxide as the base of all organic matter on earth with fundamental importance for metabolism of organisms is taught in each school and all universities of the world.
The background for these realizations were investigated among other things for approx. 200 years by scientists such as Pettenkofer, Benedict, Krogh (Nobel prize), Lundegardh and Warburg (Nobel prize).
In IPCCs Climate Change 2001: Working Group I: The Scientific Basis **you will find the following in chapter 3: "The Carbon Cycle…":3.1: "**
"The concentration of CO_2 in the atmosphere has risen from close to 280 parts per million (ppm) in 1800, at first slowly and then progressively faster to a value of 367 ppm in 1999, echoing the increasing pace of global agricultural and industrial development. This is known from numerous, well-replicated measurements of the composition of air bubbles trapped in Antarctic ice. Atmospheric CO_2 concentrations have been measured directly with high precision since 1957; these measurements agree with ice-core measurements, and show a continuation of the increasing trend up to the present."
Responsible for the relative measurements since 1958 is C.D. Keeling, University of California at San Diego, USA. He used cryogenic condensation of the samples and NDIR spectroscopy against a reference gas with manometric calibration. Today all measurements are done by this technique as a standard (WMO). Keeling's laboratory delivers the reference gases worldwide and have the calibration monopoly. .(38, 39, 40,41, 42, 43, 44, 45)
Measurement stations spreading over the world are mainly in oceanic areas to get air without contamination from vegetation, organisms and civilisation, the so called background level of CO_2.
So his initial work mainly on the active volcano Mauna Loa (Hawaii) is todays reference for determination of carbon dioxide with an accuracy of down to 0.1 ppm. (20, 21, 22, 24)
Accuracy from 1959 was much more in error and approx. 4 ppm between 1964 –1968 max. 1 ppm. (130)
A thorough review of existing literature (175 in this study) revealed in contrast to the published opinion based on the founders of modern greenhouse theory, Callendar and Keeling, that there exists some 90, 000 accurate measurements by chemical methods before 1957 back to 1857 with an accuracy better than 3%.
Accurate measurements had been done amongst others by de Saussure 1826, Pettenkofer/v.Gilm 1857, Schulze 1864/71, Farsky 1874, Uffelmann 1886, Letts und Blake 1897, Krogh and Haldane 1904, Benedict 1912, Lundegardh 1920, van Slyke 1929, Dürst and Kreutz 1934 alternatively 1940, Misra 1942 or Scholander 1946 with measuring instruments through which from 1857 (Pettenkofer) an accuracy of +/-0,0006 Vol% to under +/-0,0003 Vol% =~3 ppm (Lundegardh 1926) was achieved.
They show precise seasonal and some diurnal variation.
These pioneers of chemistry, biology, botany, medicine and physiology laid foundations for todays knowledge of metabolism, nutrition science, biochemistry and ecology. Modern climatology ignored their work till today even though it is the basis of all textbooks of the mentioned faculties and was honoured with several Nobel prizes.

2. Results of the literature review of this study:

To reconstruct historic fluctuation of carbon dioxide 137 yearly averages were used out of 175 technical papers within 1812 until 1961, the end of using chemical technique. Nearly all selected data had been received in rural areas or periphery of towns under comparable conditions with a measuring hight of approx. 2 m above ground and without large contamination of industry. Evaluation of chemical methods revealed a systematic accuracy of maximum 3% down to 1% in best cases by Henrik Lundegard 1920, a pionieer of plant physiology and ecology.

11 often used measuring techniques (gravimetric, titrimetric, volumetric and manometric) had been evolved from 1812 to modern times, from which the so called Pettenkofer method (titrimetric) was easy, fast and well understood and the optimized standard from 1857 for 100 years. Mentioned authors had calibrated their methods against each other and samples with known content. All measuring parameters, local modalities and measuring errors can be extracted out of available literature.

The available data used in this study can be researched in several comprehensive bibliographies:

Year	Autors	Cited autors and papers with data			Notes
		Gesamt	**19. Jh**	**20. Jh**	
1900	Letts and Blake (53)	252	252	-	only 19th century
1912	Benedict (51)	137	137	-	only 19th century; focus on O2-determination
1940	**Callendar (113)**	**13**	**7**	**6**	**cited Letts&Blake and Benedict**
1951	Effenberger (54)	56	32	24	cited Duerst, Misra und Kreutz
1952	Stepanova (118)				
1956	Slocum (128)	33	22	11	
1958	**Callendar (119)**	**30**	**18**	**12**	**No citing of Duerst, Kreutz and Misra**
1958	Bray (129)	49	20	19	
1986	Fraser (149)	6	6	-	
1986	**Keeling (147)**	**18**	**18**	**-**	**Only 19th century same as Callendar;**
2006	Beck (this study)	152	82	73	Only chemical determination until 1961

Table 1 Bibliographies and citation of papers.

It could be shown that between 1800 to 1961 more than 320 technical papers exist on the subject of air gas analysis containing verified data on atmospheric CO_2 concentrations.

Callendar(engineer), Keeling (chemist) and IPCC do not evaluate these chemical methods though being standard in analytical chemistry, discredited these techniques and data and rejected most as faulty and highly inaccurate because not helpful proving their hypothesis of fuel burning induced rise of carbon dioxide in the atmosphere. In using their concept of unpolluted background level they had examined about 10% of available literature and considered <1% (Müntz, Reiset, Buch) as accurate. (see references)

But history of air gas analysis was not like this (see references).

From 1857 with Pettenkofer process as a standard accuracy of 3% was enough to develop all modern knowledge of medicine, biology and physiology (photosynthesis, respiration end energy metabolism) which are taught today worldwide as a content of all text books of the mentioned faculties

Several Nobel (Krogh 1923, Warburg 1933, nominated Benedict 1923) and other awards (Schuftan Memorial Prize in Process Design in Chemical Engineering (UK) and Pettenkofer award (medicine, D) honoured these pioneering findings of modern natural science (58, 59, 60, 61, 64).

Others as Lundegardh induced a revolution of our knowlodge on ecology and plant physiology inventing modern techniques and revealed today well known facts (flame-photometer 1929, cytochrome 1950, (100))

And without the exact determination of blood gas levels with the aid of the apparatus of van Slyke hundred thousands of patients would have died in the 20th century.
Modern climate scientists based on the tasks of Keeling, Callendar and IPCC ignore their work.
In every decade from 1857 we will find several measuring series with hundreds of precise continous data.
The highest data density is achieved by W. Kreutz in the state-of-the-art meteorologic station of that time at Gießen (Germany) using the best available equipment (closed, volumetric, automatic system) designed by Paul Schuftan, the father of modern gas chromatography. He´d done more than 65 000 single measurements in 18 month from 1929 –1941 with 120 determinations a day every 90 minutes.
The longest series had been done in Paris at Montsouris laboratory with 12000 Determinations in 30 years from 1876 until 1910.
Presented data in this study are initially not modified, selected for a measuring hight of approx. 2 m above ground, extend mainly in northern hemisphere from Alaska over Europe to Pune (India).
Table 2 shows series of measurements since 1860 more than a year using the titrimetric Pettenkofer process. The Pettenkofer process and all its variants included the absorption of a known volume of air in alkaline solution ($Ba(OH)_2$, KOH, NaOH) and titration with acid(oxalic, sulphuric acid) of the produced carbonate. Basic accuracy is +-0,0003 volume% (70) optimized to 1% by Lundegardh and it can be found several comparative measurements with the other techniques.

Table 2 Series of measurements since 1860 more than a year using the titrimetric Pettenkofer process

	year	**author**	**locality**	**Amount of determinations**
1.	from 1855	v. Pettenkofer	München	many
2.	1856 (6 month)[1]	v. Gilm[1]	Innsbruck[1]	19
3.	1863 -1864	Schulze	Rostock, (D)	426
4.	1864/65	Smith	London, Manchester Scotland	246
5.	1868 - 1871	Schulze *	Rostock, (D)	1600
6.	1872 – 1873	Reiset	Dieppe, France (Northsea) (F)	92
7.	1873	Truchot	Clermont Ferrand	60
8.	1874 –1875	Farsky *	Tabor, Böhmen, (Cz)	295
9.	1874 -1875	Hässelbarth*	Dahme (D)	347
10.	1879 - 1880	Reiset	Dieppe (F)	118
11.	1883	Spring	Lüttich	266
12.	1886 - 1887	Uffelmann	Rostock	420
13.	1889 - 1891	Petermann	Gembloux (B)	525
14.	1897 - 1898	Letts&Blake	Nähe Belfast (I)	64
15.	1898 - 1901	Brown& Escombe	Kew Garden England (GB)	92
16.	1917 -1918	A. Krogh	Kopenhagen (DK)	viele
17.	1920-1926	Lundegardh	in southern Sweden (Kattegat) (S)	>3000
18.	1928	Krogh/Rehberg	Kopenhagen	
19.	1932 -1935	Buch	Northern atlantic ocean/Finland (FIN)	176
20.	1936 - 1939	Duerst	bei Bern (Schweiz) (CH)	>1000
21.	1941 -1943	Misra	Poona, India (IND)	> 250
22.	1950	Effenberger	Hamburg (D)	>40
23.	1954	Chapman et al.	Ames (IOWA, USA)	>100
24.	1957	Steinhauser	Vienna (AUS)	>500
25.	1955-1960	Fonselius et al. Bischof	Skandinavia	>3400

[1]v. Gilm: similar process as Pettenkofer, first calibrated
very similar to Pettenkofer process, sampling by tube through opening in window

Table 3 volumetric and manometric measurements

1	1875 (März)	Tissander	Paris, Ballonfahrt (volumetrisch)	<10
2	1880 - 1882	Müntz & Aubin	Bei Paris, Pyrenäen, Karibik usw. /F) volumetrisch	81+
3	1910 - 1912	Benedict	Washington (USA), volumetrisch	>264
4	1912 -1936	Haldane	volumetrisch	1500
5	**1939-1941**	**Kreutz**	**volumetrisch**	**64 000**
6	1946	Scholander	volumetrisch	>1000

The volumetric equipment before Haldane **(84)** and Benedict/Sonden/Petterson (e.g.. 1900, **51,82,83)** used by Regnault, Müntz, Tissander were **open systems** without efficient control of reacting temperature (see Schuftan 1933 (72)) So their data are partly erroneous.
Especially Müntz was highly praised by Keeling and IPCC as a source of best available data for that time.

(Further comments and detailed analysis of methods and data see full version.)
According to Callendar, Keeling and IPCC allowed variations of atmospheric CO_2 are the diurnal, the seasonal and ice age/ interglacial fluctuations. Natural concentrations are in equilibrium, mankind disturbed this natural situation.
So let´s look at the data within 160 years air gas analysis by chemical means, at first the raw data out of 138 papers:

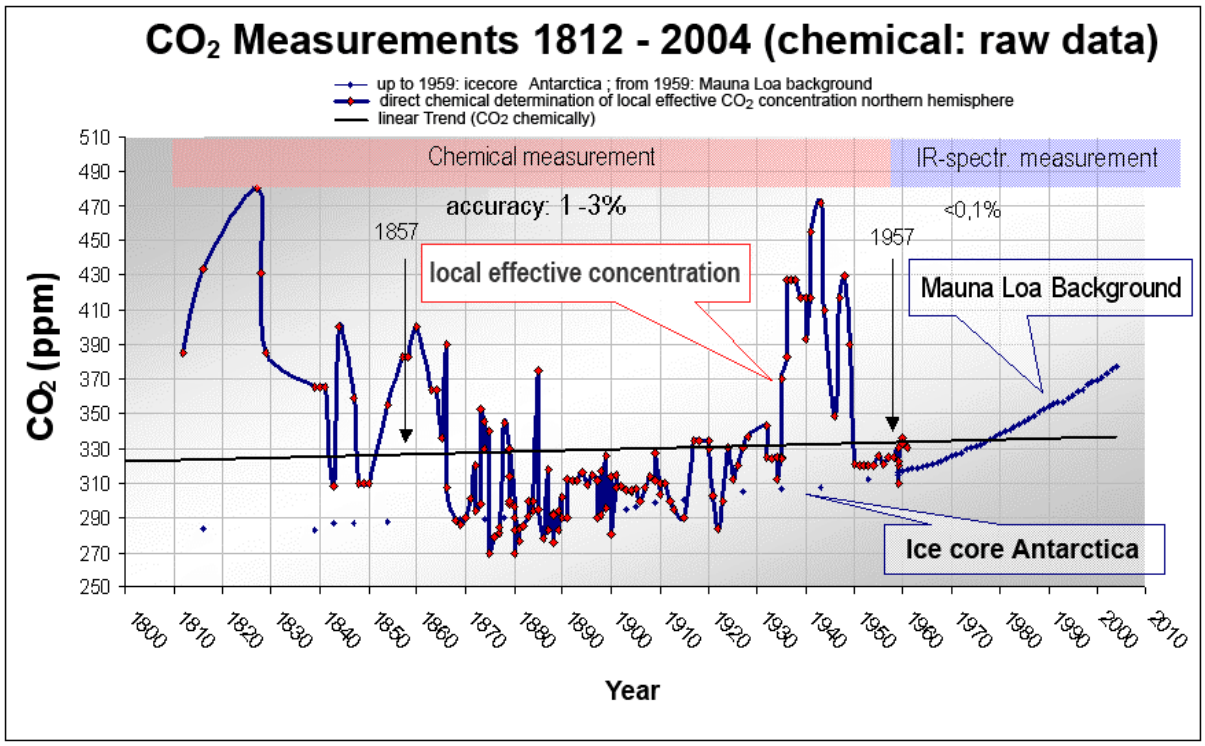

Fig. 1 138 yearly average from 1812 up to 1961 chemical determination (raw data)
And now the same data with 5 years average smoothing:

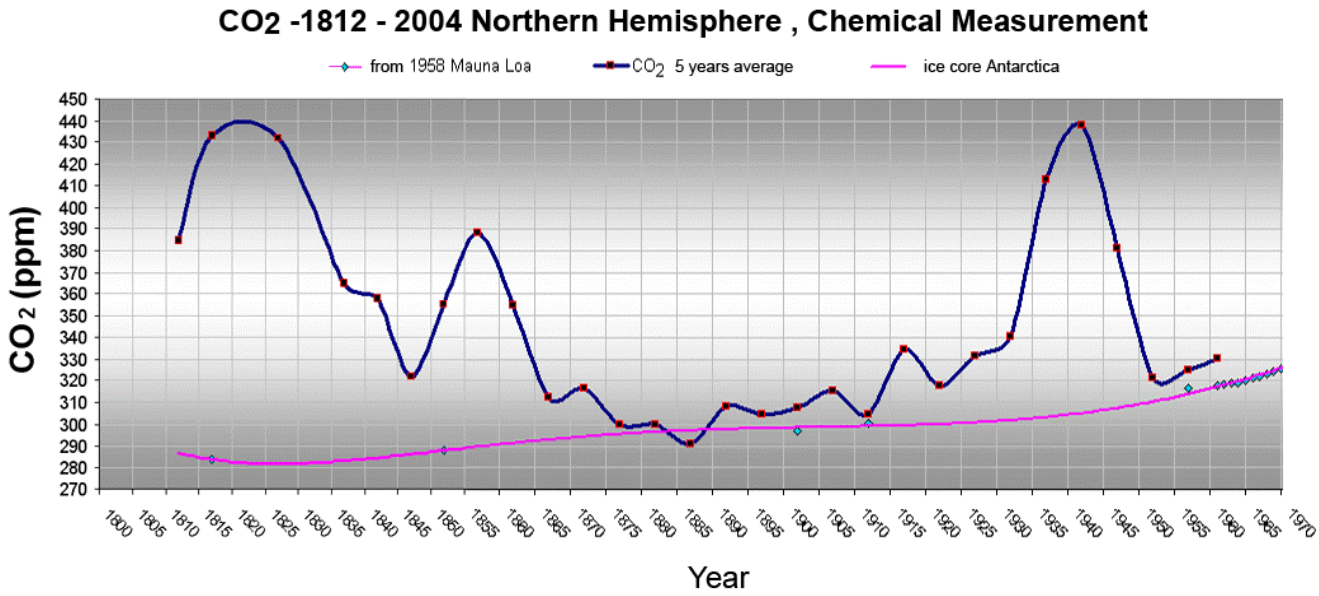

Fig. 2 138 yearly averages of local effective atmospheric CO_2 concentration from 1812 up to 1961 by chemical determination, smoothed as 5 years average (raw data); icecore reconstruction (Neftel et al. (13,14,15)) and Keeling measurements from Mauna Loa included.

It is easily seen that

1. atmospheric carbon dioxide fluctuates through 19th and 20th century contradicting the icecore reconstructions.
2. In 20th century we notice one big maximum around 1942 with more than 420 ppm and several little maxima in 1915 and 1905; in 19th century a big maximum occurred before 1870 and perhaps a big maximum in 1820 out of precise measurement area. Little maxima appeared around 1876, 1880 and 1890.
3. CO_2 concentrations rises from approx. 1880 to 1930 by some 20 ppm as Callendar speculated in 1938.
4. Big maximas with an amplitude of 100 ppm like the one in the 40s should be easily reproduced with chemical methods (3%). This is not mentioned in modern literature.

See full version for detailed analysis.

As an example for the quality of chemical measurements and real existing CO_2-maxima let´s take a closer look to the big CO_2 maximum 1942 in Fig. 3.

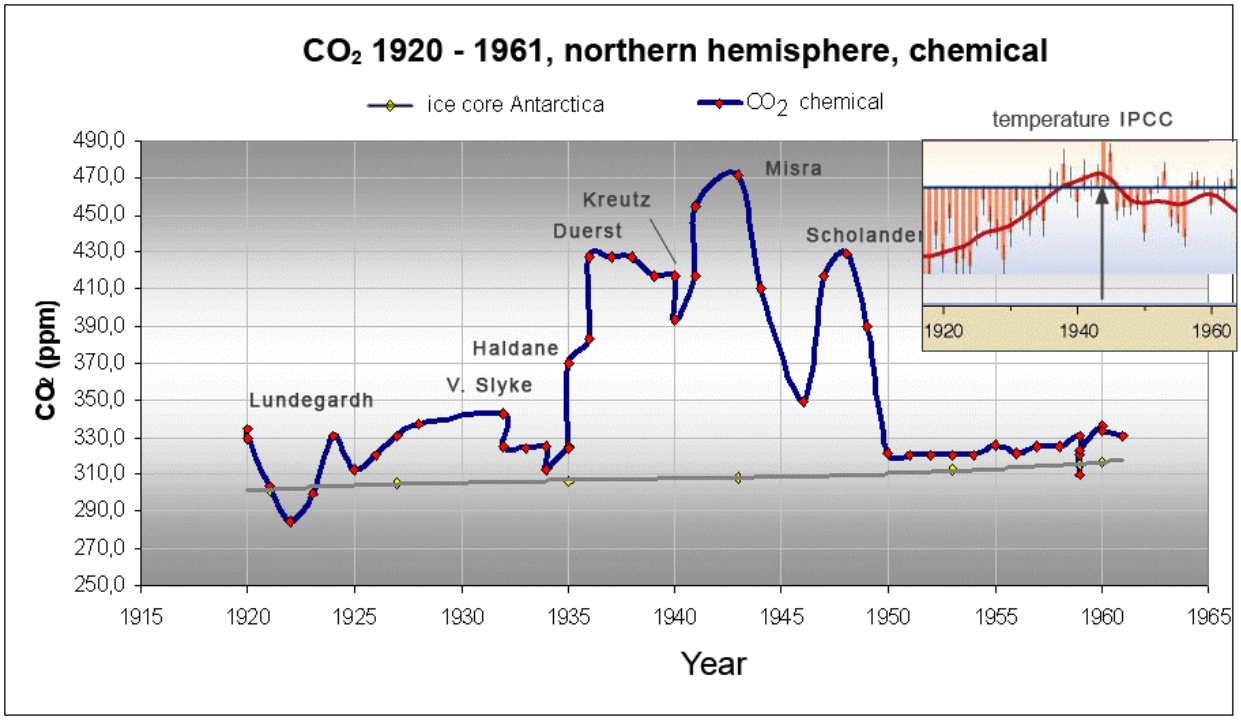

Fig. 3 The big CO2 maximum around 1942 in northrrn hemisphere detected with chemical analysis.

There are a lot of indications for this big variation:

- **High density of data** with broad geographic coverage:
- **41 series** includes approx. 70 000 single data with highest density in peak area 1939-1942,
- **Measuring stations are spread** throughout middle- and northern Europe, USA, Atlantic ocean Alaska, India and Antarctica. Continous rise since. 1925.
- **Application of different accurate standard measuring systems** with high accuracy of 2-3% designed by Krogh, Schuftan, van Slyke, Haldane, Scholander.
- **Measured by different, competent experts**: Buch, Duerst, Kreutz, Scholander, Lockhart
- Verified conditions of measuring stations, no exceptional contamination by local CO_2 sources e.g. civilisation, war, soil degassing, volcanic emissions.

The second world war cannot be responsible for high values because there is a continous rise from 1925 culminating still 1939 and second part of maximum was measured at places with no war activities. (Alaska, India)

To show quality of data and methods see results of W. Kreutz (Germany 1939 –1941):

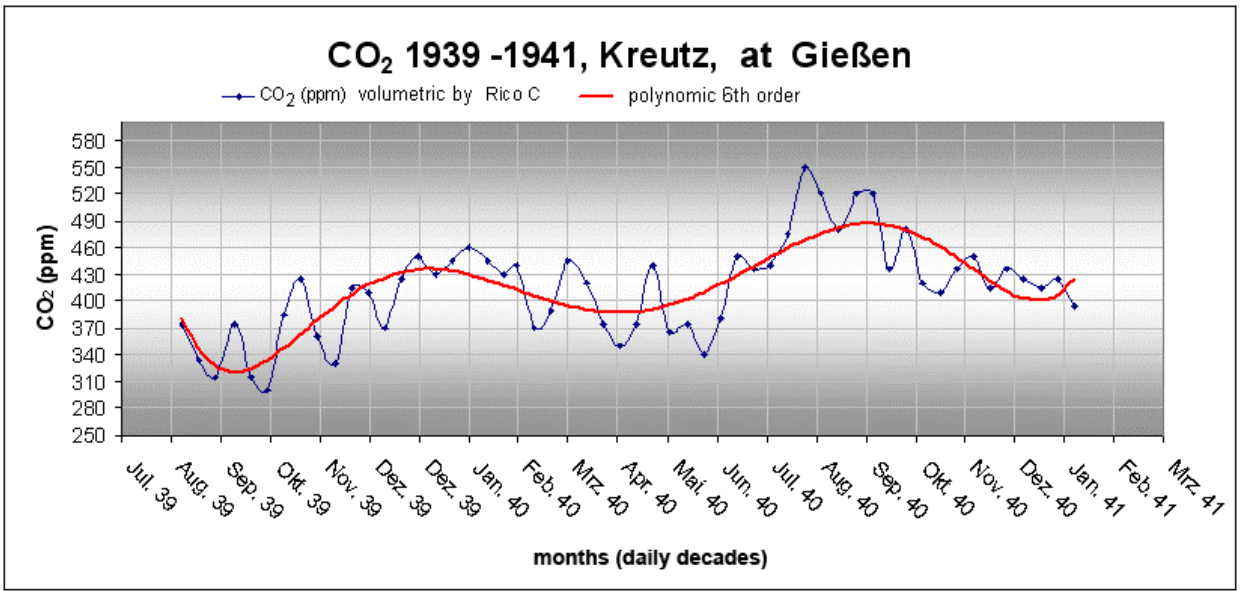

Fig. 4 CO_2 concentration at meteorological station in periphery of Gießen (Germany) 1939/40 smoothed by decade average

Climate science ignores the work of Kreutz, IPCC and Keeling have not cited him, Callendar excluded his data because it was considered out of allowed range. (119), others Slocum (128), Effenberger (54) and Bray (130) gave faulty citation of details. (see more facts in full version)

The same overall precision and accurate measurement of seasonal and diurnal variation one can see in a lot of determinations by 19th century scientist as F. Schultze (Rostock) at the Baltic sea.

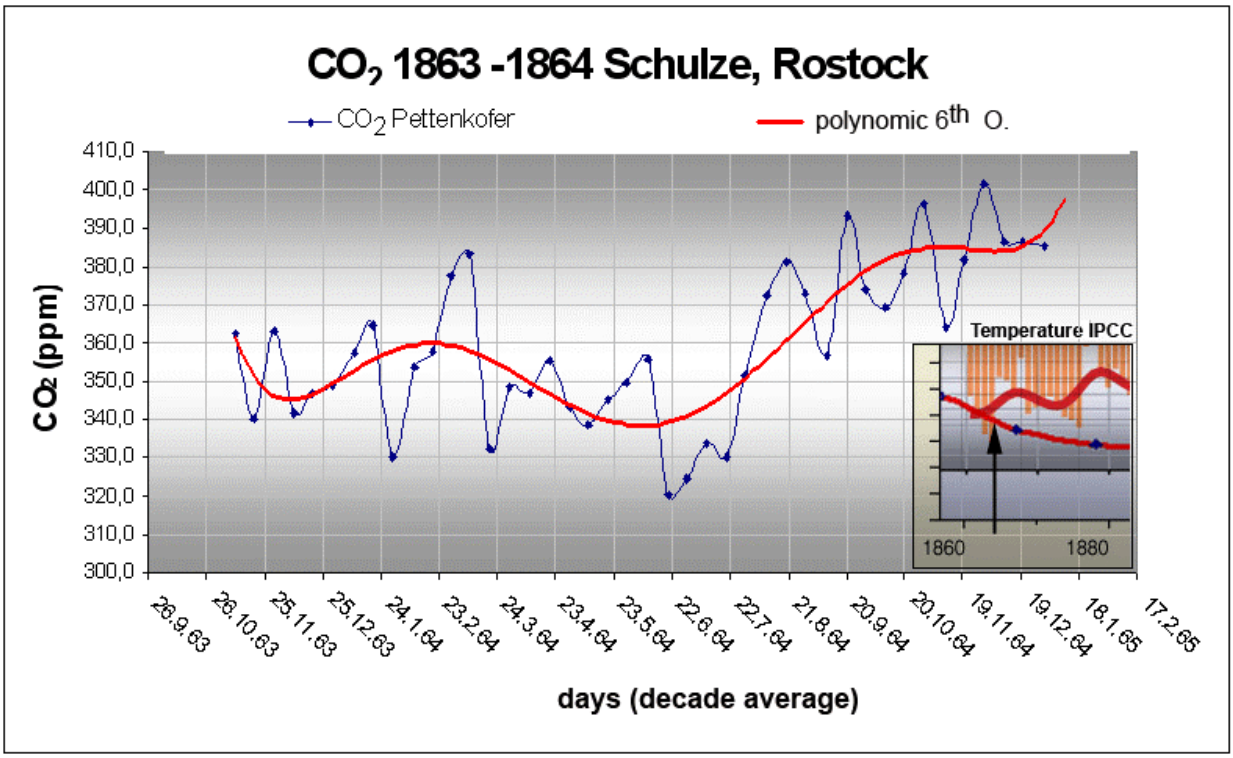

Fig. 5 CO_2 concentration at meteorological station near Rostock, Baltic sea (Germany) 1863/64 smoothed by decade average
(see much more in full version)

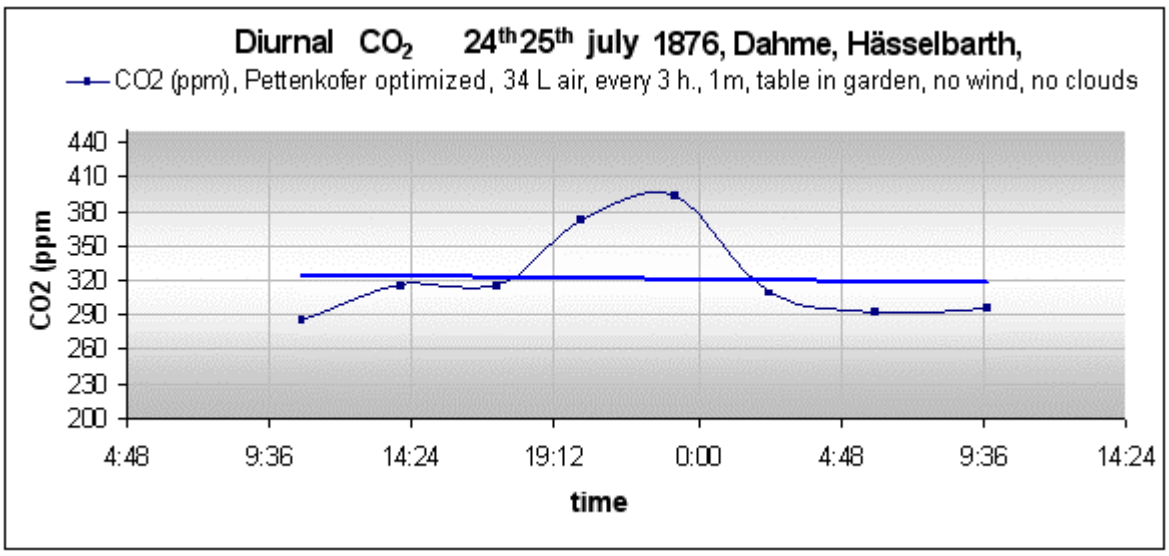

Fig. 6 Diurnal variation of CO_2 in $24^{th}/25^{th}$ of July 1876 in Dame (Prussia, Germany) by Hässelbarth

A smoothing of 138 yearly averages of CO_2 by 11 years of sunspot cycle maxima/minima leads to:

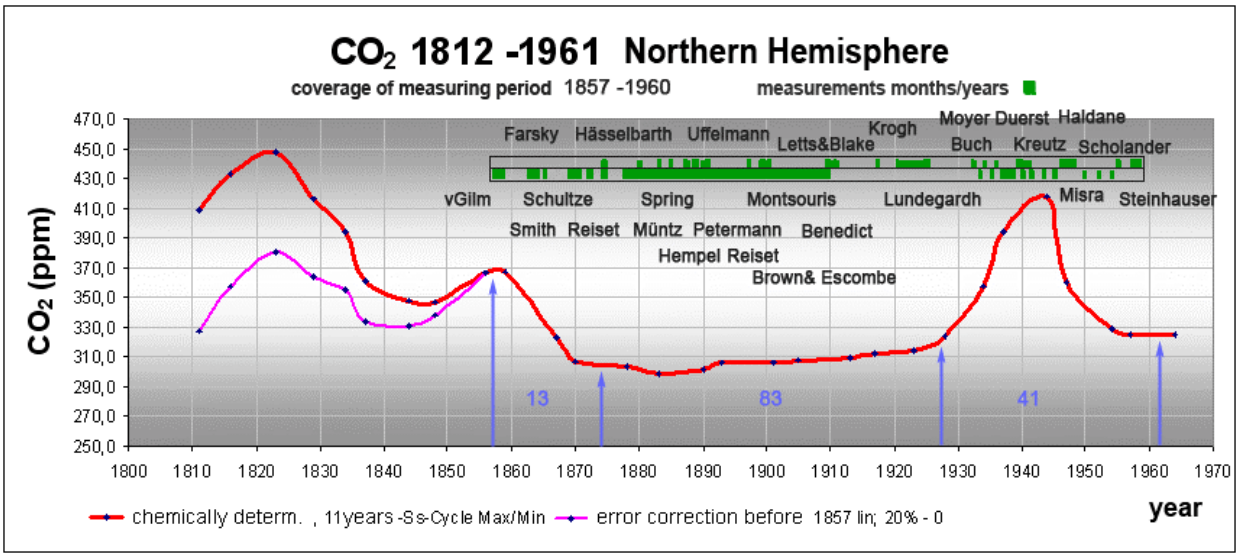

Fig. 7 Effective local CO_2 concentration chemically determined between 1812 - 1861 of northern hemisphere Nordhemisphäre (11 year averages with sunspot cycle maxima/minima) including data coverage, number of data and important scientists.

Fig. 7 shows also guessed linear error correction below accurate measuring 1857 The little maximas cannot reproduced by this smoothed curve. Result are 3 big maxima with one 1820 not exactly valuable because of missing comparative informations.
All needed details for evaluation can be found in full version.
Especially interesting is a comparison of measured atmospheric CO_2 to measured temperature.

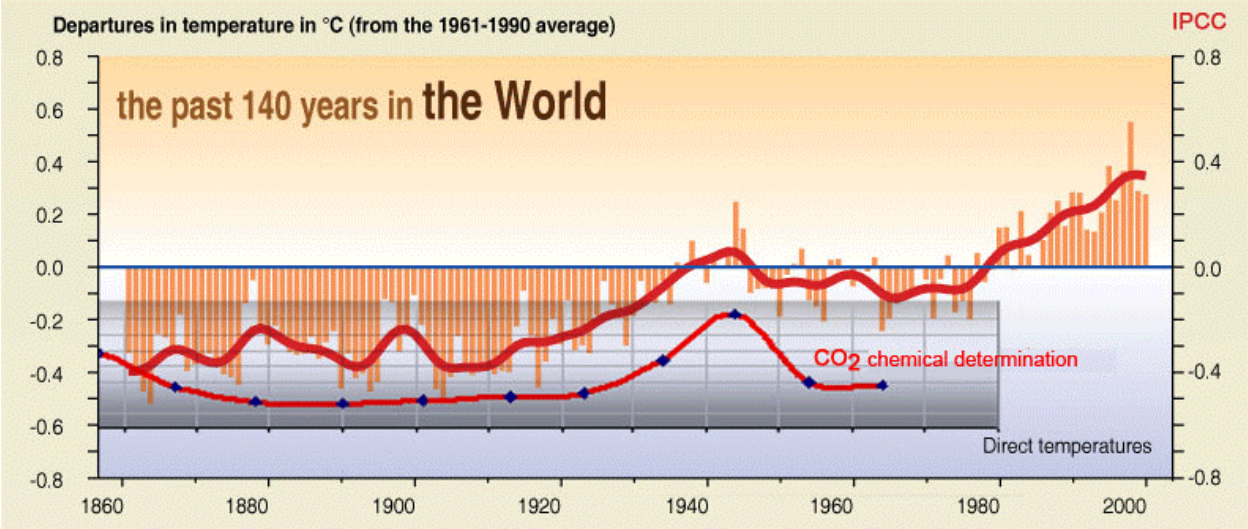

Fig. 8 Global temperature (stations, IPCC 2001) from 1860 and atmospheric CO_2 by chemical analysis The carbon dioxide maximum of 1942 perfectly fits to the measured temperatur maximum at that time. Smaller maxima cannot be seen because of 11 year smoothing.

Using the 5 year average all 8 temperature maximas within 100 years correspond accurate to CO_2-maximas. Temperature data, northern hemisphere, land from GHCN (170), Jones (171), Hansen (172).

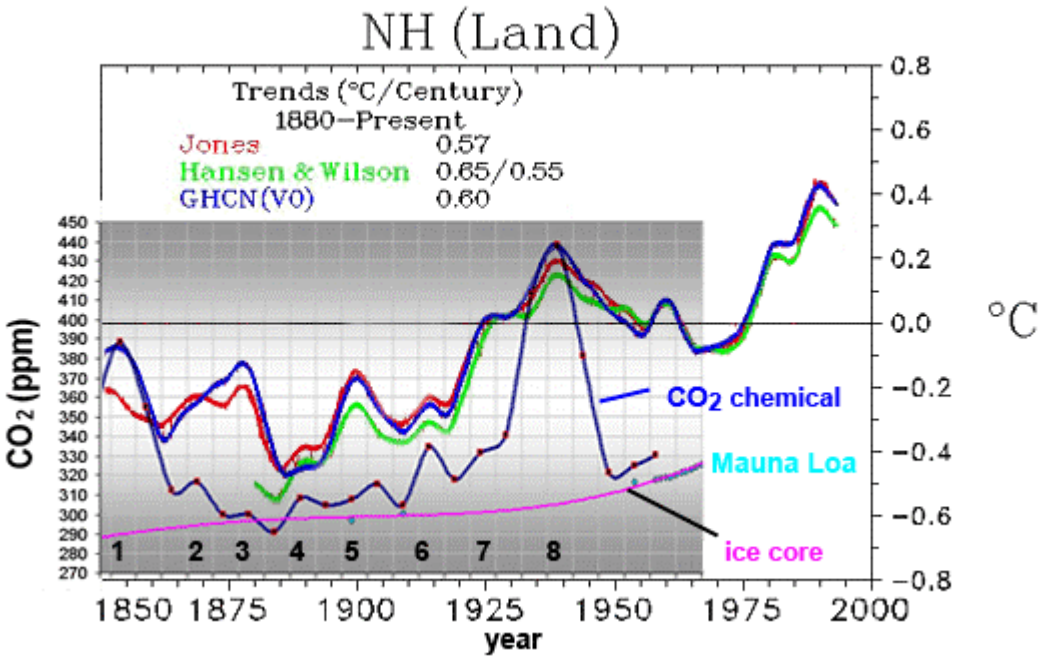

Fig. 9 Comparing measured temperature in northern hemisphere (land) from 1850 (Jones (171), Hansen (172), GHCN(170)) with CO_2 fluctuation. (5 years difference by averaging corrected) The temperature maximum around 1940 is not a result of exponential rise of CO_2. It´s the reverse, high temperature around 1940 had induced CO_2 maximum.

Summary

Accurate chemical CO_2 gas analyses of air over 180 years show a different trend compared to the literature of IPCC climate change actually published. From 1829 the concentration of carbon dioxide of air in the northern hemisphere fell down from a value of e.g. 400 ppm up to 1900 to less than 300 ppm rising till 1942 to more than 400 ppm. After that maximum it fell down to e.g. 350 ppm and rose again till today, 2006 to 380 ppm. Accurate measurements had been done amongst others by de Saussure 1826, Pettenkofer/v.Gilm 1857, Schulze 1864/71, Farsky 1874, Uffelmann 1886, Letts und Blake 1897, Krogh and Haldane 1904, Benedict 1912, Lundegardh 1920, van Slyke 1929, Dürst and Kreutz 1934 alternatively 1940, Misra 1942 or Scholander 1946 with measuring instruments through which from 1857 (Pettenkofer) an accuracy of +/-0,0006 Vol% to under +/-0,0003 Vol% =~3 ppm (Lundegardh 1926) was achieved. These pioneers of chemistry, biology, botany, medicine and physiology constituted the modern knowledge of metabolism, nutrition science, biochemistry and ecology. Modern climatology ignored their work till today even though it is the basis of all textbooks of the mentioned faculties and was honoured with several Nobel prizes. In total over 90 000 measurements within nearly every year since 180 year gave the following results:

1. There is no constant exponential rising CO_2-concentration since preindustrial times but a variing CO2-content of air following the climate. E.G. around 1940 there was a maximum of CO_2 of at least 420 ppm, before 1875 there was also a maximum.
2. Historical air analysis by chemical means **do not prove** a preindustrial CO_2-concentration of 285 ppm (IPCC),as modern climatology postulates. In contrast the average in the 19th century in northern hemisphere is 321 ppm and in the 20th century 338 ppm.
3. Todays CO_2 value of. 380 ppm, which is considered as threatening has been known several times in the last 200 years, in the 20 th century around 1942 and before 1870 in the 19th century. The maximum CO_2-concentration in the 20th century roses to over 420 pmm in 1942.
4. Accurate measurements of CO_2 air gas contents had been done from 1857 by chemical methods with a systematical error of maximal 3%. These results were ignored reconstructing the CO_2 concentration of air in modern warm period.
5. **Callendar** and **Keeling** were the most important founders of the modern greenhouse theory (IPCC) beside **Arrhenius.** Literature research confirmed that they ignored a big part of available technical papars and selected only a few values to get a validation of their hypothesis of fuel burning induced rise of CO_2 in air. Furthermore these authors discussed and reproduced the few selected historic results by chemical methods in a faulty way and propagated an unfounded view of the quality of these methods, without having dealt with its chemical basis.
6. To reconstruct the modern CO_2 concentration of air icecores from Antarctica had been used. The presented reconstructions are obviously not accurate enough to show the several variations of carbon dioxide in northern hemisphere.