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 price), Lundegardh and Warburg (nobel price).

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). Keelings laoboratory delivers the reference gases worldwide and have the calibration monopoly. .(38, 39, 40,41, 42, 43, 44, 45)

Measurements 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 the 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 thoroughly review of existing literature (175 in this study) revealed in contrast to the publisched 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 below 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 an some diurnal variation.
These pioneers of chemistry, biology, botany, medicine and physiology constituted the 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 prices.

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 others 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 und citation of papers

It could be shown that between 1800 to 1961 more than 320 technical papers exists on the subject of air gas analysis conteining 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 dioxid in the atmosphere. In using their concept of unpolluted background level theyhad 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 had been died in 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, geographicly spreading 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, Indien (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
* identical variant of 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:

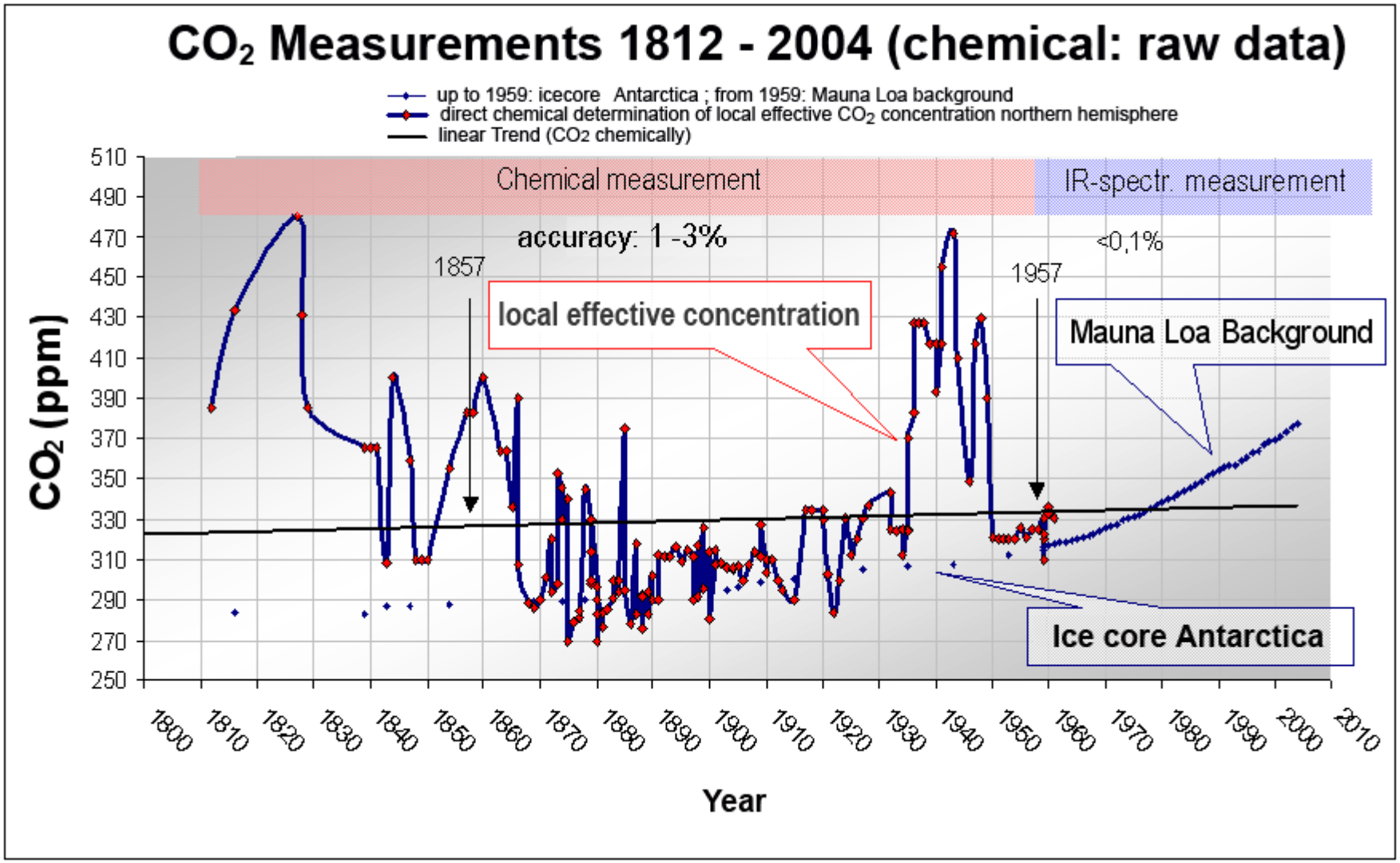

Fig. 1 138 yearly average from 1812 up to 1961 chemical determination (raw data)

And now the same data with 5 years average smoothing:

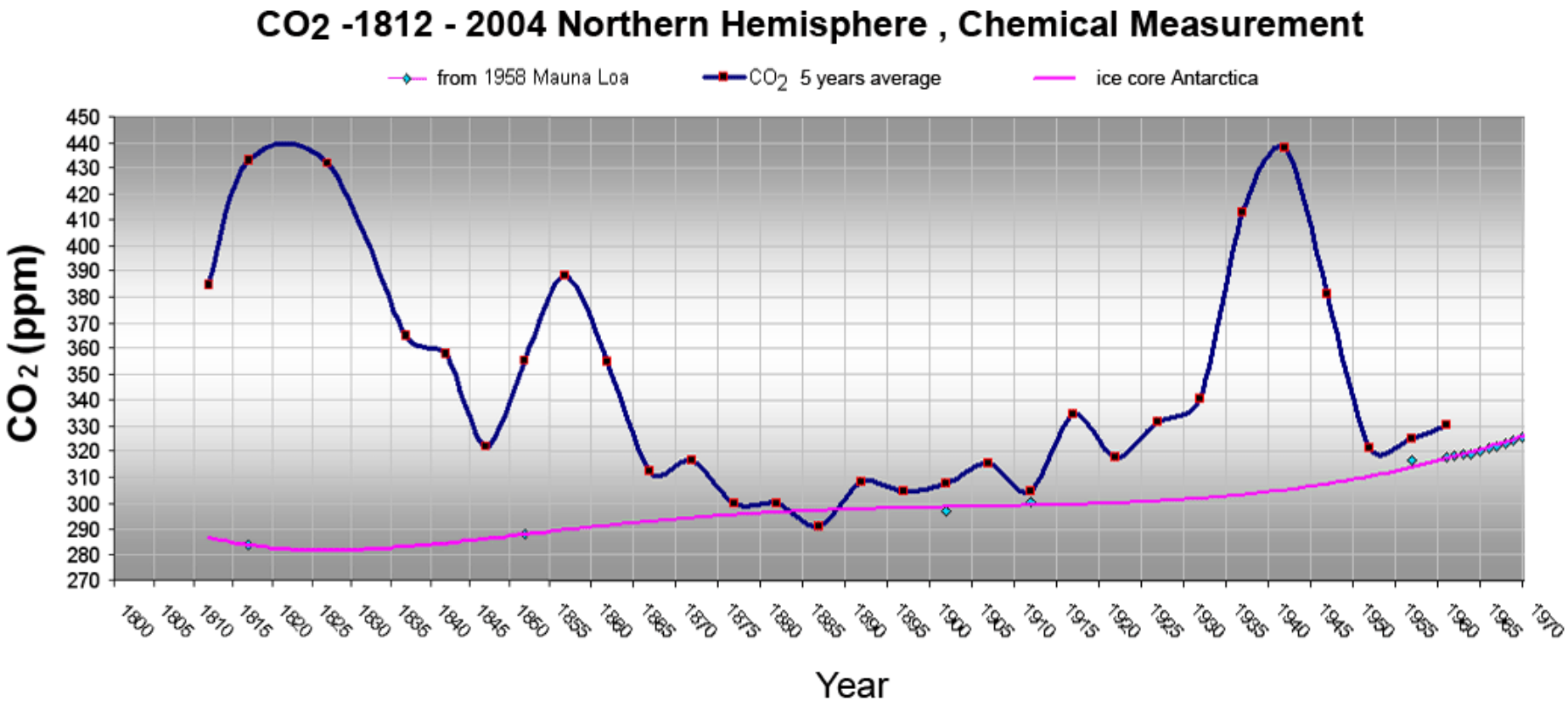

Fig. 2 138 yearly averages of local effective atmospheric CO_2 concentration from 1812 up to 1961 by chemical determination, smoothed as 5 years average (raw data); icecore reconstruction (Neftel et al. (13,14,15)) and Keeling measurements in Mauna Loa from included.

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 Calledar 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%). It do not exist in modern literature.

See full version of 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.

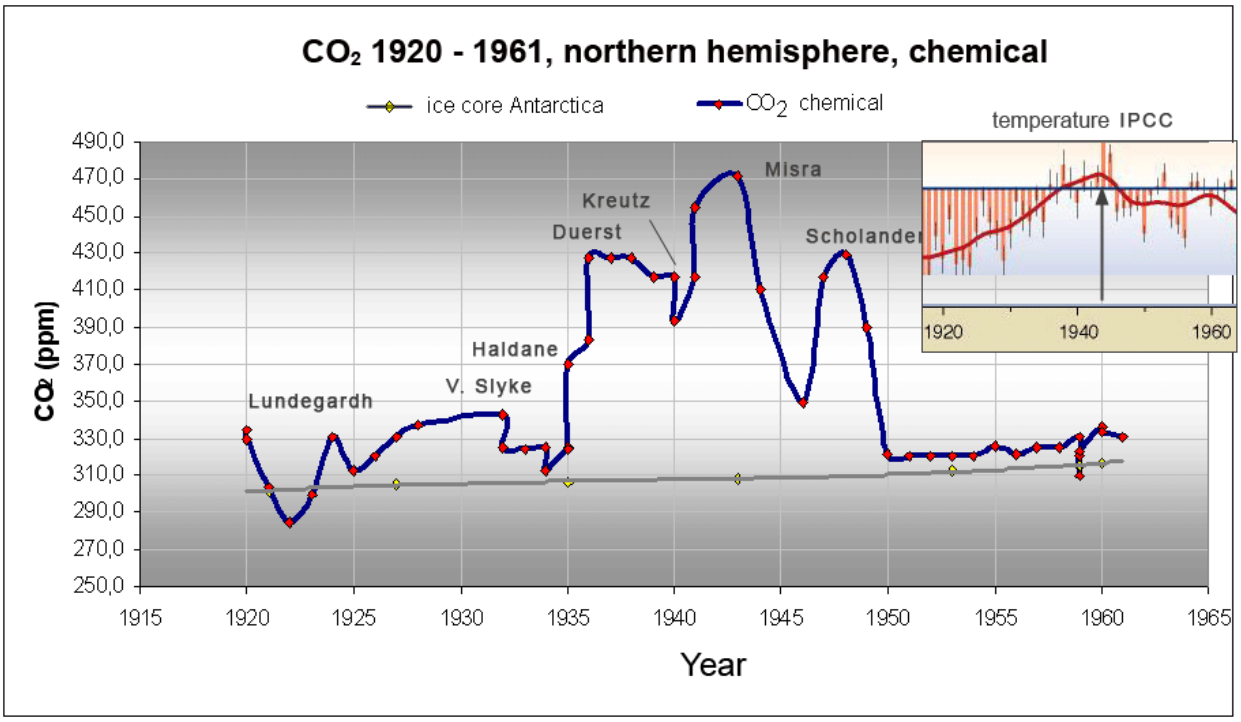

Fig. 3 The big CO2 maximum around 1942 in northrrn hemisphere detected with chemical analysis.

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):

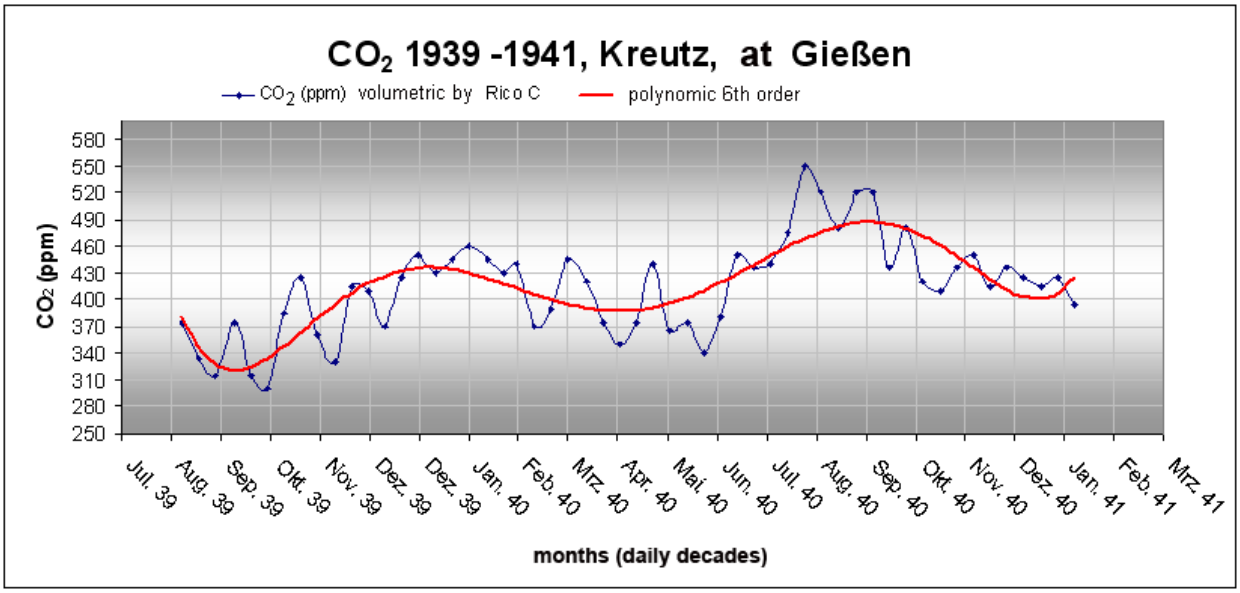

Fig. 4 CO_2 concentration at meteorological station in periphery of Gießen (Germany) 1939/40 smoothed by decade average

Climate science ignore the work of Kreutz, IPCC and Keeling have not cited him, Callendar excluded his data because of 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 adn 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.

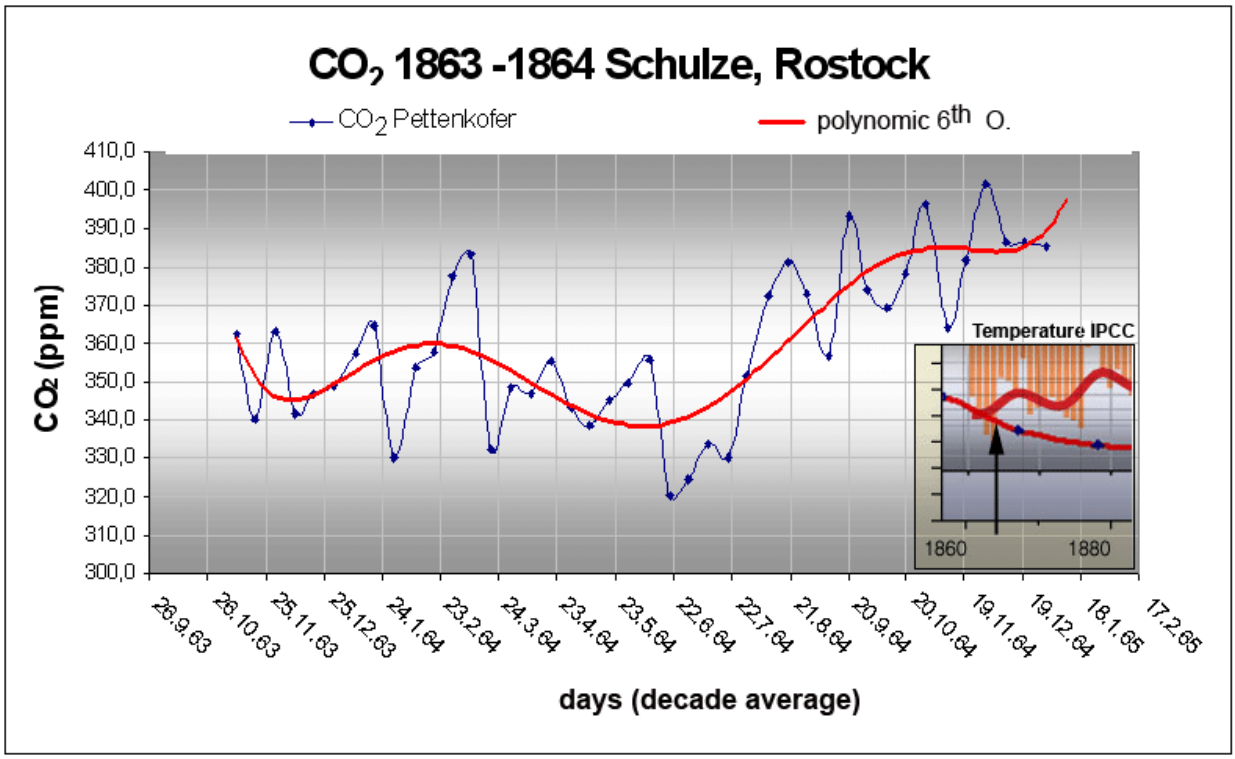

Fig. 5 CO_2 concentration at meteorological station near Rostock, Baltic sea (Germany) 1863/64 smoothed by decade average

(see much more in full version)

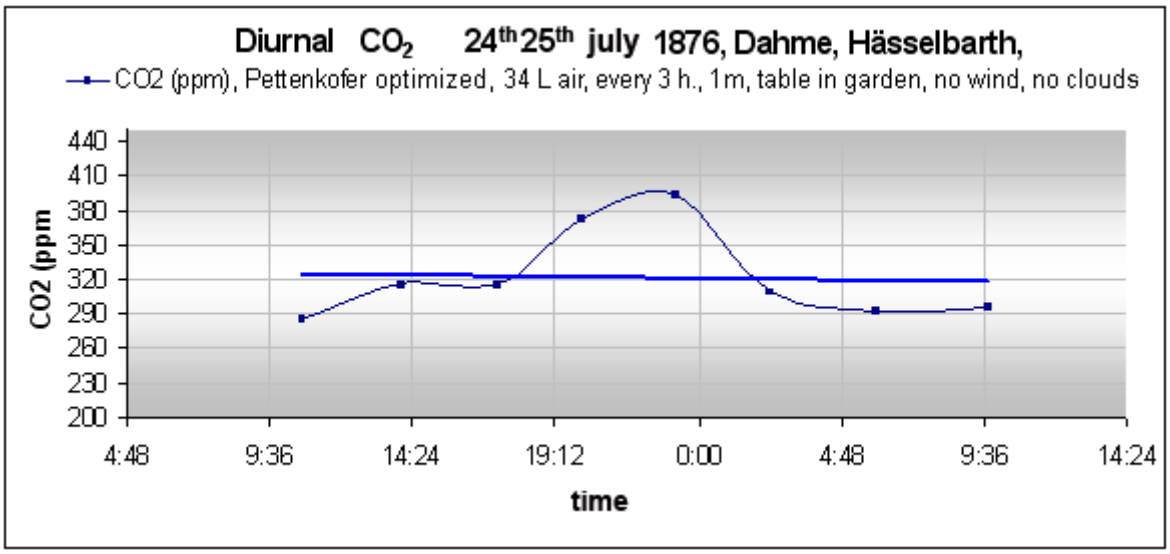

Fig. 6 Diurnal variation of CO_2 in 24th/25th of july 1876 in Dame (Prussia, Germany) by Hässelbarth

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

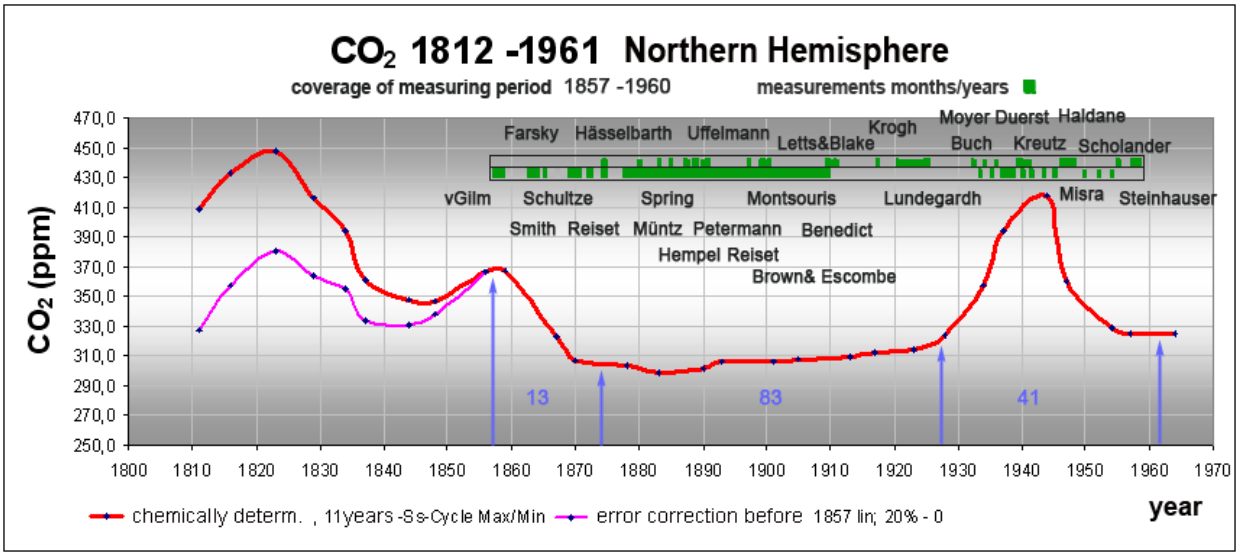

Fig. 7 Effektive local CO_2 concentration chemically determined between 1812 - 1861 of northern hemisphere Nordhemisphäre (11 year averages with sunspot cycle maxima/minima) including data coverage, number of data and important scientists.

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.

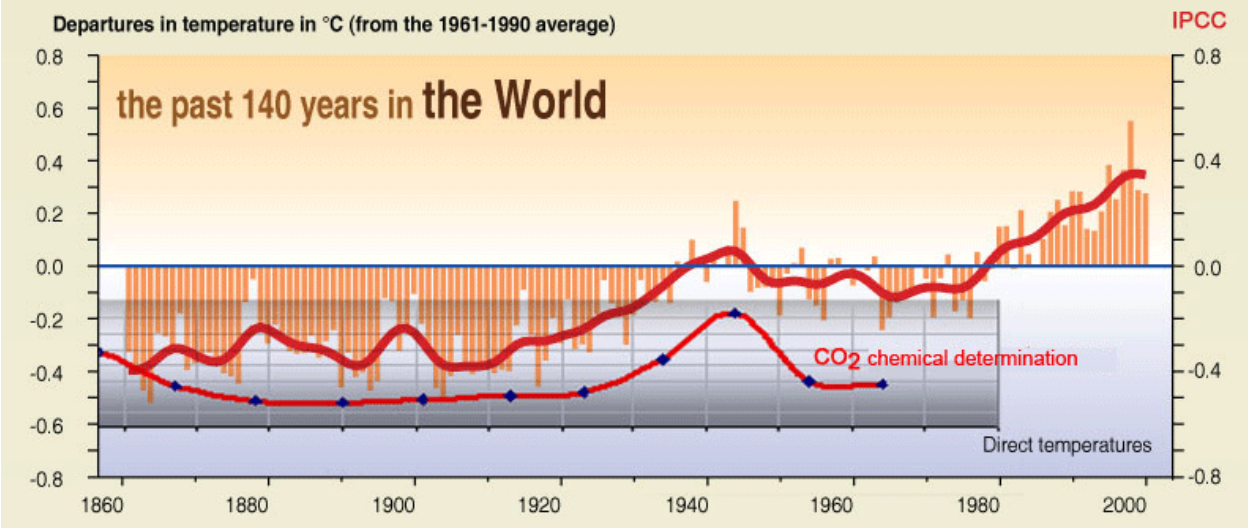

Fig. 8 Global temperature (stations, IPCC 2001) from 1860 and atmospheric CO_2 by chemical analysis

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).

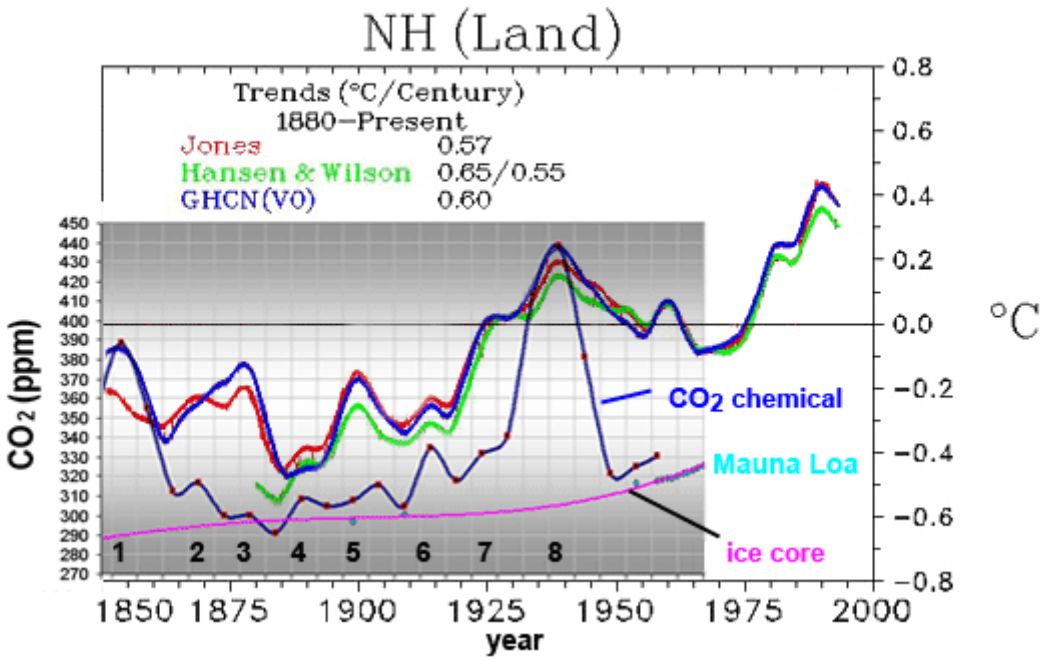

Fig. 9 Comparing measured temperature in northern hemisphere (land) from 1850 (Jones (171), Hansen (172), GHCN(170)) with CO_2 fluctuation. (5 years difference by averaging corrected)

So the there is no problem to explain temperature maximum around 1940 because 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 since 180 years show a different trend compared to the literature of 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 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 prices. 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 proove** 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 threatingly had been appeared 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. Furtheron these authors discussed and reproduced the few selected historic results by chemical methods in a faulty way and propagated an unfounded view on quality of these methods, without having dealed 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.

Content of full version,

(106 pages, 78 pictures, 8 tables

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Table 4: CO_2- air gas analysis 1800 - 2004

year	Siple ice core	chemically	CO_2 corrected from 1857	Number measurements	**authors, methods, stations, sources, notes**
	CO_2 (ppm)	CO_2 (ppm	CO_2 ppm)		
1800					0,05 Fourcroy/Humboldt nicht vewendet; (zitiert in 50, 51,52)
1802					Dalton, 0,0683 nicht verwendet (50,56)
1812		385,0		1	Thenard, bei Paris (48N 2E); Methode: Barytwasser, gravimetrisch, Werte zu niedrig, da zu kurze Einwirkzeit; in Barytwasser (5-6 Minuten); mehrere Std. Analyse für eine Probe
1816	283,8	433,0			Interpolation da kein Messwert vorhanden
1827		481,0		69	de Saussure bei Genf (46N 6E); Methode: Barytwasser, gravimetrisch, neu geordnete Werte: Mittag, gleicher Ort und Bedingungen, gravimetrisch"
1828		431,0			
1829		385,0			
1839	283,1	365,0		161	Boussingault Paris (48N 2E), Umland, Elsaß Methode nach Brunner, KOH, gravimetrisch
1840		365,0			
1841		365,0			
1843	287,4	308,6			Boussingault Paris, Andilly; Methode Brunner, KOH, gravimetrisch
1844		400,0			Boussingault Aus Effenberger, Annalen der Meteorologie 1950
1847	286,8	359,0		15	Lewy, Le Harvre (49N 0E); zitiert in Lundegardh 1924, P. 7
1848		310,0		150	Marchand, Halle (51N 11E) Prof. f. Chemie, 150 Messungen**
1849		310,0			
1850		310,0			
1854	288,2	355,0			Interpolation da kein Messwert vorhanden
1857		416,0	**383,0**	19	v. Gilm Innsbruck (47N 11E) 1857/58 Nov.-März; Pettenkofer Dez. 1857 München: 442 ppm; Mittelwert samt Sommer Korrektur 1858 = 383 ppm
1858		416,0			
1860		400,0			Boussingault Anderson,Thomas Elements of agricultural chemistry, 1860, P. 38
1863		364,0		1600	Fr. Schultze; Landwirtschaft. Versuchsstationen, Bd. 9, 1867, P.217, Bd. 10, 1868, P.515, Bd. 12, 1870, P.1; Bd. 14 1871, P. 366; Ort Rostock (54N12E) Balkon Museum Westseite 1465 Messungen; Pettenkofer: Keine Korrektur: mögliche Kontaminierung (+10%) kompensiert durch Meeresnähe
1864		364,0			
1865		336,0	**360**,0	246	Smith, Agnus Scotland; Land, Perth (56N 3E) zit. Benedict; Bunsen-Eudiometer

1866		390,0			Gorup, Erlangen mit Pettenkofer Methode; http://gorup.heim.at/Briefe/18660211-Pettenkof.htm München (48N 11E)
1866		308,0		77	Thorpe, irische See (ca. 53N 5E), in Liebigs Ann. Chemie, Bd, 145, 1868, P. 94, zit. Letts& Blake
1868		289,0			Fr. Schultze siehe oben
1869	289,3	286,0	**303**		Fr. Schultze siehe oben, verbesserte Methode; Korrektur Meer: Min+20ppm
1870		290,0	**312**		
1871		301,0	**321**		
1872		320,0		17	Henneberg in Weende (51N 9E, Göttingen) Letts& Blake
1872		294,0		92	Reiset, J, 92 Analysen, Pettenkofer modifiziert, außerhalb Dieppe (49N 1E),
1873		298,0			
1873		353,0		49	Truchot in Clermont Ferrand (45N 3E)
1874	289,5	346,0		295	Farsky,F, aus Effenberger, 1950, Tabor (49N 14E), Böhmen 295 Messungen, 1 Jahr, 1874-1875
1874		330,0		374	Hässelbarth P. versuchsstation Dahme (51N 13E), 1874/75, 347 Messungen,
1875		340,0			
1875		270,0		10	Tissandier,1875 Ballonfahrt 800-900m 0,024 23./24. März; 1000m in Paris (48° 52'N, 2° 20'E) 0,03, KOH, manometrisch; Temp. und Druck-korrigiert zitiert in La Nature 1875,http://cnum.cnam.fr/CGI/fpage.cgi?4KY28.4/337/100/433/0008/0421
1876		279,0		31	P. Claesson, Berliner chem. Berichte, 1876, P. 174, 31 Bestimmungen in Lund (55N 13E)
1877		281,8		35	Fodor, Budapest (47 N 15E), 35 Messungen Stadt 0,0418
1877		284,5		12000	Montsouris, Paris Observatory 1877-1910; Pettenkofer; Levy, Marie-Davy; nach G. Stanhill, climatic Change 4 (1982) 221-237)
1878	290,3	345,0			
1879		328,8			
1879		314,0			Macagno Observatorium Palermo (38N 13E) 20 Bestimmungen 1879, Februar - August; Quelle: Chemical News, 1880, 41, p. 97; nicht verwendet
1879		298,0			Reiset, J, siehe oben; Compt. Rend, T, p. 1007, T. 90, p1144, 1457 (1879-1880) zitiert in Lundegardh
1879		300,0		53	Armstrong, Grasmere (54N 3E), England, 53 Messungen, 0,03
1879		330,0			Legendre, Westküste Frankreich, aus Effenberger 1950
1880		297,0		89	Reiset, J, siehe oben; Compt. Rend, T, p. 1007, T. 90, p1144, 1457 (1879-1880) Ort Dieppe
1880		283,4			Nansen, Grönland: 0,031; Gerät Pettersson 1882
1880		269,8			Montsouris, siehe oben
1880		290,0		64	Müntz, Landstat. Vincennes, 64 Messungen
1881		276,8			Montsouris, siehe oben

1881		284,0		17	Müntz, Aubin , Pic de Midi, Pyrenäen (44N 1E), 2877m hoch bei Wind, 17 Messungen; Methode, KOH, volumetrisch; La Nature 1882, P. 595
1882		285,7			Montsouris, Paris
1883		291,3			
1883		300,0		266	Spring, Roland, Lüttich (50N 5E), 1883/1884 266 Messungen, aus Effenberger; Pettenkofer-Variante
1884		294,1			Montsouris
1884		300,0			Spring, Lüttich siehe oben
1885		375,0		79	Hempel Dresden (51N 13E)
1885		294,7			Montsouris
1886		278,3			
1887		318,0		420	Uffelmann Rostock, vor der Stadt (in Stadt 351ppm Jahresmittel)
1887	292,3	283,5			Montsouris
1888		293,0			Selander, N.E., Luftundersökningar vid Vaxhims fästning, Bih. Kgl. Svenska Vet. Handlingar, Bd. 13, 1888, Afd. II, No. 9; Pettenkofer Methode; Ort Stockholmer Scheren (59N 18E), Messserie, Zitiert in Lundegard, 1924
1888		275,8			Montsouris
1888		291,7			J. Reiset, Comt Rend. Paris, 1888, p.1007, Normalstation außerhalb Dieppe; Pettenkofer; Mittelwert Messserie
1889		282,9			Montsouris
1889		294,0		564	Petermann, A. in Gembloux (50N 4E), 1889-1891, 564 Messungen
1890		302,1			Montsouris
1890		290,0			Petermann siehe oben
1891		290,0			
1891		312,1			Montsouris
1892		311,4			
1893		311,9			
1894		316,7			
1895		309,1			
1896		314,7			
1897		311,5			
1897		290,0	**327,0**	64	Letts and Blake nähe Belfast (54N 5E), Boden, 46 Messungen (März-Juli 1897) , Mod. Pettenkofer, Barytwasser titriert mit HCl, Phenolphthalein; Genauigkeit getestet: -+-1ppm oder 0,0003vol%
1898		317,3			Montsouris
1898		292,0		90	Brown& Escombe 1898-1901 Kew Garden London (51N 0E) GB Pettenkofer, 3 Jahre (145, 146)
1899		325,9			Montsouris

1899	295,8	296,0			Brown& Escombe 1898-1901 Kew Garden GB Pettenkofer
1900		313,8			Montsouris
1900		280,8			Brown&Escombe (145, 146)
1901		315,0			Montsouris
1901		308,0			Brown&Escombe
1902		308,5			Montsouris
1903	294,8	306,0			
1904		305,2		50	Montsouris 1904 0,025 Vol% Krogh, Haldane Apparat: 50 Analysen West-Grönland: 0,025-0,07%; ignoriert
1904		306,1			Interpolation da kein Messwert vorhanden
1905	296,9	307,0			Montsouris
1906		300,1			Montsouris 1908 0,0256 Vol% Müntz und Laine, Kap Horn; Franz. 1908 Antarktis Expedition; ignoriert
1907		307,8			Montsouris 1908 0,02 Vol% 2. Charcot Expedition Antarktis 1908-1910 ignoriert
1908		313,8			Montsouris 1910 Müntz und Laine, Kap Horn; Franz. Antarktis Expedition
1909		311,6			Montsouris
1909	299,2	327,5		645	Benedict, F.G., Nähe Boston (42N 71W), 645 Messungen; korrigiert laut Composition of Atmosphere
1910		303,8			Montsouris
1910		310,0			Benedict, F.G., Nähe Boston, 645 Messungen, aus Effenberger 1950
1911		310,0			
1912		300,0			
1913		295,0			
1915	300,5	290,0	**314,7**		
1917		334,5		40	A. Krogh, 1920, Kopenhagen (55N 12E); A Gas Analysis Apparatus Accurate to 0·001% mainly designed for Respiratory Exchange Work; August Krogh; Biochem J. 1920 July; 14(3-4): 267–281. Genauigkeit: 0,001%, viele Messungen in der Stadt Kopenhagen, 20 cm vom Laborfenster, 1917-1918; B. Keine Korrektur da Meeresnähe durch Stadt kompensiert wird
1918		334,5			

1920		334,5			A. Krogh, 1920, Kopenhagen; A Gas Analysis Apparatus Accurate to 0·001% mainly designed for Respiratory Exchange Work; August Krogh; Biochem J. 1920 July; 14(3-4): 267–281. Genauigkeit: 0,001%, viele Messungen; Erhöhung in der Stadt: 0,001-0,007 laut Krogh:http://docp.lib.noaa.gov/rescue/mwr/048/mwr-048-10-0599c.pdf
1920		329,5	**334**	3000	Lundegardh, 1920-26 in Hallands Väderö (56N 12E; Insel Kattegat) 3-4 Sommermonate; Freiland, Methode: modifizierte Pettenkofermethode mit +-+-1% Pro Wert also 0,0003%; Korrektur wegen fehlendem Winter und Meer: Winter: Min +40 ppm; Meer: min +20ppm=+20 ppm
1921	301,6	303,1	**310,1**		siehe oben
1922		284,3	**303,0**		siehe oben
1923		300,0	**307,0**		siehe oben
1924		331,0	**336,0**		siehe oben
1925		312,5	**319,5**		siehe oben 0,0327 Wattenberg 20N-20S 291 Beobachtungen Meteor Atlantik 1925-27 Zitiert in Callendar
1926		320,0	**326,0**		siehe oben
1927	305,5	338,5			Interpolation da kein Messwert vorhanden
1928		337,0			0,027 Vol% Müller, Süd-Westgrönland, Titration: 0,024-0,03

1932		343,0			Van Slyke et al. 95 (2): 531. (Jan. 1932) Messungen 1931, New York (40N 74W) ; MANOMETRIC ANALYSIS OF GAS MIXTURES II. CARBON DIOXIDE BY THE ISOLATION METHOD; http://www.jbc.org/cgi/reprint/95/2/531; Genauigkeit innerhalb 0,0003 Vol%; 2 Messbeispiele von vielen; CO2 in NaOH, Manometrisch
1932		325,0		28	Buch, K. Nordatlantik (ca. 75N 16E), 28 Messungen: Bestimmung mit Apparat v. Krogh/Rehberg
1934		325,0		95	Buch, K. Petsamo Finnland (63 N 27E) 95 Messungen
1934		312,5	**328,1**	28	Waugh, Cornell Ithaca (42N 76E), Test eines verb. Haldane Apparates; 20 m über Boden : Genauigkeit +-1%; Mittel April - Oktober 28 Messungen: 0,552754mg/L
1935		325,0	**345,0**		Buch, K. Petsamo Finnland 95 Messungen aus Effenberger 1950; Apparat Krogh/Rehberg; Korrektur: Meer +min+20 ppm, Winter: min+40
1935		324,0	**364,**0		Buch Schifffahrt Atlantik Kopenhagen-Bosten und zurück (Juni-September 1935; 35N-59N) 317ppm (Mittel) Korrektur: Meer +min+20 ppm, Winter: min+40

1935	306,6	370,0	370,0	153	Haldane, Perthshire, Schottland, 153 Messungen (Land, 1,2m-22m Höhe über Boden), 54. Breitengrad ; (Juli- Dezember) August 1935 0,0324 (Tag) Nacht 0,0386; August/September Ayrshire Küste: 0,037 Effenberger und Haldane , Nature 4. April 1936 ohne Korrektur da Max + Min gemessen
1936		427,0	427,0	1000	Dürst Bern (46N 7E), Pettenkofer- Variante über 3 Jahre jede Woche mind. 1 Messung (>1000) Messzeit/Probe: 1,5 Min
1936					
1937					
1938					
1939		417,0	417,0	65000	W. Kreutz, Gießen (50N 8E), 25 000 Messungenn, Pettenkofer Variante, Kalilauge,manometrisch, Analyse in temperaturkonstantem Raum
1940		417,0	417,0		W. Kreutz, Gießen, 2m Messhöhe Mittelwert 0,0434
1940		393,0	393,0		Bazett; Viele Messungen 1940 , Genauigkeit +-0,005%; >12 Messungen, OH, Manometrisch, Philadelphia; A MODIFIED HALDANE GAS ANALYZER FOR ANALYSIS OF MIXTURES WITH ONE HUNDRED PER CENT ABSORBABLE GAS BY H. C. BAZETT; Jan. 1941; http://www.jbc.org/cgi/reprint/139/1/81 Keine Korrektur möglich
1941		417,0	417,0		W.Kreutz, Gießen
1941		454,7	454,0		0,054 Antarktis 1942; OXYGEN DEFICIENCY IN ANTARCTIC AIR By ERNESTE . LOCKHART AND ARNOLD COURT [U. 8. Antarktic Service, 193949411; Ross Ice shelf; Palmer Peninsula; Messungen: Sommer 1940, Dez-Jan. 1941; Fehler des Haldane-Messgerätes innerhalb 0,03%; KOH manometrisch mit Temp-korrektur. Winter 1940 (Juli-Sept): 12 Messungen: 0,054, Sommer 1940/41(Dez-Jan): 0,0704 (Mittelwert Sommer/Winter=0,064) Daten grafisch nicht verwendet
1943	307,9	471,0	467,0	600	Misra, Indien , Poona (18N 73E), 1,8 m über dem Boden , Ackerland, Pettenkofer-Methode Barytwasser, Oxalsäure, Phenolphthalein
1944		410,0	410,0		Glückauf, England Kew garden/Imperial College Tower London, GLÜCKAUF, E. 1944. Carbon dioxide content of atmospheric air. Nature 153: 620-621. Methode Gefrierkondensation trockene Luft Mittelwert 0,0345; nicht verwendet da keine chemische Vergleichsmessung
1946		349,0	349,0	25	25 Messungen (1946, vor September, Harvard (42N 71W), Massachusetts ; Scholander, J. Biol. Chem. 167 (1): 235. 1946 http://www.jbc.org/cgi/reprint/167/1/235; Genauigkeit: 0,015Vol%, Volumetrisch, KOH; Korrektur : min-5%+30+Min/2; nicht korrigiert
1947		417,0	417,0	350	350 Messungen in Barrow, Alaska (71N 176 W), 1947-1949;Messgerät: Scholander (fand selbst 1948: 0,033; Composition on groundlevel Atmosphere at Point Barrow, Alaska; Hock, Scholander et.al. 1952, Journal of Meteorolgy, Vol. 9, P. 441,442; Genauigkeit: +-0,015%
1948		429,0	429,0		siehe oben

1949		390,0	390,0		siehe oben
1950		321,0	**321,0**	450	Selm; Ohio Nähe Columbus (40N 82W) Rand Birkenwald 12m Höhe inkl. Saison Korrektur (164)
1951		320,5	320,5		
1952		320,5	**320,5**	1500	Kornfeld in Ames bei Iowa State College Televsion Tower (42N 93W), Juli - 18. Oktober (Sommer), mind. 1500 Messungen, Absorption in KOH, Ausfällung als BaCl2 und Titration mit HCl. Winterkorrektur Min+30; keine Korrektur
1953	312,7	320,5	320,5		
1954		320,0	**320,0**	1400	0,031 Mittelwert Juni/Juli-18.Oktober 1954 über Kornfeld in Iowa (41N 93E; USA); Chapman et al, gewichtet
1955		326,0	326,0	1000	Mittelwerte Skandinavisches Meßnetz (19 Stationen, Methode Pettenkofer mod. Krogh, Bischof 1960 Tellus XII, 1960, 2 P. 216
1956		321,0	321,0		
1957		325,0	325,0	549	Steinhauser, Wien (48N 16E), Hohe Warte, Pettenkofer
1958		325,0	325,0		
1959		331,0	331,0		
1959	315,0	320,0			Mauna Loa IR Gas Analyser, Keeling
1959		310,0	310,0		Hagemann Stratosphäre
1959	316,0	323,0			Keeling IR_spektrometrisch
1960		336,0	336,0		Bischof, Skandinavien, Mittelwert , mod. Pettenkofer
1960	316,9	333,0			Keeling IR_spektrometrisch
1961		330,5	330,5		Steinberg; Mittelwert Stratosphäre in 21,9 Km Höhe San Angelo Texas; J. of. Meteorology, Vol. 1, P 418, 1961
1961	317,7				Mauna Loa Keeling; ab hier IR-Spektrometrische Messung

1962	318,45			**92860**	**Sum measurements at more than 52 stations**
1963	318,99			**137**	**Total average on 150 years**

1964	319,23				Keeling IR_spektrometric
1965	320,03				
1966	321,37				
1967	322,18				
1968	323,05				
1969	324,62				
1970	325,68				
1971	326,32				

1972	327,46				
1973	329,68				
1974	330,25				
1975	331,15				
1976	332,15				Error until 1976: > 4ppm (Stanhill Climate change, 1984, 6, 409)
1977	333,9				
1978	335,5				
1979	336,85				
1980	338,69				Error untill 1981; data in months are inaccurate between 0,5 and 1ppm (Stanhill 1984)
1981	339,93				
1982	341,13				
1983	342,78				
1984	344,42				
1985	345,9				
1986	347,15				
1987	348,93				
1988	351,48				
1989	352,91				
1990	354,19				
1991	355,59				
1992	356,37				
1993	357,04				
1994	358,88				
1995	360,88				
1996	362,64				
1997	363,76				
1998	366,63				
1999	368,31				
2000	369,48				
2001	371,02				
2002	373,1				
2003	375,64				
2004	377,38				

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