

CARBON CYCLE

Vienna, 14th April, 2007

RESERVOIRS AND GLOBAL ANNUAL FLUXES OF CO₂
(gigatonnes of carbon, GT C = 10¹⁵ g C); [] IPCC 2001

RESERVOIRS

Sediments (near surface)	60,000,000		Walker & Drever, 1988
Marine dissolved inorganics	38,000	[38,000]	Bolin, 1989
Marine dissolved organics	1,000		Bolin, 1989
Soil	1,200		Prentice et al., 1990
		[land 2000]	
Terrestrial biomass	834		Prentice et al., 1990
Marine biomass	42		Jaworowski et al., 1992
Fossil fuels (exploitable)	7,200		Walker & Drever, 1988
Atmosphere	727	[730]	Rose et al., 1983

ANNUAL FLUXES

NATURAL

Iansiti et al., 1989

Ocean (-->atm.)	106	[90]	
Land (-->atm.)	63	[120]	
Mantle outgassing	0.028		(Zhang and Zinfler, 1993)
Lithosphere (-->atm.)	>0.16 ^a	(volc. + non-volc.)	(Morner and Etiope, 2002)
Aerial volcanic	0.01		(Javoy, 2005)
	0.3 ^b		(Wardell, 2002)
	0.8		(Werner and Brantley, 2003)
	~6 ^c		
Rainout	-0.27		(Liu et al., 2004)
<u>TOTAL to atmosphere</u>	<u>~170</u>		

MAN-MADE

Human respiration	0.65		(Bartsch, 2007)
Cars	0.57		ibid.
All fossil fuels, cement and land use (2003)	7.3 ^d	[6.3]	(Marland et al., 2006)

^a non-volcanic; ^b measured for 24 volcanoes (there are 300 – 600 active volcanoes worldwide); ^c calculated from Wardell 2002 for 500 volcanoes; ^d including cars

BASICS OF IPCC:

- (1) Rejection of direct measurements of CO₂ in the atmosphere**
(after Callendar and Keeling)
- (2) Assuming that proxy ice core determinations are direct atmospheric measurements** (after Bern group)
- (3) Pre-industrial atmospheric CO₂ was about 280 ppmv**
(after Callendar, Keeling, and glaciologists)
- (4) CO₂ atmospheric lifetime is 50 to 200 years**
- (5) Truncated buffering system of the ocean, treated as a distilled water, presence of calcium carbonate and other buffers ignored. BUFFER FACTOR OF ABOUT 10 assumed without experimental support. Result: increase in atmospheric CO₂ claimed to be balanced when only 10% of it is dissolved in the ocean** (after Bolin & Eriksson, 1958; Broecker, 1971; Bacastow & Keeling, 1973; Oeschger & Siegenthaler, 1978)
- (6) Mixed layer about 75 meters**
- (7) Man-made increase of atmospheric CO₂ since pre-industrial time to 1999: $367 - 280 = \underline{87 \text{ ppmv}}$ (= 23.7%)**
- (8) Man-made CO₂ in the present atmosphere**
21% of total of 717 GT C = 153 GT C ~25 annual emissions
- (9) Unsolved problem of “MISSINK SINK”, a lacking 50% of man-made atmospheric CO₂, deduced from ~ 6 GT C industrial emissions, and 3 GT C calculated from Mauna Loa data.**

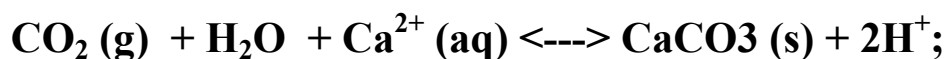
Ad (1): Rejections were not based on sound scientific grounds (as discussed in several publications, most recently in Beck's monography (Beck, 2006).

Ad (2 and 3): Pre-industrial level of CO₂ was about 340 ppmv; see discussion of ice cores, and Beck direct measurements, and proxies other than ice cores.

Ad (4): CO₂ atmospheric lifetime is about 5 – 6 years (see below)

See also below “Isotopic CO₂ mass balance calculations”: (~5 years) - discussion Segalstad.

Ad (5): BUFFERING – The (neglected) net reaction is:



**5 BUFFERS: calcium carbonate; anorthite; kaolinite; calcium silicate; and clay mineral buffers. Together they add up to almost INFINITE BUFFER CAPACITY.
Discussion of buffering system - Segalstad.**

Ad (6) Mixed layer: see below.

Ad (7 and 8): CONC. AND MASS OF MAN-MADE CO₂ – According to isotopic mass balance calculations, the mass of all past fossil fuel and biogenic CO₂ emissions remaining in December 1988 atmosphere was ~30 GT C, i.e. about 4% of the total, corresponding to 14 ppmv.

**In 1988 351 ppmv (Boden et al., 1990),
average pre-industrial 340 ppmv (Beck)
difference = 11 ppmv**

Ad (9) “MISSING SINK” (50% DEFICIT OF MAN-MADE CO₂) is a proof of wrong carbon cycle modeling.

ATMOSPHERIC LIFETIMES OF CO₂ (compiled by Segalstad, 1998)

Based on bomb carbon-14

Bien & Suess [1967]	>10
Münnich & Roether [1967]	5.4
Nydal [1968]	5-10
Young & Fairhall [1968]	4-6
Rafter & O'Brian [1970]	12
Machta (1972)	2
Broecker et al. [1980a]	6.2-8.8
Stuiver [1980]	6.8
Quay & Stuiver [1980]	7.5
Delibrias [1980]	6.0
Druffel & Suess [1983]	12.5
Siegenthaler [1983]	6.99-7.54

Based on radon-222

Broecker & Peng [1974]	8
Peng et al. [1979]	7.8-13.2
Peng et al. [1983]	8.4

Based on solubility data

Murray (1992)	5.4
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Based on carbon-13/carbon-12 mass balance

Segalstad (1992)	5.4
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Based on natural carbon-14

Craig [1957]	7 +/- 3
Revelle & Suess [1957]	7
Arnold & Anderson [1957]	10
including living and dead biosphere (Siegenthaler, 1989)	4-9
Craig [1958]	7 +/- 5
Bolin & Eriksson [1959]	5
Broecker [1963], recal. by Broecker & Peng [1974]	8
Craig [1963]	5-15
Keeling [1973b]	7
Broecker [1974]	9.2
Oeschger et al. [1975]	6-9
Keeling [1979]	7.53
Peng et al. [1979]	7.6 (5.5-9.4)
Siegenthaler et al. [1980]	7.5
Lal & Suess [1983]	3-25
Siegenthaler [1983]	7.9-10.6
Kratz et al. [1983]	6.7

Based on Suess Effect

Ferguson [1958]	2 (1-8)
Bacastow & Keeling [1973]	6.3-7.0

(UNSCEAR, 1977)

7.5

OCEAN

**CO₂ ANNUAL FLUX FROM OCEAN INTO ATMOSPHERE:
63 - 120 MT C**

DEGASSING FROM THE OCEAN

SOLUBILITY PUMP:

Thermally driven solubility pump: 70% of CO₂ = 70 GT C/y;

Biological pump: 30% = 30 GT C/y;

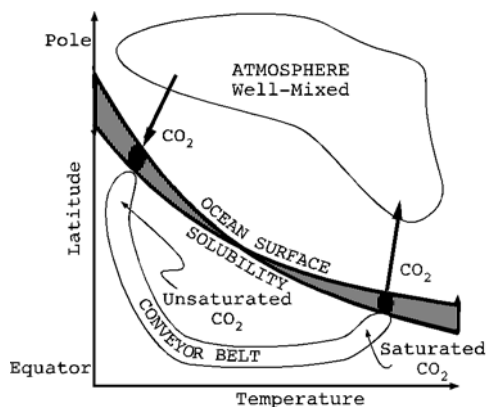
**Total = 100 BT C/y
(Volk and Liu, 1988)**

During upwelling of the deep oceanic water, cold, rich in CO₂, the water warms near the surface.

This drives a thermal solubility pump.

(Glassman, 2006):

Thermal solubility pump. The global ocean-atmosphere CO₂ circulation is governed by the pole-equator temperature difference, and by the conveyor belt. No quantification provided.

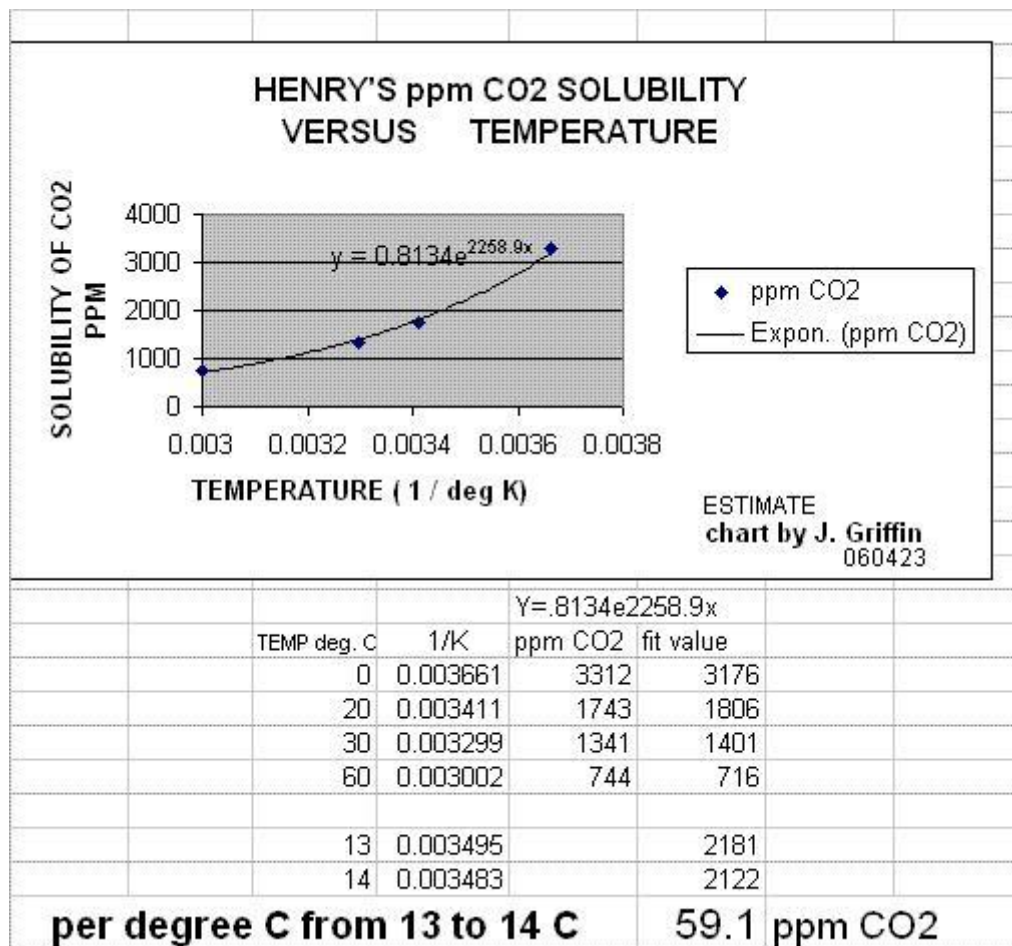


CARBON DIOXIDE STREAM

Heating the sea water by 1°C increases atmospheric CO₂ by 12.5 ppmv (Takahashi 1961).

Example: 12 °C warming of Benguela Current = 150 ppmv
 (a part precipitates as CaCO₃).

Decrease of CO₂ solubility in water: 60 ppmv per 1°C (?? to be checked) ((Griffin, 2007):



MIXED LAYER can reach a depth of up to 2000 m (Wikipedia).

In non-climatic papers usually assumed as 200 meters.

IPCC assumes 75 meters

**In the upper 75 m layer of the ocean there is enough Ca to bind
>3000 GT C.**

**This reservoir is continuously replenished from other parts of
ocean and from the lithosphere.**

**Upwelling warms the deep water in mixed layer and increases
outgassing of CO₂.**

Hurricanes mix this layer, upwelling the deep water.

**This cools the water in 30 minutes by 3°C, what corresponds to 37
ppmv CO₂).(Black et al., 2006)**

**Breaking waves form in water clouds of air bubbles circulating to
10 m depth. This is related to dissipation of turbulent kinetic
energy, leading to Langmuir circulation (down to 10 m). These
effects are observed to the depth 6 x wave height. (Thorpe and
al., 2003).**

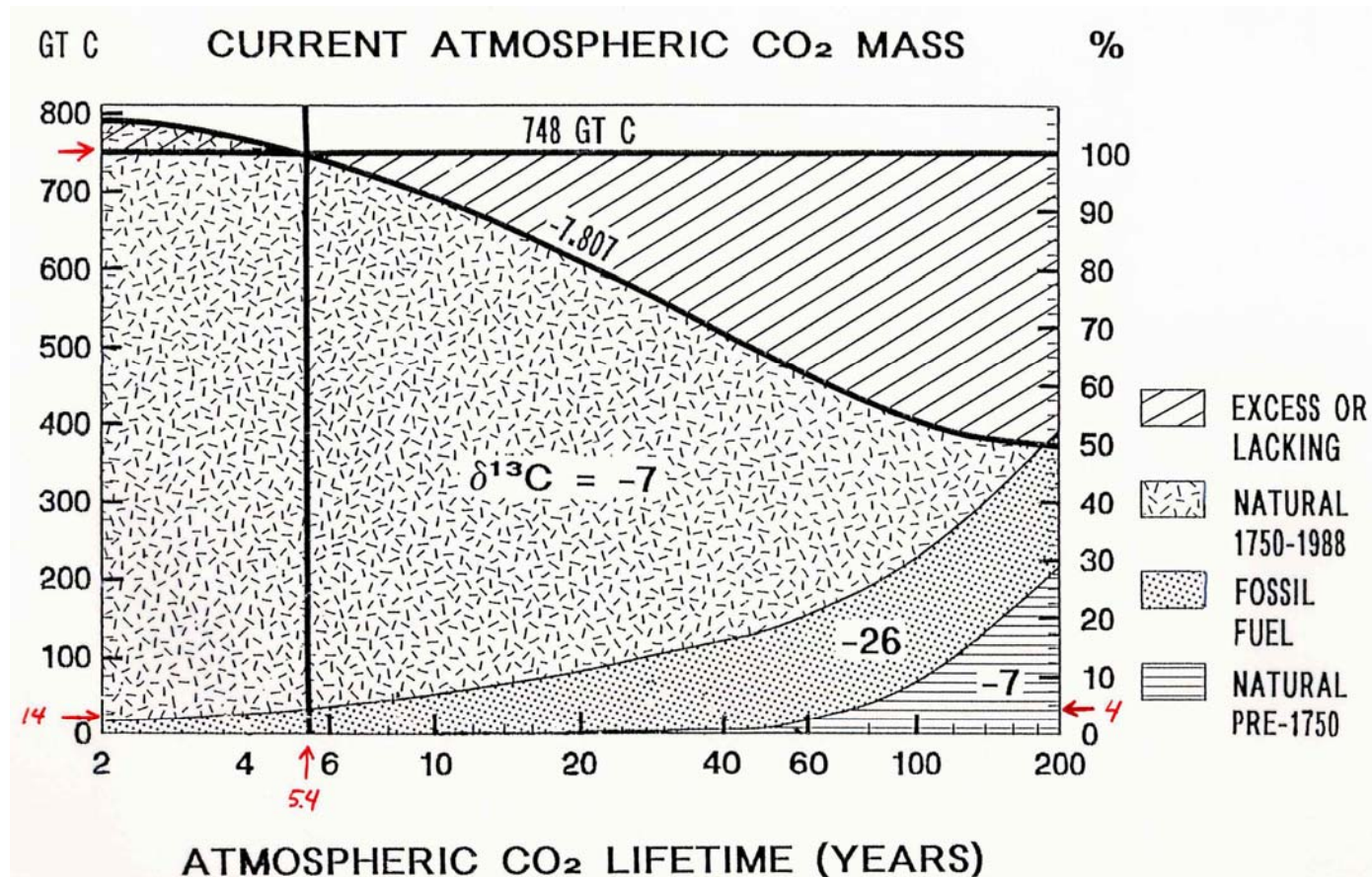
**Decrease of SST in the mixed layer observed up to 3.2°C in 11
hours. Intense breaking of large waves (up to 11 meters) injects
bubbles into the ocean. The thickness of the bubble layer increases
appr. as wind speed cubed, reaching a maximum thickness of over
10 meters. The resulting near surface bubble layer plays a key
role in gas flux across the air-sea interface. (Black et al., 2006)**

**The bubbles increase the air-ocean contact surface. This and the
influence of air bubbles on CO₂ air-ocean flux needs
quantification.**

ISOTOPIC CO₂ MASS BALANCE CALCULATION

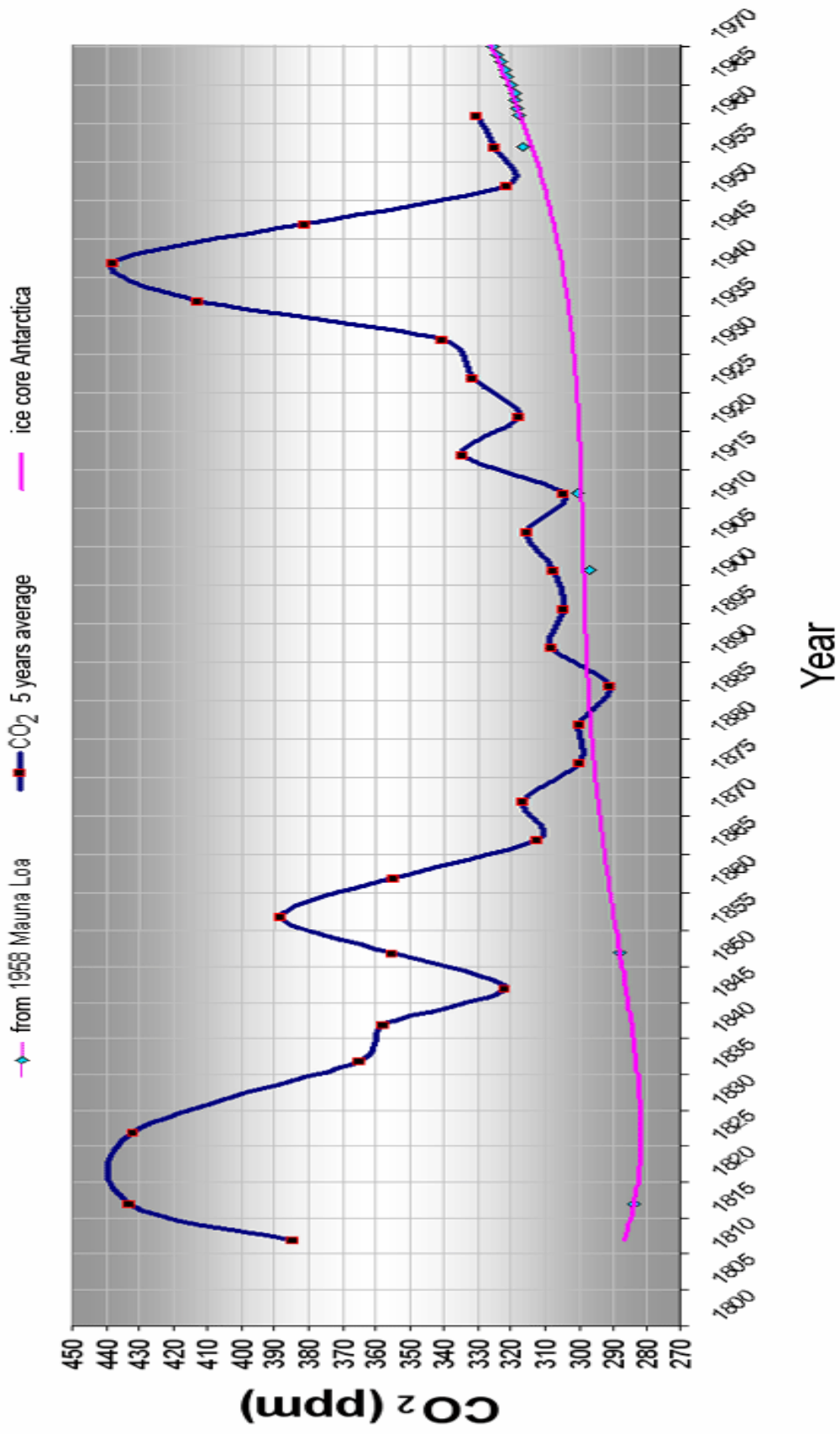
IPCC's "rough indication" lifetime 50-200 years for atmospheric CO₂ gives an atmosphere which is too light, and gives only 50% of the atmospheric CO₂ mass. This explains why the wrong IPCC model creates the artificial 50% error, nicknamed "The Missing Sink".

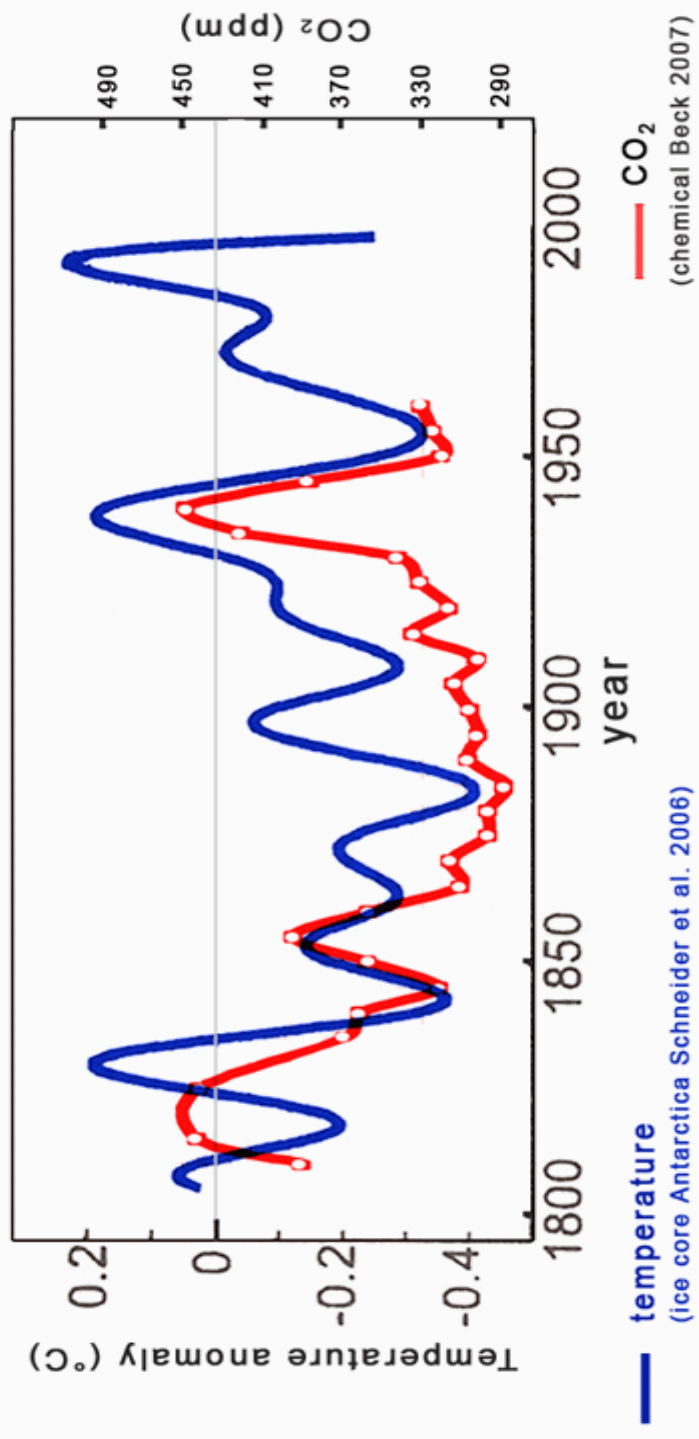
SUMMARY: ATMOSPHERIC CO₂ LIFETIME ~5 years
 ATMOSPHERIC MAN-MADE CO₂ <14 GT C
 4% (in 1988, similar now)



The December 1988 atmospheric CO₂ isotopic composition computed for its 748 GT C total mass and measured $\delta^{13}\text{C}$ of -7.807‰, fits only atmospheric lifetime of about 5 years, and a CO₂ mass of 14 GT C (= 4% of total mass) with (juvenile, biogenic or fossil fuel) $\delta^{13}\text{C}$ of -26‰.

CO₂ -1812 - 2004 Northern Hemisphere , Chemical Measurement





CO₂ IN ICE CORES

MESSAGE:

stabilized (flat) Holocene CO₂ concentrations of 270 ppmv to 280 ppmv until the industrial revolution.

ASSUMPTIONS:

- (1) Ice, and the ice cores are a closed system.
- (2) Measurements of CO₂ in ice cores are not the proxy estimates, but direct determinations in the real past atmosphere
- (3) No liquid phase occurs in ice at mean annual temp. of -24°C
- (4) Entrapment of air in ice is a mechanical process, with no chemical and isotopic fractionation
- (5) The age of gas inclusions is about 90 to several ten-thousands of years younger than the age of ice in which they are entrapped.

THESE ASSUMPTIONS WERE NEVER EXPERIMENTALLY VERIFIED, AND THEY ARE IN CONFLICT WITH MANY CO₂ AND GLACIER STUDIES.

The proxy ice core values remained low during the entire past 650,000 years, even during the six former interglacials, when the global temperature was up to 5°C warmer than now.

Either atmospheric CO₂ levels have almost no influence on climate (which is true), or Proxy ice core reconstructions of the chemical composition of the ancient atmosphere are false (which is also true).

More than 20 physical-chemical processes operating *in situ* in the polar snow and ice, and in the ice cores, cause that the ice cannot be regarded as a closed system, and that low pre-industrial CO₂ concentrations are an artifact. Drilling the cores is a brutal and polluting procedure, drastically disturbing the ice samples.

Other proxy atmospheric CO₂ reconstructions, based on stomatal frequency in fossil leaves, show that:

During the past 10,000 years CO₂ levels were higher than 300 ppmv, fluctuating up to 348 ppmv.

These stomatal proxies are supported by direct chemical measurements of CO₂ in the atmosphere (Beck, 2007), showing in the Northern Hemisphere between 1812 and 1961, CO₂ concentrations almost always higher than 300 ppmv, with 3 peaks:

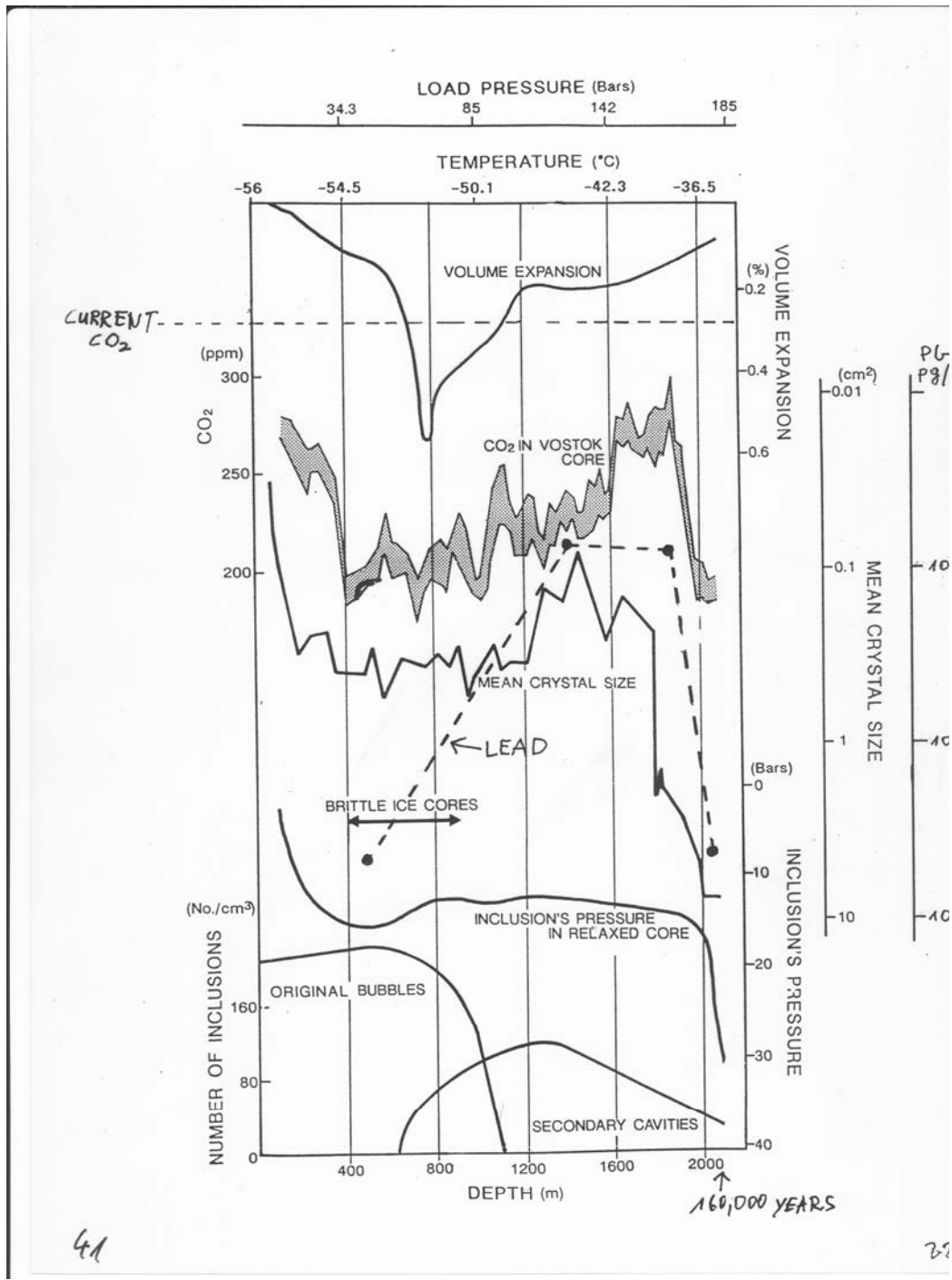
near 1820 (440 ppmv)

near 1855 (390 ppmv)

near 1942 (440 ppmv)

TU DODAC TEMPERATURE





BUFFER FACTORS AND RESIDENCE TIMES

(Bolin and Eriksson, 1959)

Carbon cycle modelling

Buffer factor = 12.5

CO₂ atmospheric lifetime 5

(Broecker et al., 1971)

Buffer factor = 10 (increases with increasing CO₂ pressure)

(Bacastow and Keeling, 1973; Keeling, 1973)

Definition of **Evasion Factor, ξ** , for long-term atm./ocean exchange, is defined as: representation of a relationship between the partial pressure of CO₂ exerted by the ocean surface water and the total inorganic carbon in this water. with an assumption on low pre-industrial level of CO₂ in the atmosphere (290 ppmv) and in sea (pp. 92 i 93).
Decrease of CO₂ in ice was related to increasing pressure and level of CO₂ clathrates

Reservoir exchange model for CO₂ is discussed.

Values of **Ksi Factor**: 9.1 in 1954 to 31.5 in 2070.

Predictions for **2070 AD**: CO₂ in air will be 6, 8 or 10 times higher than the preindustrial values of 290 ppmv (x 6 = **1740 ppmv**, a x 8 = **2320 ppmv**; x10 = **2900 ppmv**).

Upper 60 meters of ocean water contains about the same total amount of carbon as the atmosphere.

Dzeta Factor, ζ , = buffer factor for instantaneous atm/ocean exchange.

Values of **Dzeta Factor**: 9.4 in 1954 to 113.1 in 2070.

Residence time of CO₂ in the atmosphere: ^{All Siple data} ~~5~~ ^{fitting 82 years}

Predictions: **Only 6%** of the industrial CO₂ produced in 2070 AD **will enter the oceans.**

(Keeling, 1973).

Similar as Bacastow & Keeling 1973 # 9030. Evasion factor disappeared, **replaced with a buffer factor dzeta**, also based on pre-industrial CO₂ of 290 ppmv. Changes of CO₂ solubility in relation to the pressure in the ocean are not taken into account.. Buffer factor (like in Bacastow & Keeling) increases with increasing level of CO₂ in the system. Solubility of CO₂ is **2 times higher at 200 m depth and 20 times higher at 100 m depth (100 bars).**

Residence time of CO₂ in the atmosphere: 5 years *The age of all bubbles in Siple ice deposited in 1891 was „corrected” by 82 years to 1973.*

Transfer time from deep water to surface layer: 1500 years

Mixed layer (surface water): thickness not given.

(Oeschger and Siegenthaler, 1978)

Ksi Factor = buffer factor.

Models for CO₂ global exchange. Atmospheric CO₂ is in direct exchange only with dissolved gaseous CO₂ in the sea, which makes up only a small fraction of the dissolved inorganic carbon, the major part being bicarbonate (HCO₃⁻) and carbonate (CO₃⁻⁻) ions.

Buffer factor value assumed as about 10, but increases with increasing pressure (Bacastow and Keeling, 1973). Thus if the fossil CO₂ were distributed only between the atmosphere and the mixed layer (which contain the same amount of CO₂ as the atmosphere) **about 90% of the excess CO₂ would remain in the atmosphere and 10% would go to the mixed layer,**

328 ppm
in 1891 a

while the changes in the isotope ratios, $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$, would be equal in both reservoirs at equilibrium. The absolute increase of the back flux of CO_2 from ocean was larger than the decrease in its $^{14}\text{C}/\text{C}$ ratio, so that there was an enhanced ^{14}C flux from the mixed layer to the atmosphere. ??? That means that the direction of ^{14}C flow was not from its source (atmosphere and cosmic rays or nuclear explosions), but from the ocean where ^{14}C is not formed. IMPOSSIBLE. The same statement in (Keeling 1973) and earlier in Bolin & Eriksson, 1959 (cited by Keeling, 1973). The two fluxes of CO_2 : from the ocean and to the ocean are equal, and **THERE IS NO NET TRANSFER.**

Residence time in the atmosphere: 7.0 YEARS.

Mixed layer = 70 – 80 meters.

(IPCC 1990) “Turnover time” of 4 years; BUT – rejected; instead “adjustment time” or “atmospheric lifetime” of 50 – 200 years was accepted. Oceanic “biological pump” accepted, but “solubility pump” including the a major part of buffering system ignored.

“Sensitivity of atmospheric CO_2 to changes of temperature by about 1°C is small” – concluded from not changing and low ice core CO_2 concentration ranging 270 - 290 ppmv between 1000 and 1800 AD. Carbon cycle based on five aforementioned papers.

Evidence of anthropogenic CO_2 increase: (1) ice core data; (2) atmospheric increase closely parallels fossil fuel emission trends; (3) isotopic trends of ^{13}C and ^{14}C agree with emissions from fossil fuel.

CaCO_3 sink only via marine organisms; inorganic CaCO_3 reactions ignored.

(IPCC 2001) The same carbon cycle as in IPCC 1990, now based on pre-industrial level of 280 ppmv. CaCO_3 from marine organisms deposited in sediments enters surface waters and is returned to the atmosphere.

Organic CaCO_3 sink: “extremely slow, hence of limited relevance to the atmospheric CO_2 response to (man-made) emissions”.

No inorganic CaCO_3 sink. We should estimate this sink.

No atmospheric CO_2 lifetime discussed

Mixed layer not defined

In all these documents the ocean is treated as pure distilled water.

In carbon cycle models, except for boron in (Keeling, 1973), inorganic reactions with **calcium, silicate, phosphate, sulfate and fluoride** are neglected. With all these ions taken into account the value of buffer factor would be **near 0**. Including clay, the buffering capacity of the ocean is practically infinite.

In IPCC 2001 (p. 126) a confession: global ocean models ignore the observed CaCO_3 formation.

PROJECTIONS OF EMISSIONS

(Million Metric Tons Carbon Dioxide)											
Region/Country	History ^a				Projections ^a					Average Annual Percent Change, 2003-2030	
	1990	2002	2003	2010	2015	2020	2025	2030			
OECD											
OECD North America	5,759	6,691	6,801	7,505	7,997	8,513	9,096	9,735	1.3		
United States ^b	4,985	5,752	5,800	6,365	6,718	7,119	7,587	8,115	1.3		
Canada	474	570	596	683	753	799	839	873	1.4		
Mexico	300	369	405	457	526	595	670	747	2.3		
OECD Europe	4,089	4,203	4,264	4,474	4,632	4,741	4,909	5,123	0.7		
OECD Asia	1,536	2,063	2,090	2,269	2,390	2,455	2,540	2,638	0.9		
Japan	1,011	1,191	1,206	1,200	1,228	1,218	1,214	1,219	0.0		
South Korea	234	462	470	608	675	723	781	843	2.2		
Australia/New Zealand	291	410	415	462	487	515	545	576	1.2		
Total OECD	11,384	12,957	13,155	14,248	15,019	15,709	16,545	17,496	1.1		
Non-OECD											
Non-OECD Europe and Eurasia ..	4,193	2,634	2,725	3,113	3,444	3,758	4,047	4,352	1.7		
Russia	2,334	1,546	1,606	1,799	1,949	2,117	2,246	2,374	1.5		
Other	1,859	1,088	1,118	1,314	1,495	1,641	1,801	1,978	2.1		
Non-OECD Asia	3,626	5,733	6,072	9,079	10,753	12,407	14,113	15,984	3.6		
China	2,241	3,273	3,541	5,857	7,000	8,159	9,349	10,716	4.2		
India	578	1,011	1,023	1,369	1,592	1,799	2,008	2,205	2.9		
Other Non-OECD Asia	807	1,449	1,508	1,853	2,161	2,449	2,756	3,062	2.7		
Middle East	704	1,152	1,182	1,463	1,647	1,811	1,987	2,177	2.3		
Africa	649	850	893	1,188	1,363	1,477	1,593	1,733	2.5		
Central and South America	673	993	1,006	1,270	1,436	1,586	1,758	1,933	2.4		
Brazil	220	347	348	423	469	508	559	610	2.1		
Other Central/South America	453	645	659	847	967	1,078	1,199	1,323	2.6		
Total Non-OECD	9,846	11,362	11,878	16,113	18,643	21,039	23,500	26,180	3.0		
Total World	21,230	24,319	25,033	30,361	33,662	36,748	40,045	43,676	2.1		

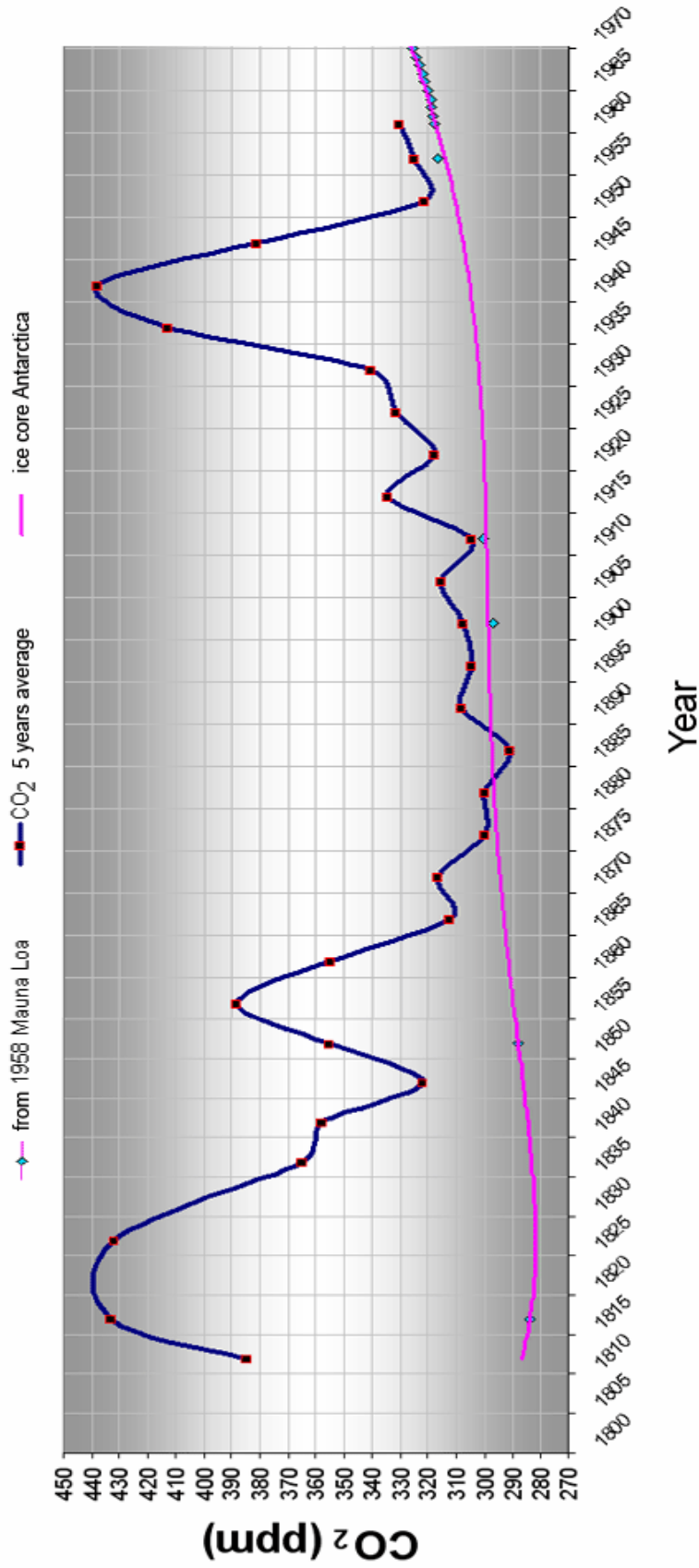
^aValues adjusted for nonfuel sequestration.

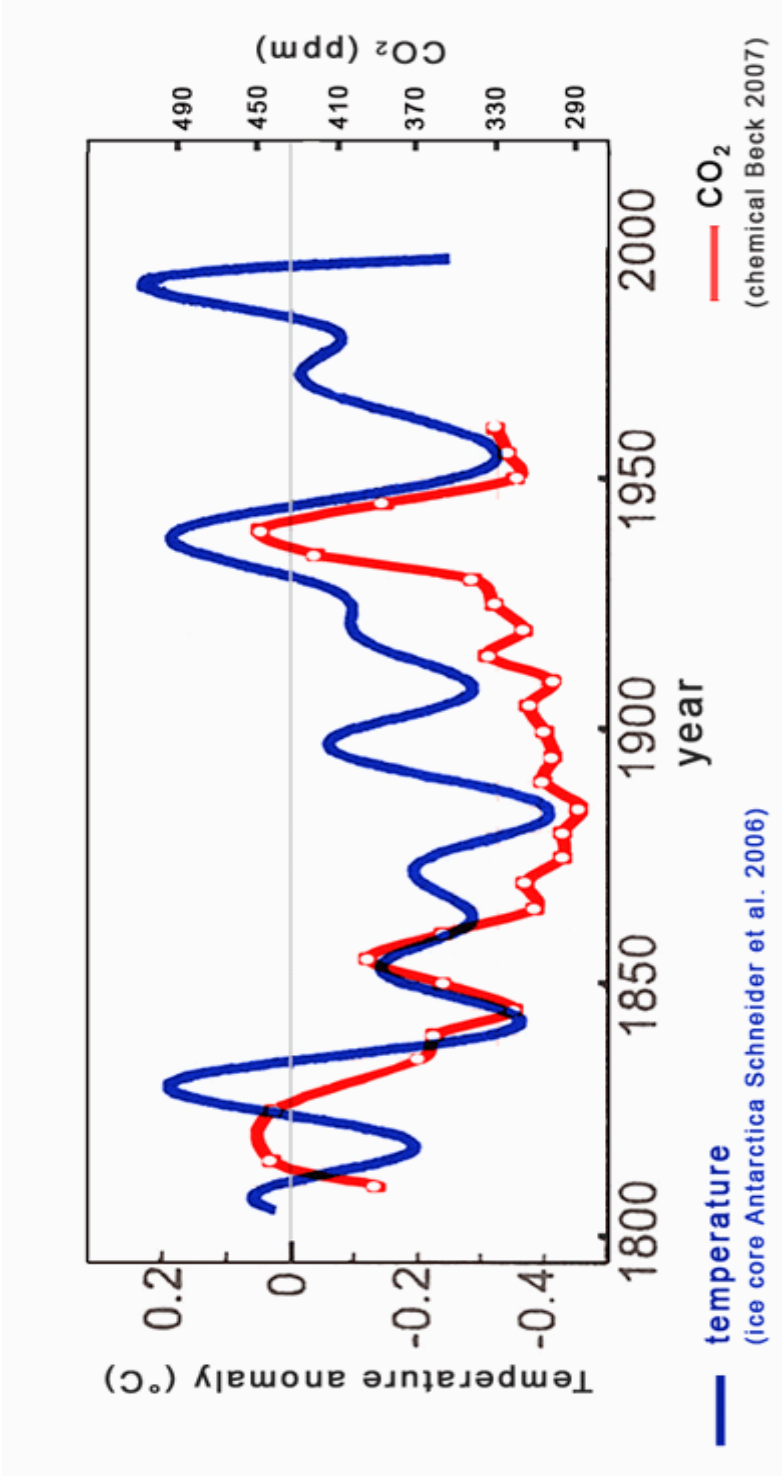
^bIncludes the 50 States and the District of Columbia.

Note: The U.S. numbers include carbon dioxide emissions attributable to renewable energy sources.

Sources: **History:** Energy Information Administration (EIA), *International Energy Annual 2003* (May-July 2005), web site www.eia.doe.gov/ieal/; and data presented in this report. **Projections:** EIA, *Annual Energy Outlook 2006*, DOE/EIA-0383(2006) (Washington, DC, February, 2006), Table 1, web site www.eia.doe.gov/oi/aeo/; and *International Energy Outlook 2006*, DOE/EIA-0484(2006) (Washington, DC, June 2006), Table A10.

CO2 -1812 - 2004 Northern Hemisphere , Chemical Measurement





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