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How Has the Atmospheric Concentration of CO Changed?

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Abstract. Carbon monoxide exerts strong control over the chemistry of the troposphere and lower stratosphere through its influence over hydroxyl radical (OH) and ozone concentrations. Thus, CO affects the oxidizing power of the atmosphere and the concentrations of greenhouse gases. Because of its short atmospheric residence time (two to three months) the determination of a secular trend in CO concentrations is very difficult. Temporal increases of CO are expected because certain sources under human control have been growing; these include fossil-fuel usage and increasing atmospheric methane. These factors and existing atmospheric data are reviewed here. From the data, it is likely that CO has increased in the Northern Hemisphere in the past 15-30 years. Southern Hemispheric data indicate no positive trend. Problems in determining trends more reliably and in model studies are outlined.

IMPORTANCE OF ATMOSPHERIC CARBON MONOXIDE

A variety of important roles for atmospheric CO leads us to want to determine its spatial and temporal variations and its secular trends. In polluted regions such as urban centers, elevated CO concentrations can be dangerous to human health and they are taken as a key indication of other kinds of pollution. In the presence of nitrogen oxides (NO_x) the atmospheric oxidation of CO generates ozone; this occurs in highly polluted air but also in relatively clean air. In very clean air, where there are subcritical amounts of NO_x, the oxidation of CO to CO₂ consumes ozone. Thus, CO and its photochemistry exert control over tropospheric ozone, an important oxidant and a potent climatic greenhouse gas.

For clarity, I should list the key atmospheric elementary reactions involving CO. For a more complete discussion see Crutzen (1987). Oxidation is initiated by



followed by



In the presence of significant amounts of NO_x , reaction with NO follows:



Photolysis of NO_2 occurs due to light of wavelength (λ) less than 425 nm:



By adding reactions (1) through (5) as if they were algebraic equations, one obtains the net reaction:



In the absence of NO_x , reactions (1) and (2) are followed by



and the net reaction is



Through these reactions CO influences atmospheric chemistry and climate in important ways—those mentioned above and more. Reactions (1) and (2) strongly control the ratio of OH/ HO_2 concentrations and thus the oxidative capacity and pathways of the atmosphere. Further, spatial concentration patterns of atmospheric ^{12}CO and ^{14}CO can be used to empirically estimate atmospheric OH concentrations (Volz et al. 1981).

SOURCES AND SINKS OF ATMOSPHERIC CARBON MONOXIDE

Some excellent effort has gone into identifying sources and sinks of atmospheric CO and the relative and absolute sizes of these sources and sinks. Two very useful compilations and analyses of CO budgets are summarized in Tables 1 and 2. Before focusing on specific entries in these tables, note several points. First, the unit of these sources and sinks is 10^{12} g CO per year. In various other budgets of atmospheric gases or studies of

Table 1 Global CO budget (10^{12} g CO yr⁻¹) from Logan et al. (1981)

	Total	Northern Hemisphere	Southern Hemisphere
Sources			
Fossil fuel use	450 (400-1000)	425	25
Oxidation of anthropogenic hydrocarbons (0-180)	90	85	5
Oxidation of natural hydrocarbons (280-1200)	560	380	180
Emissions by plants	130 (50-200)	90	40
Wood used as fuel	51 (25-150)	33	17
Forest wild fires	25 (10-50)	22	3
Forest clearing	380 (200-800)	260	120
Savanna burning	200 (100-400)	100	100
Ocean	40 (20-80)	13	27
CH ₄ oxidation	810 (400-1000)	405	405
Total	2736 (1500-4000)	1813	922
Sinks			
Soil uptake	250	210	40
Photochemistry	3170 (1600-4000)	1890	1280
Total	3420	2100	1320

carbon cycling, the unit is often elemental carbon mass (g, kg, or moles), e.g. 10^{12} g C per year.

On examining the individual entries and the total CO sources and sinks in Tables 1 and 2, one is struck by the variety of industrial, chemical, and biological processes that is involved. Incomplete combustion produces CO when fossil fuels are burned industrially and when biomass is burned, as in forest clearing for agriculture or in natural forest or grassland fires. CO itself is also photochemically produced in the atmosphere during hydrocarbon oxidation. It is also emitted directly into the atmosphere by vegetation and

Table 2 Global and tropical budget of tropospheric carbon monoxide (10^{12} gmCO/yr) from Seiler and Conrad (1987)

	Global	Tropics (30°S–30°N)
Sources		
Technological sources	640 ± 200	—
Biomass burning	1000 ± 600	800 ± 500
Vegetation	75 ± 25	60 ± 20
Ocean	100 ± 90	50 ± 45
CH ₄ oxidation	600 ± 300	400 ± 200
Oxidation of nonmethane hydrocarbons	900 ± 500	600 ± 300
Production by soils	17 ± 15	10 ± 9
Total production	3300 ± 1700	1900 ± 1100
Sinks		
Oxidation by OH	2000 ± 600	1200 ± 400
Uptake by soils	390 ± 140	105 ± 35
Flux into stratosphere	110 ± 30	80 ± 20
Total decomposition	2500 ± 750	1400 ± 430

soil microorganisms and it is taken up from the atmosphere by other soil microorganisms. The principal sink for atmospheric CO is reaction (1) in which the atmosphere, through OH radicals, oxidizes CO irreversibly to CO₂; i.e., CO is not produced from CO₂ in the atmosphere except for insignificantly slow rates in the upper stratosphere, mesosphere, and thermosphere.

Less than 20 years ago it was widely believed that the dominant source of atmospheric CO was incomplete combustion of coal and petroleum products. This view led to a deduced atmospheric residence time, τ , of about four years. Consideration of the behavior of naturally produced ¹⁴C led to an independent estimate of τ , of about one month (Weinstock 1969), and to the view that natural sources, not just anthropogenic sources, were important for CO. Stevens et al. (1972) demonstrated convincingly from ¹³C/¹²C and ¹⁸O/¹⁶O ratio measurements that natural CO sources exceed combustion globally. When one examines the CO budgets of Tables 1 and 2, or that of Thompson and Cicerone (1986), and discovers disagreements over individual sources and sinks or inconsistent listings of processes and categories, one should also recall the great progress of the last 15–20 years.

SPATIAL AND TEMPORAL VARIABILITY

The sources and sinks of Tables 1 and 2 imply that atmospheric CO varies in space and time (which is known independently from actual measurements, of course). For example, if the average global tropospheric concentration of CO is 110 ppb (1.1×10^{-7}) by volume, then the total production figure of Table 2 (3300×10^{12} g CO per year) implies that in steady state, $\tau_r = 2$ months. The comparable figure from Table 1, 2740×10^{12} g CO per year, leads to $\tau_r = 2.5$ months. Thus the atmospheric CO burden is replaced five or six times each year; spatial and temporal variability must result from such rapid turnover. Second, most of the individual sources and sinks of CO are inherently variable. Fossil-fuel usage and the inputs of anthropogenic hydrocarbons (whose atmospheric oxidation produces CO) vary with season and latitude and they depend on economic activity and industrial practices that vary with time, e.g., pollution-control devices change as do fuel mixtures. Similarly, CO emissions from plants and from biomass burning vary with season and latitude but also change due to ecological and climatic variability.

It is also important to realize that the atmospheric residence time, τ_r , is not a single, constant number because the spatial and temporal variations of the sources are not identical to those of the sinks. As outlined above, the principal atmospheric sink for CO is the hydroxyl radical, through reaction (1). In the atmosphere, the bulk rate of reaction (1) depends mostly on the OH concentration, [OH]. Photochemical models predict that [OH] is approximately ten times larger in the planetary boundary layer (PBL) than in the upper troposphere, and in the summer troposphere vs. the winter troposphere (see, e.g., Isaksen and Hov (1987)). Thus CO is short-lived in the daytime PBL compared to the upper troposphere and short-lived in the summer vs. winter, especially at middle and high latitudes. Thus, Volz et al. (1981) have shown that ^{14}CO is much more long-lived than ^{12}CO because ^{14}CO spends a significant amount of time in the upper and middle troposphere where there is less OH than in the lower troposphere. The unequal τ_r for ^{14}CO and ^{12}CO is important to recognize if ^{14}CO is used as an indicator of [OH] values (see Volz et al. 1981).

One type of CO variability is illustrated in Fig. 1: CO concentrations measured from an aircraft during Project GAMETAG in April and May 1978 from Heidt et al. (1980). There is a gradient of decreasing CO from high northern latitudes to high southern latitudes. This gradient is probably similar but smaller at all times of year (see Dianov-Klovov and Yurganov 1981).

There are also seasonal cycles evident at individual sites. For example, Fig. 2 shows data from Cape Grim, Tasmania (41°S). CO maxima are normal in late winter (August-September) and minima are usual in late

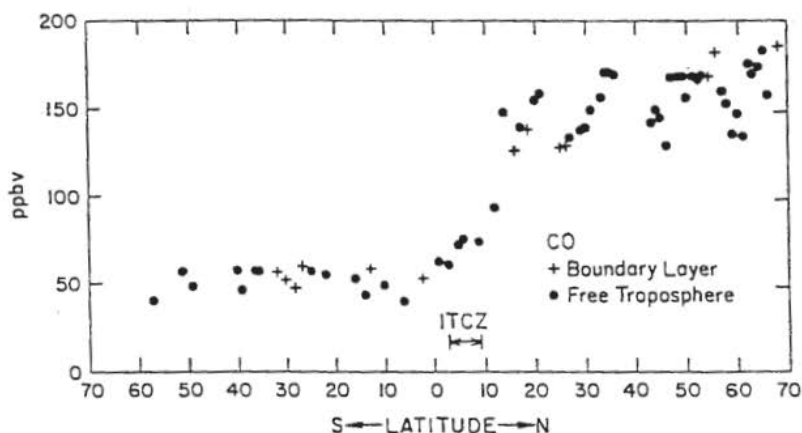


Fig. 1a—Measured latitudinal distribution of CO from southern leg-southbound and northern leg-northbound aircraft flights of April and May, 1978 (from Heidt et al. 1980).

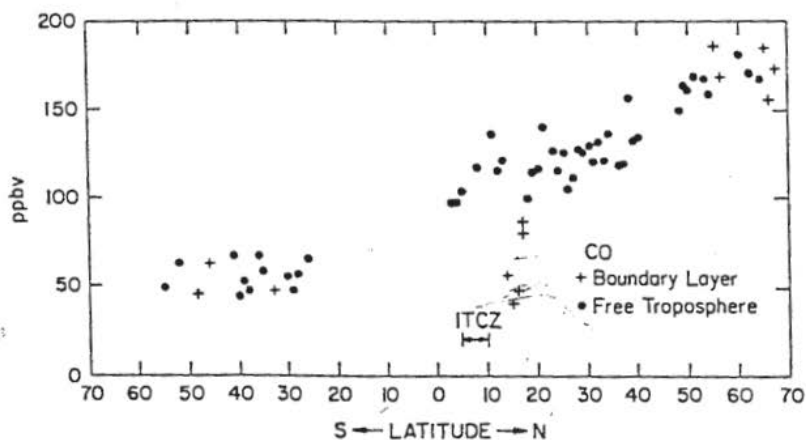


Fig. 1b—Same as 1a except for southern leg-northbound and northern leg-southbound flights.

summer (February-March). Seasonal cycles are also evident at other sites (see, e.g., Khalil and Rasmussen 1984 and Seiler et al. 1984).

TEMPORAL TRENDS: MEASUREMENTS

There are reasons to believe that atmospheric CO might be increasing with time; several of the direct anthropogenic sources of CO have already increased dramatically and some continue to increase. For discussions of

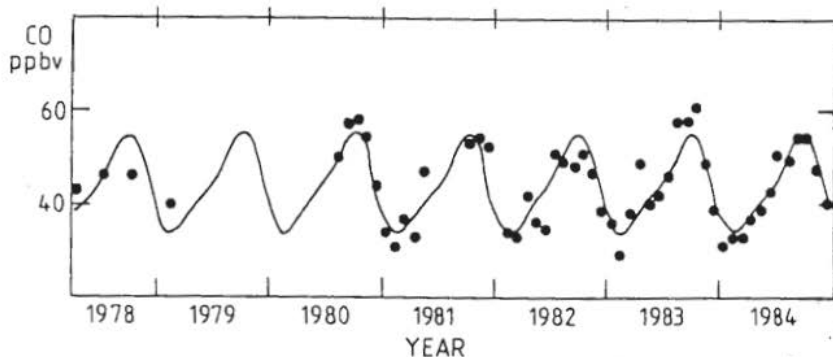


Fig. 2—Monthly mean CO concentrations, observed in samples gathered with glass and stainless steel flasks at Cape Grim, Tasmania, as a function of time. The solid line is a least squares fit that clearly shows seasonal cycles, but no long-term trend (from Fraser et al. 1986).

trends in emissions the reader is referred to Logan et al. (1981). An example of how CO emissions can be estimated for the past 100 years can be found in Thompson and Cicerone (1986). These authors used the CO source categories of Table 1 and assumed that (a) natural sources are constant with time, except for methane oxidation from essentially anthropogenic methane, (b) CO released due to combustion and oxidation of industrial hydrocarbons has varied in proportion to fossil-fuel usage rates, and (c) CO from other activities such as intentional forest clearing has varied with human population. It is also important to note that the atmospheric methane increase of the past should have caused a CO increase due to increased atmospheric production of CO during methane oxidation and also through suppression of tropospheric OH, the main CO sink.

Six published efforts to deduce CO trends will be summarized here; see Table 3. The first of these by Graedel and McRae (1980) was based on a large data set from a region (New Jersey) that is often polluted (CO concentrations over 500 ppb). From nearly continuous nondispersive infrared absorption data, Graedel and McRae studied the statistics of one-hour averages (formed from 15-minute averages). Their analysis weighted the observed CO minima very heavily. They found a significant monotonic CO increase of 180 ppb over the 1968 to 1977 period. This trend is quite credible but it probably represents only a regional effect.

For remote northern hemispheric tropospheric conditions, about 85–90% of atmospheric CO is below the tropopause and only 10–15% is in the stratosphere. Column measurements should exhibit less variability than local *in situ* sampling. Dianov-Klokov and Yurganov (1981) and Dvoryashina et al. (1984) have reported infrared absorption measurements of the total

Table 3 Published CO trend-detection studies based on CO measurements

Investigator	Method of observation	Period of observation	Location & latitude	Trend (%/yr)
Graedel & McRae (1980)	<i>In situ</i> sampling, infrared absorption	1968-1977	New Jersey 40°N	positive
Dianov-Klokov & Yurganov (1981)	Total column infrared absorption	1970-1976 compared to 1952 and 1953	Moscow 56°N	2 (winter) 0 (summer)
Dvoryashina et al. (1984)	Total column, infrared absorption	1970-1982	Various Northern Hemisphere	1.7 (winter) 1.4 (summer)
Seiler et al. (1984)	<i>In situ</i> sampling HgO/Hg	1978-1981 compared to 1971-72	Cape Point 34°S and South Atlantic	0.5 to 1.0
Khalil & Rasmussen (1984)	<i>In situ</i> sampling GC-FID	1979-1983	Cape Meares 45°N	6
Rinsland & Levine (1985)	Total column infrared absorption	1950 and 1951 compared to 1977	Jungfrauoch 46°N and Northern Hemisphere	2
Fraser et al. (1986)	<i>In situ</i> sampling GC-FID	1978-1984 1980-1984	Cape Grim 41°S Mawson, Antarctica 68°S	0 3

atmospheric column of CO based on an absorption line in the band at 4.67 μm . Dianov-Klokov and Yurganov (1981) found CO maxima in spring and minima in late summer in their data from 1970–1976, and by comparing with earlier similar data from John Shaw (at Ohio State University, 1952 and 1953), they noted about a 40% increase in the winter CO amounts (1970–1976 amounts minus the 1952 and 1953 amounts) but no significant change in summertime CO amounts. Dvoryashina et al. (1984) reported an extension of these data from 1970–1982: clear seasonal variations and trends of increasing CO at rates of 1.7% per year (winters: 1970–82) and 1.4% per year (summers: 1970–82). A possible bias in this data set should be noted. These spectroscopic measurements employ the sun as a source so that data can only be gathered in the absence of clouds, or generally during high-pressure meteorological episodes. High-pressure events favor temperature inversions in the lower troposphere. This favors the accumulation of human-produced pollutants such as CO. Therefore there is some reason for concern that the extensive-Soviet data sets might be unrepresentative of trends over larger regions such as the Northern Hemisphere.

Seiler et al. (1984) measured CO by a continuous HgO to Hg conversion technique in surface air at Cape Point, South Africa between 1978 and 1981. Clear seasonal variations were apparent but not a temporal trend. By comparison with measurements made in 1971 and 1972, that employed the same technique and which were traceable to the same absolute calibration standard, Seiler et al. placed an upper limit of 5–10% on the total CO increase from 1971 until 1981.

Khalil and Rasmussen (1984) have reported the largest CO trend to date: about 6% per year. They deduced an increase of about 20% over a 3.5 year period (July, 1979 to February, 1983) in data from gas chromatographic flame-ionization detection (preceded by methanization) of over 60,000 *in situ* surface samples at Cape Meares, Oregon. These authors used several different statistical analysis methods to discern a trend from the data; strong seasonal cycles and an asymmetric sampling distribution (with a tail to high CO values) were identified as difficulties in the analysis. In subsequent analysis of the same data, Khalil has deduced slightly smaller trends.

In 1985 Rinsland and Levine (1985) reported a re-analysis of infrared solar absorption spectra that were measured originally in 1950 and 1951 at Jungfrauoch. By employing more accurate CO spectral data and modern analysis techniques, Rinsland found that eleven CO column measurements in 1950 and 1951 yielded 76 ± 25 ppbv. Rinsland and Levine then compared this value to a nominal northern hemispheric, annual average of 130 ppb for the year 1977 (from other investigators and techniques). In this analysis they tried to average over season cycles. For the 27-year period they deduced a 2% per year average increase of northern hemispheric CO.

A new and significant data base for the Southern Hemisphere has been released recently by P.J. Fraser and his colleagues in Australia. Fraser et

al. (1986) have reported monthly mean CO mixing ratios for Cape Grim, Tasmania (41°S) for early 1978 through 1984 and for Mawson, Antarctica (68°S) for early 1980 through 1984. The data were gathered by flask sampling and gas chromatographic, flame-ionization detection analysis. Monthly means were based on smaller numbers of samples in early years, growing to over 220 samples annually at Cape Grim in 1984. Statistical analysis revealed no CO trend at all for Cape Grim but $3(\pm 1)\%$ year at Mawson. An extension to this data set (P. Fraser, personal communication) shows no trend at Cape Grim through mid 1987, a smaller positive trend (if any) at Mawson than was reported by Fraser et al. (1986) and no trends at several other sites (Barrow, Mauna Loa, Samoa and South Pole) for the period January 1984 through mid 1987.

It seems clear from all of these data that atmospheric CO has increased in the northern hemispheric troposphere since 1950, at least in certain regions, but not steadily or uniformly in space. Variable rates of change of CO probably occurred in different years and periods and in the planetary boundary layer as opposed to the free troposphere. The data suggest no positive trend in the Southern Hemisphere.

PROBLEMS IN TREND ESTIMATION

The detection of sustained temporal trends in atmospheric CO is very challenging. Like tropospheric ozone, CO is subject to meteorological variability and changing sources and sinks. Several problem areas are outstanding, including:

1. development of a sampling strategy that prescribes the number of sites and their geographical spacings and the sampling frequency necessary to discern a trend of $x\%$ per year with n years of observations to within an uncertainty, ϵ ;
2. evaluate and compare various methods for extracting seasonal cycles with varying amplitudes in the determination of temporal trends;
3. develop methods to identify sporadic events that appear as anomalous cycles or trends in the data;
4. evaluate measurement methods and calibrations to determine limits of accuracy.

Several of the difficulties with CO trend detection are interrelated. As described above, atmospheric CO concentrations are strongly influenced by sources and sinks that vary greatly with season, latitude, and longitude. Even the atmospheric residence time, τ_r , is a variable quantity. A successful trend-detection strategy must account for all of this and be capable of

dealing with differences between continental and marine regions and between the free troposphere and the PBL. A well founded strategy for CO trend detection could emerge from a new approach to ozone trend detection that has just been developed (Prinn 1988). Prinn's approach should be considered and modified as needed.

MODEL PREDICTIONS OF CO TRENDS

Given the number of variables involved in predicting future CO changes or in estimating past CO changes, and the large uncertainties in these variables, it is not surprising that few such modeling studies have been attempted. On the other hand, there are clear secular trends in factors that must influence atmospheric CO, including fossil fuel combustion (rates increased about 50-fold from 1850-1980) and atmospheric CH₄ concentrations (doubled from 1850-1980). In a recent study, Thompson and Cicerone (1986) modeled past and future CO concentrations. In one scenario, perhaps the most relevant, they adopted the CO source and sink apportioning of Table 1 and extrapolated anthropogenic sources through time according to fossil fuel usage data and trends or human population data and held constant various natural sources. Assuming CH₄ concentrations as determined from old ice core analysis and background NO_x concentrations similar to those in the background troposphere today, they calculated with a one-dimensional photochemical model that CO concentrations might have been one-third to one-half those of 1985 in 1860 and that further increases to two or three times those of 1985 could occur by 2035. These model CO increases are partly due to increased direct CO sources, larger sources due to CH₄ and nonmethane hydrocarbon oxidation, and decreased tropospheric OH in the model (due to increased CH₄ and CO). Amongst many model uncertainties, tropospheric NO_x concentrations were noted.

Another recent model study (Isaksen and Hov 1987) simulated simultaneous perturbations to tropospheric CH₄, CO, NO_x, and nonmethane hydrocarbon sources. This study used a global two-dimensional model (latitude and altitude) and focused on two time periods, 1950-2010 and 1965-1995, for various perturbation scenarios. Increasing NO_x emissions could actually increase tropospheric OH and thus decrease the effect of increasing CO sources. In fixed NO_x scenarios, Isaksen and Hov (1987) calculated OH decreases similar to those of Thompson and Cicerone (1986). These model studies and present understanding of tropospheric photochemistry clearly indicate that the behavior of tropospheric CH₄, CO, O₃, OH, and NO_x are strongly coupled. NO_x concentrations and their variations represent the biggest single uncertainty in model perturbation calculations. Transport and removal processes for NO_x are not treated very definitively in existing models.

FUTURE RESEARCH

There are several major problems, open questions, and research opportunities that concern the question of whether atmospheric CO concentrations are changing secularly, and the effects of such changes.

The optimum locations, spatial separations, and sampling frequency for CO measurements to deduce a trend of $x\%$ per year, in n years, to an uncertainty of ϵ , need to be determined. It remains to be determined how much data on vertical profiles or total columns is needed.

Regular observations continue to be needed from the Southern Hemisphere, and probably from a mixture of continental and marine sites.

The CO yield from the atmospheric oxidation of methane, isoprene, and other hydrocarbons must be determined. It is necessary to improve our understanding of the photochemical mechanisms and the atmospheric removal rates of intermediate species, such as organic peroxides and aldehydes, before we will know the yield of gas-phase CO from hydrocarbon oxidation. Carbon and oxygen isotopic methods could provide great help to these mechanistic studies and to source-apportionment research.

Much more realistic modeling of the tropospheric photochemical system and of transport of hydrocarbons and NO_x is needed before definitive predictions can be made for simultaneous perturbations to the global atmosphere.

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