

# Reports

## Carbon Monoxide in the Earth's Atmosphere: Increasing Trend

**Abstract.** *The results of an analysis of more than 60,000 atmospheric measurements of carbon monoxide taken over 3½ years at Cape Meares, Oregon (45°N, 125°W), indicate that the background concentration of this gas is increasing. The rate of increase, although uncertain, is about 6 percent per year on average. Human activities are the likely cause of a substantial portion of this observed increase; however, because of the short atmospheric lifetime of carbon monoxide and the relatively few years of observations, fluctuations of sources and sinks related to the natural variability of climate may have affected the observed trend. Increased carbon monoxide may deplete tropospheric hydroxyl radicals, slowing down the removal of dozens of man-made and anthropogenic trace gases and thus indirectly affecting the earth's climate and possibly the stratospheric ozone layer.*

Every year human activities may put some 1500 teragrams (1 Tg =  $10^{12}$  g) of CO into the earth's atmosphere. Natural sources may contribute another 1200 Tg/year (1–3). Since the anthropogenic sources of CO are linked to the production of energy and food, they are expected to increase as much as 3 to 6 percent per year, which should increase the atmospheric CO concentration 2 to 4 percent per year. We show here that now there is evidence suggesting that CO may indeed be increasing in the earth's atmosphere (nonurban troposphere) (4). This evidence is based on an enormous database consisting of more than 60,000 individual atmospheric measurements of CO taken at a remote location (Cape Meares) in Oregon over the past 3½ years.

Our results are shown in Figs. 1 and 2 and Table 1. To describe these results we

will first discuss current estimates of the global sources and sinks of CO, describe the data and their acquisition, and then discuss the methods used to extract the increase and estimate its magnitude.

According to a recent global budget of CO proposed by Logan *et al.* (1), some 450 Tg/year (400 to 1000 Tg/year) are emitted directly into the atmosphere from fossil fuel burning alone. The burning of wood, forest clearing, and savanna burning may add another 630 Tg/year (300 to 1400 Tg/year). The remaining anthropogenic sources of about 500 Tg/year (400 to 1200 Tg/year) are indirect and result from the oxidation of hydrocarbons including some 400 Tg/year which we estimate comes from the anthropogenically controlled sources of CH<sub>4</sub> (5, 6). The natural sources of CO, about 1200 Tg/year (800 to 1900 Tg/year),

include the oxidation of naturally produced hydrocarbons including CH<sub>4</sub>, emissions from plants, forest wildfires, and oceans. The principal removal processes for atmospheric CO are believed to be oxidation by OH radicals (> 80 percent) and uptake by soils (< 15 percent). Some CO may be lost in the stratosphere or taken up by plants (3). When these estimated global sources (*S*) are compared to the measured abundance (*C*), the lifetime ( $\tau = C/S$ ) of CO is calculated to be 2 to 6 months on average (3). The major sources and sinks of CO are well known now, but their magnitudes are still quite uncertain as indicated by the ranges of estimated emissions (1). Nevertheless, it can be seen that anthropogenic activities are important in the present global CO cycle, especially when the oxidation of CH<sub>4</sub> from anthropogenic sources is included. Since the lifetime of CO is relatively short and its land-based sources spread out all over the world, its concentrations vary enormously with time at any location; thus it is extremely difficult to observe a relatively small systematic increase of 2 to 4 percent per year without obtaining frequent measurements which span a long time, perhaps decades.

The strength of our data is the high frequency of measurements, up to 2000 every month. This detailed record allows us to separate the effects of local pollution and short-term cycles from the increasing trend. The span of the measurements, only 3½ years, is a shortcoming. The measurements were made with an automated Carle 211-MS gas chromatograph equipped with a methanator and a flame-ionization detector. After every ambient analysis, a calibration standard

Table 1. Increase of CO in the earth's atmosphere (based on 63,000 measurements taken at Cape Meares, Oregon, 45°N, 125°W, between July 1979 and February 1983).  $\hat{b}$  and  $\hat{\beta}$  are the estimated yearly rates of increase of CO;  $\hat{\beta} = 100(\hat{b}/\bar{C}_0)$  percent per year; ( $b_L, b_U$ ) and ( $\beta_L, \beta_U$ ) are the approximate 90 percent confidence limits. The column headed, "Is  $\beta > 0$ ?" corresponds to the statistical test of increase in CO concentration at the 5 percent level of significance ( $\alpha$ );  $\bar{C}$  is the average CO concentration during the entire study period which lasted  $n + 2$  months, and  $\bar{C}_0$  is the average concentration at the beginning of the time series selected for analysis. During September and October 1981 no data were obtained because of equipment failure.

Method of analysis	Rate of increase				Is $\beta > 0$ ?	Concentration (ppbv)		
	$\hat{b}$ (ppbv per year)	$(b_L, b_U)$	$\hat{\beta}$ (% per year)	$(\beta_L, \beta_U)$		$\bar{C}$	$\bar{C}_0$	Months of data ( $n$ )
<i>Method 1</i>								
Monthly average data with 12-month smoothing	5	(−,−)	4	(−,−)		131	124	42
Leading mode monthly average data with 12-month smoothing	7	(−,−)	6	(−,−)		119	109	42
<i>Method 2</i>								
Leading mode monthly average data with 12-month cycle subtracted								
Regression analysis	6.5	(2,11)	6	(2,11)	Yes ( $\alpha = 0.05$ )	117	104	34
Analysis by nonparametric statistical methods	7	(2,12)	7	(2,12)	Yes ( $\alpha = 0.05$ )			34
<i>Method 3</i>								
Yearly average	6	(5,8)	5.5	(4,7)	Yes ( $\alpha = 0.05$ )	117	111	36

was automatically analyzed. The standards have been carefully prepared and monitored during the experiment. No systematic drifts of CO concentrations have been found in the standards. A complete description of the experimental design, methods, accuracy, and precision is given elsewhere (5).

Now let us consider how the more than 60,000 individual measurements were statistically and mathematically analyzed. First, we must define what constitutes a measurement of the clean air or background concentration of CO and then apply mathematical methods to remove the large seasonal variations in the clean air CO concentration ( $\pm 50$  percent per year), which mask any small (2 to 4 percent per year) systematic trend that may be present.

We observed that over a month's time the frequency distribution of CO concentration at our remote, clean background site [Cape Meares, Oregon ( $45^\circ\text{N}$ ,  $125^\circ\text{W}$ )] was rarely normal. We assumed that the nonnormal frequency distributions were composed of many probably normal distributions, each reflecting a local source, except the leading mode, which we assume represents the true geophysical background concentration of CO. The leading mode is the one with the lowest mean value; most often this mean value coincided with the modal value of the entire month's distribution. We call this component distribution the leading mode. In other words, this leading mode, of true background concentration, contained more data points than any of the other modes, so that it was distinguished from other modes by this criterion. Figure 1, A and B, shows the typical nonnormal frequency distributions, whereas Fig. 1C shows a seldom observed, almost normal distribution. We analyzed each month's measurements and obtained an average monthly concentration based on the mean of the leading mode. Figure 2A shows the monthly average concentrations of all the data, and Fig. 2B shows the average monthly concentrations of the leading mode. In both cases, the largest variation of CO concentration is a yearly seasonal cycle. Highest concentrations occur in winter and lowest in summer, responding to the expected seasonal variation of OH radicals (1). Although the seasonal variations in CO are of considerable interest, they will not be discussed in detail here. We chose three different methods for removing the effects of the seasonal cycle so as to analyze the data for systematic increases in the CO concentration.

Since we wanted to eliminate all cy-

cles that last a year or integral divisors of 12 months, we calculated moving averages over 12-month periods to obtain smoothed averaged concentrations for month  $T$ ,  $\bar{C}(\Delta, T)$  (7). The average concentrations obtained are shown in Fig. 2, C and D, for monthly averages of all data and the average of the leading mode

data, respectively. The increase in CO is clearly visible in the smoothed data (Fig. 2, C and D), and its magnitude is 4 and 6 percent per year, respectively (Table 1), based on linear least-squares estimates.

The second method for eliminating cycles was to use Fourier series and write the monthly concentrations as  $\bar{C}_i$  (8).

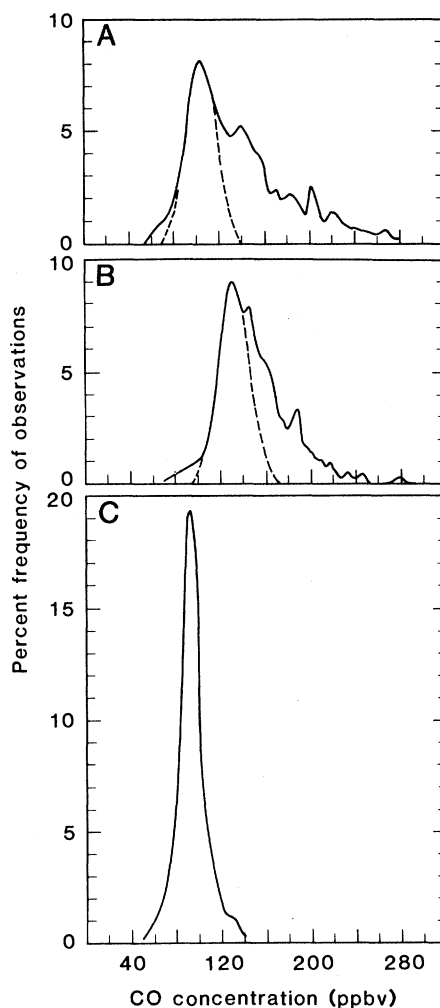
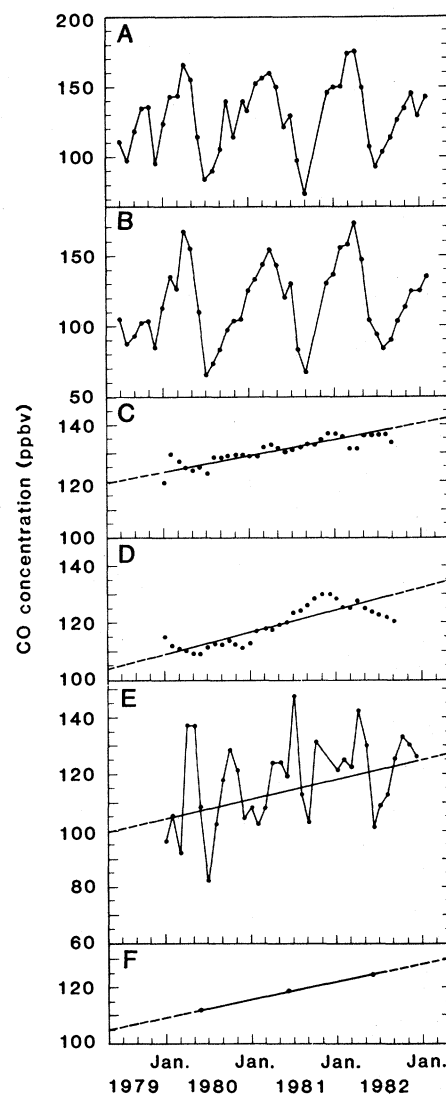


Fig. 1 (left). Typical frequency distributions of CO concentrations at Cape Meares, Oregon: (A) October 1980; (B) February 1981; (C) July 1982. Each figure part is derived from about 1800 observations. A histogram of 5-ppbv intervals is smoothed by connecting the centers of each bar (1 ppbv CO =  $10^{-9}$  molecule of CO per unit volume per molecule of air per unit volume). In (A) less than half the data lie in the first or leading mode; in (B) about half the data are in the first mode; in (C), a less frequently observed type of distribution, nearly all the data lie in the first mode. We interpret the first mode as having an approximately normal distribution and as representing the geophysical background concentration of CO; we interpret the rest as composed of other distributions arising from local anthropogenic and natural sources or long-distance transport of pollution.

Fig. 2 (right). Carbon monoxide concentrations at Cape Meares, Oregon ( $45^\circ\text{N}$ ,  $125^\circ\text{W}$ ). In (A) all the data obtained are represented as monthly average concentrations with 440 to 2200 measurements per month. The standard errors of the monthly mean are less than 2 ppbv. In (B) the monthly average data consisting of only the first mode (as shown in Fig. 1) are plotted. The seasonal cycles become more regular. We interpret these data as geophysical background concentrations. In (C) and (D) the data shown in (A) and (B), respectively, are averaged over successive 12-month periods. Note the change of vertical scale. The calculated 12-month average is plotted in the middle of the averaging period. These plots represent 12-month moving averages, in which seasonal cycles of a year or less disappear. The solid lines are the trends calculated by linear least-squares techniques. In (E) the data of (B) are plotted after the principal 12-month seasonal cycle has been subtracted. The cycle is found by Fourier analysis of the data from January 1979 to December 1980 shown in (B). The solid line is the estimated trend. In (F) average concentrations of CO during 1980, 1981, and 1982 are shown. The averages are plotted in the middle of the appropriate year. During 1979 data were not available for the entire year.



We found that a cycle lasting 12 months was most prominent, although cycles of higher frequencies also exist. We subtracted the principal (12-month) cycle from the data shown in Fig. 2B to obtain

$$\bar{C}_{i*}(T) = \bar{C}_i - C_P \cos\left(\frac{2\pi P}{T} - \theta_P\right)$$

where  $P$  indicates the principal 12-month cycles. The value of  $C_P$  is 34 parts per billion by volume (ppbv),  $\theta_P = 1.5$  radians, and  $P = 3$ . The resulting data  $\bar{C}_{i*}(T)$  are shown in Fig. 2E. Once again, the increasing trend of CO is apparent, and we estimated its magnitude by standard and nonparametric (Theil) statistical analyses (9). The trend for 1980 to 1982 was found to be significantly positive ( $\alpha = 0.05$ ) and about 6 percent per year (Table 1).

Our third method for overcoming the effects of seasonal cycles on long-term trends was to average our data (Fig. 2B) over each of the 3 years (1980, 1981, and 1982). Once again, the results (Fig. 2F) indicate an increase of about 6 percent per year. The three methods used to analyze long-term trends provide results in remarkable agreement with each other.

The full range of environmental effects from increased concentrations of CO is not known; however, CO is believed to control the concentrations of OH radicals in the troposphere. Increased CO may deplete tropospheric OH radicals, thereby reducing the yearly removal of dozens of natural and anthropogenic trace gases. In particular, this effect may add to the increase of CH<sub>4</sub>, which in turn could further reduce OH concentrations (10). Increased CO may indirectly intensify global warming and perturb the stratospheric ozone layer by increasing the lifetimes of trace gases such as CH<sub>4</sub>, CH<sub>3</sub>Cl, CH<sub>3</sub>CCl<sub>3</sub>, and CHClF<sub>2</sub> (F-22).

Carbon monoxide may be included in the group consisting of CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>, all of which have probably been present in the earth's atmosphere for a long time and are now increasing as a result of the rapid rise in the human population over the past century. The natural and anthropogenic emissions of these gases as well as their annual losses may vary from year to year, depending on natural fluctuations in climate and other processes. For long-lived species such as CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O, random fluctuations of sources and sinks do not greatly affect the global concentration since their amounts in the atmosphere at any time far exceed the yearly emissions. The case for short-lived gases such as CO is entirely different. Natural fluctuations of sources and sinks may

greatly affect the CO concentrations from year to year and even from place to place. Although we have extracted the leading mode and proposed that it represents the geophysical background concentration, long-term atmospheric measurements at other remote locations are needed to verify the global nature of the increase. It is difficult to define a firm global rate of increase for CO since it varies considerably from year to year, and it is not possible to unequivocally attribute the entire observed increase to human activities. With a longer span of observations, it should be possible to overcome these difficulties.

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#### References and Notes

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4. Two earlier studies have attempted to extract long-term trends of CO from observed concentrations. T. E. Graedel and J. E. McRae, [*Geophys. Res. Lett.* **7**, 977 (1980)] analyzed urban CO data obtained from Camden, N.J., between 1968 and 1978. A large increase in the CO concentration was suggested; however, firm rates of increase for the background (nonurban troposphere) could not be determined from the

data. L. N. Yurganov of the Institute of Atmospheric Physics, Moscow, sent us a collection of CO measurements made by his group (E. V. Dvoryashina, V. E. Dianov-Klavov, L. N. Yurganov) at Zvenigorod, U.S.S.R., between 1970 and 1982. To our knowledge the complete data and their statistical trend analysis have not yet been published. A preliminary analysis of these data suggested a possible increase of about 2 percent per year.

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6. M. A. K. Khalil and R. A. Rasmussen, *ibid.* **88**, 5131 (1983).
7. Smoothing:

$$\bar{C}(\Delta, T) = \frac{1}{\Delta} \sum_{i=T}^{T+\Delta-1} \bar{C}_i$$

where  $\bar{C}_i$  are the monthly average concentrations during month  $i$ , as shown in Fig. 2, A or B;  $\Delta$  is the interval of averaging, here 12 months;  $T$  is the time in months and ranges from 1 to  $(N - \Delta) + 1$ , where  $N$  is the total time span of data, here 44 months.

8. Fourier series:

$$\bar{C}_i = \bar{C}_0 + b_{t_i} + \sum_{k=1}^{\infty} C_k \cos(\omega_k t_i - \theta_k)$$

where  $\bar{C}_i$  are monthly concentrations,  $\omega_k = 2\pi k/T = 2\pi/\tau_k$ , and  $\theta_k = \arctan(b_k/a_k)$ ,  $C_k = (a_k^2 + b_k^2)^{1/2}$ ,  $t_i = i$ ,  $i = 1, \dots, N$ ;  $T$  is the length of months of the entire database, which for our analysis had to be confined to an integral number of years (January 1980 to December 1982) so that  $T = 36$  months;  $a_k$  and  $b_k$  are the usual Fourier series coefficients.

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11. This work was supported in part by grants from the National Science Foundation (ATM-8109047), the National Aeronautics and Space Administration (NAG1-160), Biospherics Research Corporation, and the Andarz Company.

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## Detectability of Supernova Neutrinos with an Existing Proton Decay Detector

**Abstract.** *The 8000-ton water IMB nucleon decay detector has good sensitivity to the neutrino burst associated with the collapse of stars. It is particularly sensitive to the  $\bar{\nu}_e$  charged current interactions with protons but can also record other neutrino interactions through  $\nu_e$  scattering. Signal, noise, physics objectives, and detector modifications that would enhance burst detection are discussed. The objectives include astrophysical questions about the pulse structure and power. It also may be possible with a distant source to study neutrino masses and neutrino oscillations.*

Although the IMB nucleon decay detector was developed primarily for the study of baryon stability, this detector has features that make it an ideal instrument for other physics studies. For instance, it should be suitable for the observation of neutrinos emitted during the collapse of a massive star to a black hole or neutron star. Our understanding of these phenomena has grown in recent years through the study of astrophysical gamma-ray sources and radio pulsars (1). A large amount of theoretical work has also been done; including work on the effects of the weak neutral current (2) and, more recently, on the possibility of neutrino oscillations (3).

About  $3 \times 10^{53}$  ergs of energy are dissipated in the form of neutrinos during a collapse. This corresponds to the emission of  $3.4 \times 10^{57}$   $\nu_e$  neutrinos and comparable numbers of  $\bar{\nu}_e$ ,  $\nu_\mu$ ,  $\bar{\nu}_\mu$ ,  $\nu_\tau$ , and  $\bar{\nu}_\tau$  neutrinos. These neutrinos have a spectrum and time structure that characterizes their source. The  $\bar{\nu}_e$  spectrum (4) extends from 5 to 20 MeV with a mean energy of 13.3 MeV. The neutrino flux falls as  $1/r^2$ . At a distance of 1 kpc ( $3.1 \times 10^{21}$  cm) from the source the  $\nu_e$  flux is  $2.8 \times 10^{13}$  cm<sup>-2</sup>. The  $\bar{\nu}_e$  flux is  $1.7 \times 10^{13}$  cm<sup>-2</sup>.

Our detector consists of 8000 tons of water. The oxygen in the water is virtually inert to neutrinos of this energy. The