Carbon Monoxide: Residence Time in the Atmosphere

Abstract. A lower limit of 0.1 year for the residence time of carbon monoxide in the atmosphere is derived from radiocarbon measurements. The action of certain microorganisms and atmospheric photochemical reactions are possible mechanisms for the removal of carbon monoxide. This value can be compared with 2.7 years, a value deduced from estimated rates of carbon monoxide production and global measurements of atmospheric concentrations of carbon monoxide.

Carbon monoxide was first reported in 1949 to be a minor constituent of the atmosphere by Migeotte (1), who assigned certain lines in the 4.7-μm region of the solar spectrum to atmospheric carbon monoxide. Bates and Witherspoon (2) estimated that the life of carbon monoxide in the atmosphere is less than 4 years. This estimate was based on a production rate for CO in 1951 of $8 \times 10^{17}$ molecule cm$^{-2}$ year$^{-1}$ (1.9 $\times$ 10$^{14}$ g year$^{-1}$) and a global concentration of 0.1 part per million (the lower of two values observed by Migeotte and Nevin in Switzerland) (3). Although these considerations suggested to them that CO was not accumulating in the atmosphere, they did not feel that the removal mechanism could be identified with certainty at that time.

Of the particular removal mechanisms for CO that they considered, the action of soil bacteria [in particular, Bacillus subtilis (4)] and the observations of Jones and Scott (5) were deemed the most significant, although the data were not suitable for quantitative analysis. Jones and Scott, in studying the disappearance of carbon monoxide from sealed-off mine shafts after a coal mine fire, found that many materials from the mine or its vicinity were capable of removing carbon monoxide from air. A more recent estimate of the lifetime of CO in the atmosphere has been made by Robinson and Robbins (6) who followed the approach of Bates and Witherspoon (2). They estimated the global CO production to be 2.1 $\times$ 10$^{14}$ g year$^{-1}$ in 1966 and the average atmospheric concentration at the 0.1 ppm (based on recent atmospheric measures in remote areas). They derived a residence time for CO of 2.7 years in agreement with the previous estimate. I report here an independent method for estimating the lifetime of CO in the atmosphere that is related to the radiocarbon-dating method.

The radiocarbon-dating method (7) is based on the production of $^{14}$C in the atmosphere by the reaction $^4$He(p,n)$^{14}$C and the subsequent formation of radioactive CO$_2$. Measurements of the $^{14}$C content of samples from the terrestrial biosphere and of contemporary shells, which were independent of latitude and longitude (8), indicated that this radioactive CO$_2$ is uniformly distributed over the surface of the earth. That $^{14}$C was in a steady state in nature was indicated by the fact that the specific activity of $^{14}$C measured in living things agreed with that calculated from the $^{14}$C formation rate and the global carbon inventory (9). The success of this method for dating is well established (10).

However, in proposing the method, Libby assumed that the radioactive $^{14}$C atoms would become CO$_2$ within a few hours after their formation. Subsequently, Pandon et al. (11) studied the chemical fate of $^{14}$C produced in an atomic reactor in the presence of air and found that it was principally fixed as CO. They confirmed this result with $^{14}$C produced in a heavy ion accelerator (12), where the possibility that the radioactive CO might have been produced in the reactor experiment by radiation decomposition was eliminated. Thus, if $^{14}$C is initially fixed as CO, the rate of conversion of radioactive CO to radioactive CO$_2$ provides an independent method for determining the lifetime of CO in the atmosphere. MacKay et al. did, in fact, report measurements of the specific activity of atmospheric CO$_2$ (12) from which the lifetime of CO can be estimated.

In collaboration with L. C. Matsch, they separated three samples of atmospheric CO from liquefied air produced by the Linde Air Products Company in their South Buffalo plant between 21 January and 7 March 1960. The sampling periods comprised 1 to 3 weeks and gave results for the $^{14}$C specific activity of $+9.3$, $-39.3$, and $-27.9$ percent deviation relative to the 95 percent deviation of an oxalic acid sample (National Bureau of Standards) defined as zero age in 1955. The CO content of the air was approximately 0.3 ppm. Although they expected the specific activity of atmospheric CO to

References and Notes

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be much greater than that of CO₂, the data are nevertheless consistent with a relatively short lifetime for CO and with dilution of the radioactive CO by CO produced by combustion. If the radioactive CO is uniformly distributed in the atmosphere like radioactive CO₂, then we can derive the content of radioactive CO in the atmosphere. If we take the average specific activity of the South Buffalo samples to be 12.3 disintegrations min⁻¹ g⁻¹ and the decay constant of ¹⁴C to be 9.6 × 10¹² disintegrations min⁻¹ g⁻¹, the ratio of radioactive CO to stable CO in the samples is 1.3 × 10⁻¹². If we use 0.3 ppm for the atmospheric concentration of radioactive CO for these samples, the global concentration of radioactive CO is then 4 × 10⁻¹² ppm. The mass of the atmosphere is 5 × 10²¹ g, which gives 1 kg for the mass of ¹⁴C in the atmosphere as CO. If we assume that the removal mechanism for CO is in concert with respect to CO and that the radioactive CO in the atmosphere is in a steady state, the effective rate constant for the removal of radioactive CO is then 3 × 10⁻⁷ sec⁻¹ (the rate of formation of ¹⁴C is 1.3 × 10¹⁹ atom sec⁻¹) (9). The lifetime of CO in the atmosphere is then 3 × 10⁶ seconds or 0.1 year.

This value is probably too low, because radioactive CO, which is principally produced in the stratosphere, may be converted to radioactive CO₂ in significant amounts before it mixes into the troposphere. The same process would have a much smaller effect on the CO produced by combustion on the earth's surface because in that case the total removal would be limited by mass transport up to the larger quantity of CO from the troposphere to the stratosphere. A likely process for the conversion to CO to CO₂ in the stratosphere is the reaction (2)

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \]

The same reaction could be an effective mechanism for the removal of CO in the troposphere, but Bates and Witherspoon did not consider it likely. If we assume that CO is in a steady state at a concentration of 0.1 ppm in the atmosphere, we can calculate the concentration of OH required to maintain the steady state from

\[ [\text{OH}] = \frac{P}{k[\text{CO}]} \]

where P is the rate of CO production (3.5 × 10¹⁴ molecule cm⁻³ sec⁻¹) derived from Robinson and Robbins's estimate (6) of 2.1 × 10¹⁴ g year⁻¹ and an atmospheric volume of 4.1 × 10²⁴ cm³, and k is the second-order rate constant, 2 × 10⁻¹³ cm³ molecule⁻¹ sec⁻¹ (13). The concentration of OH required to maintain CO at a concentration of 0.1 ppm is then 7 × 10¹⁴ molecule cm⁻³. This is not unreasonably high but could only be realized by a regenerative chain mechanism for OH because of the large amount of CO involved. The following steps coupled with the previous reaction is one possibility:

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]

and

\[ \text{H} + \text{HO}_2 \rightarrow 2\text{OH} \]

Thus consideration of the data on radioactive carbon provides additional support for a short lifetime for CO in the atmosphere. This should help to dispel further the concern that CO is accumulating in the atmosphere and represents a longtime hazard to human health. A quantitative assessment of the CO removal processes remains to be worked out, but the action of certain microorganisms and of photochemical processes offer reasonable, possible explanations.

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References and Notes
8. ibid., p. 15.
9. ibid., p. 7.
10. F. Johnson, ibid., chap, 7.
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Spectrographic Detection of Topographic Features on Mars

Abstract. Observations of the martian carbon dioxide band at 1.05 microns made with a three-channel multislit spectrophotometer indicate gross height variations in the vicinity of Syrtis Major and surrounding desert regions. Syrtis Major appears to be very high with essentially no detectable carbon dioxide above it. The data appear to confirm local trends and, in magnitude at least, the large variations of height found in earlier radar observations. A one-to-one correlation of height with albedo is not evident in the results. Elevated areas are found in both desert and dark regions. In several regions dark areas are associated with relatively steep slopes.

The question of the relative altitudes of the dark and bright areas on Mars has been hotly debated in recent years. Traditionally the dark areas are considered to be lowlands. This view is based mainly on the idea that they would be warmer and therefore more likely to support the life forms that were thought responsible for the remarkable regenerative property of the dark areas (1). This supposition received some support when the dark areas were in fact generally found to be some 8°K warmer than the bright regions. Others (2) have shown that the temperature variations have little to do with height differences. They assert that temperature is more closely connected with the local surface albedo. They propose that the regenerative property is a purely mechanical, wind-driven phenomenon and have concluded that the dark areas are probably higher than the bright deserts. Some quantitative evidence for this view has been provided by early radar data (3) as well as by certain observations of cloud phenomena (4). More recently, radar mapping (5) along a narrow belt at 23°N latitude has indicated very large height variations of some 12 km. However, there does not appear to be any obvious correlation between the radar height contour and albedo changes.

We have devised a three-channel, multislit photometer which, together with the 13.4-m spectrometer of the McMath Solar Telescope of Kitt Peak National Observatory, is capable of de-