

The Stratosphere as a Chemical Sink for Carbon Monoxide

JEROME PRESSMAN AND PETER WARNECK

GCA Corporation, Bedford, Mass.

(Manuscript received 27 June 1969, in revised form 5 September 1969)

ABSTRACT

Past and recent data on atmospheric CO levels indicate no significant increase of average concentrations—despite the increasing anthropogenic emission rate—so that one or more natural sinks for CO seem to be operative. It is shown that the stratosphere provides a sink for CO on account of the reaction $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$. The radical OH is produced photochemically in a moist ozonosphere with a time constant several orders of magnitude less than that of the CO oxidation reaction, so that almost all the CO entering the stratosphere will be destroyed. The rate limiting factor is the transport of CO rich air through the tropopause. To determine the significance of the stratosphere sink, two theoretical models for the tropospheric CO behavior are considered. Although the theory provides several constraints for the rate of CO removal from the atmosphere, it is found that the uncertainties concerning measurements and source functions preclude the derivation of a reliable value for the total CO removal rate. An estimate indicates that the stratospheric sink contributes significantly, but only partially, to the overall removal of CO from the atmosphere.

1. Introduction

The increasing concern over the current high rate of carbon monoxide emission into the atmosphere—mainly from automobile exhaust—has stimulated a search for the natural processes that are effective in removing CO from the atmosphere. In the absence of such processes, an accumulation of CO clearly should occur. A current estimate for the yearly global CO emission rate is 200 million tons, corresponding to an atmospheric CO concentration increase of 0.05 ppm per year unless a portion of the carbon monoxide is scavenged. A variety of measurements performed over the past 20 years at locations remote from direct urban pollution have shown considerable short-time fluctuations of CO concentrations, but the average concentration levels seem to have remained essentially constant (see Table 1). Thus, it appears that one or more atmospheric CO removal processes are operative.

Jaffe (1968) has recently reviewed the fate of CO in the atmosphere and has discussed conceivable CO removal reactions. One of the processes considered by him is oxidation by OH radicals. We have independently considered this possibility and have found that it is effective in the lower stratosphere, where OH is formed photochemically. Very recent CO measurements by Seiler and Junge (1969) above and below the troposphere indeed show a drastic decrease of the CO concentration in the stratosphere, in accord with the theoretical prediction.

The discussion of stratospheric CO removal requires a variety of background information which is summarized in the next section. Subsequently, the significance of the stratosphere as a sink for CO is demon-

strated. Finally, two theoretical models are considered to determine the compatibility of the stratospheric CO removal rate with the measured atmospheric CO concentrations. It is concluded that if the CO production is essentially anthropogenic in origin, the stratospheric sink would provide a sizable contribution to the overall removal rate of CO from the atmosphere.

2. CO measurements, sources, and transport to the stratosphere

This section serves to summarize data needed later for a determination of the effectiveness of stratospheric CO removal. The required information includes the average CO concentration levels, the CO production rate, as well as the rate of transport of air from the troposphere to the stratosphere.

Isolated measurements of CO concentrations in the atmosphere have been made since 1949 when Migeotte first detected the CO 4.7 μ band in the solar spectrum, but only recently have measurements been carried out systematically. Table 1 presents a summary of all the observations of which we know to date. The recent observers attempted to avoid areas of urban pollution, so that the newer data represent atmospheric background concentrations. This conclusion is supported by the similarity of the CO concentration values observed over the continents and the Pacific ocean. The CO concentrations vary considerably with the wind direction, most likely because the sources are mainly in the cities and distribution must occur by advective motion of air. The majority of the data were obtained in the Northern Hemisphere, but Robinson and Robbins (1969b) also measured CO concentrations in the Southern Pacific

TABLE 1. Atmospheric CO concentration measurements.

| Observer | Location | Year | Concentration (ppm) |
|-------------------------------|---------------------------------|---------|--|
| Benesch <i>et al.</i> (1953) | Jungfrauoch | 1950-51 | 0.031-0.14 |
| Locke and Herzberg (1953) | Ottawa | 1952 | 0.11-0.22 |
| | Ohio | | 0.19 |
| | Jungfrauoch | | 0.15 |
| | Mt. Wilson | | 0.16 |
| Shaw (1958) | Columbus, O. | 1952-53 | 0.13 |
| Shaw (1959) | Columbus, O. | 1959 | 0.04-2.2, average 0.11 |
| Robbins <i>et al.</i> (1968) | Camp Century, Greenland | 1965 | 0.24-0.90 |
| | North coast, Calif. | 1965 | 0.8 |
| | Crater Lake, Ore. | 1965 | 0.03-0.3 |
| | Patrick Pt., Calif. | 1965 | 0.04-0.8 |
| Robinson and Robbins (1968) | North Pacific | 1967 | 0.03-0.8 |
| Cavanagh <i>et al.</i> (1969) | Pt. Barrow, Alaska | 1967 | 0.06-0.12, average 0.10 |
| Robinson and Robbins (1969a) | Inge Lehmann Station, Greenland | 1967 | 0.05-0.7 0.11 background average |
| Robinson and Robbins (1969b) | Southern Pacific | 1968 | 0.06 (variable) |

Note: The first four entries were taken from Junge (1963a).

and found them lower than in the Northern Hemisphere. Clearly, the data in Table 1 do not indicate the average CO concentration in the troposphere because they do not include the polluted areas. However, since the oceans cover 70% of the earth's surface and since, in addition, the CO sources are concentrated on the northern continents, a value of 0.15 ppm appears to provide a reasonable estimate for the average CO concentration.

The major source of CO emitted from fossil fuel combustion is derived from gasoline-powered motor vehicles. A much smaller portion of CO production stems from coal combustion, industrial operations, furnaces, etc. The contribution from natural sources is uncertain, although several exist (Jaffe, 1968; Robinson and Robbins, 1969b). Since 1945, the number of automobiles has increased almost linearly with time, so that CO emission rates have been continually revised. The early estimate of Bates and Witherspoon (1952) was 120×10^6 tons per year for the total emission. A 1962 report of the U. S. Department of Health, Education and Welfare (Terry, 1962) estimated the rate of CO emission from automobile exhaust in the United States alone as 90×10^6 tons per year. Jaffe (1968) in a careful analysis of all man-made sources for the year 1966 derived at a similar value, 88×10^6 tons per year in the United States. His estimate for the global total CO emission is 200 million tons per year. More recently, Robinson and Robbins (1969b) revised that estimate to 257×10^6 tons per year of which 75% is due to automobile exhaust emission. This value still excludes the contribution of conceivable natural sources. To obtain an estimate of the source function, the yearly emission rate must be combined with the variation of the automobile popula-

tion. During the 15-year period, 1945-60, the number of cars on the road increased by a factor of 2 (Barr, 1967) and is still increasing approximately linearly, whereas before 1945 it remained essentially constant for a comparable time period. Therefore, one can approximate the source function of worldwide CO production by $P = P_0(1 + \alpha t)$, where 82×10^6 tons per year corresponds to a fractional global concentration increase per year of $P_0 = 2.0 \times 10^{-8}$, $\alpha = 0.074$, and $t = 0$ for the year 1945. The projected production rate for the year 1952 then is 120×10^6 tons per year, in accord with the estimate by Bates and Witherspoon (1952), that for 1966 is 200×10^6 tons per year in accord with the estimate by Jaffe (1968), and that for 1969 is 218×10^6 tons per year [only slightly below the corresponding estimate of Robinson and Robbins (1969b)]. If it is considered that the production of CO occurs predominantly in the Northern Hemisphere, the source function is slightly different. We shall assume that for the Northern Hemisphere $P_N = P_{N_0}(1 + at)$, with $P_{N_0} = 1 \times 10^{-8}$ per year and $a = 2\alpha = 0.148$ per year. In the Southern Hemisphere, the production rate is taken as constant, $P_{S_0} = P_{N_0}$.

The effectiveness of the stratosphere as a chemical sink for CO depends to a large extent upon the rate at which CO can be transported into the stratosphere. The exchange of air between the troposphere and the stratosphere is limited by the tropopause layer which acts as a barrier to convective transport. A considerable volume of research has been devoted to the problem of stratosphere-tropospheric interchange, motivated by the need for quantifying the rate of radioactive fallout from the stratosphere, for understanding the variation in the tropospheric concentration of ozone and the

stratospheric concentration of water, and for understanding the general meteorological problem of atmospheric circulation. A variety of tracers, both natural and man-made, have been utilized to determine the rate of exchange between the stratosphere and the troposphere. Progress prior to 1963, as summarized in several reviews (Junge, 1963a, b; Sheppard, 1963; Kellogg, 1964; Newell, 1963), led to the following approximate time constants: 1) Mixing in the troposphere, in a given hemisphere, is relatively fast and occurs within a few weeks. 2) The exchange between the northern and southern tropospheres is slower, requiring about one year. 3) The storage time of air in the lower stratosphere, below 20 km, with which we are concerned here, is 1–2 years. 4) Mixing within a hemisphere is of the same order of magnitude, but air exchange between the northern and southern stratosphere is again slower, taking ~ 5 years.

More recently, additional measurements and refined data analyses have specified the transport coefficients and residence times more quantitatively (see Table 2). In addition, the transport mechanism of air within the stratosphere and across the tropopause has been detailed. The earlier model of meridional circulation by Brewer (1949) and Dobson (1956) has been modified to include large-scale quasi-horizontal eddy diffusion, and the latter has been shown to predominate in the overall transport process (Freely and Spar, 1960; Newell, 1961, 1963; Reed and German, 1965). It has also been established that transfer through the tropopause depends on the latitude (Martell, 1968; Gudiksen *et al.*, 1968; Fabian *et al.*, 1968). It is greatest at middle latitudes (40–50°) and appears to be connected with the tropopause discontinuity and concomitant jet stream occurring in that region (Reiter *et al.*, 1967; Danielsen, 1968; Smith, 1968).

Table 2 summarizes the results of recent tracer studies in terms of the time constants associated with the transfer of air between the various atmospheric reservoirs, where τ_{ST} is the time constant for the transfer from the stratosphere to the troposphere, τ_{SS} that for exchange between the northern and southern stratospheres, and τ_{TT} that for the exchange between the two

tropospheres. The first of these is the most significant value for the purpose of the present study. The recent results provide quite consistent values for the residence time of air in the stratosphere. The average is $\tau_{ST} = 1.5 \pm 0.5$ year. To derive from this value the average flux of air through the tropopause requires some assumptions concerning the depth of the stratosphere and the location of the tropopause. Since the exchange occurs predominantly at middle latitudes, it seems appropriate to base the estimate on the tabulation of the U. S. Standard Atmosphere (1962). Thus, the tropopause is assumed to occur at 11 km, and the corresponding pressure and temperature are 227 mb and 217K, respectively. The total number of molecules per cm^2 column, residing in the altitude range 11–20 km, is $N_S = 3.61 \times 10^{24}$, while that in the troposphere below 11 km is $N_T = 1.66 \times 10^{25}$. On the basis of these quantities, the rate of stratospheric air entering the troposphere through the tropopause is found to be $\sigma = 7.8 \times 10^{16}$ molecules $\text{cm}^{-2} \text{sec}^{-1}$. This flux must be balanced by a similar flux from the troposphere to the stratosphere. The magnitude of this derived flux is smaller than, but still within the same order of magnitude as, the flux derived by Junge (1962) from the seepage of ozone into the troposphere.

As noted above, the derived exchange rate is based entirely on observations of transfer of air from the stratosphere to the troposphere. Studies of the reverse process are not as numerous but from meteorological case studies, tracking individual parcels of air near the tropopause in the vicinity of the jet stream, estimates for the transfer rate have become available. Reiter *et al.* (1967) concluded that per hour 3×10^{16} gm of air flowed through the tropopause into the stratosphere, corresponding to an average flux of $\sigma = 3.5 \times 10^{16}$ molecules $\text{cm}^{-2} \text{sec}^{-1}$. Smith (1968), using tritium as a tracer in conjunction with moisture flux data, derived an air flux of 4.4×10^{20} gm month^{-1} leaving the troposphere, corresponding to an exchange rate of $\sigma = 6 \times 10^{17}$ molecules $\text{cm}^{-2} \text{sec}^{-1}$. This value undoubtedly is too high because it would lead to a stratospheric residence time of only about two months, but it is of interest that Smith found an exact balance of inflow and outflow through the

TABLE 2. Comparison of exchange times (years) for atmospheric reservoirs*.

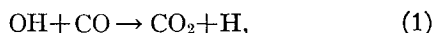
| Investigator | Tracer | τ_{ST} | τ_{SS} | τ_{TT} |
|-------------------------------|--|----------------------|---------------|---------------|
| Lal and Rama (1966) | C ¹⁴ | 0.8 \pm 0.3 0.2 | | 1.2 |
| Feely <i>et al.</i> (1966) | C ¹⁴ Sr ⁹⁰ | 2.2 1.2 | | |
| Nydal (1967) | C ¹⁴ | 3.5 \pm 0.8 | 3–5 | 0.5 \pm 0.2 |
| Peirson and Cambray (1967) | Ce ¹⁴⁴ , Cs ¹³⁷ , Sr ⁹⁰ | 1.37 \pm 0.05 | 3.5 \pm 1.0 | |
| Young and Fairhall (1968) | C ¹⁴ | 1.5 | | |
| Gudiksen <i>et al.</i> (1968) | W ¹⁸⁵ | 1.2 \pm 0.5 | | |
| Fabian <i>et al.</i> (1968) | Sr ⁹⁰ | 1.56 \pm 0.13 | 3.3 \pm 0.3 | |
| Nydal (1968) | C ¹⁴ | 2.0 \pm 0.5 | 5.0 \pm 1.5 | 1.0 \pm 0.2 |

* τ_{ST} , transfer from the stratosphere to the troposphere; τ_{SS} , transfer between the northern and southern stratospheres; τ_{TT} , transfer between the northern and southern tropospheres.

tropopause. Thus, these estimates can serve to substantiate the exchange rate $\sigma = 7.8 \times 10^{16}$ molecules $\text{cm}^{-2} \text{sec}^{-1}$ derived above from the transfer of air from the stratosphere to the troposphere.

3. The stratosphere as a chemical sink for CO

The most abundant chemically active entity in the stratosphere is ozone. Although laboratory experiments have shown that ozone oxidizes CO (Hartek and Dondes, 1957), the reaction is very slow and it is doubtful whether a direct bimolecular reaction is involved. Rather, it appears that the oxidation is caused by oxygen atoms generated by the O_2 thermal decomposition. If a direct CO oxidation by ozone were effective in the atmosphere, it should also occur in the troposphere due to the considerable seepage of ozone downward through the tropopause. However, Seiler and Junge (1969) have found that the CO mixing ratios below the tropopause are similar to those near the ground, whereas above the tropopause they decrease rapidly. Thus, the reaction with ozone seems negligible. In the stratosphere, oxidation of CO by ozone will also be assumed negligible because of the effectiveness of another oxidation reaction



which can consume essentially all the CO entering the stratosphere. This reaction will now be discussed.

The presence of OH radicals in the ozonosphere results from the interaction of photochemically generated, excited oxygen atoms with water vapor. The effects of moisture upon the ozonospheric photochemistry has been studied recently by Hunt (1966) and by Leovy (1969). The photochemical mechanism is complex and involves a variety of species which could conceivably react with CO. However, only reaction (1) will be considered here because OH appears to be the most efficient CO oxidant. Reaction (1) is relatively fast. At 217K, the temperature prevailing in the lower stratosphere, the rate coefficient is $k_1 = 1 \times 10^{-13}$ $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ (Schofield, 1967). Nevertheless, the rate of destruction of OH radicals by (1) is estimated to be less than that due to other reactions in the photochemical mechanism, so that the OH concentrations are not greatly perturbed. The H atoms produced in

TABLE 3. Number densities for OH (after Leovy), total number densities (U. S. Standard Atmosphere), and their products for the low stratosphere.

| Altitude (km) | n_{OH} (10^6 molecules cm^{-3}) | n (10^{18} molecules cm^{-3}) | $n_{\text{OH}} \times n$ (10^{24} molecules ² cm^{-6}) |
|---------------|---|--|--|
| 11.0 | 0.60 | 7.60 | 4.56 |
| 12.5 | 0.80 | 6.00 | 4.80 |
| 15.0 | 1.20 | 4.06 | 4.88 |
| 17.5 | 1.80 | 2.74 | 4.92 |
| 20.0 | 2.60 | 1.85 | 4.82 |

(1) are very rapidly ($\sim 10^{-4}$ sec) converted to HO_2 by attachment to oxygen. Leovy (1969) has shown that the ratio of OH and HO_2 radical concentrations adjusts to a steady state within less than $\tau = 100$ sec. The supply rate of OH then is $\bar{n}_{\text{OH}} \Delta z / \tau \geq 10^6 \times 9 \times 10^5 / 10^2 \geq 9 \times 10^9$ molecules $\text{cm}^{-2} \text{sec}^{-1}$, where \bar{n}_{OH} is the approximate average OH concentration in the altitude region $\Delta z = 9$ km above the tropopause. This supply rate is greater than the rate of transport of CO into the stratosphere from the troposphere (unless the fractional CO concentration in the troposphere exceeds 0.12 ppm), so that an adequate supply of OH radicals for the oxidation of CO in the stratosphere is provided. If it is assumed that reaction (1) is the predominant CO loss reaction, the average fractional concentration of CO in the stratosphere, f^* , is governed by

$$\frac{df^*}{dt} = \left[-\frac{1}{2} k_1 f^* \left(\int_{\text{strat}} n_{\text{OH}} n dz \right) / N_S \right] + \left(\frac{\sigma}{N_S} \right) (f - f^*). \quad (2)$$

Here, n_{OH} is the number density of OH, n the total number density, both being functions of the altitude z , $N_S = \int_{\text{strat}} n dz$ is the total square centimeter column count of the number density in the stratosphere, f the fractional CO concentration in the troposphere, and $\sigma = 7.8 \times 10^{16}$ molecules $\text{cm}^{-2} \text{sec}^{-1}$ is the atmospheric flux entering the stratosphere through the tropopause. The factor $\frac{1}{2}$ in the second term takes into account that photochemical OH generation occurs only during the day and that at night the OH concentration reduces substantially. The integration is performed over the 11–20 km altitude domain, so that $N_S = 3.6 \times 10^{24}$ molecules cm^{-2} . Steady-state concentrations of OH were calculated by Leovy (1969) and by Hunt (1966) only at altitudes > 15 km. For the lower altitude regime, we have applied an extrapolation to the published data. The number densities employed in the evaluation of the integral and their products are shown in Table 3 for several altitudes. The product of the two number densities is essentially constant $n_{\text{OH}} \times n = 4.8 \times 10^{24}$, so that the computation of the integral is facilitated. The time constant for the depletion of CO is

$$\tau_r = 2N_S / \left(k_1 \int_{\text{strat}} n_{\text{OH}} n dz \right) = 1.7 \times 10^7 \text{ sec},$$

or about a half-year. Since the time constant of the reaction is of the same order as the time required for vertical mixing of air in the lower stratosphere, a reasonably uniform CO mixing ratio will be established and a balance is achieved between the consumption of CO and its supply through the tropopause. Thus, $df^*/dt = 0$, and the ratio of the CO concentration in the stratosphere to that in the troposphere is

$$\frac{f^*}{f} = (\sigma / N_S) / \left(\frac{1}{\tau_r} + \frac{\sigma}{N_S} \right) = 0.26.$$

The net flux of CO into the stratosphere is given by

$$\sigma(\text{CO}) = \sigma f \left(1 - \frac{f^*}{f} \right) = 5.8 \times 10^{16} f$$

[molecules cm⁻² sec⁻¹]. (3)

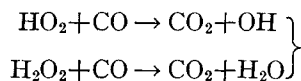
To determine the significance of this process, it may be assumed that it provides the only CO sink in the atmosphere. If CO production and losses have achieved a steady state, and if the CO production rate is $P = 2 \times 10^8$ tons per year = 2.7×10^{10} molecules cm⁻² sec⁻¹ (Jaffe, 1968), one obtains for the tropospheric CO concentration

$$f = \frac{P}{\sigma} / \left(1 - \frac{f^*}{f} \right) = 4.7 \times 10^{-7}.$$

Comparison of this value, 0.47 ppm, with the measured tropospheric CO concentrations (Table 1) shows that the calculated CO concentration is 2-3 times greater than the observed concentration averages. Nevertheless, the similarity of magnitude indicates that the stratospheric CO removal medium discussed here provides a significant sink for CO. Since the assumption of a steady-state CO concentration in the troposphere probably is unrealistic in view of the increase of the CO emission with time, the stratosphere may be even more effective as a CO sink than the above calculation indicates. This problem will be pursued further in the next section.

The ratios of CO concentration in the stratosphere to that in the troposphere observed by Seiler and Junge (1969) are, on the average, smaller than the value $f^*/f = 0.26$ derived here, indicating a more efficient CO consumption in the stratosphere than Eq. (2) and Table 3 imply. The difference may be due to an inadequate photochemical theory, to the influence of circulation in the lower stratosphere which would increase the OH concentrations, or to additional reactions oxidizing CO. Some of the reaction rate coefficients employed by Leovy (1969) and Hunt (1966) require revision due to recent laboratory data. Two of the most important reaction rates [for O(¹D) with nitrogen and water vapor] have changed by more than an order of magnitude, but their ratio has changed by only a factor of 2. Since in the model the equilibrium OH concentration is proportional to the $\frac{1}{3}$ power of the ratio of rate coefficients, the changes of values causes a negligible effect. Snelling and Hampson (1969) have reviewed such factors critically, and have concluded that below 40 km, the calculations of Leovy provide an adequate description of the atmospheric photochemistry. No assessment appears to have yet been made of the downward transport of OH into the lower stratosphere, but the increase of OH concentration due to this effect would not be sizable. On the other hand, moist ozone photochemistry predicts the presence of species other than OH which may oxidize CO. For example, HO₂

radicals and H₂O₂ are predicted with concentrations orders of magnitude greater than that of OH. The reactions.



are conceivable but no information is available at present on their rates.

While these factors are important in describing the details of CO oxidation in the stratosphere, it has been shown here that the OH+CO reaction consumes most of the carbon monoxide entering the stratosphere. Hence, the uncertainty of the size of the stratospheric CO sink is determined more by the uncertainty in the transport of air across the tropopause than by additional reactions in the stratosphere. In the following discussion the estimate given by Eq. (3) will be employed.

4. Models for the behavior of CO in the atmosphere

If it is true that the sources of CO are mainly man-made, carbon monoxide may provide a useful atmospheric tracer. Obviously, the determination of the vertical CO concentration profile in the lower stratosphere would furnish information on the rate of CO removal above the tropopause. If such measurements verify that the stratosphere is a sizable sink for CO, and if the mechanism of CO removal can be detailed, CO as a tracer would enable the determination of the flux of air entering the stratosphere through the tropopause.

Two other aspects of atmospheric CO result from the time dependence of the anthropogenic source function and from the fact that the sources are located mainly in the Northern Hemisphere. Hence, if it is correct to assume that the anthropogenic sources predominate over other, natural sources, measurements of atmospheric CO concentrations in both hemispheres over an extended period of time should provide information concerning the source function, the inter-hemispheric transport, as well as the overall rate of CO removal from the troposphere. With the required field data slowly becoming available, it is of interest to consider theoretical models and to determine their compatibility with the measurements. Two such models are discussed below.

a. Model 1

The first model assumes that the exchange of air between the two hemispheres is much more rapid than the removal of CO from each hemisphere by any first-order destruction mechanism. Then the two hemispheres can be treated as one reservoir. For example, this model is applicable if the stratosphere is the major sink and the removal rate is of the magnitude derived in the preceding section. For this case, the CO residence

time in the troposphere is 9 years, i.e., much longer than the time for interhemispherical air exchange which is about 1 year (Table 2). The time variation of the fractional CO concentration in the troposphere is determined by

$$df/dt = -K_S f + P(t), \quad (4)$$

where $P(t)$ is the source function and K_S the rate coefficient for CO removal which is equal to the inverse residence time of CO in the troposphere. For the stratosphere as the sink one obtains.

$$K_S = 3.15 \times 10^7 \left[\frac{\sigma(1-f^*/f)}{N_T} \right] = 0.11 \text{ per year}$$

from Eq. (3) using 3.15×10^7 sec per year. Since it appears that the anthropogenic CO production was reasonably constant until 1945, and then increased linearly, it will be assumed that $P = P_0(1 + \alpha t)$ and that at $t=0$ the CO concentration is that of the steady-state value $f_0 = P_0/K_S$. For these conditions, the solutions to (4) is

$$\frac{f}{f_0} = 1 + \alpha t - \left(\frac{\alpha}{K_S} \right) [1 - \exp(-K_S t)]. \quad (5)$$

Owing to the presently inadequate knowledge of P_0 and K_S , it is preferred to investigate the behavior of f/f_0 rather than f directly. Note that f/f_0 increases with increasing K_S whereas f decreases. Using for α the value of 0.074 per year (Section 2), the increase of the CO concentration as a function of time is that shown in Fig. 1. After an induction period depending on K_S , the CO concentration rises linearly with time. The induction period increases with decreasing K_S , so that a small CO removal rate lessens the impact of an in-

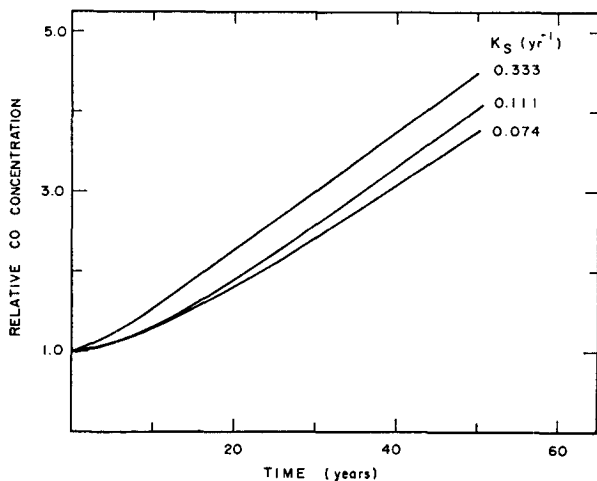


FIG. 1. Relative CO concentration, f/f_0 , as a function of time for a linearly increasing CO production rate, and different CO removal rates K_S . Interhemispherical exchange is assumed to be rapid.

crease in the CO production rate. For $K_S = 0.11$, corresponding to the stratospheric sink considered above, the CO concentration increases by a factor of 2 after 22 years, whereas for $K_S = 0.33$, the CO concentration increases by a factor of 2.5 during about the same period of time. Comparison with the data shown in Table 1 indicates that the uncertainty in the measurements is of the similar magnitude as the predicted increase in concentration, so that at the present time the validity of this model cannot be evaluated.

A modification of the above model results when the seasonal variation of the exchange of air between the troposphere and the stratosphere is taken into consideration in a manner similar to that used by Junge and Czeplak (1968) in their estimation of the seasonal injection of ozone into the troposphere. However, a detailed treatment of the modified model will not be given here, because sample calculations indicated that the effect of the seasonal variation upon the tropospheric CO concentration is almost negligible. The reason for the small influence is that since the fraction of the tropospheric air involved in the exchange is much smaller than the fraction of stratospheric air, the amplitude of the resulting CO fluctuation is only a few per cent of the total tropospheric CO concentration, too small to be detectable by present measurement techniques.

b. Model 2

The second model to be discussed here takes into account the restricted exchange of air between the two hemispheres. Again the nature of the CO removal mechanism is left unspecified, except that it is assumed to be a first-order process. It is further assumed that the time-dependent source is located in the Northern Hemisphere and that the CO removal rate is the same in both hemispheres. This model is described by the coupled equations

$$\frac{d}{dt} f_N = -K_S f_N - K_T (f_N - f_S) + P_N(t), \quad (6a)$$

$$\frac{d}{dt} f_S = -K_S f_S + K_T (f_N - f_S) + P_S(t), \quad (6b)$$

where f_N and f_S are the fractional concentrations of CO in the northern and the southern troposphere, respectively, K_S the rate coefficient for CO removal in each hemisphere, $K_T = 1/\tau_{TT}$ is the coefficient for exchange of air between the hemispheres, and P_N and P_S the source functions for the Northern and Southern Hemisphere, respectively. Similar to the first model, the production rate in the north is taken to be a linear function of time, $P_N = P_{N_0}(1 + \alpha t)$, with $\alpha = 2\alpha$, but the source function for the south is assumed to be constant $P_S = P_{S_0} = P_{N_0}$. If the initial CO concentrations are set equal to the steady-state value $f_0 = f_{N_0} = f_{S_0}$

= P_{N_0}/K_S , the solutions to the Eqs. (6) are

$$\frac{f_N}{f_0} = 1 + \frac{a}{2(K_S + 2K_T)} \left[2(K_S + K_T)t - \left(\frac{K_S + 2K_T}{K_S} \right) [1 - \exp(-K_S t)] - \left(\frac{K_S}{K_S + 2K_T} \right) \{1 - \exp[-(K_S + 2K_T)t]\} \right], \quad (7a)$$

$$\frac{f_S}{f_0} = 1 + \frac{a}{2(K_S + 2K_T)} \left[2K_T t - \left(\frac{K_S + 2K_T}{K_S} \right) [1 - \exp(-K_S t)] + \left(\frac{K_S}{K_S + 2K_T} \right) \{1 - \exp[-(K_S + 2K_T)t]\} \right]. \quad (7b)$$

The time dependence of the CO concentration in the two hemispheres is rather similar to that of the simpler first model. In fact, the first model provides the average CO concentration, $(f_N + f_S)/2f_0$, for the Northern and Southern Hemispheres combined. In the Northern Hemisphere, the CO concentration increases faster than the average, whereas in the Southern Hemisphere the increase is less than the average. The extent to which the CO increase deviates from the average depends on K_S (and on K_T). Fig. 2 shows, for two values of K_S , that the effect of increasing K_S is to increase the rate at which the CO concentration rises in the Northern Hemisphere, with a corresponding decrease of the rate in the Southern Hemisphere. Again the range of value for K_S which is compatible with the CO measurements is limited due to the failure to observe a significant increase of the CO concentration in the Northern Hemisphere, during the past 20 years (Table 1). Apparently, the effective CO sink cannot be greater than $K_S = 1.0$; otherwise, the change in the CO concentration predicted by the model should be detectable.

Another constraint is given by the ratio, f_N/f_S , of the CO concentration in the north to that in the south. After long times, the ratio approaches the value

$$\left(\frac{f_N}{f_S} \right)_{t \rightarrow \infty} = \frac{K_S + K_T}{K_T}, \quad (8)$$

i.e., $f_N/f_S = 1.33$ for $K_S = 0.33$ and $K_T = 1.0$, and $f_N/f_S = 2.0$ for $K_S = K_T = 1.0$, respectively. These values, however, are reached only very slowly, as Fig. 2 shows. After 20 years, the corresponding ratios are, approximately, $f_N/f_S = 1.20$ and $f_N/f_S = 1.50$, respectively.

The data of Robinson and Robbins (1969b) indicate that the CO concentration in the Southern Hemisphere

is indeed lower than that in the Northern. The limited number of observations available at the present time favor a ratio of average CO concentrations of about $f_N/f_S = 2$. On the basis of the foregoing discussion, this large a ratio would require $K_S > 1.0$ which is not consistent with the value $K_S \leq 1.0$ derived above from the time-dependence of the source function. However, if a smaller K_T is chosen, the discrepancy can be alleviated.

The absolute size of the effective CO sink can be estimated from the absolute value of the average atmospheric CO concentration. The simplest way to evaluate K_S in this manner would be to use the relationship, $f_0 = P_0/K_S$, which holds for $t = 0$, but the lack of reliable measurements at that time makes the value for f_0 extremely uncertain. Instead, it is more appropriate to apply (7a) in the approximation

$$f_N = \frac{P_{N_0}}{K_S} \left[1 + \left(\frac{K_S + K_T}{K_S + 2K_T} \right) at - \frac{a}{2K_S} - \frac{K_S a}{2(K_S + 2K_T)^2} \right] \quad (9)$$

with $t = 22$ years, and to insert for f_N the 1967 CO measurement average at remote locations, $f_N = 1.0 \times 10^{-7}$ (Cavanagh *et al.*, 1969; Robinson and Robbins, 1969a).

Then, with $K_T = 1.0$ per year it is found that $K_S = 0.25$ per year. Although this value cannot be considered reliable and probably is accurate only within a factor of 2 owing to the existing uncertainties in the measurements and the source function, it lies well within the range of K_S values consistent with the constraint pro-

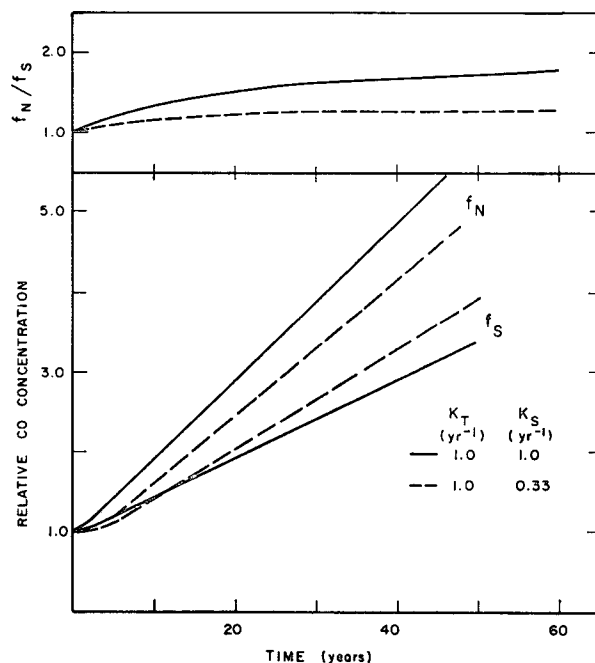


FIG. 2. Relative CO concentrations in the Northern Hemisphere, f_N/f_0 , and in the Southern Hemisphere, f_S/f_0 , and their ratio, f_N/f_S as a function of time for a linearly increasing production rate of CO in the Northern Hemisphere, taking interhemispherical exchange into account.

vided by the predicted temporal behavior of the CO concentration. Note also that the influence of K_T in (9) is much less marked than in (8). Comparison of the derived estimate for the effective rate of CO removal from the atmosphere with the value derived for the stratospheric sink, $K_S=0.11$, indicates that the stratosphere contributes significantly, but only partially, to the total rate of CO removal. Hence, the stratosphere consumes 11% per year of the total CO inventory of the troposphere. The stratosphere will be less effective, if the atmospheric CO concentration increases markedly beyond present levels, because then the OH kinetics in the stratosphere may be seriously perturbed.

5. Conclusions

The main aim of the present paper has been to show that the oxidation of CO by reaction with OH radicals in the stratosphere can provide a sizable sink for atmospheric CO. On the basis of two theoretical models, an attempt has then been made to determine whether the size of the stratospheric sink is compatible with present knowledge of anthropogenic CO sources and available measurements of atmospheric CO concentrations over the past 20-year period. The analysis presented provides several constraints for the rate of CO removal from the atmosphere that is comparable with the CO concentration data. The constraints include the absolute value for the atmospheric CO concentration, the ratio of CO concentrations in the Northern and Southern Hemispheres, and the temporal behavior of these parameters. Despite these restrictions, it has not been possible to derive a reliable value for the rate of CO removal, because of the present uncertainties in the measured CO concentrations and the source function estimates. The uncertainties stem from differing measurement techniques, large fluctuations of atmospheric CO concentrations, the few measurements made in the Southern Hemisphere, and the ensuing lack of a discernible increase of the average CO concentrations over the past two decades. Clearly, more detailed measurements are required before these uncertainties can be removed.

To determine if the CO sources are indeed anthropogenic in origin, it will be necessary to study their time-dependence by atmospheric CO measurements over the next decades. The fact that to date no increase in the atmospheric CO concentrations has been discernible indicates either that the effective CO sink is too small to allow a rapid adjustment between CO production and removal, or that a constant natural source exists which is larger than the anthropogenic sources. In the first case, the stratosphere would provide a sizable contribution to the CO removal. However, a significant increase in the CO concentration level should then occur in the future. A failure to detect such an increase over the next decades would indicate that the anthropogenic emission represents only a minor portion of the total CO budget and that natural sources

predominate. In that case, sinks much larger than that provided by the stratosphere must be operative. In addition, the concentration gradient from the Northern to the Southern Hemisphere should not be appreciable. Since the recent measurements by Robinson and Robbins (1969b) provide evidence for a higher CO concentration in the north compared with that in the south, it appears that the anthropogenic CO emission constitutes the major source. Consequently, the stratosphere must presently be included in the consideration of atmospheric sinks for carbon monoxide.

Acknowledgments. The work upon which this publication is based was performed under joint sponsorship of the National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, Public Health Service, Department of Health, Education and Welfare, and the Coordinating Research Council, Inc.

REFERENCES

- Barr, H. I., 1967: Hearings before the Subcommittee on Air and Water Pollution of the Committee of Public Works, U. S. Senate 90th Congress. First Session on Problems and Progress Associated with Control of Automobile Exhaust Emissions, p. 515.
- Bates, D. R., and A. E. Witherspoon, 1952: The photochemistry of some minor constituents of the earth's atmosphere. *Mon. Notices Roy. Astron. Soc.*, **112**, 101-124.
- Benesch, W., M. Migeotte and L. Neven, 1953: Investigation of atmospheric CO at the Jungfrauoch. *J. Opt. Soc. Amer.*, **43**, 1119-1123.
- Brewer, A. W., 1949: Evidence for a world circulation provided by the measurements of helium and water vapor distribution in the stratosphere. *Quart. J. Roy. Meteor. Soc.*, **75**, 351-363.
- Cavanagh, L. A., C. F. Schadt and E. Robinson, 1969: Atmospheric hydrocarbon and carbon monoxide measurements at Point Barrow, Alaska. *Environ. Sci. Tech.*, **3**, 251.
- Danielsen, E. F., 1968: Stratospheric-tropospheric exchange based on radioactivity, ozone and potential vorticity. *J. Atmos. Sci.*, **25**, 502-521.
- Dobson, G. M. B., 1956: Origin and distribution of the polyatomic molecules in the atmosphere. *Proc. Roy. Soc. London*, **A236**, 187-193.
- Fabian, P., W. F. Libby and C. E. Palmer, 1968: Stratospheric residence time and interhemispheric mixing of strontium 90 from fallout in rain. *J. Geophys. Res.*, **73**, 3611-3616.
- Feeley, H. W., and J. Spar, 1960: Tungsten 185 from nuclear bomb tests as tracer for stratospheric meteorology. *Nature*, **188**, 1062-1064.
- , H. Seitz, R. J. Lagomarsino and P. E. Biscaye, 1966: Transport and fallout of stratospheric radioactive debris. *Tellus*, **18**, 316-328.
- Gudiksen, P. H., A. W. Fairhall and R. J. Reed, 1968: Roles of mean meridional circulation and eddy diffusion in the transport of trace substances in the lower stratosphere. *J. Geophys. Res.*, **73**, 4461-4473.
- Harteck, P., and S. Dondes, 1957: Reaction of carbon monoxide and ozone. *J. Chem. Phys.*, **26**, 1734-1737.
- Hunt, B. G., 1966: Photochemistry of ozone in a moist atmosphere. *J. Geophys. Res.*, **71**, 1385-1398.
- Jaffe, L. S., 1968: Ambient carbon monoxide and its fate in the atmosphere. *J. Air Pollution Control Assoc.*, **18**, 534-540.
- Junge, C. E., 1962: Global ozone budget and exchange between stratosphere and troposphere. *Tellus*, **14**, 363-377.
- , 1963a: *Air Chemistry and Radioactivity*. New York, Academic Press, 382 pp.

- , 1963b: Studies of global exchange processes in the atmosphere by natural and artificial tracers. *J. Geophys. Res.*, **68**, 3849–3855.
- , and G. Czeplak, 1968: Some aspects of the seasonal variation of carbon dioxide and ozone. *Tellus*, **20**, 422–434.
- Kellogg, W. W., 1964: Pollution of the upper atmosphere by rockets. *Space Sci. Rev.*, **3**, 275–316.
- Lal, D., and Rama, 1966: Characteristics of global tropospheric mixing based on man-made C^{14} , H^3 , and Sr^{90} . *J. Geophys. Res.*, **71**, 2865–2874.
- Leovy, C. B., 1969: Atmospheric ozone: An analytic model for photochemistry in the presence of water vapor. *J. Geophys. Res.*, **74**, 417–426.
- Locke, J. L., and G. Herzberg, 1953: The absorption due to CO in the infrared spectrum. *Can. J. Phys.*, **31**, 504–516.
- Martell, E. A., 1968: Tungsten radioisotope distribution and stratospheric transport processes. *J. Atmos. Sci.*, **25**, 113–125.
- Migeotte, M. V., 1949: The fundamental band of carbon monoxide at 4.7μ in the solar spectrum. *Phys. Rev.*, **75**, 1108–1109.
- Newell, R. E., 1961: The transport of tracer substances in the atmosphere and their implications for the general circulation of the stratosphere. *Geofis. Pura Appl.*, **49**, 137–158.
- , 1963: Transfer through the tropopause and within the stratosphere. *Quart. J. Roy. Meteor. Soc.*, **89**, 167–204.
- Nydal, R., 1967: On the transfer of radiocarbon in nature. *Symp. on Radioactive Dating and Methods of Low-Level Counting*, U. S. Doc. SM 87/29, Intern. Atomic Energy Agency, Vienna, 119–129 pp.
- , 1968: Further investigation on the transfer of radiocarbon in nature. *J. Geophys. Res.*, **73**, 3617–3634.
- Peirson, R., and I. Cambray, 1967: Interhemispheric transfer of debris from nuclear explosions using a simple atmospheric model. *Nature*, **216**, 755–758.
- Reed, R. J., and K. E. German, 1965: A contribution to the problem of stratospheric diffusion by large-scale mixing. *Mon. Wea. Rev.*, **93**, 313–321.
- Reiter, E. R., M. E. Glasser and J. D. Mahlman, 1967: The role of the tropopause in stratospheric-tropospheric exchange processes. Atmos. Sci. Paper No. 107, Colorado State Univ., Fort Collins, 80 pp.
- Robinson, E., and R. C. Robbins, 1968: Evaluation of CO data obtained on Eltanin Cruises 27, 29 and 31. *Antarct. J.*, **3**, 194–196.
- , and —, 1969a: Atmospheric CO concentrations on the Greenland ice cap. *J. Geophys. Res.*, **74**, 1968–1973.
- , and —, 1969b: Gaseous atmospheric pollutants from urban and natural sources. *J. Air Pollution Control Assoc.* (in press).
- Robbins, R. C., K. M. Borg and E. Robinson, 1968: Carbon monoxide in the atmosphere. *J. Air Pollution Control Assoc.*, **18**, 106–110.
- Schofield, K., 1967: An evaluation of kinetic rate data for reactions of neutrals of atmospheric interest. *Planetary Space Sci.*, **15**, 643–670.
- Seiler, W., and Junge, C., 1969: Decrease of carbon monoxide mixing ratio above the polar tropopause. *Tellus*, **21**, 477–449.
- Shaw, J. H., 1958: The abundance of atmospheric carbon monoxide above Columbus, Ohio. *Astrophys. J.*, **128**, 428–440.
- , 1959: A determination of the abundance of nitrous oxide carbon monoxide, and methane in ground-level air at several locations near Columbus, Ohio. Sci. Rept. No. 1, Contract AF19(604)-2259, Air Force Cambridge Research Center, 33–34.
- Sheppard, P. A., 1963: Atmospheric tracers and the study of the general circulation of the atmosphere. *Rept. Progr. Phys.*, **26**, 213–267.
- Smith, R. M., 1968: A preview on the determination of mass return flow of air and water vapor into the stratosphere using tritium as a tracer. *Tellus*, **20**, 76–81.
- Snelling, D., and Hampson, J., 1969: Water vapor concentration and neutral reactions in the mesosphere and stratosphere. Aeronomy Rept. No. 32, Univ. of Illinois, Urbana, Meteorological and chemical factors in D-region aeronomy—Record of the Third Aeronomy Conf., 223–234.
- Terry, L. L., 1962: Motor vehicles, air pollution and health. A report of the Surgeon General to the U. S. Congress in Compliance with Public Law 86–493, The Schenck Act, 87th Congress, 2nd Session, House Doc. No. 489.
- U. S. Standard Atmosphere, 1962*: Washington, D. C., Gov't. Printing Office, 278 pp.
- Young, J. A., and A. W. Fairhall, 1968: Radiocarbon from nuclear weapons tests. *J. Geophys. Res.*, **73**, 1185–1200.