NASA CONTRACTOR REPORT

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NASA CR-2081

A REVIEW OF CARBON MONOXIDE SOURCES, SINKS, AND CONCENTRATIONS IN THE EARTH'S ATMOSPHERE

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Prepared by
GENERAL ELECTRIC COMPANY
Philadelphia, Pa. 19101
for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JUNE 1972

1. Report No. NASA CR-2081	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle A REVIEW OF CARBON MONOXIDE SOURCES, SINKS, AND CONCENTRATIONS IN THE EARTH'S ATMOSPHERE		5. Report Date June 1972
		6. Performing Organization Code
7. Author(s) **M. H. Bortner, R. H. Kummler (Wayne State University), and L. S. Jaffe (George Washington University)**		8. Performing Organization Report No.
9. Performing Organization Name and Address **General Electric Company** **Space Division - Space Sciences Laboratory** **P. O. Box 8555** **Philadelphia, PA 19101**		10. Work Unit No. **630-52-00-01-23**
		11. Contract or Grant No. **NAS1-10139**
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Contractor Report
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Carbon Monoxide is a toxic pollutant which is continually introduced into the earth's atmosphere in significant quantities. There are apparently some mechanisms operating which destroy most of the CO in the atmosphere, i.e., a carbon monoxide "sink." These mechanisms have not as yet been established in a quantitative sense. This report discusses the various possible removal mechanisms which warrant serious consideration. Particular emphasis is given to chemical reactions (especially that with OH), soil bacteria and other biological action, and transport effects. The sources of carbon monoxide, both natural and anthropogenic, are reviewed and it is noted that there is quite possibly a significant undefined natural source. Atmospheric CO concentrations are discussed and their implications on carbon monoxide lifetime, sinks and sources are considered.

17. Key Words (Suggested by Author(s)) **Carbon monoxide** **Air pollution** **Sink mechanisms** **Atmospheric chemistry**	18. Distribution Statement **Unclassified - Unlimited**

19. Security Classif. (of this report) **Unclassified**	20. Security Classif. (of this page) **Unclassified**	21. No. of Pages 55	22. Price* $3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

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FOREWORD

This report was prepared for NASA as part of contract NAS1-10139 with Langley Research Center under the Advanced Applications Flight Experiments (AAFE) Program. The objective of this contract is the development of the Carbon Monoxide Pollution Experiment ("COPE"). This experiment is designed to obtain data for the investigation of mechanisms by which CO is removed from the earth's atmosphere. The approach uses an orbiting platform to remotely map global CO concentrations and determine vertical CO profiles using a correlation interferometer measurement technique being developed by Barringer Research Ltd. The instrument is to be capable of measuring CO over the range .02 to 20 atm.-cm. and of measuring other trace atmospheric constituents. The support of NASA and the cooperation of Mr. P. J. LeBel, NASA LRC Technical Project Manager on the "COPE" program, are much appreciated.

A REVIEW OF CARBON MONOXIDE SOURCES, SINKS, AND CONCENTRATIONS IN THE EARTH'S ATMOSPHERE

By M. H. Bortner, R. H. Kummler* and L. S. Jaffe**
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INTRODUCTION

Carbon monoxide (CO) is the most widely distributed and the most commonly occurring air pollutant. It was one of the first five air contaminants designated by the National Air Pollution Control Administration as serious possible health hazards. In addition to the obvious problem in some urban areas, which was the foremost justification for that emphasis, it was later recognized (refs. 1, 2, 3, 4) that a global anomaly exists and a potential global problem was suggested as well. Total emissions of CO to the atmosphere exceed those of all other pollutants combined (ref. 4). Automobile and industrial fossil fuel combustion produces roughly 3.0×10^8 tons (2.8×10^{14} g) of CO per year (ref. 5) compared to the 8.1×10^8 tons (7.4×10^{14} g) of CO presently in the atmosphere (ref. 2) and chemists had not been able to identify a reliable lower atmospheric mechanism to destroy CO once it was produced. If there were no mechanism of destruction (i.e., a CO sink) then, based on the above figures, the CO concentrations would be expected to double in two or three years. This apparently is not occurring at present but it is impossible to extrapolate CO concentrations without a knowledge of the sink mechanism. Thus, the potential of CO as an ecological problem in the future cannot be determined. There is, therefore, substantial interest in ascertaining the global balance of CO. Such a consideration involves a knowledge of the sources, the present global concentration, and sinks of CO, all of which will be reviewed in this work. The interest in CO by the scientific community is continually growing so that applicable information on the CO sink problem can be expected to increase. Thus considerable improvement and updating of the information discussed herein can be expected in the future.

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CO SOURCES: ANTHROPOGENIC

The estimate given above of 3×10^8 tons year^{-1} is mainly that produced from man-made sources.

Table I gives data for known sources broken down by man-made and natural sources.

Fossil fuel combustion is the major man-made source of CO and the only major source which has been identified with certainty. The detailed breakdown of the various sources has been the subject of numerous recent reviews (refs. 2-4) and is easily verified from a knowledge of the world-wide fuel consumption statistics (refs. 5,6) and emission factors (ref. 7) for various combustion processes. The source data are summarized in Table I where a total CO source function of 337×10^6 tons/year is found. There is almost certainly an additional natural source, but a discussion of its magnitude is indirect and will be covered later.

The comparative production of CO from various combustion sources of different types is shown in Table II in terms of the amount of CO emitted per unit of fuel. It will be noted that various types of fuel and various uses of any one specific fuel often produce considerably different amounts of CO.

GLOBAL CO CONCENTRATIONS

Solar spectroscopic measurements (ref. 8) in 1952 first detected the presence of atmospheric CO and spectral observations over the next ten years (refs. 9,10), repeatedly confirm the presence of 0.1 - 0.3 ppm CO although not necessarily in "clean air" regions. There have been many subsequent measurements of CO in clean air, primarily using the HgO reduction method (ref. 4,11), which also measures other species oxidizable by HgO. Some of these measurements are collected in Table III and details of the CO variations at Pt. Barrow (ref. 12) are given in Figure 1. The latitudinal variations of CO have been obtained on cruise ships, first by Robinson and Robbins (ref. 13) on the Eltanin cruise 31, and second by Junge (refs. 14,15) on the Meteor expedition. These data are presented in Figure 2, which generally shows the sharp transition of CO concentration between the northern hemisphere and southern hemisphere in the troposphere. The concentrations in the northern hemisphere is variable, but averages nearly twice that of the southern hemisphere. The general interpretation of this latitude effect has been attributed to the larger fossil fuel consumption in the more heavily industrialized northern hemisphere. Stevens (ref. 16) has noted, however, that the results may be due to the seasonal change which occurs during equator crossing. To our knowledge, no inverse data exists showing higher southern hemispheric concentrations, so that it is likely that both

TABLE I. - CO SOURCES

	Fuel Consumption World (ref. 6) 10^6 ton-yr^{-1}	CO Emission World (ref. 5) 10^6 ton-yr^{-1}	CO Emission USA (ref. 3, 4) 10^6 ton-yr^{-1}	CO Emission USA (ref. 3, 4) % of Man-Made
Man-Made Sources				
Mobile Sources			63.8	67.5
Motor Vehicles	380	193	59.2	62.7
Gasoline			59.0	62.5
Deisel			0.2	0.2
Aircraft			2.4	2.5
Boats			0.3	0.3
Railroads			0.1	0.1
Other Motor Fuel			1.8	1.9
Stationary Sources			1.9	2.0
Coal	3089	12	0.8	0.8
Oil			0.1	0.1
Gas			0	0
Wood	1260	44	1.0	1.0
Industrial Processes		24	11.2	11.9
Petroleum Refineries		6		
Solid Waste			7.8	8.3
Miscellaneous			9.7	10.3
Incineration	500	25		
Total Man-Made		304	94.4	100.0
Natural Sources				
Forest Fires	18×10^6 acres/yr.	11	7.2	
Ocean		10		
Terpine Photochemistry		12		
Total		337	101.6	

TABLE II.- CO EMISSION FACTORS
(Per Unit of Fuel)(refs. 4, 7)

Gasoline engines	2910 lb/1000 gal.
Deisel engines	60 lb/1000 gal.
Coal, power plants	0.5 lb/ton
Coal, industrial	3 lb/ton
Coal, domestic and commercial	50 lb/ton
Natural gas, power plants	Negligible
Natural gas, industrial	0.4 lb/10^6 ft^3
Natural gas, domestic and commercial	0.4 lb/10^6 ft^3
Oil, larger than 1000 hp	0.04 lb/1000 gal.
Oil, smaller than 1000 hp	2 lb/1000 gal.
Oil, refinery boilers and heaters	Negligible
Gas, refinery boilers and heaters	Negligible
Gas, compressor engines	Negligible
Catalytic units, fluid	13700 lb/1000 bbl fresh feed
Catalytic units, moving bed	3800 lb/1000 bbl fresh feed
Refuse incineration, municipal	0.7 lb/ton
Refuse incineration, industrial single chamber	20 - 200 lb/ton
Refuse incineration, industrial multiple chamber	0.5 lb/ton
Refuse incineration, domestic	300 lb/ton

TABLE III. - SAMPLE OF COLLECTED CO MEASUREMENTS IN REMOTE AREAS - Continued

Place	Date	Local Time	Wind Direction and Velocity (mph)	CO Concentration (ppm)	Ref.
Camp Century, Greenland	7/3/65	1245	SE-8	0.90	11
	7/3/65	1245	SE-8	0.85	
	7/5/65	0800	SE-15	0.24	
	7/5/65	0805	SE-15	0.32	
North Coast, California	6/23/65	1400	W-8	0.85	
	6/24/65	1400	W-10	0.80	
Coastal forest (California)	6/24/65	1130	Calm	0.80	
Crater Lake, Oregon (7,000 ft. elevation)	9/27/65	9005	NE-22	0.30	
	9/28/65	0835	Lt. and Var.	0.08	
	9/28/65	1650	W-4	0.06	
	9/29/65	0910	Lt. and Var.	0.03	
	9/29/65	1700	Lt. and Var.	0.05	
Patrick Point, California coast	10/02/65	1630	S-5	0.04	
	10/03/65	1800	W-10	0.04	
	10/04/65	1145	W-10	0.04	
	10/05/65	0840	E-2	0.80	
	10/05/65	1320	W-5	0.06	
	10/06/65	1320	Lt. and Var.	0.34	
	10/06/65	1650	W-8	0.06	
Pt. Barrow, Alaska	9/2/67	1030		0.122	12
	9/2/67	1140		0.089	
	9/2/67	1230		0.064	
	9/2/67	1340		0.146	
	9/2/67	1440		0.125	
	9/2/67	1550		0.134	
	9/2/67	1630		0.105	
	9/2/67	1730		0.127	
	9/2/67	1820		0.102	
	9/2/67	2145		0.102	
	9/2/67	2230		0.119	
	9/2/67	2330		0.100	
	9/3/67	0030		0.107	
	9/3/67	0130		0.080	
	9/3/67	0230		0.119	
	9/3/67	0330		0.123	
	9/3/67	0430		0.090	
	9/3/67	0530		0.097	
	9/3/67	0630		0.110	
	9/3/67	0730		0.105	
	9/3/67	0830		0.105	
	9/3/67	0930		0.092	

TABLE III. - SAMPLE OF COLLECTED CO MEASUREMENTS IN REMOTE AREAS - Concluded

Place	Date	CO Concentration (ppm)	Ref.
Lower Troposphere			
European surface data			
Mainz	1967-1969	0.11 - 2.0	14
Deuselbach	1969	0.15 - 1.2	
Clean-air conditions			
Northern Hemisphere			
North Atlantic	1969	0.17 - 0.21	
Tenerife below trade wind inversion	1968	0.17 - 0.2	
Tenerife above trade wind inversion	1968	0.1 - 0.14	
Southern Hemisphere			
Southern Atlantic	1969	0.1 - 0.12	
South Africa	1968	0.1 - 0.14	
Upper Troposphere			
Transpolar flights	1968	0.1 - 0.15	
Transequatorial flight	1968	0.1 - 0.14	
Lower Stratosphere	1968	< 0.003	
Equilibrium Pressure of CO in Seawater	1969	~ 5	
Air in Contact with Earth Surface			
Nighttime	1969	~ 0.02	
Daytime with sunshine	1969	~ 0.6	

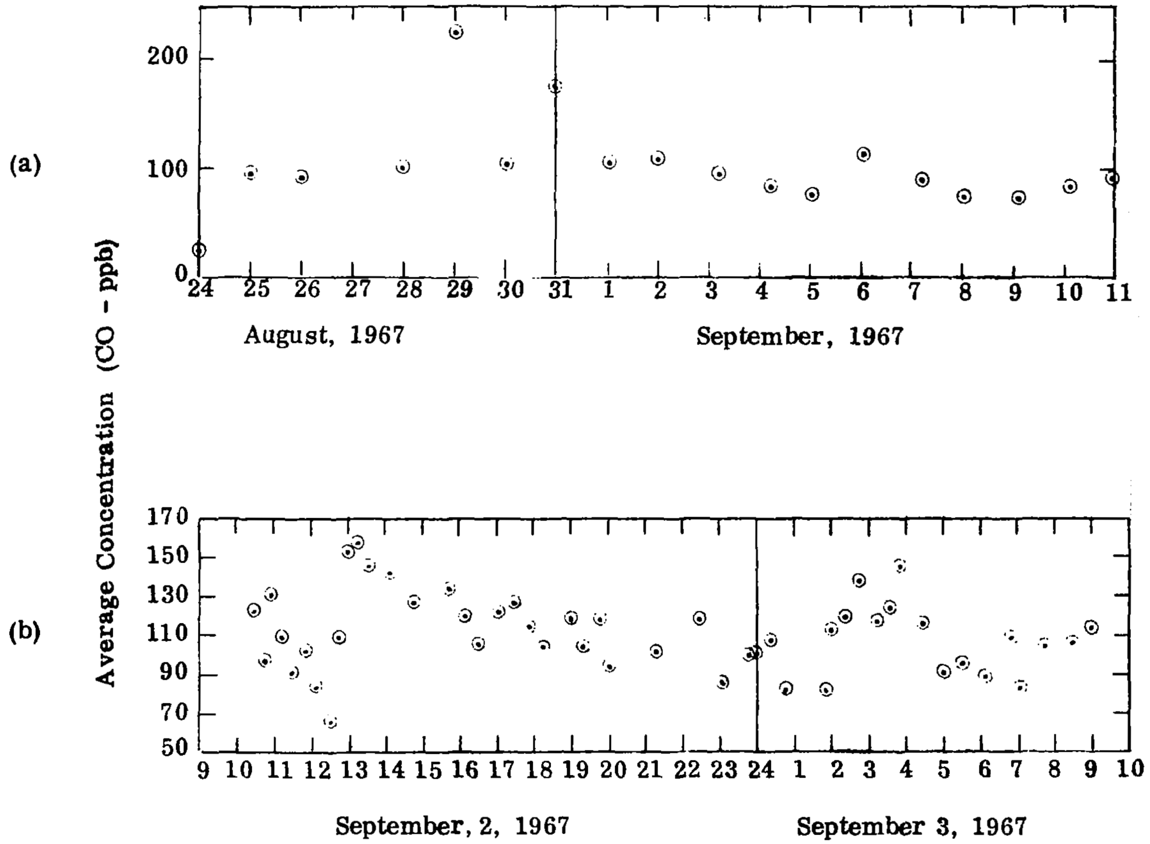


Figure 1. CO Concentration Variation at Pt. Barrow, Alaska (ref. 12).
(a) Mean Daily Concentration
(b) Hourly Concentration

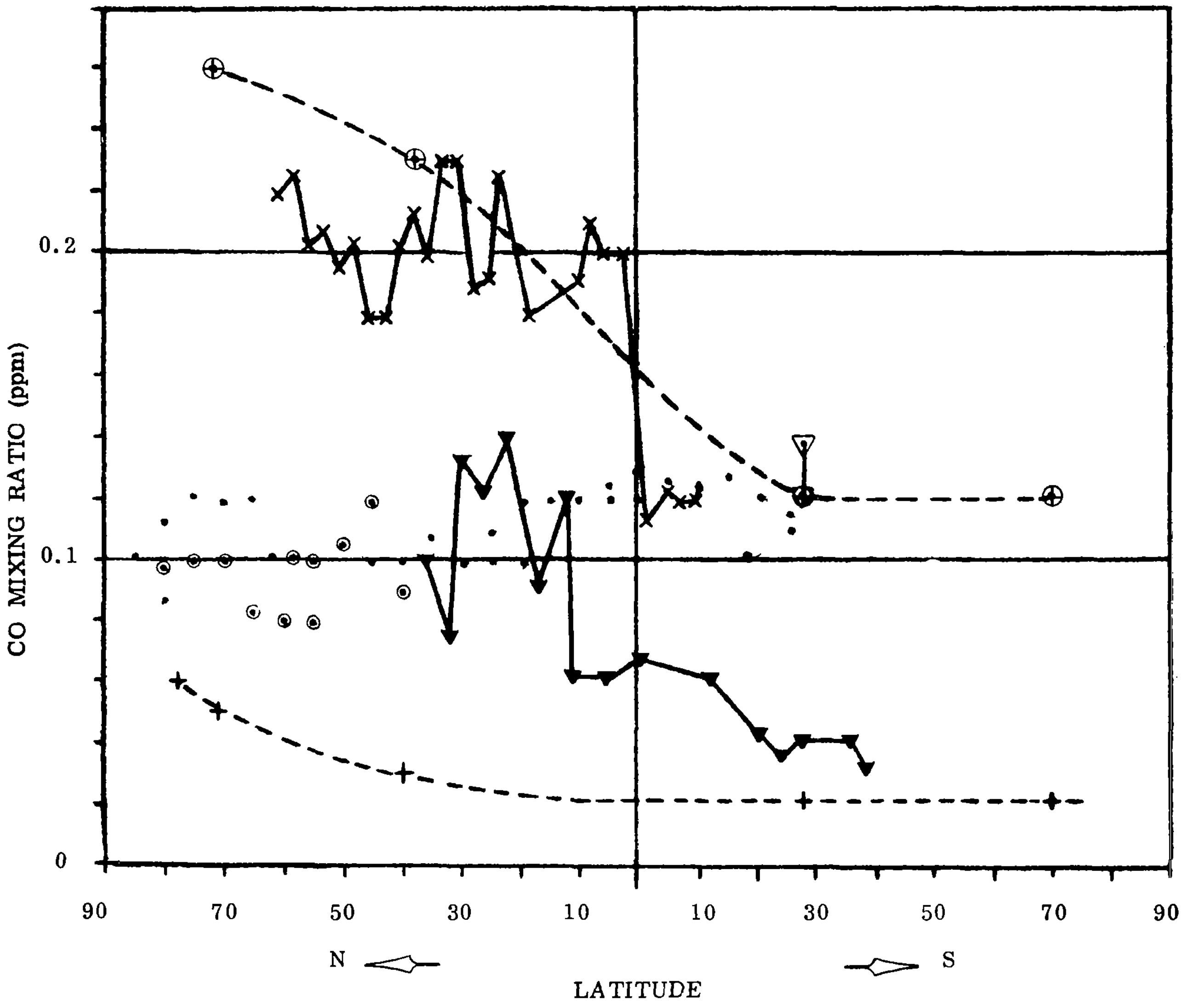


Figure 2. Data on the Global Distribution of CO. (See Legend, Page 9.).

Figure 2. Data on the Global Distribution of CO - Legend.

Data on the global distribution of CO as a function of latitude from Junge, Seiler, and Warneck (ref. 15). CO measurements by Robinson and Robbins (ref. 13): full triangles represent Eltanin cruise 31 (Nov. - Dec. 1967) from San Francisco to New Zealand; +'s represent the lowest CO concentrations at several locations on the northern and southern Pacific; ⊕ represent the highest CO concentrations at the same location. CO measurements by Seiler and Junge (ref. 14): x's represent Meteor expedition (spring, 1969) on the sothern and northern Atlantic; open triangles represent variation of the CO concentration at 28 °S near Johannesburg (South Africa) over a period of three weeks; .'s represent CO concentration in the upper troposphere at altitudes of 10 km over the Atlantic; ʘ's represent CO concentration in the upper troposphere at altitudes of 10 km over the northern Pacific.

natural and man-made sources are present in greater quantity in the north or large sinks exist in the south if antropogenic sources are small compared to natural sources on a global basis. On ocean cruises diurnal variations have been observed, and a typical example is shown in Figures 3 and 4 from Swinnerton (ref. 17). Figure 5 shows the ratio of measured dissolved CO to equilibrium CO calculated by Lamontague (ref. 18) from Henry's Law. Diurnal variations are seen in these data and in those of the surface water and the air in Figure 4. No such variation is seen in the data (ref. 18) of Figure 3 because of relatively high winds at the time of the measurements.

A nominal value for CO in an unpolluted area is of the order of 0.1 ppm (while a sink region would be expected to be appreciably lower than this). However, over the last twenty years there is no apparent increase in the global averaged CO concentrations. Urban areas have much more CO than this in their atmospheres (ref. 4). Concentrations of tens of parts per million are common under such conditions. Limits which human beings can safely be exposed to have been established by EPA (9 ppm for 8 hours, 35 ppm for 1 hour) (ref. 19) but are somewhat arbitrary because of the lack of data needed for the establishment of such limits.

Robinson and Moser (ref. 5) have recently suggested new values for global average concentrations, specifically

Northern hemisphere	0.20 ppm
Southern hemisphere	0.06 ppm
Global	0.13 ppm

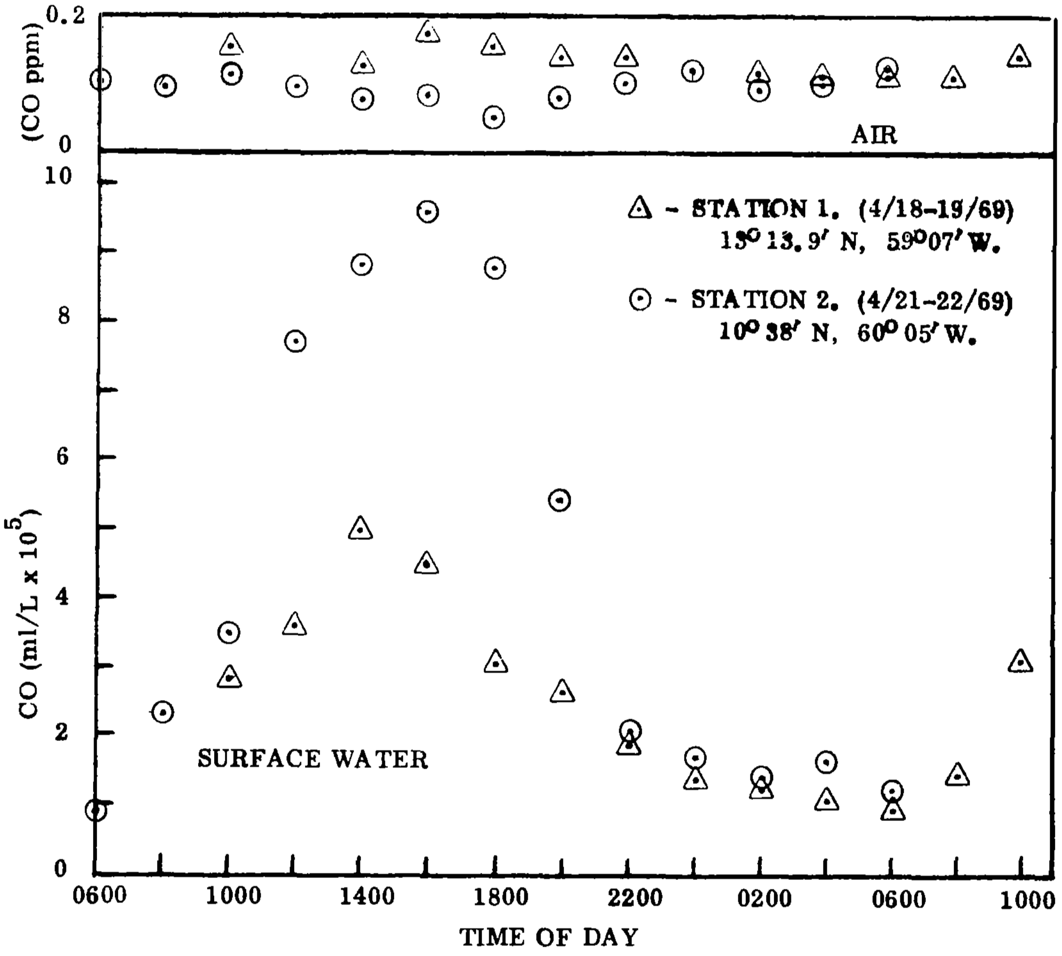
Seiler and Junge (ref. 14) have data showing similar, though less drastic, hemispheric effects. This implies that either the source is primarily in the northern hemisphere or the sink is primarily in the southern hemisphere or both. This can be shown as follows.

If the concentration of CO is not changing appreciably

$$\frac{dn_{CO}}{dt} = 0$$

But the rate of change of CO concentration is equal to the difference in its rate of formation (i.e., its production, P), and its rate of removal (i.e., $k_1 n_{CO}$) where k_1 is the effective first-order rate constant for the total removal mechanism and is equal to the reciprocal of its lifetime, and n_{CO} is the CO concentration. Thus

$$P_{CO} - n_{CO} k_1 = P_{CO} - \frac{n_{CO}}{\tau_{CO}}$$



CO DISTRIBUTION

Figure 3. Concentration of CO in Surface Waters and in the Atmosphere as a Function of Time of Day (ref. 17). Little or no diurnal variation was observed in the air data because of relatively high winds.

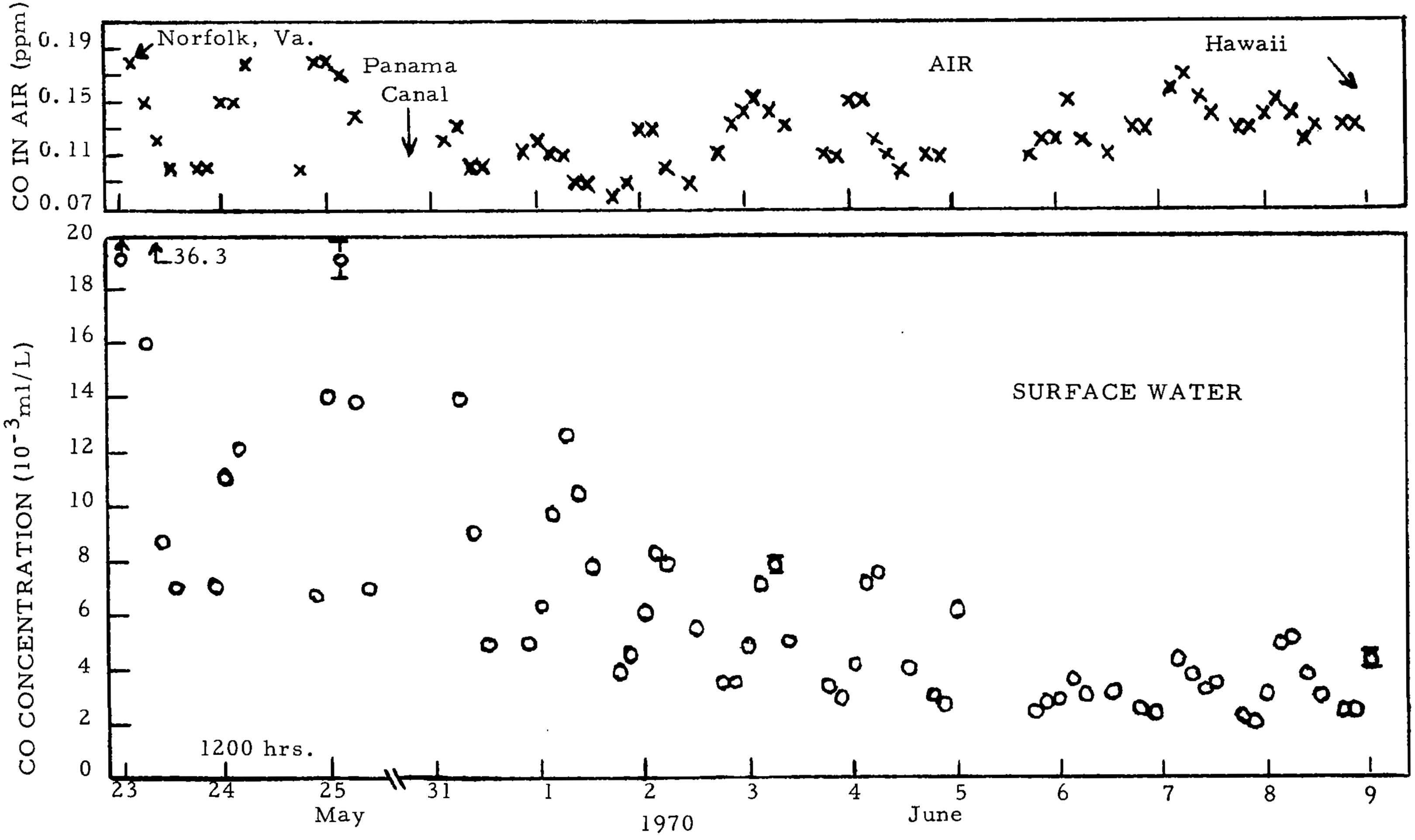


Figure 4. Concentrations of CO in Surface Waters and in the Atmosphere. Taken during a cruise from Washington, D. C. to Hawaii (ref. 18) showing diurnal variations in both air and surface water.

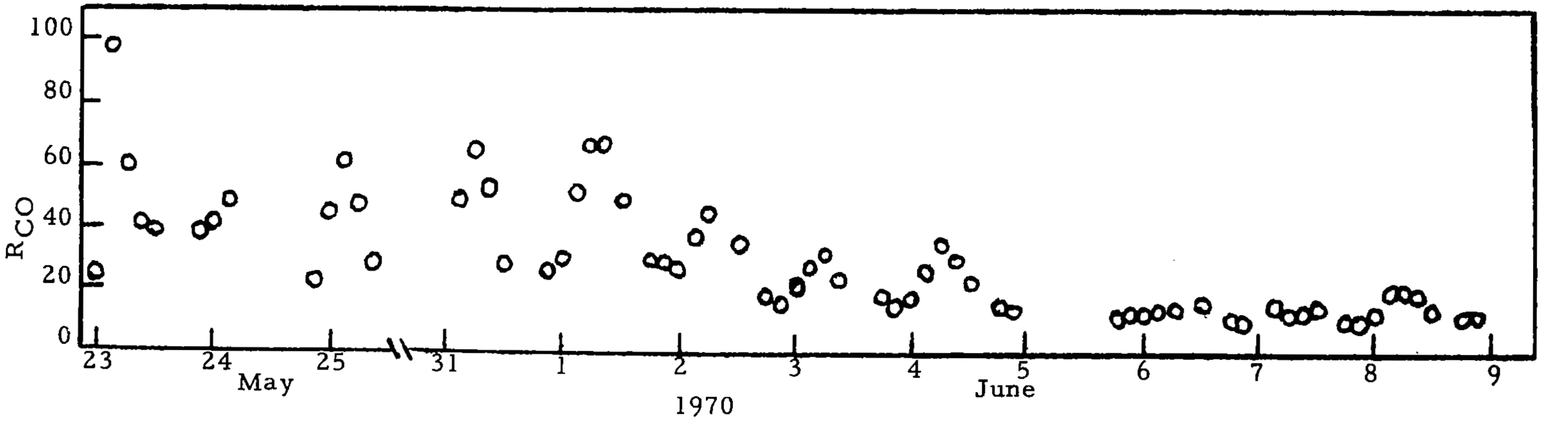


Figure 5. Ratio of Measured Concentrations of CO Dissolved in Ocean Water to CO Equilibrium Partial Pressures (ref. 18). Calculated by Henry's Law, showing diurnal variation.

or

$$P_{CO}\,\tau_{CO} - n_{CO} = 0$$

or

$$P_{CO}\,\tau_{CO} = n_{CO}$$

Considering the world total rates as the sum of the rates for the two hemispheres

$$P_{total} = P_N + P_S = n_{N_{CO}}\,\tau_{N_{CO}}^{-1} + n_{S_{CO}}\,\tau_{S_{CO}}^{-1}$$

where N and S refer to the hemispheres.

Assuming little interaction (transport) between the two hemispheres

$$P_N = \frac{n_N}{\tau_N} \quad \text{and} \quad P_S = \frac{n_S}{\tau_S}$$

so that

$$\frac{P_N}{P_S} = \frac{n_N\,\tau_S}{n_S\,\tau_N}$$

or

$$P_N\,\tau_N - P_S\,\tau_S = n_N - n_S$$

But

$$n_N > n_S \quad \text{or} \quad n_N - n_S > 0$$

so that

$$P_N\,\tau_N > P_S\,\tau_S$$

or

$$\frac{P_N}{P_S} > \frac{\tau_S}{\tau_N}$$

$$\frac{P_N}{P_S} > \frac{k_{1_N}}{k_{1_S}}$$

The ratio of the first-order rate constants is the ratio of the removal rates.

If the sinks are similar in the two hemispheres,

i.e.

$$\tau_N = \tau_S$$

$$\frac{P_N}{P_S} = \frac{n_N}{n_S} = \frac{.2}{.06} = 3.33$$

and thus 77% of the total production would be in the northern hemisphere and 23% would be in the southern hemisphere. If, on the other hand, the sink is primarily in the southern hemisphere

and

$$P_N = P_S$$

$$\frac{\tau_N}{\tau_S} = \frac{n_N}{n_S} = \frac{.20}{.06} = 3.33$$

If $P_N > P_S$

$$\tau_N < 3.33\ \tau_S .$$

CO ATMOSPHERIC LIFETIMES: SUMMARY OF THE ANOMALY

At this point, we know the anthropogenic production source strength, P, and it may be postulated that there is a CO sink, regardless of its nature, which is indeed acting to maintain a constant CO concentration of roughly 0.1 ppm. If this is true, then we may set the time derivative of the CO concentrations, $dn_{CO}/dt = 0$ in the steady state. A general equation for the temporal variation of the CO concentration may also be written as

$$\frac{dn_{CO}}{dt} = \text{Production} - \text{Loss}$$

The loss rate of CO is undoubtedly proportional to the CO concentration to the first power (i.e., first order in CO) and may be expressed as $n_{CO}\,k_1$ or n_{CO}/τ, where τ is the effective lifetime of CO. Thus, at steady state,

$$n_{CO} = P\tau ,$$

which lead Robinson and Robbins (ref. 20) to the result,

$$\tau = 2.7 \text{ years}$$

Note that a constant n_{CO} implies a decreasing τ as P increases with increasing fossil fuel consumption, a highly unlikely possibility.

As Weinstock (ref. 21) has shown, it is possible to directly measure the CO lifetime without knowledge of the global source strength by a variation of the carbon dating technique, using ^{14}C (radioactive decay time, t = 5720 years) as a tracer. In this process, the atmospheric neutron flux converts ^{14}N to ^{14}C via:

$$n + {}^{14}N_2 \rightarrow {}^{14}C(HOT) + p + {}^{14}N .$$

The neutron flux in the atmosphere has been measured by Libby (ref. 22) so that the rate of production of translationally hot ^{14}C can be calculated to be 1.3×10^{19} atom/sec. over the entire globe (ref. 21). The high energy ^{14}C can then react with O_2, probably via

$$^{14}C(HOT) + O_2 \xrightarrow{\text{fast}} {}^{14}CO + O .$$

The rate of such reaction is not known but must be rapid as is consistent with Pandow's observation that ^{14}C is fixed as ^{14}CO and not $^{14}CO_2$. Thus, the rate of ^{14}C production $P(^{14}C)$ is assumed equal to the rate of ^{14}CO production. Then, by some unknown process which is presumably the same process by which ^{12}CO is converted to $^{12}CO_2$,

$$^{14}CO + ? \rightarrow {}^{14}CO_2 + ?$$

While the latter process is unknown, it is the rate controlling step for ^{14}CO conversion. If we assume a steady state for ^{14}CO,

$$\frac{d(^{14}CO)}{dt} = P_{^{14}C} - \frac{n_{^{14}CO}}{\tau_{^{14}CO}} = 0,$$

and measure the concentration of ^{14}CO, then from Weinstock (ref. 21), it may be calculated that

$$\tau_{^{14}CO} = 0.1 \text{ year.}$$

If there is no reason for ^{14}CO to be any more reactive than ^{12}CO, this implies a natural production source which is twenty times as large as fossil fuel combustion. Still, there are several weaknesses to this calculation. First, the atmospheric ^{14}CO production of Libby (ref. 22) occurs to a large extent in the stratosphere, where it is well known that CO + OH will result in a very short lifetime (ref. 1). Weinstock indicates that his value is probably too low because his calculations of the CO oxidation rate in the troposphere were based on data pertaining to CO oxidation in both troposphere and the stratosphere. A more exact calculation increases the lifetime of CO by roughly a factor of two to 0.2 yr. This may be qualitatively seen from Figure 6, where it is evident that the production rate of ^{14}CO is roughly symmetric about the tropopause (10 - 12 km). If it is assumed that no mixing occurs between the stratosphere and troposphere, then the error is a factor of two. Second, the reaction of $^{14}C + O_2$ undoubtedly produces excited (electronically or vibrationally) ^{14}CO, rather than ground state ^{14}CO. It is likely, however, that quenching of this state is completely dominant over reactions so that it can be assumed that ^{14}CO reaction with OH is as slow as ^{12}CO reaction with OH. Third, and perhaps more serious as suggested by Junge (ref. 15), is the fact that the neutron flux from the exosphere may not be the only significant source of ^{14}CO. Junge (ref. 15) concluded that, on the global average, no anthropogenic sources of ^{14}CO exist. However, it remains to be shown that the sample of ^{14}CO collected by McKay (ref. 23) in one location is in fact representative of the global average required for Weinstock's calculation (ref. 21), and, more important, what is the biosphere input to the ^{14}CO production which may exceed the anthropogenic input? If a value of 1.2×10^{-12} for a $^{14}C/^{12}C$ ratio (as appropriate to fuel) (ref. 24) can be assumed appropriate for all sources, and if the natural source is 10 times as large as the anthropogenic source (3.1×10^{14} g ^{12}CO/yr) as Weinstock estimates (ref. 21), then the corresponding ^{14}CO production is 340 g ^{14}CO yr^{-1} or 8.6×10^{-2} molecules ^{14}CO cm^{-2} sec^{-1} for the northern hemisphere, while cosmogenic ^{14}CO production has been calculated by Junge (ref. 15) to be 0.85 ^{14}CO molecules cm^{-2} sec^{-1}. Hence, Weinstock's calculation (ref. 21) holds for these assumptions of the applicability of McKay's measurement and an invariant ^{14}CO to ^{12}CO production ratio. Within these assumptions the calculation indicates that there is a total source function which is ten times as large as the anthropogenic source function; this implies a sink ten times as large as that necessary to explain constant (CO) concentrations with fossil fuel consumption only.

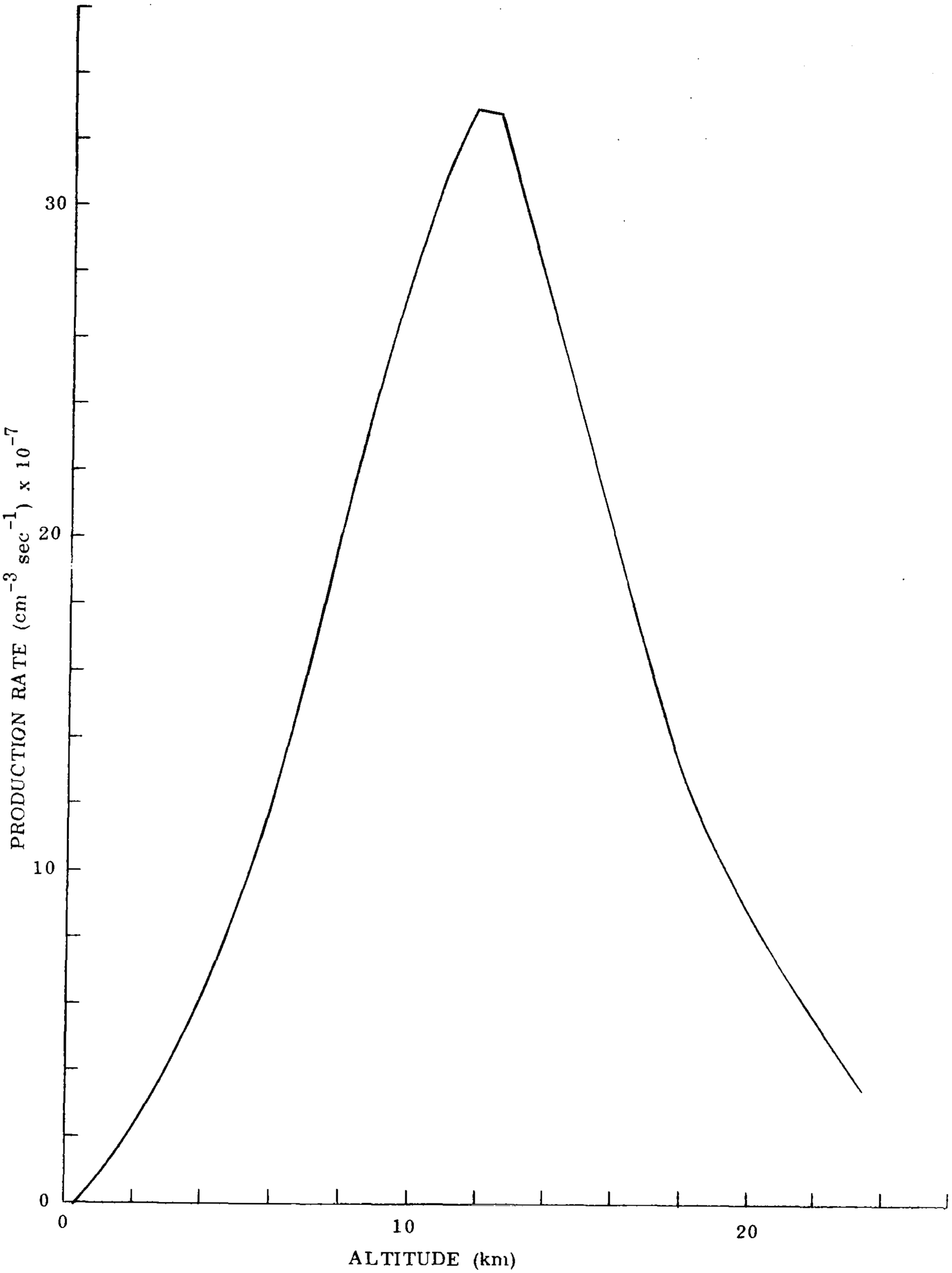


Figure 6. C^{14} Production Rate.

SOURCES: NATURAL

Further evidence that natural sources of CO exceed vehicular sources is being provided by Stevens (ref. 25) at Argonne National Lab under sponsorship of the Coordinating Research Council's (Automobile Manufacturers Association, the American Petroleum Institute and the Environmental Protection Agency through the Air Pollution Control Office) Air Pollution Research Advisory Committee project CAPA-4-68 under the leadership of B. Weinstock. Stevens is isotopically analyzing the CO from the atmosphere as well as that from motor vehicle and natural sources to ascertain the contribution of each to the atmosphere. The isotopic abundance of both ^{13}C and ^{18}O relative to ^{12}C and ^{16}O are used. Automobile exhaust contains $^{13}C/^{12}C$ ratios characteristic of the petroleum field in which the gasoline originated and $^{18}O/^{16}O$ ratios characteristic of atmospheric oxygen. The measured $^{18}O/^{16}O$ ratio varies from a high in atmospheric CO_2 to a low in oxygen in ocean and rain water, with atmospheric O_2 in between. At least three different isotopic compositions have been identified to date in atmospheric CO. At least two are clearly distinct from automobile exhausts and are at least 10 times as abundant as the auto exhaust contribution (ref. 25). The third may also be different, but variations in isotopic composition from various petroleum fields apparently have precluded a definative statement at present. One of the smaller groups (although there is a large spread in the data) appears to be of marine origin. This substantiates at least qualitatively the calculations of Swinnerton (ref. 26) which suggest that the ocean is a source, albeit a small one. The C seems to be of marine origin and the O is definitely not from atmospheric O_2, but is more like rain water. The technique of Stevens, then, can be applied to biological as well as anthropogenic sources with the hope of matching the source isotopic ratio to the most abundant atmospheric CO isotopic ratio. Thus far marine CO, trees, and plants have been studied, and preliminary investigations have suggested that soil and humus emissions are less significant than the first three. Some plants and trees, notably Austrian Pine and Balsam, do emit CO but with variable $^{13}C/^{12}C$ ratios which show no correlation with the atmospheric CO. Algae also produce CO. None of these sources investigated (ref. 25), however, correlate well with atmospheric CO. Thus, while the above studies indicate that anthropogenic sources can be excluded as the major CO source, the data of Stevens indicate another source which has not yet been identified.

Recently atmospheric methane (ref. 27) and formaldehyde (ref. 28) have been suggested as natural sources of CO. McConnell, McElroy and Wolfsy (ref. 27) have noted that the annual source of methane is of the order of 9×10^{14} gram and argue that the most likely product of this is carbon monoxide, by the following mechanism. Methane is converted to CH_3 by reaction with OH or with $O(^1D)$ (with photolysis playing a role at high altitudes). By a three-body reaction CH_3 is converted to CH_3O_2 which ultimately forms formaldehyde, H_2CO. Formaldehyde is photodissociated to form HCO which reacts with oxygen primarily to form CO. If all of the methane were converted to CO this would produce about 1.5 x 10^{15} gram CO/year, about five times as much as from anthropogenic sources. Of course there are many side paths to this chemical mechanism and uncertainties in many of the rates. However, this does indicate a significant natural source for CO.

Calvert (ref. 28) has considered formaldehyde as a source of CO. The chemistry producing CO from formaldehyde is the same as that suggested by McConnell (ref. 27). A rough calculation of CHO radical concentration using $k(OH + H_2CO) = 7 \times 10^{-12}$ (ref. 29) and $k(CHO + O_2) = 1 \times 10^{-13}$ (ref. 30), and a H_2CO density of 5×10^{10} cm^{-3} with the OH and HO_2 densities given above, gives data to calculate a rate of CO formation of 1.3×10^6 molecules cm^{-3} sec^{-1}. From this a lifetime of 0.4 years is found for average solar conditions. Including this reaction system, it is seen that OH can participate in both the creation and loss of CO. The source function postulated is large enough to be the natural source postulated by Weinstock (ref. 21) and may be significantly larger than the man-made CO.

Oceans have been found to be a source of CO in some regions, rather than a sink, as previously thought to be a possibility. Seiler and Junge (ref. 14) confirm the earlier work by Swinnerton (ref. 17) that the surface waters of the Atlantic have much larger CO concentrations (10 - 40 times greater) than the atmospheric equilibrium CO, see Figure 7. These investigators also found that the CO mixing ratio generally varies between 0.10 and 0.15 ppm. Midtropospheric data from the subtropics show no marked difference between the two hemispheres.

More recently Lamontagne, Swinnerton, and Linnenbom (ref. 18) in an ocean cruise from Washington, D. C. via the Panama Canal to Hawaii found the surface waters of the Atlantic and Pacific Oceans to be supersaturated with carbon monoxide and an apparent non-equilibrium of CO at the air-sea interface (see Figure 5). Swinnerton, et al (ref. 31) recently simultaneously measured the CO content of the atmosphere and of the surface water at 29 different points during an oceanographic cruise between Washington, D. C. and Puerto Rico. These investigators found that the actual measured CO concentration of the surface waters (W) at all sampling points ranged from 7 to about 90 times (averaging about 28 times) the aforementioned theoretical CO concentrations of the surface water (T) based on the concentration of the gas in the water if the only source were the atmosphere. Pure gaseous carbon monoxide at 1 atm pressure is soluble to a limited degree in sea water, on the order of 32 to 17 ml gas STPD/liter of water over a surface water temperature range of -2^oC to $+ 30^oC$ and a chlorinity range of 15 to 21 g Cl per kg. H_2O, respectively (ref. 32) (convertible to salinites of 27.1 to 37.9, respectively). As an illustration, at 25^oC, the solubility of CO is 18 ml/liter of sea water (volume of gas (STPD) absorbed by a unit volume of water when the pressure of the gas equals 1 atm (760 mm) at a salinity of 36 parts per thousand (ref. 32). This solubility rate is roughly between the solubilities of O_2 and N_2, but is considerably less than the solubilities of CO_2 and SO_2 in water. (The solubility coefficients of O_2, N_2, and CO in sea water and in pure (distilled) water differ by about 10%). The precise degree of solubility, however,

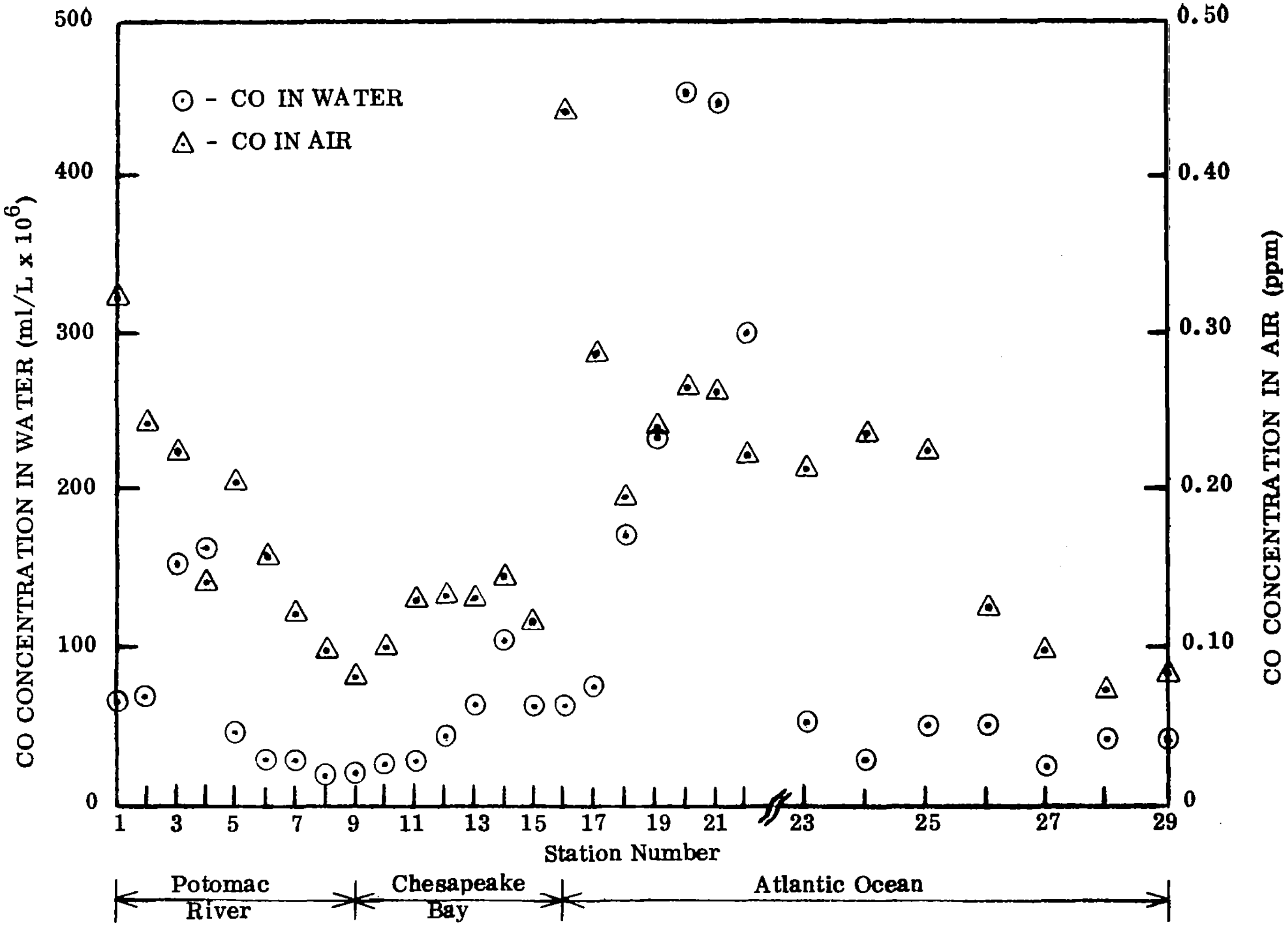


Figure 7. Concentration of CO in Surface Waters and the Atmosphere, Swinnerton, et al (ref. 17).

is a function of the partial pressure of the gas in the atmosphere. Thus, based on an atmospheric CO background level of 0.01 to 0.2 ppm as found in clean air regions, the solubility of CO in sea water will be 1.8×10^{-7} to 3.6×10^{-6} ml CO/liter of water at equilibrium between the atmosphere and surface waters, assuming that the atmosphere is the sole source of the gas. These data indicate that atmospheric CO from land sources may not be the principal source of CO in the water since the highest values of W/T were found in the open water. Marine biological sources of CO such as marine algae and siphonophores and/or other marine sources apparently contribute substantial quantities of CO to the surface waters exceeding that obtained from the atmosphere. These findings (ref. 31), confirmed in a more recent study (ref. 26), indicate that the ocean in the areas studied is not a sink for atmospheric CO but, indeed, serves as an additional natural source, with the transient exchange or net transport of CO being from water to the atmosphere due to the supersaturated condition of the surface waters with respect to the partial pressure of CO in the atmosphere over the ocean. These same investigators (ref. 17) have also investigated the carbon monoxide content of rainwater in Washington, D. C., that collected on an ocean cruise between Washington, D. C. and Hawaii, and in Hawaii. The latter two sites are remote from any industrially produced CO. In all cases, all rainwater samples were supersaturated with CO. The rainwater samples collected in the daytime had significantly higher CO levels than those samples collected at night. Rainwater contains relatively high concentrations of dissolved organic carbon, as much as 10 times the quantity found in surface organic water. It is also known that photochemical reactions on dissolved organic carbon in surface ocean waters can produce carbon monoxide. Dissolved organic matter appears to constitute the major reservoir of organic materials in the oceans. The authors (ref. 17) suggested that it is a source from which CO might be produced in the illuminated zone of the surface waters. It is possible that a chemical process is not actually needed to explain the supersaturation, however. If equilibrium between CO and condensed water vapor in clouds may be assumed, then the low temperature in the lower stratosphere would permit a far greater gas solubility (even with the reduced pressure) at altitudes where the droplet nuclei originate than is found at ground level temperatures. Once the nuclei have collected to form droplets, diffusion to the surface to reestablish equilibrium at a new temperature will be extremely slow and hence it is reasonable that supersaturation occurs. The degree of supersaturation would also be expected to be highly variable depending upon the altitude of droplet formation. This point needs more study.

Junge, et al (ref. 15) have estimated the total rate of production of CO from the ocean, Q, by:

$$Q \quad = \quad Ak\,\Delta p \qquad\qquad \text{g CO yr}^{-1}$$

where

A = ocean area = 1.5×10^{18} cm^3

Δp = pressure difference at the surface, $\sim 3.3 \times 10^{6}$ atm (corresponding to a supersaturation of 20 times equilibrium)

The exchange coefficient, k, is unknown. Keeling and Bolin (ref. 33) and Munich, as quoted by Junge (ref. 15) have obtained that information for O_2 and CO_2. Junge (ref. 15) selects the value of 15 g O_2 cm^{-2} yr^{-1} atm^{-1} = k as an estimate of the exchange coefficient for CO and on that basis computes 0.75×10^{14} g CO yr^{-1}, or 24% of 3.1×10^{14} for the anthropogenic contribution. Swinnerton, et al, (ref. 26) estimated an upper limit of 5% based on a region of a typically high biological activity. It is difficult to reconcile these two estimates except by selecting a lower value for k.

CO SINKS

The potential sinks (ref. 1) may be classified as:

(1) transport to and reaction in the stratosphere

(2) ground level and tropospheric chemistry

(3) biological sink

  (a) activity in the soil

  (b) activity in the ocean

(4) horizontal transport

Vertical Transport

If transport to the stratosphere is sufficiently rapid, then, as we have previously shown (ref. 1), the reaction of CO + OH is rapid enough to destroy CO. The rates per CO molecule of this reaction are calculated in Table IV for various conditions with graphical representation of these values as a function of altitude given in Figure 8. Details of this calculation are given later.

To evaluate the transport strength a solution of the continuity equation is needed.

TABLE IV. - RATE OF CO + OH REACTION
(Per Second Per CO Molecule)

Altitude (km)

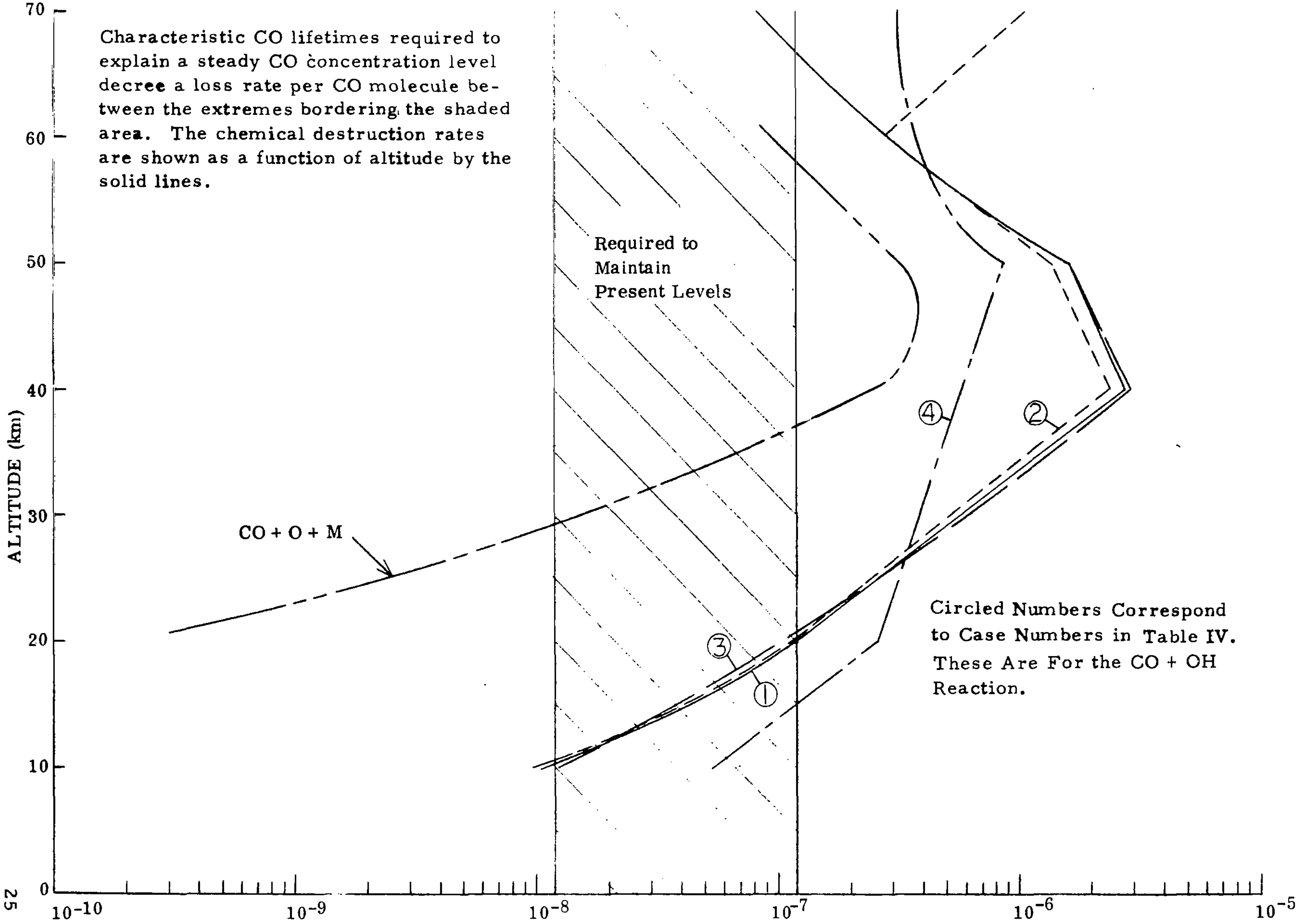
Case		10	20	30	40	50	60	70
1	T [a]	223.3	216.6	226.5	250.4	270.6	255.8	219.7
	k [b]	1.07(-13)	1.00(-13)	1.10(-13)	1.38(-13)	1.61(-13)	1.44(-13)	1.03(-13)
	n(OH) [c]	1.05(5)	1.2(6)	5.1(6)	2.07(7)	1.0(7)	2.0(6)	8.0(5)
	Rate	1.07(-8)	1.2(-7)	5.61(-7)	2.76(-6)	1.61(-6)	2.88(-7)	8.24(-8)
2	T [a]	217.2	214.2	216.0	234.6	259.3	250.9	254.4
	k [b]	100(-13)	9.65(-14)	9.90(-14)	1.20(-13)	1.48(-13)	1.39(-13)	1.32(-13)
	n(OH) [c]	1.0(5)	1.2(6)	5.1(6)	2.0(7)	1.0(7)	2.0(6)	8.0(5)
	Rate	100(-8)	1.16(-7)	5.05(-7)	2.40(-6)	1.38(-6)	2.78(-7)	1.06(-6)
3	T [a]	237.0	206.7	232.3	254.0	270.2	253.1	218.9
	k [b]	1.22(-13)	8.87(-14)	1.17(-13)	1.42(-13)	1.61(-13)	1.41(-13)	1.06(-13)
	n(OH) [c]	1.0(5)	1.2(6)	5.1(6)	2.0(7)	1.0(7)	2.0(6)	8.0(5)
	Rate	1.22(-8)	1.07(-7)	5.97(-7)	2.84(-6)	1.61(-6)	2.82(-7)	8.48(-8)
4	T [a]	223.3	216.6	226.5	250.4	270.6	255.8	219.7
	k [b]	107(-13)	1.00(-13)	1.10(-13)	1.38(-13)	1.61(-13)	1.44(-13)	1.03(-13)
	n(OH) [d]	5.0(5)	2.6(6)			5.4(6)	2.5(6)	3.0(6)
	Rate	5.4(-8)	2.6(-7)			8.7(-7)	3.6(-7)	3.1(-7)

a. The four cases use different temperature models as noted. These are average, cold, and hot profiles (ref. 36) Case 4 uses the temperature profile of Case 1.

b. Rate constant calculated by $k = 1.1 \times 10^{-12} e^{-1030/RT}$ as given by Schofield (ref. 37).

c. OH profile given by Bortner and Kummler (ref. 38).

d. OH profile given by Leovy (ref. 39) up to 20 km, and by Hesstvedt (ref. 40) from 45 km up.



Characteristic CO lifetimes required to explain a steady CO concentration level decree a loss rate per CO molecule between the extremes bordering the shaded area. The chemical destruction rates are shown as a function of altitude by the solid lines.

Circled Numbers Correspond to Case Numbers in Table IV. These Are For the CO + OH Reaction.

Figure 8. Rate of CO Removal per CO Molecule. $(\text{Seconds})^{-1}$

The continuity equation for CO vertical transport (following Keneshea and Zimmerman (ref. 34) or Hesstvedt (ref. 35) can be written in one dimension as:

$$\frac{\partial n_{CO}}{\partial t} = P_{CO} - L_{CO} - \frac{\partial \Phi}{\partial z} \qquad (1)$$

where n is the number density of CO, P and L are the chemical production and loss rates of CO, and Φ is the vertical flux of CO. In the lower atmosphere this flux is solely due to turbulent transport so that the vertical velocity resulting from eddy motion is given by:

$$v(z) = -K(z)\left[\frac{1}{n}\frac{\partial n}{\partial z} + \frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H_m}\right] \qquad (2)$$

where K is the eddy diffusion coefficient, T the kinetic temperature, H_m the scale height for the mean molecular weight of the atmosphere, all functions of altitude and time. Thus $\Phi = nv$ is also spatially and temporally variable.

In the steady state $\partial n/\partial t = 0$. Furthermore, it may be assumed as a first order approximation that photodissociation of CO_2 may be neglected as source of CO in the lower atmosphere and thus the continuity equation becomes:

$$\int L dz = -\Phi$$

which suggests that the larger the chemical loss term in the lower atmosphere, the larger the vertical flux of CO and hence the shorter the effective "transport" lifetime (which can be given as $H^2_{CO}/K = \tau_T$).

If the transport lifetime of CO is to be more rapid than that of other species, then it must be the first term of equation (2) which must dominate since K, $1/T\ \partial T/\partial z$, and H_m are the same for all species.
Thus,

$\Phi \doteq -K\frac{\partial n}{\partial z}$, if transport is to be important, and equation (1) becomes

$$H = +\frac{\partial}{\partial z} K \frac{\partial n}{\partial z}$$

$$\int L dz = K\frac{\partial n}{\partial z}$$

Thus, the lower the eddy diffusivity, the steeper the gradient expected. In particular, at the tropopause the rate of mass transport is low and hence the gradient would be expected to be large. This model, qualitatively proposed by Kummler, et al (ref. 1) has been substantiated by Seiler and Junge (ref. 14) who showed in several transpolar flights above and below the tropopause there was a decrease of carbon monoxide mixing ratio above the polar tropopause. The CO mixing ratio in the troposphere fluctuated between 0.1 and 0.2 ppm with values around 0.1 ppm below the tropopause, in agreement with measurements in clean surface air. In the stratosphere the values rapidly dropped below 0.03 ppm and often reached the detection limit of the instrument (refs. 4, 11) (HgO technique). The decrease or increase in mixing ratio usually occurred within a few minutes of crossing the tropopause. The data give strong evidence that the tropospheric CO mixing ratio drops rapidly to very low levels in the stratosphere.

Pressman and Warneck (ref. 41) indicate that 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. The OH radical in the ozonosphere is primarily generated by the reaction (ref. 1)

$$O(^1D) + H_2O \rightarrow 2\,OH,$$

and the photolysis of H_2O and H_2O_2 with the subsequent CO_2 formation by the reaction (ref. 1)

$$OH + CO \rightarrow CO_2 + H$$

which can consume essentially all of the CO entering the stratosphere. They estimate, based on certain limitation, that "the stratospheric sink contributes significantly, but only partially, to the overall removal of CO from the atmosphere". Hesstvedt (ref. 35) substantiates the contention (ref. 1) that OH combines with the CO in the lower stratosphere. He predicts continuous decreases of CO with height in that region of the vertical profile extending from the upper troposphere, where a mixing ratio of 0.1 ppm is obtained 2 km below the tropopause, to the lower stratosphere, where the mixing ratio has dropped to 0.02 ppm, 2 km above the tropopause. His best estimate of the mixing ratio is shown in Figure 9. Seiler (ref. 42) has found a reduction in the mixing ratio from 0.12 to 0.04 ppm on passing from the troposphere to the stratosphere. The CO + OH reaction is discussed in detail in the next section.

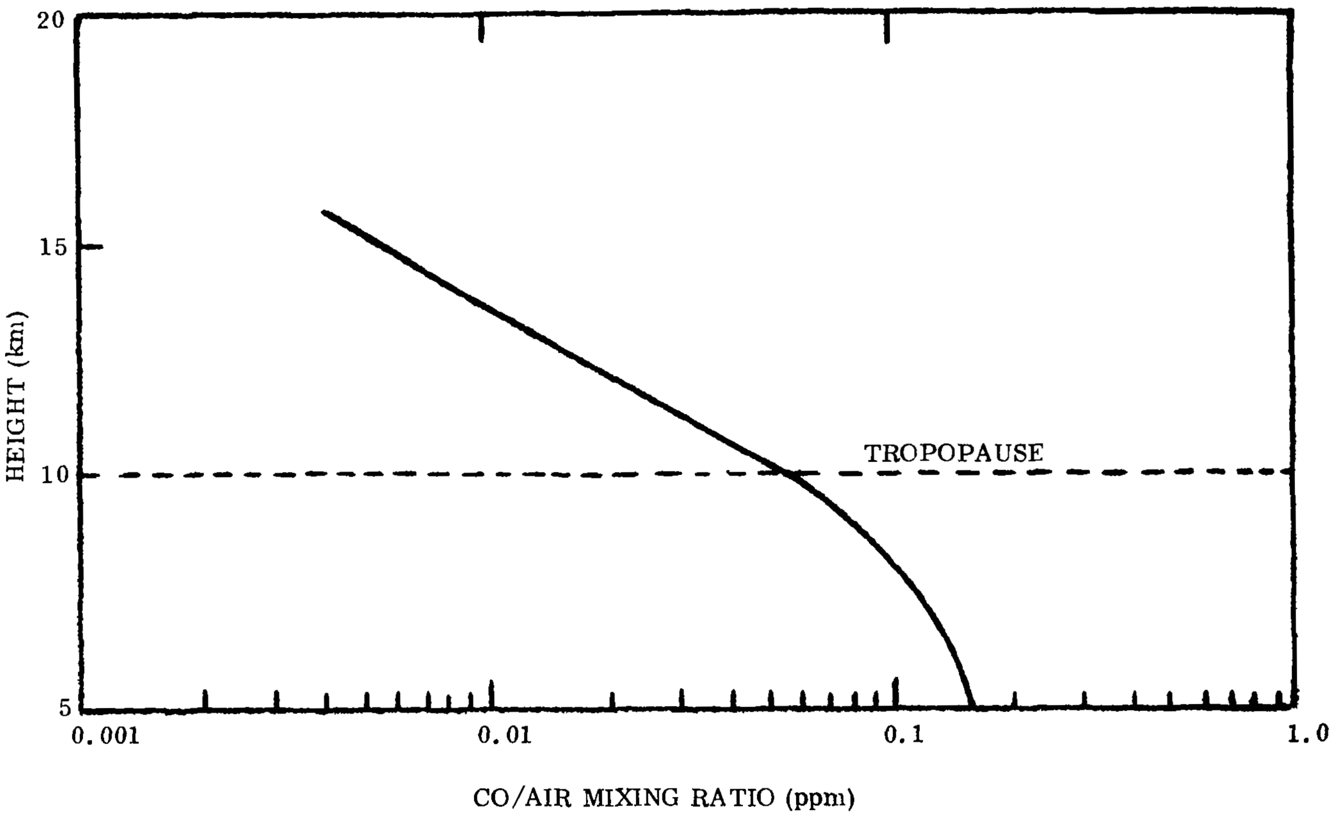


Figure 9. Mixing Ratio (theoretical) of Carbon Monoxide as a Function of Height (ref. 35)

Ground Level and Atmospheric Chemistry

A thorough consideration of the CO balance in the atmosphere must take into account the strongly interacting CO_2 balance. Accordingly, Figure 10 is a diagrammatic representation (ref. 1) of the combined CO/CO_2 atmospheric breakdown. Figure 10 notes that the lower atmospheric chemical conversion of CO to CO_2 is potentially a major CO sink. All processes of importance appear to lead to CO_2, which in turn, through the "greenhouse" effect, globally affects the weather. In Figure 11, the most likely chemistry is illustrated (ref. 1). Also included in Figure 11 are possible reactions whereby the necessary co-reactants with CO are formed.

Any analysis of the chemical conversion scheme illustrated in Figure 11 must be consistent with the following set of facts: (1) as pointed out earlier, the annual rate of CO discharge into the atmosphere is not matched by the known rates of CO removal; (2) yet the global CO background is more or less constant; (3) on the other hand, the global CO_2 background is increasing steadily (refs. 20, 43); (4) therefore, the aggregate rate of chemical conversion of CO to CO_2 must be such as to: (a) match the rate of CO emission, when taken in combination with non-chemical CO sinks, and (b) generate CO_2 at a rate such that, when considered together with the various CO_2 sinks (including upper-atmospheric dissociation) and the other CO_2 sources, there is a net increase in CO_2 concentrations.

It is clear form the above considerations that additional chemical mechanisms (i.e., aside from those treated in earlier works) (refs. 20, 44 - 47) must be important in the CO to CO_2 conversion. In Figure 11, two of these proposed additional reactions are indicated by heavy outlining. A more detailed discussion of the CO removal kinetics, with emphasis on these two reactions, follows.

General considerations. - Table V lists a number of reactions that potentially account for the removal of CO. With them are listed the best available rate constants (in units such that the concentrations are to be expressed in molecules cm^{-3}), and an estimated lifetime of CO at ground level would result from each reaction as calculated, using the listed rate constants and estimated concentrations (ref. 38) of the species reacting with CO. The lifetime is to be compared with that discussed above.

For the surface reactions, estimates given in Table V are not quantitative at this time. Where the surface is charcoal, crude rate data (refs. 48, 49, 50) indicate that this reaction would probably be sufficiently fast to remove CO if enough surface of this type were available (e.g., in soot). However, owing to effects of the crystallographic nature of surfaces, the amounts of such surfaces available, the temperature dependence, and the pressure dependence, this conclusion is extremely tenuous today.

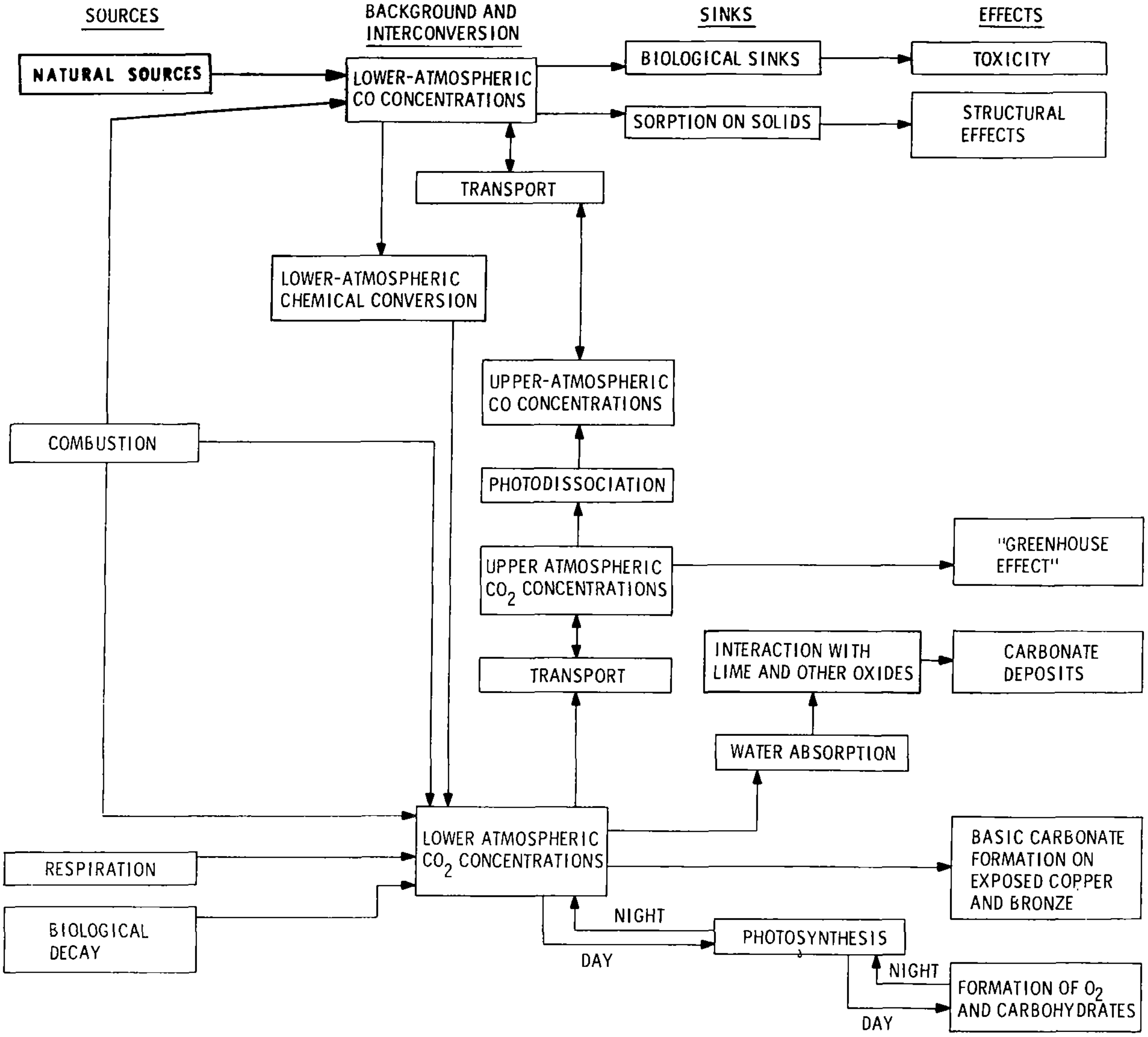


Figure 10. Atmospheric CO/CO_2 Balance

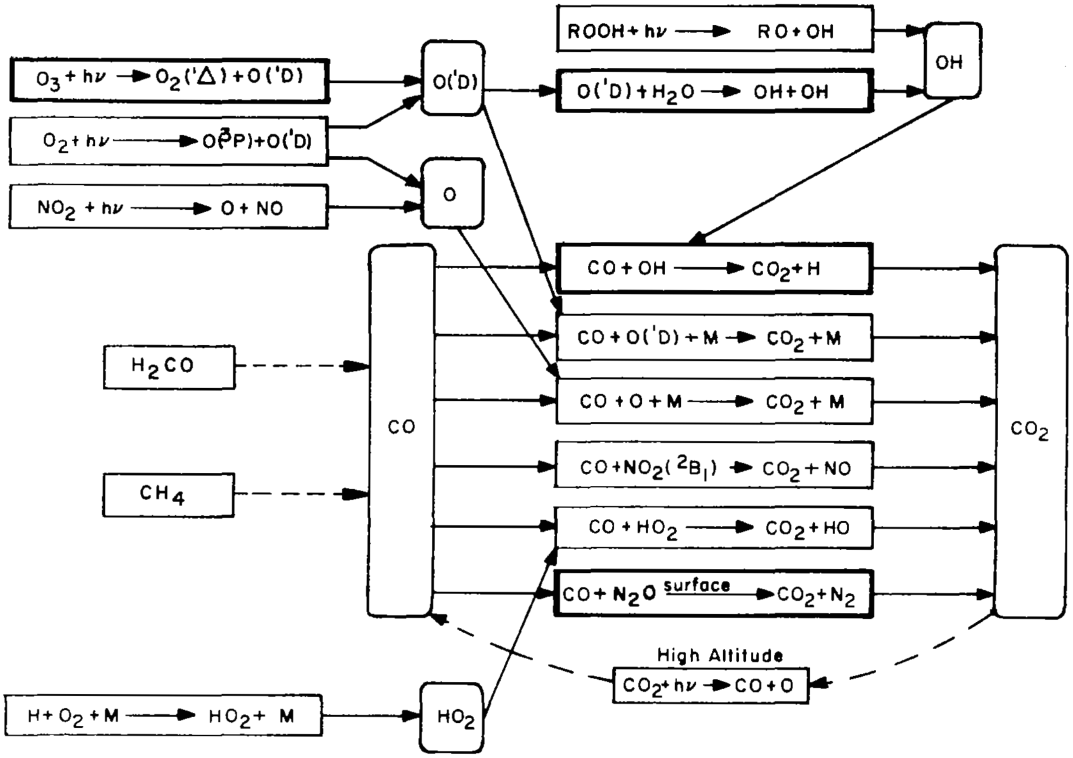


Figure 11. Detailed CO/CO_2 Chemical Conversion Scheme

TABLE V.- REACTIONS CONSUMING CO

	Reactions	Rate Constant Concentrations in Molecules/cc	τ_{CO}(Yr)	Ref.
1.	$CO + OH \rightarrow CO_2 + H$	$1.1 \times 10^{-12} e^{-520/T}$	.13	37
2.	$CO + O(^1D) + M \rightarrow CO_2 + M$	$< 1 \times 10^{-31}$	$> 1 \times 10^{5}$	37
3.	$CO + O + M \rightarrow CO_2 + M$	$1 \times 10^{-30} \exp(-1750/T)$	2×10^{1}	37
4.	$CO + NO_2 \rightarrow CO_2 + NO$	$2 \times 10^{-11} e^{-16000/T}$	1×10^{20}	Est.
5.	$CO + NO_2(^2B_1) \rightarrow CO_2 + NO$	1×10^{-12}	$1 \times 10^{12}/\eta_{NO_2(^2B_1)}$	Est.
6.	$CO + HO_2 \rightarrow CO_2 + OH$	2.5×10^{-17}	1×10^{10}	Est.
7.	$CO + N_2O \rightarrow CO_2 + N_2$	1×10^{-25}	7×10^{13}	48 - 50
8.	$CO + N_2O \xrightarrow{surface} CO_2 + N_2$	$2.4 \times 10^{1} e^{-6000/T}$ (*)	$7 \times 10^{-1\pm2}$	48 - 50
9.	$CO + O_3 \rightarrow CO_2 + O_2$	$< 2 \times 10^{-26}$	2×10^{5}	51
10.	$CO + O_2(^1\Delta_g) \rightarrow CO_2 + O$	$< 9 \times 10^{-27}$	$> 3 \times 10^{10}$	52
11.	$CO + O_2(^1\Sigma_g) \rightarrow CO_2 + O$	$< 2 \times 10^{-25}$	$> 2 \times 10^{8}$	52

(*) This rate constant for the surface reaction is 1st order in CO, zero order in N_2O.

From the estimated lifetimes in Table V, only the reaction with OH (1) and that with N_2O on surfaces (8) appear to be fast enough at ground level to be important. There are the two reactions indicated by heavy outlining in Figure 11; they require much better rate data than are presently available.

Reaction with OH (CO + OH) → CO_2 + H. - This reaction had at one time been dismissed as being too slow for importance. However, in view of newer data and some uncertainties, it required reconsideration recently. The rate is given by k_1 (CO)(OH), where k_1 is the reaction rate constant of the reaction and (CO) and (OH) are the concentrations of these species. The values of the rate constant at 300 K are subject to some uncertainty since at such low temperatures, values must usually be obtained by a lengthly extrapolation from data acquired at somewhat higher temperatures.

An analysis (ref. 37) of all available data suggests a rate constant expression:

$$k_1 = 1.1 \times 10^{-12}\ e^{-520/T}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$$

which has a value at 300 K of $2.0 \times 10^{-13}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$, appreciably higher and more reliable than that used in the past. Thus, this reaction is actually faster than calculations some time ago had indicated it to be.

The most uncertain factor in the rate expression, k_1(CO)(OH), is the concentration of the OH radical. The atmospheric concentration is too low to be measured, but such a limit is well above that needed to make this reaction important. The reactions controlling the interaction of $O(^1D)$, OH, and CO include the following.

10. $O_3 + h\nu \rightarrow O_2 + O(^1D)$ $k_{10} = 1.5 \times 10^{-5}\ \mathrm{sec}^{-1}$

11. $O(^1D) + H_2O \rightarrow 2\,OH$ $k_{11} \approx 1 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$

1. $CO + OH \rightarrow CO_2 + H$ $k_1 = 2 \times 10^{-13}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$

12. $O(^1D) + M \rightarrow O + M$ $k_{12} = 5 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$

In this system, as stated earlier, the $O(^1D)$ reacts with water vapor to form the OH radical. The $O(^1D)$ is formed primarily by photodissociation of ozone and is consumed in reaction 12 by quenching with the major air components, N_2 and O_2, here represented collectively by the general collision partner M.

The first order rate constant shown for ozone dissociation (Reaction 10) assumes (ref. 53), of course, ground-level intensity of the solar radiation, using available measured flux data for the Los Angeles area (ref. 54). (It is recognized that this will vary slightly with the location as well as with time of day and year.) The rate constant k_{11}, is a rather uncertain quantity in this analysis and requires experimental investigation, but k_{12} is well enough known (ref. 55) for the present calculation. Reaction 1 is most rapid in the stratosphere and can certainly account for the removal of CO if the CO is transported to the stratosphere as discussed above.

More recent considerations of the OH chemistry consider the possible cycle

$$\begin{aligned} CO + OH &\rightarrow CO_2 + H \\ H + O_2 + M &\rightarrow HO_2 + M \\ CO + HO_2 &\rightarrow CO_2 + OH \end{aligned}$$

This cycle regenerates the OH so that if the reactions of OH and HO_2 with CO are much faster than any other reactions of OH or HO_2 this cycle would remove CO faster than previously thought. Levy (ref. 57) has calculated a sum of the steady-state OH and HO_2 concentrations to be 4.8×10^8 cm^{-3} for non-time conditions. The rate constant for the CO + HO_2 reaction is unknown. In Table V it was estimated to be 2×10^{-17} cm^{+3} sec^{-1} but it could be much higher. It is unlikely that it is as large as that for the CO + OH reaction. Levy estimates the OH concentration to be 4×10^6 cm^{-3} so that the CO removal rate would be 6×10^{-7} sec^{-1} per CO molecule giving a lifetime of 2×10^6 sec or about 0.1 yr. If an average solar flux is used, a lifetime of about 0.4 yr is obtained. Of course, in any calculation of the effect of OH and HO_2 on CO concentrations in the atmosphere, it is necessary to include other removal mechanisms for OH and HO_2. Among these are:

$$\begin{aligned} OH + OH &\rightarrow H_2O + O \\ OH + HO_2 &\rightarrow H_2O + O_2 \\ HO_2 + HO_2 &\rightarrow H_2O_2 + O_2 \\ OH + H_2CO &\rightarrow H_2O + CHO \\ CHO + O_2 &\rightarrow CO + HO_2 \\ OH + NO + M &\rightarrow HNO_2 + M \\ OH + NO_2 + M &\rightarrow HNO_3 + M \\ HO_2 + NO + M &\rightarrow HNO_3 + M \end{aligned}$$

The chemical kinetic system discussed above controls the $O(^1D)$ and OH. Used in combination with assumed concentrations of 1 x 10^{13} molecules cm^{-3} (0.4 ppm) for ozone, 3 x 10^{17} molecules cm^{-3} (1%) for water vapor, and 3 x 10^{12} molecules cm^{-3} (0.1 ppm) for CO, the concentrations of $O(^1D)$ and OH are found to be 1.2 x 10^{-1} molecules cm^{-3} (4 x 10^{-15} ppm) for $O(^1D)$ and 1.2 x 10^6 (4 x 10^{-8} ppm) for OH. The rates and lifetimes given in Table V are obtained. This lifetime is consistent, within reasonable error limits, with previous estimates of 0.2 (ref. 56) and 2.7 (ref. 2) years, thus indicating that the overall scheme represented by reactions (10), (11),)1), and (12) is probably important. This analysis applies primarily to contaminated air (the O_3 concentration is much lower in clean air). Rates of CO + OH reaction at various altitudes with various temperature and OH profiles are given in Table IV. However, Levy (ref. 57) showed that for clean air OH concentrations that are also consistent with a lifetime of 0.4 years.

Surface Reaction with N_2O $(CO + N_2O \xrightarrow{surface} CO_2 + N_2)$. - The gas-phase reaction of CO with nitrous oxide (i.e., reaction (7)) is too slow to be of any importance in the atmosphere. However, certain surfaces have been found to catalyze this reaction to a point where it could be important. Specifically, the reaction on charcoal (refs. 48 - 50) on pyrex and quartz (ref. 58), and on copper (ref. 59) has been reported to be sufficiently fast to make this a potentially important process.

In real situations, of course, this probably depends on the effects of other surfaces that may be available to the reactants (e.g., bricks, building stone, glass, dust, sand, soils, water droplets, metals, fly ash, concrete, soot, etc.). Data relating to the catalytic efficiency with respect to reaction needed before any meaningful calculations could be carried out to determine the importance of reaction (8) in CO removal.

The rate of the surface reaction between two reactants is given generally by:

$$\text{Rate} = k\,\theta_1\,\theta_2$$

where θ_1 is the fraction of the surface covered by molecule i and is proportional to the partial pressure of i in the gas phase, the sticking probability for the molecule i as it hits an empty site, and the reciprocal of the evaporation probability of molecule i from the surface considered. It is readily seen that the rate of reaction can be a fractional order for any reactant. For the CO - N_2O surface reaction on quartz, CO exhibits the reaction because CO sticks readily, even at 550 C (ref. 60).

It is possible that some other gas, e.g., ozone, will react at a significant rate with CO on appropriate surfaces. However, of the potential surface reactants, N_2O is present in large concentrations over the entire globe. In any event, this catalytic mechanism would only be active over the appropriate catalytic surface and could be distinguished on that basis.

Laboratory photochemical simulations. - Numerous laboratory efforts to identify a homogeneous gas phase chemical mechanism for removal of CO from the atmosphere consistent with likely atmospheric concentrations have been frustrated by the extremely slow reactions involved. The recent apparent exception is the work of Dimitriades and Whisman (ref. 61) who derived a lifetime of 0.2 - 0.3 years, consistent with the carbon dating lifetime of Weinstock (ref. 21). The oxidizing agent operative in the Dimitriades and Whisman study was not identified (O and O_3 were specifically excluded as possibilities), but it was suggested that $O(^1D)$, $O_2(^1\Sigma_g)$, or $O_2(^1\Delta_g)$ might be possibilities. However, the work of Fisher and McCarty (ref. 52) specifically excludes the molecular oxygen singlet states as far too unreactive with CO, and the quenching rate constant for $O(^1D)$ by N_2 ($\sim 8 \times 10^{-11}$ cc/sec) is far too rapid to permit a substantial concentration of $O(^1D)$ to accumulate. A reasonable upper limit based on ozone photolysis as an $O(^1D)$ source can be estimated from the work of Kummler, et al (ref. 53) to be 1/cc which precludes the possibility of $O(^1D)$ involvement even if it reacts with CO on every collision. Since the OH radical concentration is dependent upon the $O(^3P)$ or $O(^1D)$ concentrations, only in a Los Angeles photochemical environment can OH substantially diminish the CO concentration, and turbulent transport effectively prevents even that possibility by diluting the reactants. Thus, even if effective lifetimes of 0.3 years can be obtained on the basis of Los Angeles concentrations, it must be remembered that the air masses do not remain undiluted for more than a few days to a week.

As illustrated in Table V, the rate constants and the upper limits for all known oxidizing agents preclude homogeneous gas phase reactions on a scale necessary to explain atmospheric CO loss. Moreover, it is highly unlikely in the diverse experiments of Dimitriades and Whisman (ref. 61) that even an unknown species would remain at constant concentration from experiment and throughout any given experiment thereby permitting an apparent first order reaction to be observed. Even if an excited state of NO_2 or a hydrocarbon (of which we know little) were significant, it is unlikely that the excited state could remain constant throughout the consumption of the ground state molecule.

There is much more plausible explanation for the results of Dimitriades. It is more consistent with the first order kinetics to assume that the reaction occurs on the walls of the reaction vessel by a heterogeneous catalytic process. As noted in the Air Quality Criteria Document for CO (ref. 4), there is at least one example of heterogeneous CO conversion which is rapid enough on some surfaces to explain the atmospheric CO conversion. While the global distribution of such surfaces is unknown, and hence extrapolations of global lifetimes from laboratory measurements is unwise, it is probable that the rate is rapid enough to explain laboratory experiments of the magnitude reported by Dimitriades and Whisman (ref. 61). This can be verified, of course, by the standard technique normally applied to such slow reactions: varying the surface to volume ratio and the surface type and determining the effect upon the apparent first order rate constant. Without such evidence, it is equally probable that the agreement of Dimitriades with Weinstock is largely fortuitous. If interpreted in the same fashion as the Dimitriades and Whisman data, for example, the work of Fisher and McCarty (ref. 52) in a much different reaction vessel would result in a minimum lifetime of over 30 years.

In conclusion, it is rather unlikely that homogeneous gas-phase kinetics at ground level can explain the CO sink anomaly (ref. 62), it is possible that heterogeneous chemistry is operative; but it is more probable that a biological or transport sink is required to convert CO and CO_2. An earlier laboratory study by Harteck and Reeves (ref. 63) also confirmed that CO, in the presence of O_2 or other absorbing molecules such as O_3, when subjected to high-intensity, ultraviolet radiation in an evacuated chamber, is oxidized to CO_2, but the results are equally difficult to interpret.

Biological Sinks

Biological processes can cause either the formation or the destruction of CO. The rate of CO_2 consumed annually by photosynthesis is given by Johnson (ref. 64) as 1.1×10^{17} gm. To within 0.01%, this rate is matched by oxidation of organic materials. If such an oxidation is inefficient to three parts in 10^5 then this represents a net CO source equal to that of anthropogenic fossil fuel consumption. If the photosynthesis process could reduce 3×10^{-5} as much CO and CO_2, then the CO sink for fossil fuels would be likewise accounted for. Since we know nothing about the possibility of either processes, it has been very attractive to postulate the existence of a biological sink for CO, thus assuming that they are also not mutually cancelling. That biological processes can be effective in removing CO has been shown in the laboratory is noted by Robinson and Moser (ref. 6) citing the work of Inman (ref. 65) who tested the effect of bacteria on CO in chambers.

A potential biochemical removal process for CO is the binding of CO to the porphyrin-type compounds that are widely distributed in plants and animals. In particular, the heme compounds, such as hemoglobin found in man and animals, which are analogous to porphyrin compounds found in plants, are known to bind CO. It must be noted, however, that practically all of the CO absorbed by these heme compounds is eventually discharged from the blood of man and animals and only a small fraction is retained (ref. 66). Nevertheless, this type of process in vegetation may have important potential for scavenging atmospheric CO. Permanent removal from the environment, however, would depend on whether CO subsequently entered into some reaction process to form CO_2 when the porphyrin compound is degraded.

Biological Removal (Terrestrial)

Another possible removal mechanism of atmospheric CO is the presence, in significant numbers, of microorganisms and plants that can metabolize CO. The earth's surface is a possible agent in the removal of CO from the atmosphere. Carbon monoxide in contact with the soil may be oxidized to CO_2 or converted to methane (CH_4) by common specific anaerobic methane-producing soil microorganisms, Methanosarcina Barkeri and Methanobacterium formicum, in the presence of moisture.

This action has been demonstrated in the laboratory by Schenellen (ref. 67) who showed that pure cultures of these bacteria utilize CO as a source of carbon and convert CO into methane. Schenellen found that Ms. Barkeri is capable of effecting a considerable conversion of CO to CH_4 according to the equation:

$$4\ CO + 2\ H_2O \rightarrow CH_4 + 3\ CO_2$$

Stephenson (ref. 68), however, indicates that CO, in the absence of H_2, reacts with water in these bacteria in two stages as follows:

$$4\ CO + 4\ H_2O \rightarrow 4\ CO_2 + 4\ H_2\ ,$$

and

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O\ .$$

In the presence of H_2, these bacteria convert CO directly into methane and water:

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$

Yagi (ref 69) reported the conversion in vitro of CO to CO_2 by cell-free extracts of the sulfate reducing bacteria, Desulfovibrio desulfuricans in the presence of sulfite as an oxidant. (The bacterial extracts were prepared by subjecting the cell suspension to sonic disintegration.) The enzyme conversion of CO into CO_2 by the bacterial extract was demonstrated by means of $C\ ^{14}O$ as a tracer. This study confirms other known studies of the oxidation of CO to CO_2 by several kinds of bacteria and corroborates the potentiality of soil bacteria serving as a sink for atmospheric CO.

Only recently, under sponsorship of the CRC's APRAC project CAPA-4-68, has a systematic effort begun at SRI under Inman (ref. 65) to identify a potential biological CO sink. The original effort was to have focused on plant life, but it was soon noted that the plants had little to do with the rapid (120 ppm in 2 - 3 hours) uptake of CO above the sample. The results were confirmed by field tests as well.

Sterile soil with and without plants did not deplete the CO concentration above, whereas soil with a high organic content and perhaps a high pH (with some exceptions) tended to eliminate CO rapidly. Thus, it was concluded that microorganisms present in the soil can remove CO from the atmosphere. General observations made on preliminary data suggest that: (1) the maximum rate of CO removal occurs at 30°C; (2) sterilization, (3) anaerobic conditions, (4) abnormally high salinity, and (5) antibiotic and fungicide treatment of the soil, inhibit CO removal, suggesting strongly that the removal mechanism was a bacteria or fungi rather than a physical or chemical process. Some of the more active soils were capable of removing as much as 500 tons/sq. mi. /yr. based on scaling up the sample and a crude measure of the U.S. soil capacity was given as 570 x 10^6 metric tons/yr. (ref. 65). Thus far 16 fungi capable of CO removal alone have been identified but no bacteria have yet exhibited similar properties. A summary of the data has been provided by Inman (ref. 70) as shown in Table VI.

In the discussion above of the difference in the concentrations of CO in the northern and southern hemisphere, it was noted that this could be due to the presence of the primary sink in the southern hemisphere. In light of Inman's work (ref. 65) this is reasonable since much of the hot, humid soil of high organic content exists there. This is perhaps ideal for anaerobic bacteria.

Horizontal Transport

Kwok, et al (ref. 71) have included CO convective transport in an atmospheric circulation model for a four week simulation of dispersion from the North American Continent, Europe and Asia. It took about two days for the American sources to reach the north Atlantic and after six days discernible contours linking the two sources were evident. The resulting contour map is shown in Figure 12. This may be regarded as a limiting case, since horizontal eddy diffusion and CO sinks were neglected, and any natural source was neglected as well. The study does show the obvious rapid convective mixing which occurs in the northern Hemisphere, and the very slow interchange between hemispheres. However, the work of Kwok, et al, also demonstrates the inherent difficulty and potential danger of employing a finite number of clean air monitoring stations across the globe in an effort to measure the spatial and temporal atmospheric burden of CO. It is highly preferable to obtain total systematic continuous global coverage within as short a time as possible to properly weigh the observations. This cannot be easily achieved with a few dozen stations, but is readily accomplished by remote sensing from an orbiting platform.

Meteorological phenomena will affect the exposure of air masses to diverse conditions. Examples can be cited: Tradewinds over land masses vs winds just completing a marine traverse; duplication of coverage before and after a storm front; confierous forrests (Canada, Siberia, Amazon, etc.); large bodies of fresh water with high organic content (i.e., Lake Erie vs Lake Superior); and climate such that

TABLE VI. - RATE OF REMOVAL OF CO FROM TEST ATMOSPHERES AT 25 °C BY VARIOUS SOILS (Ref. 62)

Location of Soil[a]	Vegetation	pH	Sand: Silt:Clay	% Organic	CO Uptake[b] mg/hr/m^2
Eureka-Arcata	Coast Redwoods	5.7	53:34:13	25.1	16.99
H. Cowell St. Pk.	Oak	5.3	73:12:15	11.2	15.92
H. Cowell St. Pk.	Coast Redwoods	5.7	57:26:17	13.6	14.39
Lake Arrowhead[c]	Ponderosa Pine	6.2	65:24:11	17.4	13.89
Redding	Grass-legume Pasture	5.1	53:32:15	21.0	11.94
Riverside[c]	Grapefruit[d]	6.6	75:14:11	4.3	11.48
Yosemite Valley	Grass Meadow	5.05	49:42:9	20.6	10.52
Kauai, Hawaii	Forest	4.74	58:18:24	22.8	9.90
San Bernardino Freeway[c]	None	7.2	55:30:15	2.2	6.89
Mojave Desert	Chaparrel	7.9	79:6:15	2.4	6.46
Woodland	Oak Stubble[d]	6.6	33:32:35	2.1	6.23
Riverside (Desert)[c]	Chaparrel	7.35	85:4:11	1.0	4.31
Yosemite Wall	White Fir	5.1	65:18:17	5.7	3.48
Corcoran	Cotton (fallow)[d]	7.1	57:22:21	2.8	3.48
Hanford	Almond[d]	6.95	53:26:21	3.5	2.82
Boynton Beach, Florida	Weeds (fallow)[d]	6.0	86:0:14	1.4	2.65
Oahu, Hawaii	---	4.93	40:26:34	15.3	2.16

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a. All soils collected in California unless otherwise noted.

b. Average rate at end of test period; 2-3 determinations.

c. Locations where high levels of air pollution occur due to combustion of fossile fuels and photochemical smog.

d. Land under cultivation or with recent history of cultivation.

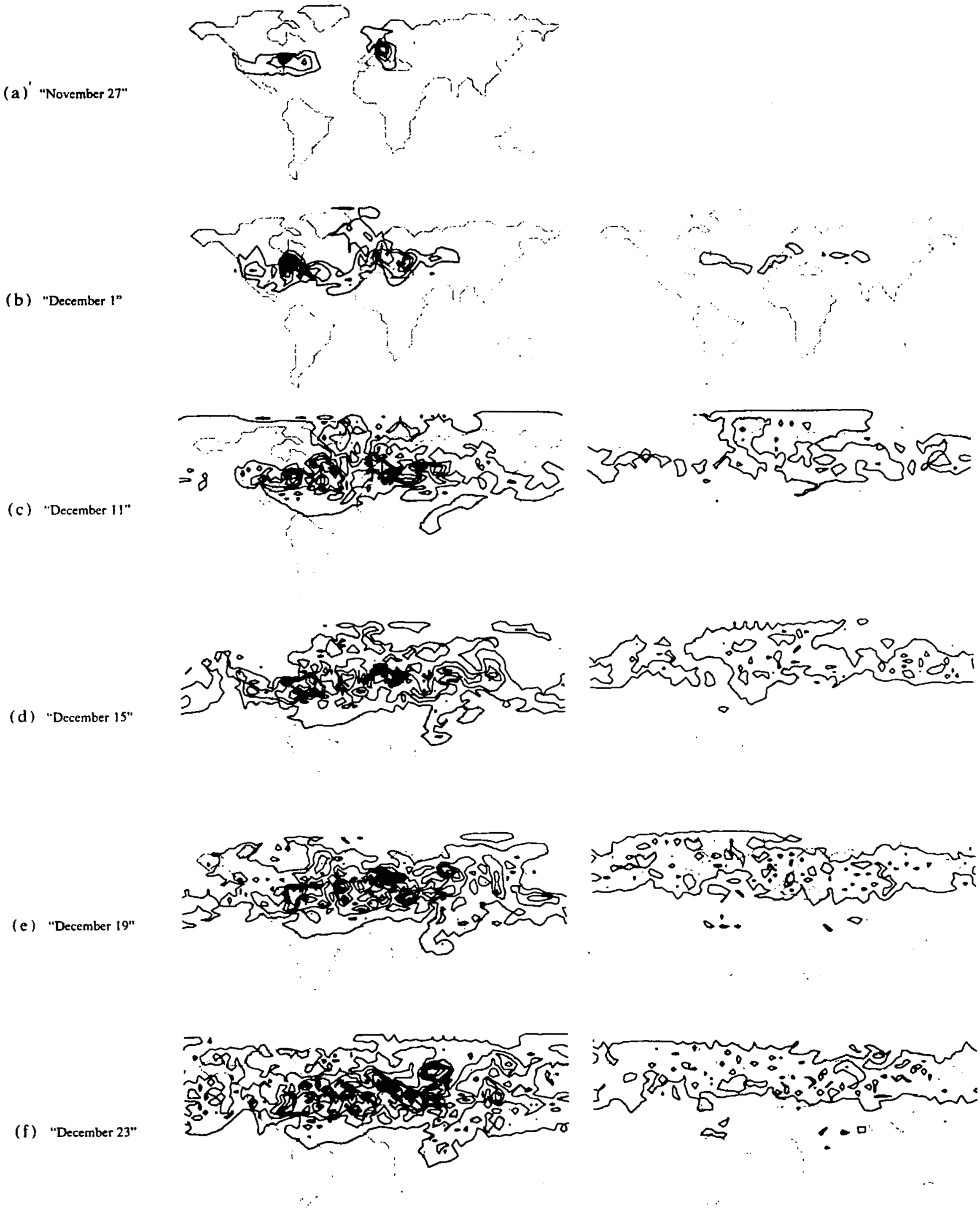

Figure 12. Simulated CO Concentration Contours for the Days Indicated at 00:00 GMT. The Contour Interval is 10 (CO) ppb. Diagrams on the left are the lower-layer contours; those on the right are the upper-layer contours (ref. 71).

the mean temperature is about 30 C. In Figures 13 - 15, global maps are presented (ref. 72) which illustrates mean temperature, tradewinds and areas of high organic content (ref. 73) which should be emphasized in CO sink data analysis.

Ocean Sink

There is no evidence at present that the oceans are a sink for CO since no process or reaction has been discovered that would remove CO from the atmosphere (refs. 20, 45). As mentioned previously, Swinnerton, et al (ref. 31) recently simultaneously measured the CO content of the atmosphere and of the surface water. These investigators found that the actual measured CO concentration of the surface waters at all sampling points was much greater than that of a concentration of CO in water in equilibrium with the CO measured above the water. These findings (ref. 31) indicate that the ocean in the areas sutdied is not a sink for atmospheric CO, but, indeed, serves as an additional natural source. This evidence, however, does not preclude the possibility of the ocean serving as a sink for atmospheric CO as well. In the case of CO_2, it has been demonstrated that the oceans are a major sink for atmospheric CO_2 as well as a source for release to the atmosphere (ref. 74).

CONCLUSIONS

The problem of carbon monoxide in the atmosphere is still replete with unsettled questions. Although over the past several years significant new information has been obtained relating to sinks, to sources, and to concentrations, none of these questions have been definitely and quantitatively answered. The present status of information concerning the sink question indicates that the most likely sinks are interaction with soil bacteria, reaction with OH near the ground, and transport to and reaction with OH in the stratosphere. With these singly, or in combination, lifetimes of a few tenths of a year could be accounted for although for the definite establishment of a sink mechanism both better data on various parameters involved and better CO concentration data are needed.

Sinks are most likely rather extensive covering significant global areas. Since they are extensive and could occur anywhere on the globe, a satellite-based remote measurement technique is ideally suited for the measurement. Of course, if the sink covers the entire globe, the measurement of concentrations will not show the sink region. If it is localized to some extent to regions which are rather extensive, as would be effected by most sink mechanisms, the measurement of CO densities with spatial resolution of the order of 25 to 50 miles should provide the information needed to locate the sink.

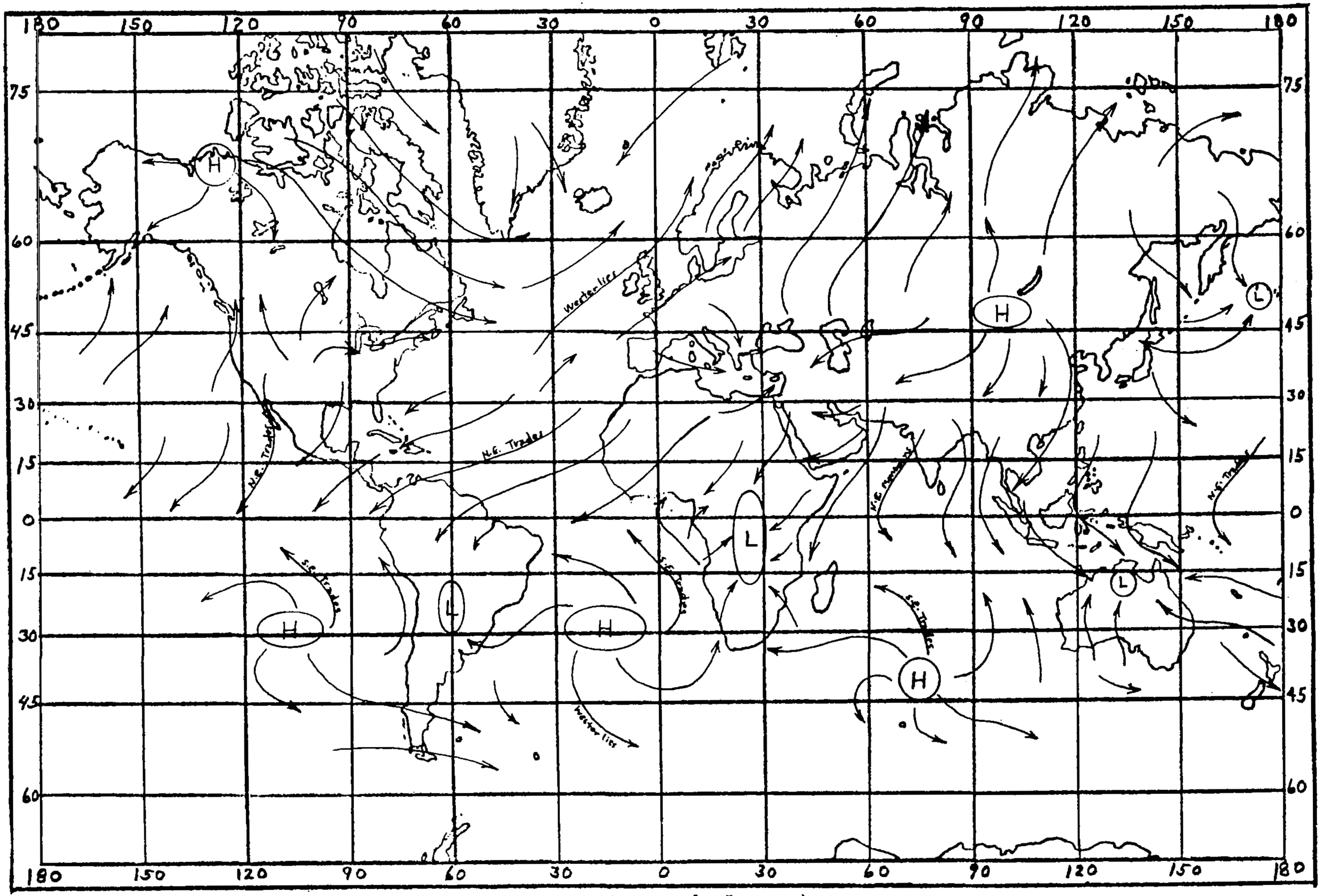

Figure 13. Prevailing Surface Winds (January)

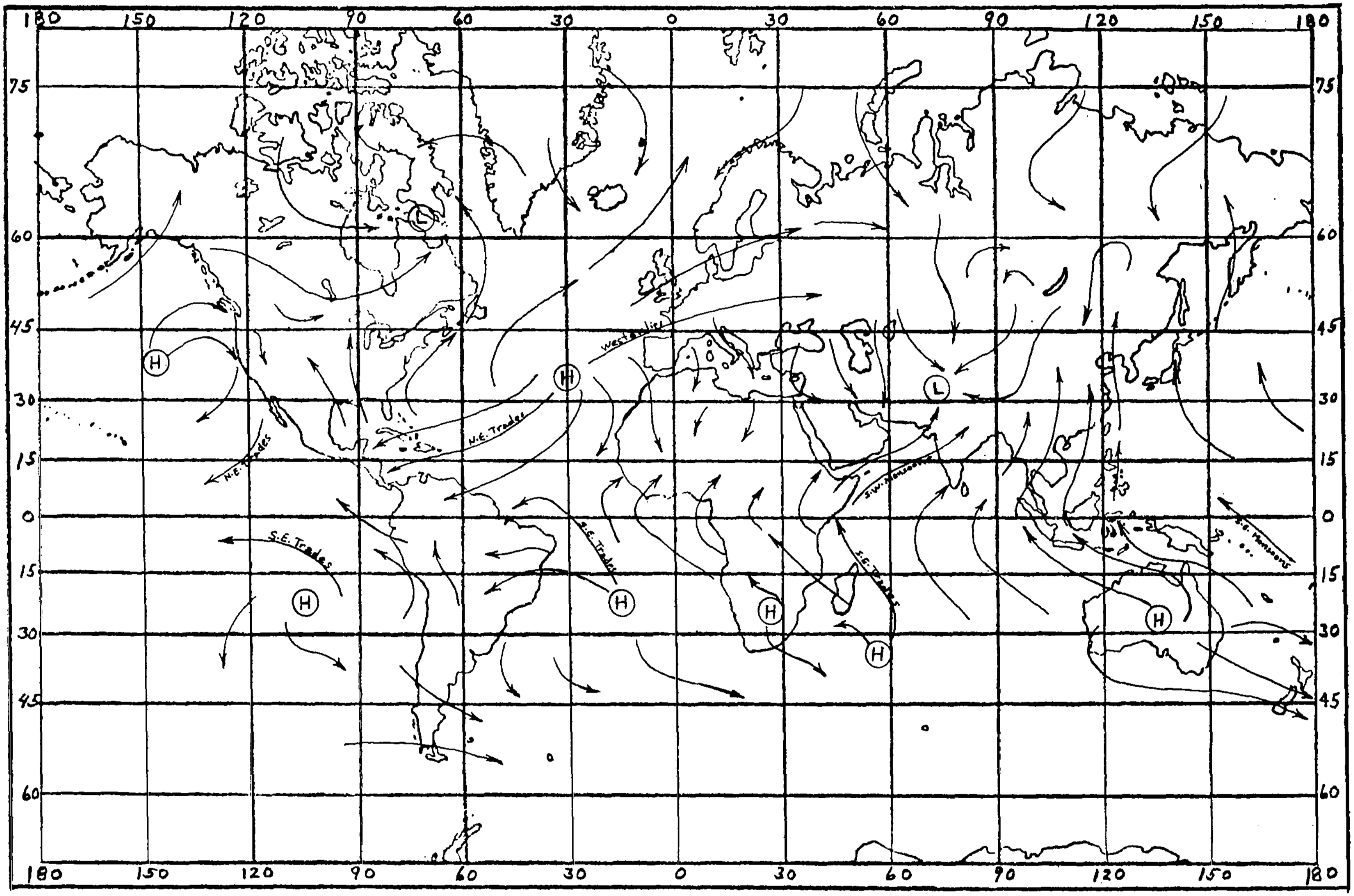

Figure 14. Prevailing Surface Winds (July)

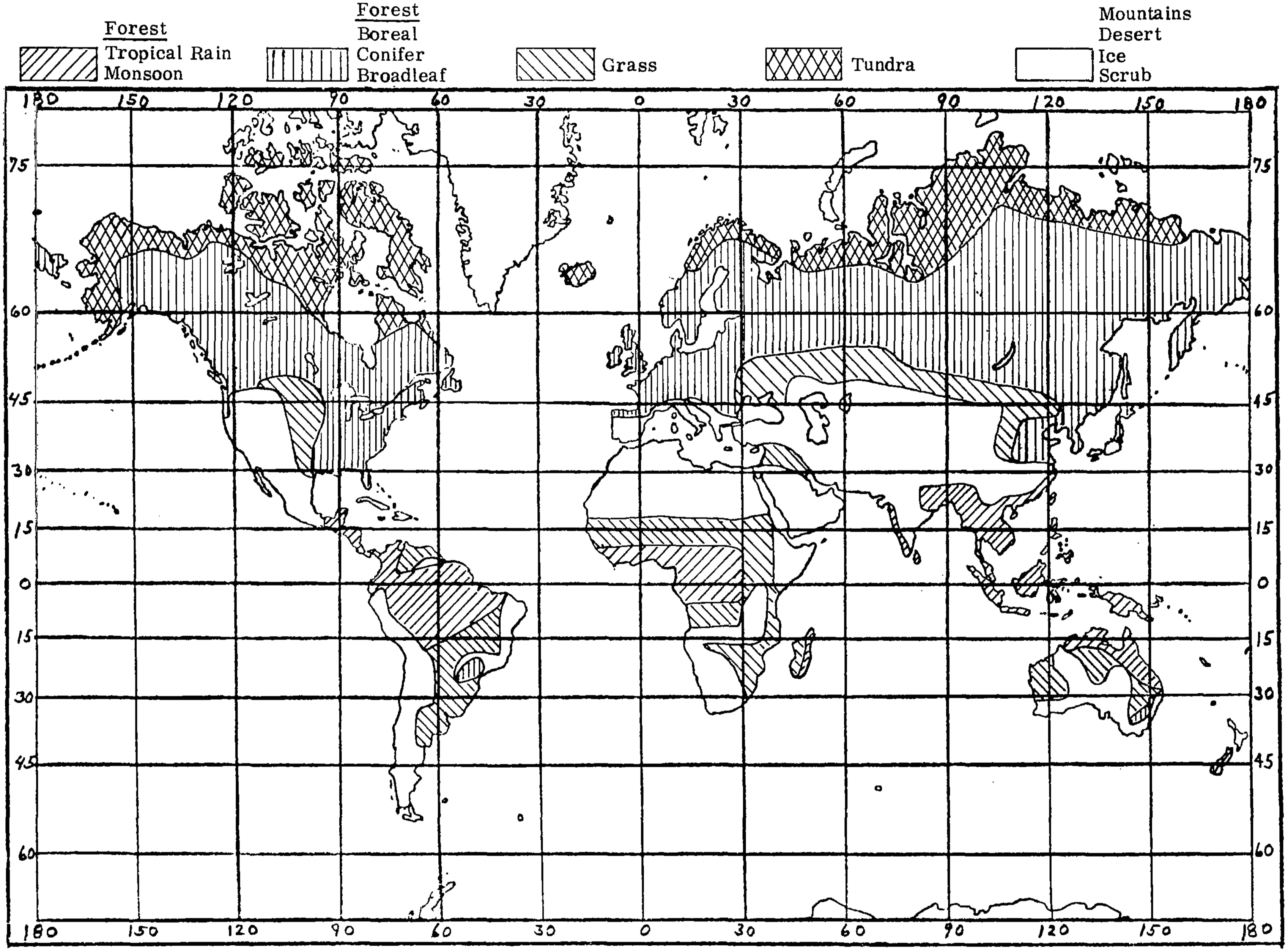

Figure 15. World Vegetation Types

The carbon monoxide produced by the various sources has time to circulate around the globe at least mixing in each hemisphere although perhaps not enough time for appreciable interhemispheric transfer. There may or may not be time enough for transfer of significant amounts to the stratosphere. Just how much mixing is possible depends on the sinks and the resultant lifetime which is probably somewhere between 0.1 and 1 year, most likely around 0.4 year.

There are logical indications that there exists some unidentified significant natural source of CO. If the lifetime is of the order of a half a year or less there is almost certainly some unidentified source. If this is the case, it suggests that the sink strength is much larger than previously supposed. Data are needed to determine this.

All parts of the CO question require further investigation. Data are needed on both localized and global CO measurements, at ground level, in the troposphere and in the stratosphere. Data possibly best found by global atmospheric measurements are needed on other sources. Data are needed related to certain sink processes. Most important are various laboratory data such as these required for the analysis of atmospheric chemistry and for those required to quantify biological CO removal processes. The sink mechanism problem can be solved only by obtaining sufficient atmospheric CO measurement data, supporting atmospheric measurements of related species, supporting laboratory data, and ground measurements of the characteristics of any sink region found, thus permitting the quantitative determination of the sink strength and allowing extrapolation to determine the trend of world-wide CO concentration in the future.

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NASA-Langley, 1972 —— 13 CR-2081