Carbon Monoxide: Natural Sources Dwarf Man's Output

Man releases nearly 270 million tons of carbon monoxide into the atmosphere each year, primarily as a result of incomplete combustion of gasoline in automobiles. This amount is more than half of the 530 million tons of CO normally present in the troposphere, and environmentalists have long feared that such a large output of CO would seriously distort the composition of the atmosphere.

It appears that such worries were unfounded. While localized buildup of CO in cities may still represent a serious health hazard, man's CO production is relatively insignificant when considered on a global basis. Experimental results revealed last month by a team from Argonne National Laboratory provide the first substantive—albeit indirect—evidence that natural sources produce more than 3.5 billion tons of CO per year in the Northern Hemisphere alone, or more than ten times the amount produced by man.

The Argonne project—performed under a contract from the Coordinating Research Council, a nonprofit organization directed by the American Petroleum Institute, the Automobile Manufacturers Association, and the U.S. Environmental Protection Agency—relied on the observation that CO emissions have distinctive isotopic compositions characteristic of the source. By analyzing the isotopic composition of CO samples collected at many locations and at various times of the year, the Argonne group was able to trace the origin of several different species of CO. And by comparing the average isotopic composition of atmospheric CO with that of a CO species whose production rate is known, they could then estimate the production rates of other species.

The experimental procedure was straightforward but rather tedious. For each isotopic determination, 87-liter samples were collected at 2 to 3 atmospheres pressure and stripped of moisture, carbon dioxide, and oxides of nitrogen. The remaining CO was then oxidized to CO$_2$, which is more easily purified, and the ^{18}O/^{16}O and ^{13}C/^{12}C ratios were determined with an isotope-ratio mass spectrometer. Appropriate calculations then provide the ^{18}O enrichment and the ^{13}C depletion of the CO sample with respect to accepted oxygen and carbon isotopic references.

With this procedure, five major species of CO (Table 1) were identified in atmospheric samples collected at various times of the year, says Charles M. Stevens, head of the Argonne team. Two of these species (less enriched) are characterized by an ^{18}O enrichment of about 0.5 percent. These species were present all year and accounted for the dominant proportion of atmospheric CO. The remaining three species (more enriched) showed an ^{18}O enrichment varying from 1.6 to 3.3 percent. Production of each of these is associated with a specific season of the year, and each may represent a mixture. All five species exhibit a ^{13}C depletion ranging from 2.2 to 3.0 percent.

The general seasonal characteristics of atmospheric CO in rural Illinois, Stevens tells *Science*, are consistent with the presence of a relatively constant concentration (0.10 to 0.15 ppm) of the less enriched species, and variable concentrations of the more enriched species (0.15 to 0.5 ppm in winter, 0.03 to 0.30 ppm in summer). Measurements at many locations indicate that the constant concentration of the less enriched CO (varieties 1 and 2) occurs throughout the world.

The production rate of the less enriched species—as well as that of the other species—can be estimated, Stevens says, by determining the average relative concentration, on a global basis, of automobile CO and using this figure as an internal standard for isotopic dilution calculations. This process provides a production rate for the less enriched species of more than 3 billion tons per year in the Northern Hemisphere.

These species probably arise from oxidation of methane in the troposphere. Various investigators have found that methane is produced in swamps, rice paddies, and tropical regions by decomposition of organic matter under water. Measurements at various locations, Stevens says, indicate that an average acre of swamp or paddy emits about 3000 pounds of methane per year (complete conversion of which would produce 5000 pounds of CO). Elmer R. Robinson and Robert C. Robbins of Stanford Research Institute have estimated that global meth-

Table 1. Identifiable species of atmospheric CO in rural Illinois.

Variety	^{18}O Enrichment * (%)	^{13}C Depletion † (%)	Principal occurrence	Source	Production rate in Northern Hemisphere
AGA‡	2.46	2.74			
1	0.5	3.0	Principal species everywhere. Increased abundance in summer	Methane	$>3 \times 10^9$ ton/year
2	0.5	2.4	In varying amounts with 1. Increased concentration in winter and spring. Also in marine air of low northern latitudes	Probably methane	
3	1.6–1.8	2.8	Lesser abundant heavy oxygen species during summer	Unknown	$\sim 5 \times 10^7$ ton/month during summer
4	2.6–3.3	2.2–2.6	Major species during autumn	Degradation of chlorophyll	2–5 $\times 10^8$ tons during autumn
5	2.0–2.5	2.7	Major species during winter and early spring	Primarily anthropogenic	3–6 $\times 10^7$ ton/month during winter

* With respect to the accepted oxygen isotopic standard, standard mean ocean water. † With respect to the accepted carbon isotopic standard, Peedee belemnite. ‡ AGA, average global automobile. [Source: Argonne National Laboratory]

ane production is at least 1.6 billion tons per year, and two other research groups have independently concluded that all this methane is eventually converted to CO.

J. C. McConnell, M. B. McElroy, and S. C. Wofsy of Harvard University have calculated (*1*) from photochemical considerations that the predominant atmospheric reaction of methane below 80 kilometers is its oxidation by hydroxyl radicals. Small quantities of methane are also converted to CO by reaction with metastable oxygen atoms or, above 80 km, by direct photolysis of methane by solar radiation. They further conclude that the resultant CO is converted to CO_2, also by reaction with hydroxyl radicals, and that the average residence time of CO in the atmosphere is 0.3 year.

Bernard Weinstock of Ford Motor Company, Dearborn, Michigan, has reached similar conclusions (*2*) by consideration of the ^{14}CO balance in the atmosphere and estimates an annual global CO production of 6 billion tons. He calculates also that the average residence time of methane in the atmosphere is 1.5 years and that of CO is 0.1 year. Weinstock's experimental data was obtained in winter, Stevens points out, and the residence time of CO declines to about 10 days in summer because of the increased solar radiation. Because both formation and destruction of CO are dependent on the concentration of hydroxyl radical, however, the concentration of CO produced from methane is independent of the amount of solar radiation and the residence time.

The more enriched species of CO arise from many sources. Variety 3 occurs principally in the summer, Stevens says, and may be associated with the growth of plants. The $^{18}O/^{16}O$ ratio for this species is similar, for example, to that of CO from bagged tree branches or from cut green plants. He estimates that about 200 million tons of variety 3 are emitted during the summer.

The second species of more enriched CO (variety 4) occurs in a large burst during the fall, and is assumed to arise from dying plants. Another Argonne team, headed by Joseph J. Katz and Henry L. Crespi, reported in June that the degradation of each mole of chlorophyll in plants produces at least 1 mole of CO, and perhaps much more. Stevens has found also that the isotopic ratios of variety 4 are identical to those of large CO concentrations found in isolated areas of forests during autumn. The estimated emission of this species is 200 to 500 million tons for a 6-week period.

Katz and Crespi also found that CO is produced by the chemical processes associated with the biosynthesis of photosynthetic pigments in algae and, presumably, other plants. Because the growing season is much longer than the dying season, however, this form of CO does not occur in a large burst, and is thus not readily identifiable. It may well be part of a mixture of CO species observed by Stevens during the spring, and may contribute an amount of CO equal to that produced by dying plants.

Anthropogenic CO Enhanced in Winter

The final identifiable species (variety 5) of atmospheric CO is produced during the winter, and is presumed by Stevens to arise principally from automobile emissions and combustion of fuel for residential heating. An increased concentration of CO from such sources would be expected because of the reduced solar radiation in winter and the concomitant decrease in the scavenging rate for CO, he argues. The actual concentration of this species in the northern midlatitudes may thus be as great as eight times the average hemispheric concentration.

Production of CO by residential heating may also be enhanced by a seasonal factor of 4 or 5. Stevens thus estimates that atmospheric CO in winter could consist of as much as 10 percent from residential heating and 50 percent from all anthropogenic sources—even though the average contribution from anthropogenic sources during the year is less than 10 percent. The collective production rate of these species is estimated to range from 30 to 60 million tons per month during winter.

There are, of course, other sources and sinks of CO that have not yet been studied by Stevens' method. The largest additional source is probably the ocean. Most marine species produce CO, and John W. Swinnerton and his associates at the Naval Research Laboratory, Washington, D.C., for example, have found that the surface waters of the western Atlantic are supersaturated with CO. They calculate that the oceans produce about 55 percent of the amount of CO produced by anthropogenic sources, or about 150 million tons per year.

The largest CO sink, other than the atmosphere, appears to be microorganisms in the soil. A Stanford Research Institute group led by Royal B. Ingersoll has found (*3*) that most soils contain bacteria that convert CO to CO_2. The average soil in temperate climates, they suggest, can convert about 210 tons of CO per square mile per year. The soil surface of the United States alone, therefore, is capable of removing about 600 million tons of CO from the atmosphere per year. Other suggested sinks include transport of CO to the stratosphere for photolytic decomposition, and conversion into CO_2 by fungi.

Many aspects of the atmospheric CO balance still remain unexplained or require additional experimental confirmation. Of particular interest are a knowledge of the isotopic composition of atmospheric methane and an exact knowledge of the atmospheric concentrations and distribution of hydroxyl radical, CO, and methane. One expected source of information is a carbon monoxide pollution experiment (COPE) being undertaken for the National Aeronautics and Space Administration by General Electric Company, Valley Forge, Pennsylvania.

General Electric, in cooperation with Barringer Research of Toronto, Ontario, is developing a correlation interferometer in which reflected sunlight is used to measure concentrations of CO and methane in the earth's atmosphere. The interferometer will ultimately be mounted in an earth-orbiting satellite to provide global data about the distribution of the two gases. The orbiting instrument will also be used to obtain vertical concentration profiles for the two gases by measuring incident sunlight through various layers of the atmosphere. These profiles should indicate where in the atmosphere the conversion of methane to CO is occurring.

Equally important is measurement of the concentration of hydroxyl radicals in the troposphere to confirm that the concentration is sufficiently high for complete conversion of the methane. Several groups are now working on the development of laser spectrometers that have sufficient sensitivity to measure the low concentrations (2.3 million molecules per cubic centimeter) predicted, but it may be 2 years or more before such measurements can be made. This measurement, combined with those from the COPE experiment, should finally provide a greater understanding of the CO balance in the atmosphere.

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References

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2. B. Weinstock, *Science* **176**, 290 (1972).
3. R. B. Ingersoll, *ibid.* **172**, 1229 (1971).