(*13*). Although NaCl at a concentration of 100 to 200 mg/liter may not be harmful to the general population, it is of concern to persons on salt-restricted diets. The American Heart Association recommends that water containing more than 22 mg of sodium per liter (59 mg of NaCl per liter) should not be used when patients are on diets with an intake of sodium restricted to < 1 g/day (*14*). The normal adult intake of sodium is about 4 g/day (*1*). In this regard the water supplies of some 62 communities in Massachusetts were considered to contain excessive amounts of sodium in 1970 (*15*). It is thought that the bulk of the sodium originates from the use of salt on roads.

EDWIN E. HULING
THOMAS C. HOLLOCHER
Environmental Studies Program,
Brandeis University,
Waltham, Massachusetts 02154

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Carbon Monoxide Balance in Nature

Abstract. *Consideration of the steady-state equations for stable carbon monoxide and for radioactive carbon monoxide in the troposphere leads to the conclusion that carbon monoxide is produced at a rate of* 5×10^{15} *grams per year, a value some 25 times greater than the rate of carbon monoxide production from combustion. The concomitant residence time for carbon monoxide is 0.1 year, in agreement with a previous estimate of Weinstock. Hydroxyl radicals are shown to account for both the production of this large amount of carbon monoxide by methane oxidation and for its removal by carbon monoxide oxidation. The average concentration of hydroxyl radicals in the troposphere required to achieve this effect is* 2.3×10^6 *molecules per cubic centimeter, with a daytime concentration of twice that. Levy and McConnell, McElroy, and Wofsy have deduced concentrations of hydroxyl radicals in the troposphere of the same magnitude from purely photochemical considerations, in support of this model.*

In an earlier publication (*1*) Weinstock pointed out that the residence time of CO in the atmosphere could be derived from radiocarbon data because the "hot" ^{14}C nuclei produced by the ^{14}N(np) reaction of cosmic-ray neutrons are first fixed as CO (*2*) before being converted into CO_2. A residence time of 0.1 year for ^{14}CO was then derived from measurements of the concentration of ^{14}CO in the atmosphere (*3*) and an estimate of its rate of formation (*4*). This 0.1-year value was suggested as a lower limit because a significant fraction of the ^{14}CO is formed in the stratosphere and may be converted to $^{14}CO_2$ there, before mixing into the troposphere. The same residence time was presumed to apply for stable CO. On the other hand, a residence time for stable CO of 2.7 years had been derived from estimates of the global production rate of CO and the average concentration of CO in the atmosphere (*5, 6*). The discrepancy of an order of magnitude between these two independent estimates of the CO residence time would be resolved if the global production rate used in the 2.7-year calculation had been underestimated by an order of magnitude. Presumably this overlooked source would be from "living" carbon and would also be a significant source of ^{14}CO. In this report the residence time of CO derived from ^{14}CO data and that from data on stable CO are brought into agreement and the amount of CO produced by nature is concomitantly derived. A quantitative explanation is then offered for the major aspects of the formation and removal of CO in nature.

The balance of CO in the troposphere can be expressed in terms of two steady-state equations, the first for stable CO and the second for radioactive ^{14}CO:

$$\frac{d(\mathrm{CO})}{dt} = P_1 + P_2 - k(\mathrm{CO}) = 0 \qquad (1)$$

$$\frac{d(^{14}\mathrm{CO})}{dt} = NP_1 + P_3 - k(\mathrm{CO}) = 0 \qquad (2)$$

In these equations, $d(\mathrm{CO})/dt$ and $d(^{14}\mathrm{CO})/dt$ are the rate of change with time of the total number of moles of stable CO and of radioactive ^{14}CO in the troposphere, respectively. These are equal to zero in the steady state. The quantity P_1 is the unknown rate of production of CO (in moles per year) from "living" carbon that is introduced into the troposphere. This will contain ^{14}CO of mole fraction N equal to 1.17×10^{-12} (*7*). The rate of introduction of ^{14}CO into the troposphere from this source is then NP_1 moles per year. The quantity P_2 is the rate of production of CO from "dead" carbon (fossil fuels) estimated to be 7×10^{12} mole year^{-1} (*6*); P_3 is the rate of production of ^{14}CO in the troposphere by cosmic-ray neutrons, 290 mole year^{-1} (*8*). The same first-order rate constant, k (per year), is assumed to apply for the removal of both CO and ^{14}CO from the troposphere; (CO) is the total amount of stable CO in the troposphere, $1.7 \times$

10^{13} mole (*9*), and (^{14}CO) is the total amount of ^{14}CO in the troposphere, 45 mole (*10*).

Equations 1 and 2 can be solved for P_1 and k. On the basis of the values given in the preceding paragraph for the other terms in the equations, P_1 is 1.8×10^{14} mole year^{-1} or 5×10^{15} g year^{-1}. This amount is 25 times greater than that estimated from the combustion of fossil fuels (*6*). The value of k for the removal of CO from the troposphere is calculated to be 11 year^{-1}. The residence time of CO is the reciprocal of this or 0.09 year. This value is coincidentally in agreement with the previous estimate of 0.1 year (*1*), which had been suggested as a lower limit because the ^{14}CO produced above the tropopause was also included in the production rate. However, since NP_1, 210 mole year^{-1}, largely compensates for the amount of CO produced above the tropopause by cosmic-ray neutrons, 370 mole year^{-1}, the two values are the same. Consideration of the uncertainties of the data and of the assumptions made gives rise to an estimate of the uncertainty in the values of P_1 and of k of about 50 percent.

In Weinstock's earlier report (*1*), the reaction

$$CO + OH \rightarrow CO_2 + H \qquad (3)$$

was suggested as a possible mechanism for the major removal of CO from the atmosphere with the reservation that OH would have to be maintained in sufficient concentration. This required OH concentration is the ratio of the first-order rate constant k divided by k_3, the bimolecular rate constant for Eq. 3. If we take k to be 11 year^{-1} or 3.5×10^{-7} sec^{-1} and k_3 to be 1.5×10^{-13} cm^3 molecule^{-1} sec^{-1} (*11*), the average OH concentration required to maintain CO in the steady state is then 2.3×10^6 molecule cm^{-3}. Levy (*12*) has recently developed a photochemical steady-state model for the surface atmosphere, in part to derive the OH concentration, and obtained 1.2×10^6 molecule cm^{-3} for the average daytime concentration, in reasonable agreement with the above value. McConnell *et al.* (*13*), using a model similar to Levy's, have calculated OH concentrations as a function of height, which also are in agreement with the above value. They estimated that the OH concentration is 3×10^6 molecule cm^{-3} up to an altitude of about 6 km and that it decreases from this value to 1×10^6 molecule cm^{-3} at the tropopause.

The residence time of CO in the atmosphere would be given by the reciprocal of k_3(OH), if Eq. 3 is the major removal process for CO. Levy calculated 0.2 year for the CO lifetime, and McConnell *et al.* calculated 0.3 year. These values are in reasonable agreement with the value of 0.09 year derived here from the radiocarbon data. Since the OH concentration should fall off rapidly in the absence of sunlight, the lifetime calculated by Levy would have to be increased by a factor of 2. Presumably, McConnell *et al.* have taken that into account in deriving their lifetime. Conversely, the average OH concentration derived here would have to be doubled to give the daylight value to allow for the fact that Eq. 3 is operative only half the time. The agreement between the two approaches is nevertheless gratifying, particularly in view of the probable greater uncertainty of the photochemical calculations.

Two other mechanisms have been considered for the removal of CO from the troposphere. One is transport into the stratosphere where CO would be rapidly converted to CO$_2$, and the other is consumption of CO by living organisms. Pressman and Warneck (*14*) have analyzed the stratospheric sink mechanism and concluded that it could remove 11 percent of the tropospheric CO inventory per year; that is, the residence time would be 9 years. More recently, Junge *et al.* (*9*) have constructed a model from which they derive a residence time of 2.7 years for CO in the troposphere with respect to the stratospheric sink. In either case, the stratosphere is not an important sink with respect to a residence time of the order of 0.1 year. Inman *et al.* (*15*) have discussed the possibility of CO removal by constituents of the soil and reported studies of CO removal rates by biological action in some soils. They conclude that soil can be a significant factor for CO removal. From the samples they studied, Inman *et al.* estimated that the soil surface of the continental United States could remove 6.5 times the amount of CO produced in the United States by combustion. This magnitude is too preliminary to be included in our analysis, but it is in the direction of improving the agreement between the two approaches used. The residence time derived from the radiocarbon data would be unaffected, but that derived from the photochemical model would have to be decreased if another significant sink were present. Conversely, the OH concentration derived from the radiocarbon analysis would have to be decreased whereas that from the photochemical model would be unaffected.

For OH radical concentrations of the order of 10^6 molecule cm^{-3}, the oxidation of CH$_4$ by OH

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (4)$$

with the subsequent conversion of CH$_3$ to CO, provides a significant source for the natural production of CO. McConnell *et al.* have estimated the rate of CO production to be 3.7×10^{11} molecule cm^{-2} sec^{-1} (9.9×10^{13} mole year^{-1}) from this source (*16*), from which they conclude that, "The internal combustion engine may locally determine the atmosphere CO abundance . . . however, the global level is governed by natural sources and oxidation of methane is likely to be a major contribution." If k_4, the rate constant for Eq. 4, is 9.2×10^{-15} cm^3 molecule^{-1} sec^{-1} (*17*), if the global concentration of CH$_4$ in the troposphere is 1.5 parts per million (ppm) (*18*), and if (OH) is 2.3×10^6 molecule cm^{-3} as derived here, the amount of CO produced by CH$_4$ oxidation is 1.45×10^{14} mole year^{-1} or 4×10^{15} g year^{-1}. This value is in good agreement with P_1, 1.8×10^{14} mole year^{-1}, that was derived here from the radiocarbon data. This agreement may be regarded as confirmation of the possibility that the OH radical plays a major role in both the tropospheric formation and removal of CO.

Other natural sources for the production of CO are known, the most significant one reported to date being the oceans. Swinnerton and his co-workers (*19*) have shown that the oceans are supersaturated with respect to CO and therefore are a source of CO. This finding has been confirmed by Seiler and Junge (*20*). A number of sources of CO have been identified in the marine environment (*21*). In addition, Swinnerton and his co-workers reported a diurnal variation of the CO concentration at the ocean's surface, which suggests a biological origin. They estimated that the amount of CO produced in the oceans is 5 percent of that produced by combustion, whereas Junge *et al.* (*9*) estimated it to be 29 percent. These values are small with respect to P_1, but other significant natural sources may be found to augment it. If these additional sources were added to the estimated production of CO by CH$_4$ oxidation, the total would be closer to the value of P_1 derived here.

If CH_4 is being removed from the atmosphere at a rate of 1.45×10^{14} mole year^{-1} or 2.3×10^{15} g year^{-1}, then a source of CH_4 of this magnitude is required to maintain the steady state. Koyama (*22*) has estimated a yearly production of CH_4 of 2.7×10^{14} g, of which about two-thirds was from paddy fields. Ehhalt (*23*) has suggested that Koyama's estimate was too low, and Robinson and Robbins (*6*) revised Koyama's estimate by including swamp lands and hot, humid tropical areas as additional CH_4 sources. Their estimate of CH_4 production is 1.45×10^{15} g year^{-1}, in agreement with the value deduced here. The lifetime of CH_4 derived from our analysis is 1.5 years.

Another point is worth consideration with respect to the role of the OH radical as the major source and removal mechanism of CO in the troposphere. Bainbridge and Heidt (*18*) have found that the mixing ratio of CH_4 is nearly constant with increasing altitude up to the tropopause, and Junge *et al.* (*9*) report a similar constancy for the CO mixing ratio. These observations may be taken as further confirmation of the determining role of OH in the CO-CH_4 cycle in nature (*24*).

In summary, it has been shown that the residence time of CO in the troposphere is about 0.1 year and that the major mechanism for the removal of CO is oxidation by OH in the troposphere. Concomitantly, the major source of CO is the oxidation of CH_4 by OH in the troposphere, amounting to a production rate of 5×10^{15} g year^{-1}, some 25 times greater than the production rate of CO from the combustion of fossil fuels. The average OH concentration in the troposphere required to maintain this balance is 2.3×10^6 molecule cm^{-3}, or twice this value during sunlight. This model could be confirmed by a measurement of the concentration of the OH radical in remote areas. Such a determination would have added importance because the OH radical also appears to play a dominant role in the overall chemistry of the troposphere as indicated by Levy (*12*) and by McConnell *et al.* (*13*), who derive a similar magnitude for the OH concentration from photochemical considerations.

BERNARD WEINSTOCK
HIROMI NIKI
Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121

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3 December 1971

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Synergy of Ethanol and Putative Neurotransmitters: Glycine and Serine

Abstract. *The putative neurotransmitters, glycine and serine, significantly enhanced the sleeping time (loss of the righting reflex) that was induced by ethanol in mice. The observed synergistic effect between ethanol and the amino acids is probably not related to an alteration of ethanol metabolism, but rather to an interaction of these compounds in the central nervous system.*

Glycine may act as an inhibitory transmitter in the brain and spinal cord areas in many animal species (*1*). It was reported recently that glycine is synthesized in brain almost exclusively by serine hydroxymethyltransferase (E.C. 2.1.2.1) (*2*). Serine, a less potent depressant amino acid than glycine, decreases the firing of spinal neurons that are spontaneous or are chemically evoked (*3*).

The inhibitory actions of ethanol in the central nervous system have been well documented (*4*). Synergistic effects on its duration of action have been observed between ethanol and other agents such as barbiturates, serotonin and its metabolites, and γ-hydroxybutyrate (*5*).

We report here on the interaction of ethanol with glycine or with serine, amino acids known to be depressants, and the demonstration that these agents enhance the soporific action of ethanol in mice.

The measured response, sleeping time, was defined as the length of time required for an animal to regain the