Reports

Anthropogenic CO Emissions: Implications for the Atmospheric CO-OH-CH_4 Cycle

Abstract. *Present anthropogenic emissions of CO are apparently large enough to perturb the natural CO-OH-CH_4 cycle, which plays a crucial role in the self-cleansing processes in the troposphere. A significant increase in global concentrations of CO, CH_4, CH_3Cl, and other trace gases may result from a decrease in the OH concentration caused by continued CO emissions. Even if the CO emissions were maintained at the present rate, increases in CO and CH_4 by the year 2025 might be as large as 50 and 25 percent, respectively. The time constants associated with the perturbations of the CO-OH-CH_4 cycle are of the order of a few decades. Perturbation of this cycle may also indirectly affect stratospheric chemistry.*

The importance of the hydroxyl radical (OH) in atmospheric chemistry was first recognized by Bates and Nicolet (*1*) and by Bates and Witherspoon (*2*). Many investigators (*3*) now emphasize that OH plays a crucial role in many tropospheric self-cleansing processes and controls the concentrations of many less soluble trace gases such as CH_4, CO, H_2S, SO_2, CH_3Cl, $CH_xCl_yF_z$, and CH_xBr_y.

In this report, the effects of increasing anthropogenic emissions of CO on tropospheric OH and the subsequent evolution of the CO-OH-CH_4 cycle are examined. It is assumed here that the reactions

$$OH + CH_4 \rightarrow CH_3 + H_2O \qquad (1)$$

and

$$OH + CO \rightarrow CO_2 + H \qquad (2)$$

are the principal sinks for CH_4 and CO (*3, 4*) and that subsequent oxidation of CH_3 provides the principal natural source of CO. Moreover, reactions 1 and 2 are the major loss processes for tropospheric OH (*5*). A simplified odd hydrogen (H, OH, HO_2, H_2O_2) cycle is shown in Fig. 1. Present CO emissions due to combustion of fossil fuel have been estimated as approximately 4×10^8 metric tons per year (*6*), compared with an estimated natural production of about 1 to 3×10^9 metric tons per year (*6, 7*), primarily from the oxidation of CH_4 (reaction 1). An increase in the global CO concentration may suppress the tropospheric OH concentration (*4*).

If CH_4 were initially in a steady state, then the height-integrated removal rate, denoted by

$$L(CH_4) = \int_0^\infty k_1[OH][CH_4]dz \qquad (3)$$

would balance the mean surface flux, $\phi(CH_4)$, a quantity presumably independent of OH perturbations. It follows that any decrease in tropospheric OH would lead to a net increase in CH_4 in the atmosphere as long as $L(CH_4)$ is less than $\phi(CH_4)$. It is argued here that, even if the anthropogenic source levels off in the future, the time constant for CH_4 to approach a new steady state would be on the order of a few decades, much longer than its residence time of about 3 to 7 years (*3, 7*). This is partially due to both the subsequent increase in the natural source of CO and the further decrease in OH as the quantity $L(CH_4)$ approaches $\phi(CH_4)$.

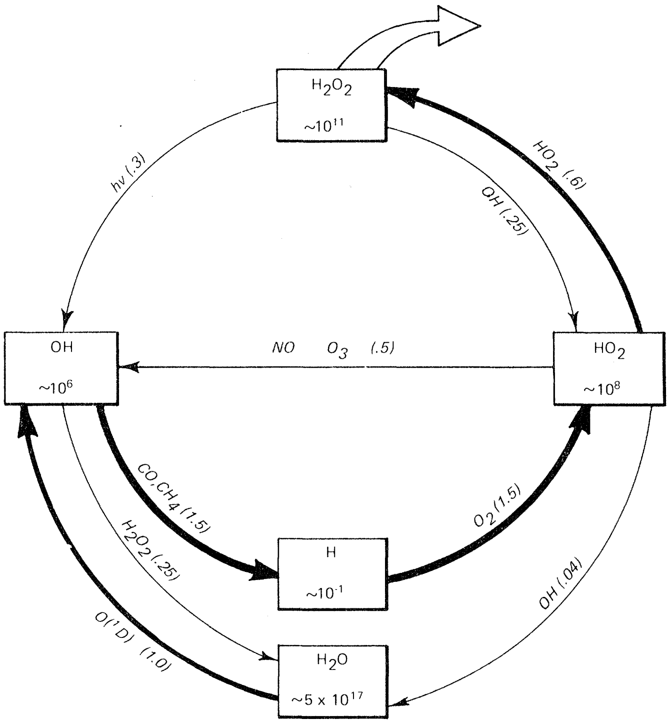

Fig. 1. Simplified odd hydrogen cycle in the lower troposphere. The concentration given in each box is in molecules per cubic centimeter. Reaction rates (10^6 cm^{-3} sec^{-1}) at 1 km are labeled on each path. Bold arrows denote major tropospheric pathways. The rate of the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ should be 1.2 instead of 0.6 if it is interpreted as a loss process for HO_2. Likewise, the rate of the reaction $H_2O_2 + h\nu \rightarrow 2OH$ should be 0.15 if it is interpreted as a loss process for H_2O_2. Reactions involving CH_2O and CH_3O_2H are relatively unimportant and are ignored in this simple scheme.

Three models for different future CO emissions were chosen for detailed studies. Concentrations of HO_x, CO, NO_x, and CH_4 were computed in every time step by solving the appropriate one-dimensional, time-dependent coupled diffusion equations (*8–10*). The results are summarized in Fig. 2, a through c. The increase in the lifetime of CH_4 (*11*) that results from the corresponding decrease of the OH concentration in each model is shown in Fig. 2a. Figure 2a presents some details of the results obtained with model A. The quantity $L(CH_4)$ increases after the year 1971. This would imply a corresponding increase in CO emission. The relative increase in global CO and CH_4 concentrations is shown in Fig. 2, b and c. In both models A and A′ (constant CO release after 1971), the global CO and CH_4 concentrations require an extensive period of time to attain their new steady levels. The continued growth of CO and CH_4 after 1971 is a consequence of the inertia and the strong coupling associated with the atmospheric CO-OH-CH_4 cycle. It is expected that much larger increases in CO and CH_4 concentrations would result in continued growth of CO emissions (model C and C′). Should a sharp drop in CO emission occur (model B), the CO and CH_4 concentrations are not expected to fall close to their levels in the 1950's.

The calculated present global CO concentration is about 20 to 38 percent higher than that in the 1950's; the corresponding CH_4 level is currently about 10 to 20 percent higher. The precise magnitude of increase depends primarily on the assumed surface flux of CH_4. The predicted CO increase is not inconsistent with CO data reported by Seiler (*7*), and the predicted CH_4 increase may be substantiated or refuted by a long-term measurement program.

An increase in the abundance of CH_4 associated with a decrease in tropospheric OH may have important effects; it may (i) increase stratospheric odd hydrogen (H, OH, HO_2) and H_2O abundances, which may affect stratospheric chemistry; (ii) tie up more Cl radical through the reaction $Cl + CH_4 \rightarrow HCl + CH_3$ (*12*), which could lead to an increased concentration of ozone if the Cl radical plays an important role in the ozone destruction process (*13*); and (iii) contribute to the atmospheric greenhouse effect because CH_4 and stratospheric H_2O have infrared absorption bands (*14*, *15*).

A decrease in OH may also increase the abundance of a number of important trace gases such as H_2S, CH_3Cl, and CH_3Br. Increasing the supply of these gases to the stratosphere could affect stratospheric ozone chemistry (*16*). It might also lead to a problem in disposing of technological products such as CHF_2Cl, $C_2H_3Cl_3$, and C_2Cl_4, which rely on tropospheric OH for their principal sinks. If an OH decrease results in a net depletion of stratospheric ozone, more ultraviolet radiation may reach the troposphere, leading to enhanced OH production through the reaction $O(^1D) + H_2O \rightarrow 2OH$, where $O(^1D)$ is produced by photolysis of tropospheric ozone. However, if total ozone increased as a result of decreasing tropospheric OH, then the OH concentration would be further suppressed.

The major conclusions that can be drawn from the present study are: (i) present anthropogenic CO emissions are sufficiently large to perturb the global CO-OH-CH_4 cycle; (ii) the time constants associated with these perturbations are about 10 to 30 years, depending primarily on the assumed surface flux of CH_4; (iii) changes in tropospheric OH may indirectly affect stratospheric ozone chemistry, which could lead to either positive or negative feedback effects; and (iv) increasing amounts of CH_4 and stratospheric H_2O may contribute to the atmospheric greenhouse effect. It seems clear that concern over anthropogenic CO emissions should be broadened to include the possible impacts on the global tropospheric CO-OH-CH_4 cycle. A long-term measurement program for atmospheric CO, CH_4, and OH concentrations would be useful to validate photochemical models of the troposphere.

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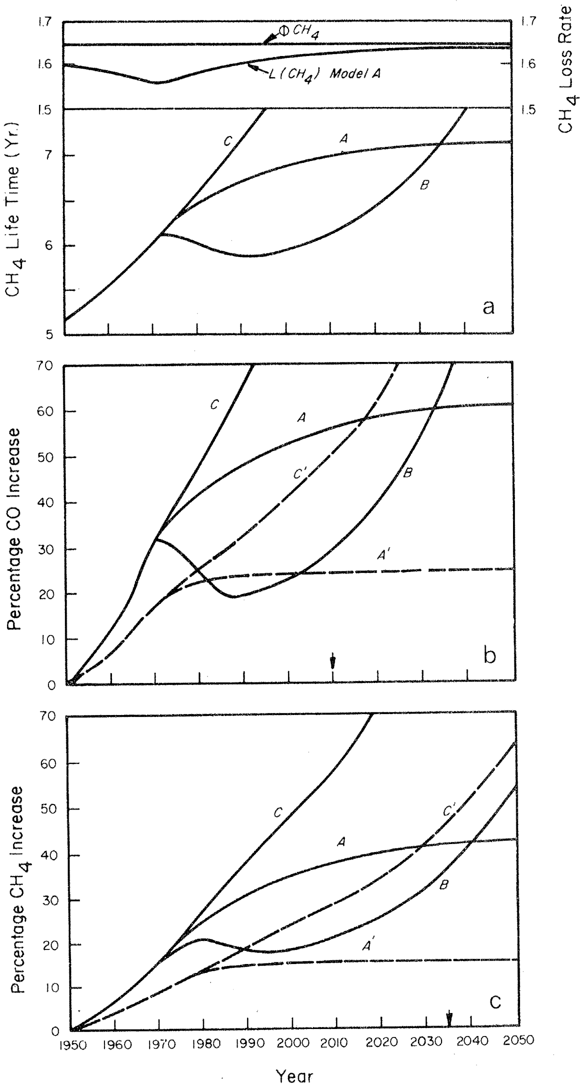

Fig. 2 (a) The lower part shows the lifetime (in years) of CH_4 for three different anthropogenic CO releases. Emissions of CO were assumed to be 400×10^6 ton/year or 5.3×10^{10} cm^{-2} sec^{-1} in 1971. The growth rate for models A, B, and C was taken as 4 percent per year in the period 1940 through 1970 (*17*). For the three models the assumed CO emissions were: model A, zero growth rate after 1971; model B, a 5 percent per year drop in the period 1971 through 1985 and a 2 percent increase after 1985 (*17*, *18*); and model C, an indefinite 1.33 percent per year increase after 1971. The lifetime (τ) of CH_4 was computed as discussed in (*11*). The global average OH concentrations near the surface may be inferred from τ. The upper part shows the height-integrated loss rate (10^{11} molecule cm^{-2} sec^{-1}) for the reaction $OH + CH_4 \rightarrow H_2O + CH_2$ as a function of time (model A). The corresponding methane flux $\phi(CH_4)$ is drawn for reference. The quantity $L(CH_4)$ was set equal to $\phi(CH_4)$ in the year 1940; $L(CH_4)$ may also be interpreted as the natural CO source. (b) Global CO increase (relative to 1950) computed with models A, B, and C of different CO emission rates and mean surface fluxes of CH_4. In models A, B, and C it is assumed that $\phi(CH_4) = 1.65 \times 10^{11}$ cm^{-2} sec^{-1}, which corresponds to $\tau(CH_4) \cong 5.2$ years. In models A' and C' $\phi(CH_4) = 3.3 \times 10^{11}$ cm^{-2} sec^{-1}, which corresponds to $\phi(CH_4) \cong 2.7$ years. The arrow indicates the year when CO doubling occurs in model C. (c) Global CH_4 increase computed with models of different CO emission rates and mean surface fluxes of CH_4. The arrow indicates the year when CH_4 doubling occurs in model C.

References and Notes

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2. D. R. Bates and A. E. Witherspoon, *Mon. Not. R. Astron. Soc.* **112**, 101 (1952).
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5. Major uncertainties in the odd hydrogen cycle arise from the regeneration process for OH by reactions such as $HO_2 + NO \rightarrow OH + NO_2$. Regeneration of OH from HO_2 or H_2O_2 increases the OH concentration by about 50 percent, according to our calculations. Evidently, if regeneration of OH is not the dominant source of OH, the OH concentration would be approximately inversely proportional to the CO and CH_4 concentrations.
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7. W. Seiler, *Tellus* **26**, 116 (1974).
8. The computations allowed for time-dependent vertical flow of N_2O, NO_x, CH_4, CO, and HO_x (*9*). The O_3 and H_2O profiles were taken from McElroy *et al.* (*10*). The surface flux of CO was estimated as 3.5×10^{10} cm^{-2} sec^{-1}, and may be due to terpenes, hydrocarbons, and other natural sources. Methane and CO were assumed to be in a steady state before 1940. Time-dependent integration started in 1940. Transport was treated by using the expedient concept of eddy diffusion. Diffusion coefficients and lists of chemical reactions were taken from (*4*). The rate constant for the reactions $CO + OH \rightarrow CO_2 + H$ and $CH_4 + OH \rightarrow CH_3 + H_2O$ are $2.0 \times 10^{-13} \exp(-115/T)$ and $5.5 \times 10^{-12} \exp(-1900/T)$, respectively. The initial column abundances for CH_4 and CO are 2.45×10^{19} and 1.02×10^{18} cm^{-2}, respectively.
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11. The lifetime of CH_4 is defined by

$$\tau(CH_4) = \frac{\int_0^\infty [CH_4]dz}{\int_0^\infty k_1[OH][CH_4]dz} = \frac{H}{H_\alpha k_1[OH]_0}$$

where H and H_α are the atmospheric scale height and the scale height for reaction 1, respectively; $[OH]_0$ denotes the concentration (cm^{-3}) of OH near the surface; and the ratio H/H_α is approximately 2.
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13. An increase in stratospheric CH_4 would transform the active Cl radicals (Cl, ClO) into the relatively inert form HCl through the reaction $CH_4 + Cl \rightarrow CH_3 + HCl$. Conversely, an increase in CH_4 may also increase stratospheric OH, which reacts with HCl to release Cl. For a given stratospheric odd chlorine (Cl, ClO, HCl, $ClONO_2$) mixing ratio, calculations indicate that a doubling of the stratospheric CH_4 concentration would decrease stratospheric column Cl and ClO by as much as 25 percent and increase OH and HO_2 by about 2 and 10 percent, respectively.
14. The effect of increasing CH_4 and stratospheric H_2O on the global mean temperature was discussed recently by Wang *et al.* (*15*). Their calculations, based on a one-dimensional radiative-convective model, show that a doubling of the CH_4 and stratospheric H_2O concentrations might cause increases in the surface temperature of 0.3° and 1.0°K, respectively.
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16. The gases CH_3Cl and CH_3Br are major natural chlorine and bromine carriers. They are decomposed in the stratosphere, releasing active Cl and Br radicals, which are potent catalysts for the destruction of ozone [S. C. Wofsy, M. B. McElroy, Y. L. Yung, *Geophys. Res. Lett.* **2**, 215 (1975)].
17. U.S. Department of Health, Education, and Welfare, *Air Quality Criteria for Carbon Monoxide* (Washington, D.C., 1970).
18. The 4 percent annual increase in the rate of CO emissions in the period 1940 through 1970 was taken from (*17*). The 1971 CO emission rates were estimated from (*6*). The 5 percent annual decrease in the CO emission rate (model B) in the period 1970 through 1985 is based on the assumption that there will be a large increase in the number of vehicles equipped with emission control systems. An increase of 2 percent per year after 1985 was assumed to take into account growth of the vehicle population.

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Origins of Sulfur in Coal: Importance of the Ester Sulfate Content of Peat

Abstract. *The sulfur found in coal stems in large part from sulfur incorporation at the peat-forming stage. Ester sulfate (a carbon-oxygen-sulfur linkage) is a major contributor to the sulfur in peat and thus is an important determiner of the quantity and forms of sulfur eventually found in coal.*

The high sulfur content of many coals restricts their use. Although various sulfur forms in coal such as pyrite, sulfate, and total sulfur have been quantified, the organic sulfur in coal has not been characterized with respect to the type of bonding present. Organic sulfur can represent a significant portion of the total sulfur and the total dry weight of coal. It accounts for over 50 percent of the total sulfur in many cases, and in Rasa coal organic sulfur represents 11 percent of the dry weight (*1*). Sulfur in coal is difficult to characterize because of the considerable polymeric and aromatic matrix of coal.

The sequence peat → lignite → bituminous coal → anthracite coal is the primary metamorphic progression in coalification (*2*). We report here on an investigation of the incorporation of organic sulfur in the peat-forming stage. Peat-forming systems in the Okefenokee Swamp, Georgia, and the Everglades, Florida, were selected as suitable modern progenitors of coal (*3*).

A peat-forming system is a dynamic system composed of a living plant community, surface litter, water, minerals, microorganisms, burrowing animals, and peat. Peat can be thought of as a highly organic soil. Earlier studies on organic sulfur in inorganic soils have led to the characterization of two forms of organic sulfur: (i) a carbon-sulfur linkage such as that found in sulfur-containing amino acids (such as cysteine) and heterocyclics (such as thiophenes) and (ii) a carbon-oxygen-sulfur linkage (referred to as "ester sulfate") represented by chondroitin sulfate and phenolic sulfates (*4*).

Using techniques developed for inorganic soils, we have characterized organic forms of sulfur in peats and related these to events deemed important to the origins of sulfur in coal. Two areas of the Okefenokee Swamp were selected for study: (i) Chesser Prairie, a freshwater-marsh environment consisting of the plants *Nymphaea, Orontium,* and *Eleocharis* associated with 180 cm of peat (*p*H 4.0) and (ii) Minnie's Lake, a freshwater-swamp environment where *Taxodium* is the dominant plant in association with 320 cm of peat (*p*H 4.0). The marine area of the Little Shark River in the Florida Everglades was the third site selected for study; at this site *Rhizophora mangle* L. is the dominant plant species in association with 360 cm of peat (*p*H 7.0). All three sites have been more fully described elsewhere (*5*).

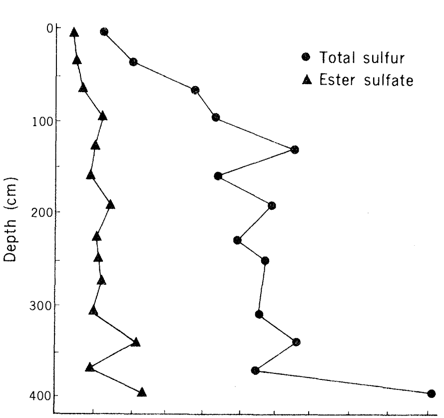

Fig. 1. Distribution of sulfur forms in peat from the mangrove environment (Little Shark River) of southern Florida.

In each of the peat profiles, samples were taken at approximately 25-cm intervals. A preliminary extraction with lithium chloride (aqueous) and then chloroform led to the removal of sulfate and elemental sulfur, respectively. We determined the total sulfur in the original sample at each level, using the Johnson-Nishita (*6*) method as modified by Tabatabai and Bremner (*7*).

The analysis of the ester sulfate content of the peat samples was carried out on samples from which the sulfate and elemental sulfur had been removed. The procedure developed by Freney was used (*8*), in which a reducing solution consisting of hydriodic acid, hypophosphorous acid, and formic acid reduces the sulfur to hydrogen sulfide (*2*). The reducing solution used here will reduce all forms of sulfur except carbon-bonded sulfur. Nitrogen, in the Johnson-Nishita apparatus, carries the hydrogen sulfide to a solution of zinc acetate and sodium acetate. The resulting zinc sulfide reacts with *p*-aminodimethylaniline and ferric ammonium sulfate to produce methylene blue, which is measured spectrophotometrically at 665 nm.

Sulfides and ester sulfate were determined by this technique. Sulfide (quantified independently by other techniques) was found to be negligible in the fraction insoluble in lithium chloride–chloroform in the samples from the two freshwater sites (two orders of magnitude lower than the ester sulfate content) (*2*). Sulfide values were significant in the samples from the marine site (at least equal to the ester sulfate content) and were subtracted from the values of sulfur reducible by hydriodic acid to give the absolute values for ester sulfate.

Table 1 shows the results of an analysis of two peat cores from the Okefenokee Swamp and one from the Everglades; the values for total sulfur represent the mean of individually determined peat levels from each profile. Figure 1 shows the ester sulfate content of peat from the Little Shark marine site as a function of sediment depth; the total sulfur content at the same site is plotted for comparison.

The data reveal a number of points: (i) the total sulfur content of the marine peat is considerably higher than that of the freshwater peats; thus, coals derived from near-marine and brackish environments would have considerably more sulfur associated with them than coals from freshwater sites; (ii) the overall differ-