Chemical Events in the Atmosphere and their Impact on Environment
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THE PHOTOCHEMISTRY OF TROPOSPHERIC TRACE SPECIES: THE CENTRAL ROLE OF RADICALS AND THEIR POSSIBLE VARIABILITY

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Abstract

In the presence of sunlight, reduced species emitted into the atmosphere from the earth's surface are oxidized, converted to soluble forms, and then returned to the biosphere-lithosphere-hydrosphere. The free radical OH, predicted to be present in the atmosphere at levels of about 10^5-10^6 molecular cm^{-3}, is believed to be the primary species in initiating the oxidation of most of these reduced atmospheric compounds. The concentration of the OH radical in the remote troposphere is primarily controlled by the atmospheric levels of H_2O, O_3, CO, CH_4 and NO_x. However, it appears that anthropogenic activities can significantly affect the atmospheric levels of O_3, CO, CH_4, and NO_x and thus may have conceivably caused a perturbation in OH levels on a global scale. A recent analysis of CH_4 in ice cores which indicated that CH_4 has increased significantly over the past 400 years suggests that OH levels have in fact undergone a secular variation in the recent past.

Introduction

While scholars have speculated about the atmosphere's composition since the days of the pre-Socratic Greek philosophers, the first significant scientific advances in atmospheric chemistry date back only to the 18th century studies of Joseph Priestley, Antoine-Laurent Lavoisier, and Henry Cavendish. It was these scientists who first established that the major constituents of Earth's atmosphere are nitrogen (79% by volume) and oxygen (20%), with lesser amounts of water and carbon dioxide.

During the 19th and early 20th centuries, many prominent chemists and physicists further advanced our knowledge in this area. Sir William Ramsey documented the presence of the noble gases argon, helium, krypton, neon, and xenon in the atmosphere. Other investigators found evidence for small quantities of methane, hydrogen, ozone, carbon monoxide, sulfur dioxide, and hydrogen sulfide in the air and nitrate, sulfate, chloride, and ammonium ions dissolved in rainwater. Thus by the middle of the 20th century, a good deal of qualitative information on the chemical composition of the atmosphere had been gathered.

Since the 1950s, rapid advancement in chemical analytical techniques and high-speed computers has led to an explosion of knowledge concerning atmospheric composition. The atmosphere has been found to be a reservoir for a myriad of trace gaseous and aerosol species with concentrations below 1 ppmv (1 part per million per volume of air). And, in spite of their relatively low concentrations, these atmospheric trace gas and aerosol species often can have a major impact on the environment. Some gases, for instance, because of their toxicity, can affect plant and animal life; others can affect climate via the "atmospheric greenhouse effect". Aerosols, on the other hand, can have a significant effect upon cloud formation and precipitation patterns.

Recognizing the potential of atmospheric trace species for altering or influencing the global environment, it may reasonably be asked: Why are these species present in the atmosphere? Can their presence, for example, be explained directly in terms of planetary thermodynamics? In fact, as indicated in Table 1, simple calculations show that most trace species are present in the atmosphere at much higher levels than would he predicted solely on the basis of thermodynamic equilibrium with nitrogen, oxygen, carbon dioxide, and water. Clearly, kinetic mechanisms involving a combination of chemical, physical, and biological processes are controlling the trace gas composition of the atmosphere. It is the identity of these kinetic mechanisms and their relationship to natural life cycles that have been of fundamental interest to atmospheric chemists in recent decades and are the subject of this work.

TABLE 1 - *Atmospheric Trace Gas Composition is Controlled by a Complex Combination of Processes.*

Species	Thermodynamically equilibrated concentration [a] (Mole fraction)	Actual atmospheric concentration (Mole fraction)	Reliability with which global distribution is known	Principal sources	Principal sinks
CH_4	10^{-145}	1.6×10^{-6}	High	Biogenic	Photochemical
CO	6×10^{-49}	$(0.5 - 2) \times 10^{-7}$	Fair	Photochemical, anthropogenic	Photochemical
O_3	3×10^{-30}	$10^{-8} - 10^{-7}$	Fair	Photochemical	Photochemical
$NO+NO_2$	2×10^{-10}	$(10^{-12} - 10^{-8})$ [b]	Low	Lightning, anthropogenic, photochemical	Photochemical
HNO_3	1×10^{-9}	$(10^{-11} - 10^{-9})$ [b]	Low	Photochemical	Rainout
NH_3	2×10^{-60}	$(10^{-10} - 10^{-9})$ [b]	Low	Biogenic	Photochemical rainout
N_2O	2×10^{-19}	3×10^{-7}	High	Biogenic	Photochemical
H_2	2×10^{-42}	5×10^{-7}	High	Biogenic, photochemical	Photochemical
OH	5×10^{-28}	$10^{-15} - 10^{-12}$ [c]	Very low	Photochemical	Photochemical
HO_2	4×10^{-28}	$10^{-13} - 10^{-11}$ [c]	Very low	Photochemical	Photochemical
H_2O_2	1×10^{-24}	$10^{-10} - 10^{-8}$	Very low	Photochemical	Rainout
H_2CO	9×10^{-96}	$10^{-10} - 10^{-9}$	Low	Photochemical	Photochemical
SO_2	0	$(10^{-11} - 10^{-10})$ [b]	Fair	Anthropogenic, photochemical volcanic	Photochemical
CS_2	0	$(10^{-11} - 10^{-10})$ [b]	Low	Anthropogenic, biogenic	Photochemical
OCS	0	10^{-10}	Fair	Anthropogenic, biogenic, photochemical	Photochemical
CH_3CCl_3	0	$(0.7 - 2) \times 10^{-10}$	Fair	Anthropogenic	Photochemical

a) Thermodynamically equilibrated concentration is that calculated by assuming thermodynamic equilibrium with a gas mixture containing 0.78 atm N_2, 0.21 atm O_2, 0.01 atm H_2O, and 3.3×10^{-4} atm CO_2 at a temperature of 298 K. *b*) Lower concentration limits cited may not necessarily reflect actual minimum concentrations but rather the lower limit on detection sensitivity of current instrumentation. *c*) Concentrations of these transient species become much lower at night.

Solar Radiation

One of the key components of these kinetic mechanisms is the presence of solar radiation. Chemical reactions between the major constituents of the troposphere occur at negligible rates. However, the formation of more chemically active species under the influence of light gives rise to rapid reaction chains that play a major role in controlling the trace composition of the atmosphere. Because it is driven by the absorption of photons, the chemistry of the lower atmosphere often is referred to as tropospheric photochemistry. Of course, all photons from the sun do not take part in tropospheric photochemistry. Most ultraviolet solar photons are absorbed in the upper levels of the atmosphere and never penetrate the tropopause (c.f. Leighton, 1961). Photons with wavelengtbs shorter than 240 nm are absorbed by oxygen and nitrogen molecules in the thermosphere, and ozone, found primarily in the stratosphere, is a key absorber of photons in the spectral region between 240 and 300 nm. Thus, for the troposphere we need consider only those chemical reactions that are activated by photons with wavelengths of 300 nm or longer, as illustrated in Fig. 1.

One of the key distinguishing features between the chemistry of the troposphere and that of the stratosphere is that ultraviolet photons sufficiently energetic to break an oxygen-oxygen bond are present in the stratosphere but not in the troposphere. As first noted by William J. Humphreys in 1910, this photodissociation of stratospheric oxygen molecules leads to the generation of ozone and, as a result, much higher concentrations of ozone are found in the stratosphere than in the troposphere.

The Earth-Atmosphere Interface

A variety of biological and geological processes can result in the emission of gases from Earth's surface to the atmosphere. These surface emissions, which can have a major effect on atmospheric composition, appear to be highly variable in both the types of species released and the rates at which they are emitted into the atmosphere. Although data are quite limited, those available suggest that different biotic provinces, such as tropical evergreen forests, deciduous midlatitude forests, swamps and wetlands, alpine tundra, and deserts each emit a unique array of gases.

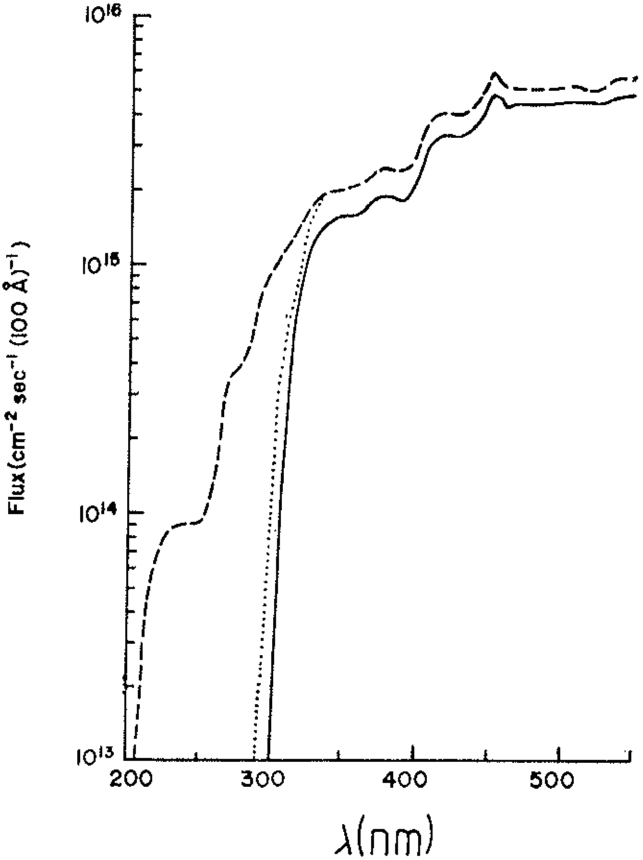

FIG. 1. The flux of solar radiation as a function of wavelength; λ. The broken line is the flux of solar radiation at the top of the atmosphere. The flux of solar radiation at the ground for solar zenith angles of 0° and 45° is represented by the dotted line and solid solid line respectively.

Even the oceans should not be looked upon as having a homogeneous interface with the atmosphere; there is growing evidence that the biological diversity of the oceans is quite large. Given the diversity of ecosystems on Earth it is quite likely that we will continue to find that the "natural" troposphere is highly inhomogeneous in its chemical composition.

In spite of the complexity of biogeospheric surface emissions, one generalization is in order: The vast majority of trace species emitted into the atmosphere are in reduced oxidation states (such as bydrogen sulfide, ammonia, and methane). By contrast, materials returned to the surface from the atmosphere, usually by dissolution in rain drops or by dry deposition, are hightly oxidized (such as sulfuric acid, nitric acid, and carbon dioxide). The link between these reduced and oxidized species is supplied by atmospheric photochemical reactions, thus giving rise to a chemical cycle whereby reduced gases are emitted into the atmosphere, photochemically oxidized, and then removed from the atmosphere.

That reduced atmospheric gases are oxidized is not surprising; the large atmospheric abundance of oxygen thermodynamically favors their oxidation. However, molecular oxygen rarely is directly responsible for oxidizing these reduced gases. The oxygen-oxygen bond is relatively strong (120 kcal/mole) and thus molecular oxygen does not react readily with most reduced gases at atmospheric pressures and temperatures.

In the early 1900s, reduced atmospheric species were believed to be oxidized by ozone and hydrogen peroxide; today, highly reactive free radical species (present in the atmosphere at levels of 10 ppt per volume of air or less) are recognized as being responsible for a large part of this oxidation. The recognition of the importance of these free radical species has constituted the major scientific breakthrough in tropospheric photochemistry during the past decade.

Tropospheric OH Free-Radical Photochemistry

Because free radicals have an unpaired electron in their outer shell, and thus an affinity for adding a second electron, they can act as strong oxidizers of atmospheric trace gases. Of the free radicals present in the atmosphere, OH, the hydroxyl species, appears to be the most pivotal in tropospheric chemistry. The chemical mechanism responsible for the presence of hydroxyl radicals in the troposphere was first proposed by Levy (1971) and further refined by Crutzen (1973), McConnell *et al.* (1971), and Wofsy *et al.* (1972).

As illustrated in Figure 2, the production of hydroxyl radicals is initiated by the photolysis of ozone. Ozone, present in the troposphere at concentrations ranging from 10 to 100 ppbv, has a bond energy of 26 kcal/mole. Solar photons having wavelengths between 315 and 1200 nm can dissociate ozone and produce an oxygen atom in its ground electronic state:

$$\text{(R1)} \quad O_3 + h\nu\,(1200 > \lambda > 315\ \text{nm}) \rightarrow O\,(^3P) + O_2$$

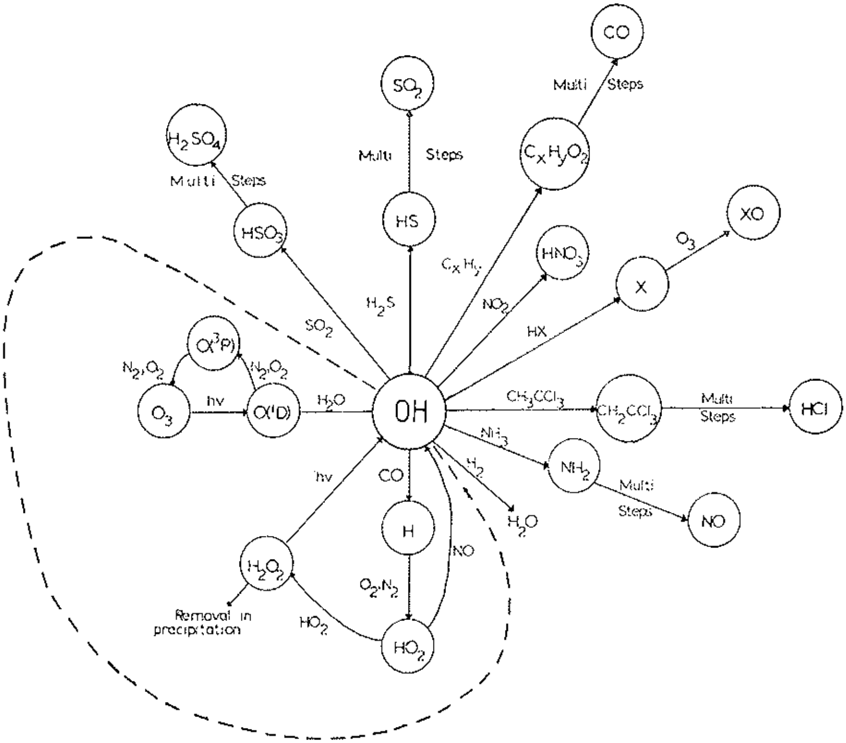

FIG. 2. The photochemistry of tropospheric OH. The reactions inside the dotted line play a major role in determining the concentration of OH.

The O (^{3}P) atom rapidly reforms ozone by combining with O_2 in a three-body reaction:

$$\text{(R2)} \qquad O(^3P) + O_2 + M \rightarrow O_3 + M \, (M = N_2 \text{ or } O_2)$$

Thus, the sequence of these two reactions is a null cycle with no net chemical effect.

When ozone absorbs a photon in the near-ultraviolet with a wavelength shorter than 315 nm, an electronically excited oxygen atom is produced:

$$\text{(R3)} \qquad O_3 + h\nu \, (\lambda < 315 \text{ nm}) \rightarrow O(^1D) + O_2$$

The O (^{1}D) → O (^{3}P) transition is forbidden and therefore O (^{1}D) has a relatively long radiative lifetime of 110 seconds. In the lower atmosphere, rather than relax radiatively, 0 (^1D) most often collides with nitrogen or oxygen molecules:

(R4) $O(^1D) + M \rightarrow O(^3P) + M$ ($M = N_2$ or O_2)

This ultimately leads to the regeneration of ozone by the three-body reaction (R2), resulting in another null cycle. Occasionally, however, O (^1D) collides with water to generate two hydroxyl radicals:

(R5) $O(^1D) + H_2O \rightarrow 2OH$

This reaction sequence is the primary source of tropospheric hydroxyl radicals.

The removal of hydroxyl from the atmosphere occurs most frequently as a result of reactions with carbon monoxide or methane:

(R6) $CO + OH \rightarrow CO_2 + H$

(R7) $CH_4 + OH \rightarrow CH_3 + H_2O$

However, several complications arise in hydroxyl chemistry when one considers the ultimate fate of the hydrogen and methyl radicals formed in these two reactions. Both radicals combine rapidly with molecular oxygen to form hydroperoxyl radicals (i.e. HO_2 and CH_3O_2). But the hydroperoxyl radical can regenerate OH:

R(8) $HO_2 + NO \rightarrow NO_2 + OH$

R(9) $HO_2 + O_3 \rightarrow 2O_2 + OH$

It also can lead to chain termination via the reactions

(R10) $HO_2 + OH \rightarrow H_2O + O_2$

or

(R11) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

followed by the removal of hydrogen peroxide in rain.

The chemistry of the methylperoxyl radical (CH_3O_2) and its products is quite complicated and the kinetics of many of the reactions still are quite tentative. A likely scheme for the degradation of CH_3O_2 is presented in Figure 3. The major features of this scheme are the production of H_2CO, then CO, and ultimately CO_2 and the conversion of OH radicals to HO_2 radicals in the process of oxidizing CH_3O_2 to CO. As we shall see later, this production of HO_2 plays a major role in the photochemistry of tropospheric ozone.

An order of magnitude estimate of the OH concentration in the remote troposphere may be obtained by considering OH to be in a photochemical equilibrium established by reactions (R3), (R4), (R5), (R6), (R7) and that no regeneration of OH from HO_2 occurs. Under these assumptions,

$$n(OH) = 2F \frac{n(O_3)\,J_3}{n(CO)\,k_6 + n(CH_4)\,k_7} \tag{1}$$

where

$$F = \frac{n(H_2O)\,k_5}{n(H_2O)\,k_5 + n(M)\,k_4} \tag{2}$$

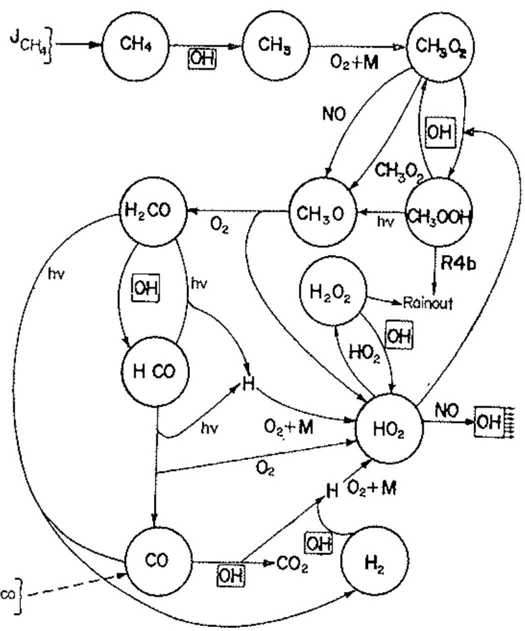

FIG. 3. A tentative scheme for methane oxidation reaction sequence. J_{CH4} and J_{CO3} represent non-photochemical sources of CH_4 and CO.

is the fraction of O (^{1}D) atoms which form OH, n (X) is the number density of the species X and J_m and k_m are the photolysis frequency and rate constant of the mth reaction. Adopting the parameters listed in Table 2, which are appropriate for the remote marine troposphere, Eqn. (1) predicts a diurnally averaged OH level of about 0.8×10^6 molecules cm^{-3}.

While Eqn. (1) predicts OH levels in the remote troposphere in reasonably good agreement with the predictions of more elaborate photochemical models which properly treat the HO_2/OH coupling, for conditions appropriate for less remote regions where enhanced NO_x levels are commonly encountered Eqn. (1) does not accurately calculate the OH concentrations. This is because as NO_x levels increase, a greater fraction of the HO_2 radicals produced from the methane oxidation reaction sequence react with NO via (R8) to regenerate OH. Thus as illustrated in Figure 4, the levels of OH calculated in a complete photochemical model increase substantially as NO_x levels increase from the pptv level (typical of remote marine conditions) to the more polluted ppbv level. For NO_x levels in

TABLE 2 - *Parameters Used for Order-of-Magnitude Estimate of OH Levels in Remote Troposphere.*

A. CONCENTRATIONS

Species	*Number Density, n* (molecular cm^{-3})
O_3	7×10^{11}
CO	3×10^{12}
CH_4	4×10^{13}
H_2O	4.5×10^{17}
$M = N_2 + O_2$	2.5×10^{19}

B. RATE CONSTANT (for T = 290° K)

	Reactions	*Constant*
(R3)	$O_3 + h\nu \rightarrow O(D) + O_2$	$J_3 = 4.5 \times 10^{-6}$ s^{-1} (diurnal average)
(R4)	$O(^1D) + M \rightarrow O(^3P) + M$	$k_4 = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}
(R5)	$O(^1D) + H_2O \rightarrow 2OH$	$k_5 = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}
(R6)	$OH + CO \rightarrow CO_2 + H$	$k_6 = 2.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}
(R7)	$OH + CH_4 \rightarrow CH_3 + H_2O$	$k_7 = 6.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

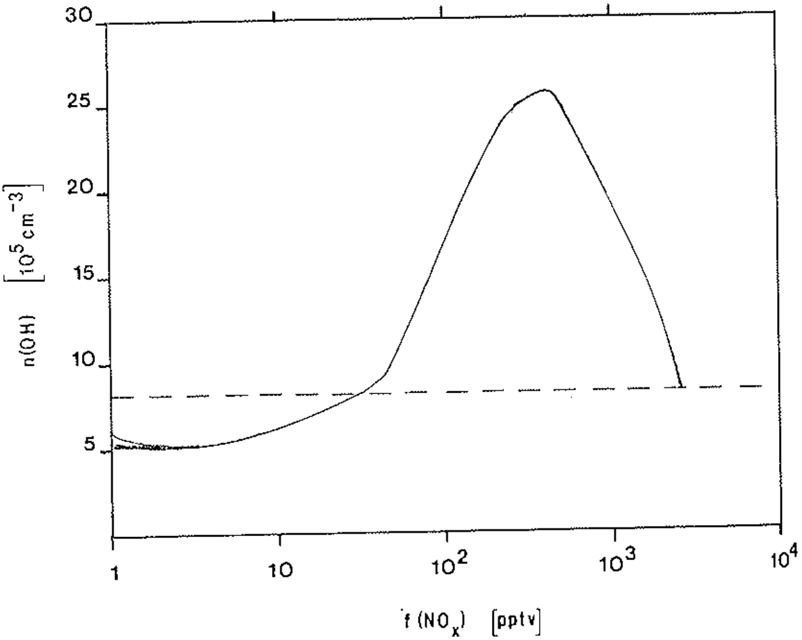

FIG. 4. Calculated diurnally averaged OH concentrations as a function of the assumed NO_x mixing ratio, f (NO_x). The broken line is the OH concentration predicted from Eqn. (1) and the solid line is the concentration obtained from a complete photochemical model.

excess of a ppbv, however, OH is calculated to decrease as NO_x increases due to the growing importance of an alternate OH loss pathway.

$$\text{(R12)} \quad NO_2 + OH \xrightarrow{M} HNO_3.$$

Thus we find that in addition to O_3, H_2O, CO, and CH_4, NO can play a major role in determining the concentration of tropospheric OH.

Figure 5 illustrates the OH levels calculated by a 2-dimensional diagnostic, photochemical model in which the observed levels of species such as H_2O, O_3, CO, CH_4, and NO_x were specified and the OH concentration was determined assuming photochemical equilibrium. The salient features of this predicted distribution are: 1) diurnally and seasonally averaged OH levels of the order of 10^5-10^6 molecular cm^{-3}; and 2) the highest OH levels are found in the tropics where high humidity and a large O (^1D)-producing actinic flux cause a large rate of OH primary production.

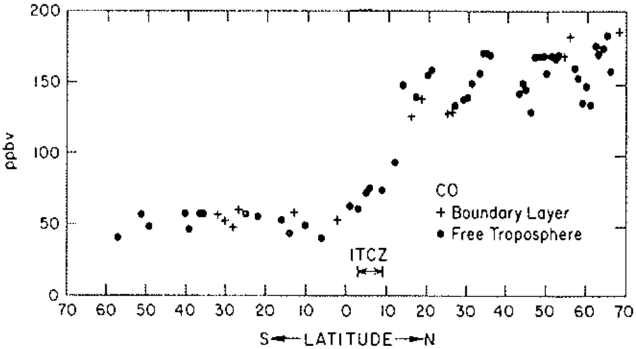

FIG. 5. Model calculated, diurnally and seasonally averaged OH concentrations as a function of altitude and latitude. The globally averaged OH concentration is predicted to be 7×10^5 molecular cm^{-3}.

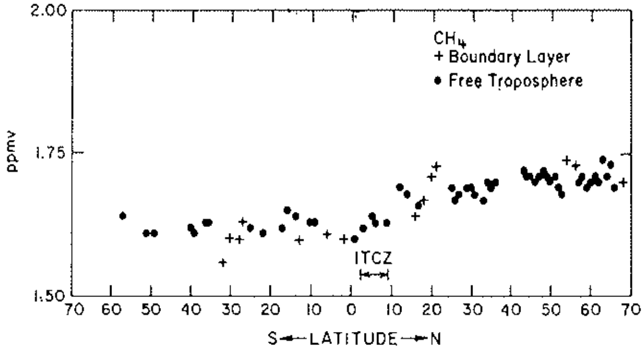

FIG. 6. Concentrations of atmospheric CO and CH_4 observed by Heidt *et al.* (1980) during Project GAMETAG.

Model-predicted OH levels of the order of 10^5 to 10^6 molecules cm^{-3} in conjunction with laboratory data demonstrating the highly reactive nature of this radical (cf. Demore *et al.*, 1982) imply that OH controls the rate at which a large number of other atmospheric species are oxidized and removed from the atmosphere. Specifically, OH is believed to initiate the oxidation of CH_4, CO, non-methane hydrocarbons (C_xH_y), H_2S. SO_2, NH_3, NO_2, and a variety of halogenated hydrocarbons (see Figure 2). It is for this reason that OH is currently viewed as the pivotal species in controlling the atmospheric component of the biogeochemical cycling of the elements. However, until model-predicted levels of OH are confirmed by direct atmospheric measurements the above conclusions must remain tentative.

Thus far, two approaches have been taken to verify the accuracy of the photochemical theory. One involves a direct comparison of measured OH levels with those predicted by a photochemical model. For this comparison to be meaningful, all parameters used in the model to calculate OH must be measured simultaneously with OH. These parameters include temperature and solar flux, as well as the concentrations of H_2O_2, CH_3OOH, CH_2O, H_2O, O_3, CO, CH_4, and NO. Unfortunately, performing this experiment has proved to be quite difficult. At this time, several of the above species either have not been measured at all, or, if they have been measured, serious questions remain about the accuracy of the measurements.

The measurement of OH itself has presented a major challenge to atmospheric chemists. Even though measurements have been reported in the literature that tend to be in qualitative agreement with model calculations, the accuracy of the data continues to be the subject of much scientific debate. Currently, at least seven independent groups in the U.S. and Europe are addressing this problem. Thus, direct comparison of measured OH levels with model-predicted values continues to be one of the challenging frontiers of global tropospheric chemistry.

An alternate, indirect test of OH photochemical theory, originally proposed by Singh (1977) involves the global distribution of methylchloroform (CH_3CCl_3). This chemical currently is used as a cleaning and degreasing agent; its release into the troposphere is believed to be its only atmospheric source. Since methylchloroform is removed from the atmosphere by reaction with hydroxyl radicals, the concentration of hydroxyl determines its lifetime. Using the history of methylchloroform emissions and its present atmospheric distribution and abundance, it is possible to infer its lifetime. This lifetime then can be compared to the lifetime obtained from model-calculated OH levels in the atmosphere. At present, the lifetime estimates from both methods agree within a factor of two or less. Model-calculated OH levels imply a CH_3CCl_3 lifetime of about 5-8 years (Chameides and Tan, 1981; Logan *et al.*, 1981); note that the profile illustrated in Figure 5 yields a lifetime of 8 years. This lifetime agrees quite well with the values inferred from observational data by Singh (1977) and Rowland *et al.*, (1980) although it is somewhat smaller than the 11 year lifetime estimated by Prinn *et al.* (1983) from data gathered in the Atmospheric Lifetime Experiment. Thus it appears that free radical photochemical theory is at least qualitatively correct. However, large uncertainties are associated with both estimates and this qualitative agreement still could prove fortuitous.

Because tropospheric OH is photochemically controlled, a complete understanding of OH requires an understanding of the processes which control the distributions of the species which influence the OH photochemical equilibrium. Of these species the most important are O_3, H_2O, CH_4, CO, and NO_x. The levels of atmospheric H_2O are largely controlled by the processes of evaporation and condensation and are not discussed here; brief discussions of the atmospheric cycles of the other species are presented below.

Atmospheric CH_4 and CO

The central role of hydroxyl radicals in atmospheric chemistry is well illustrated by examining the atmospheric cycles of methane and carbon monoxide. A quantitative assessment of both of these species was carried out in the 1920s in Belgium by Marcell Migeotte, who detected their absorption lines in the spectrum of infrared solar radiation reaching Earth's surface.

The major sources of atmospheric methane are biogenic. They include the anaerobic fermentation of organic material in swamps, tropical rain forests, paddies, and in the digestive systems of livestock as well as termites (Ehhalt, 1974; Zimmerman *et al.*, 1982). It is interesting to note that while virtually all the CH_4 emitted to the atmosphere is biogenically produced, man's activities influence a large fraction of the production — specifically that produced by enteric fermentation in livestock and CH_4

production in cultivated rice paddy fields. The major loss or sink process for CH_4 is (R7), its reaction with OH. Calculations indicate that (200-300) × 10^{12} g C as CH_4 are cycled through the atmosphere in this manner.

Of the (200-300) × 10^{12} g of C as CH_4 oxidized annually by OH approximately (150-200) × 10^{12} g C are converted to CO via the sequence of reactions illustrated in Figure 3. The remaining (50-100) × 10^{12} g C are heterogeneously removed each year from the atmosphere via rainout and washout of CH_3OOH and H_2CO. In addition to the source from methane oxidation, carbon monoxide is produced from OH-initiated oxidation of non-methane hydrocarbons, incomplete combustion (principally automotive) of fossil fuels, and the burning of biomass, such as wood, agricultural wastes, and forests. A recent analysis of the carbon monoxide budget suggests that of the total CO source strength of about (600-1500) × 10^{12} g C as CO produced annually, the burning of fossil fuels and biomass accounts for about 25-50% of the total (Logan *et al.*, 1981). As with methane the major sink for carbon monoxide is reaction with hydroxyl radicals.

It is interesting to note that the sources of both methane and carbon monoxide are mostly continental rather than oceanic. Because most of the world's land mass is in the northern hemisphere, the largest sources of both compounds are there. One might expect, therefore, to find an interhemispheric asymmetry for both methane and carbon monoxide. However, as can be seen in Figure 6, whereas considerably more carbon monoxide is found in the northern hemisphere, methane has a nearly constant mixing ratio of 1.65 ppmv with only a slight change in abundance across the ITCZ near the equator.

Differences in the latitudinal distributions of methane and carbon monoxide result from their respective atmospheric lifetimes. Based on the globally averaged hydroxyl radical concentration of about 7 × 10^5 per cc and the appropriate rate constant, the atmospheric lifetime of methane is estimated to be about seven years and that of carbon monoxide about 65 days. Because long-lived species tend to be mixed uniformly throughout the troposphere by the winds, the uniform distribution of methane is consistent with its long lifetime. The lifetime of carbon monoxide is sufficiently short to prevent it from being mixed thoroughly throughout the troposphere. As a result, its distribution more closely resembles the distribution of its sources.

Atmospheric Nitrogen Oxides

The principal reactive nitrogen oxide species found in the lower troposphere are NO, NO_2, and HNO_3, with nitric acid being more abundant by a factor of 2-10 in the remote troposphere. As illustrated in Figure 7, these three species are coupled chemically by a series of reactions that act to cycle them among each other. As with CO, large quantities of NO are produced as a by-product of burning fossil fuels and wood. Logan (1983) estimates, for instance, that fossil fuel burning produces about 20×10^{12} gN as NO yr^{-1} and biomass burning another 12×10^{12} gN as NO yr^{-} out of total global NO source strength of about 43×10^{12} gN as NO yr^{-1}. However, while measurements of tropospheric NO, NO_2, and HNO_3, are quite sparse, those that are available indicate that the distribution of nitrogen oxides is not so strongly affected by man-made urban sources as that of CO. The reason for this apparent difference is the relatively rapid rate at which nitrogen oxides are removed from the atmosphere. After being emitted into the atmosphere, NO is converted rapidly to NO_2 by reaction with ozone; NO_2 reacts with the critically important OH radical to form nitric acid. And nitric acid, which is highly soluble, is removed by such heterogeneous processes as dissolution in rain, attachment to aerosols and suspended particulates, and dry desposition on Earth's surface. In the lower troposphere, this process leads to a net nitrogen oxide lifetime of only a few days to a week — much shorter than that of CO. Thus, although NO and NO_2 may reach levels of 500 ppbv in urban centers and levels of

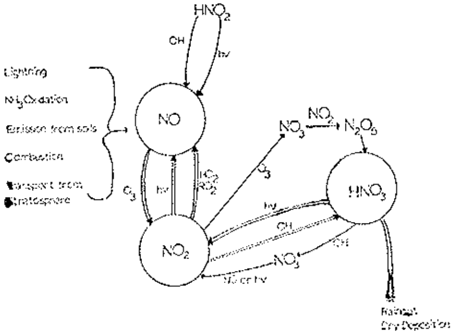

FIG. 7. The photochemistry of reactive nitrogen oxide species. Double-lined arrows represent primary reactive pathways and single-lined arrows represent secondary reactive pathways.

1 ppbv in much of the continental U.S., their removal is so rapid that little is transported to remote regions. For instance, observations by McFarland *et al.* (1979) indicate that NO levels in the remote Pacific are in the 1-20 pptv range.

It therefore appears that remote levels of tropospheric nitrogen oxides are dominated by natural rather than anthropogenic sources; these sources include the generation of NO by lightning, the direct release of NO and NO_2 from soils and marine waters, the OH oxidation of biogenically produced NH_3, and the downward transport of stratospherically-produced nitrogen oxides. Of these, the lightning source, estimated to produce about 4×10^{12} gN yr^{-1} by Barucki and Chameides (1983), looks to be quite significant. The stratospheric source which produces only about 0.3×10^{12} gN yr^{-1} could be important in the mid and upper-troposphere (Kley *et al.*, 1981). The nitrogen oxide sources from soil emissions and NH_3 oxidation are still highly uncertain but the possibility that they contribute significantly to the nitrogen oxide budget cannot be ruled out.

Tropospheric Ozone

Ozone is of major interest to tropospheric chemists for two reasons: It leads to the production of hydroxyl radicals, and it is a greenhouse gas. For many years, tropospheric ozone was believed to be chemically inert. Scientists held that the ozone present in the troposphere was formed initially in the stratosphere — where ultraviolet radiation is of high enough energy to dissociate oxygen — and mixed down into the troposphere. It was postulated further that ozone was removed from the atmosphere primarily by reacting with Earth's surface.

Several investigators have shown that several aspects of the global ozone distribution support this "*transport theory*" (c.f. Junge, 1962; Danielsen and Mohnen, 1977; Fabian and Pruchniewicz, 1977; Routhier and Davis, 1980). For one thing, tropospheric ozone concentrations increase with altitude, presumably indicating a stratospheric source. Positive correlations between ozone and species of stratospheric origin, such as the radionclide ^{7}Be, also have been pointed to as evidence in support of the transport theory. Similarly, numerous observations showing that levels of tropospheric ozone above 1 km frequently are correlated negatively with water strongly suggest a stratospheric source for ozone.

However, growing awareness in the early 1970s that free radicals are a ubiquitous component of the atmosphere led researchers to realize that ozone, rather than being chemically inert, is produced and destroyed by tropospheric photochemical processes and that these chemical processes could play a major role in the overall tropospheric ozone budget (Crutzen, 1973; Chameides and Walker, 1973).

In fact, evidence gathered by Seiler and Fishman (1981), appears to support the hypothesis that ozone can be produced photochemically in the remote troposphere. They found, for instance, that in several cases measurements in the free troposphere (the region above 1 km) show concentrations of ozone that are correlated positively with levels of carbon monoxide, a photochemical precursor of ozone.

The primary photochemical loss process for O_3 arises from the sequence of reactions which produces OH, i.e. (R3) and (R5). Tropospheric ozone generation by photochemistry can arise from the oxidation CO and hydrocarbons via reaction sequences such as

$$\begin{array}{ll}
(R6) & CO + OH \rightarrow CO_2 + H \\
(R13) & H + O_2 + M \rightarrow HO_2 + M \\
(R12) & HO_2 + NO \rightarrow OH + NO_2 \\
(R14) & NO_2 + h\nu \rightarrow NO + O \\
(R2) & O_2 + O + M \rightarrow O_3 + M \\
\hline
 & \text{NET:}\ CO + 2O_2 + h\nu \rightarrow CO_2 + O_3
\end{array}$$

and

$$\begin{array}{ll}
(R7) & CH_4 + OH \rightarrow CH_3 + H_2O \\
(R15) & CH_3 + O_2 + M \rightarrow CH_3O_2 + M \\
(R16) & CH_3O_2 + NO \rightarrow CH_3O + NO_2 \\
(R14) & NO_2 + h\nu \rightarrow NO + O \\
(R2) & O_2 + O + M \rightarrow O_3 + M \\
\hline
 & \text{(NET)}\ OH_4 + 2O + h\nu \rightarrow CH_3O + O_3
\end{array}$$

Model calculations indicate that these photochemical sources and sinks for tropospheric O_3 are quite large compared to downward transport from the stratosphere and loss at earth's surface. While about 7×10^{10} O_3 molecular cm^{-2} s^{-1} are transported across the tropopause (Mahlman *et al.*, 1980) and about 8×10^{10} molecular cm^{-2} s^{-1} are lost at the earth's surface, O_3 is calculated to be produced photochemically at an average rate of 1.6×10^{11} molecular cm^{-2} s^{-1} and destroyed photochemically at a rate of 1.5×10^{11} molecular cm^{-2} s^{-1}.

While O_3 is not directly affected by anthropogenic emissions, note that as emissions of hydrocarbons CH_4, O, and NO_x increase they tend to enhance the rate of O_3 production and could eventually enhance tropospheric O_3 levels on a global scale as they already have on a local and regional scale. In fact Fishman *et al.* (1979) have argued on the basis of the observed asymmetry between northern and southern hemispheric ozone that CO and NO_x emissions primarily from fossil fuel burning have already led to an increase in O_3 levels in much of the northern hemisphere.

That enhanced NO_x emissions could significantly affect O_3 in the troposphere is illustrated in Figure 8. The O_3 concentrations shown in Figure 8 were calculated with a one-dimensional, photochemical, eddy diffusion model for a "Low-NO_x Case" and a "High-NO_x Case". In the "Low-NO_x Case", a vertically distributed lightning source of 1.2×10^9 cm^{-2} s^{-1}, a stratospheric HNO_3 source of 3×10^8 cm^{-2} s^{-1}, and a small surface source of 2.5×10^8 cm^{-2} s^{-1}, were found to lead to surface NO_x mixing ratio of 25 pptv, the levels typically observed in the remote Pacific Ocean. In the "High-NO_x Case", an additional anthropogenic NO_x surface source of 2.5×10^9 cm^{-2} s^{-1}, was included and this resulted in a surface NO_x mixing ratio of 100 pptv, a level more typical of rural North America, Europe and the north Atlantic. As illustrated in Figure 8, the enhanced NO_x levels in the "High-NO_x Case" led to an approximate 30% rise in the calculated O_3 levels in the lower and mid-troposphere.

Long-Term Variations in Tropospheric Composition

Because of the central role of OH in tropospheric chemistry any variation in the concentration of OH in the troposphere is cause for concern. A change in OH levels would probably lead to changes in the concentration of a variety of greenhouse gases thereby causing a perturbation in the climate. The rates of formation of acids and atmospheric oxidants would

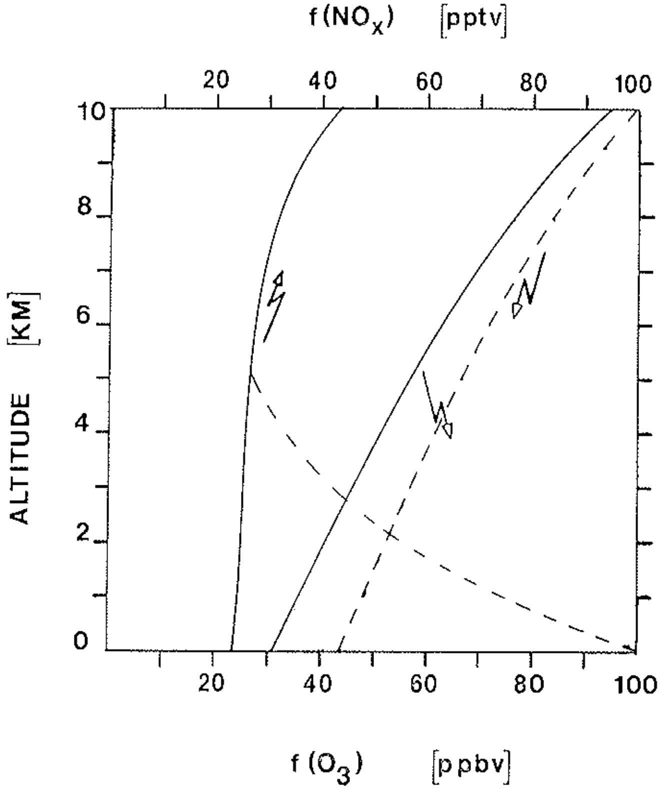

Fig. 8. The calculated NO_x and O_3 mixing ratios, f, as a function of altitude for the "Low-NO_x Case" (solid line) and "High-NO_x Case" (broken line).

also change. Furthermore the rate of injection into the stratosphere of compounds such as CH_3Cl, which affect the levels of stratospheric ozone, would also be perturbed.

In fact evidence is beginning to mount that just such a perturbation in OH levels may have already occurred over the past few centuries and is continuing today. The fact that anthropogenic activities — through ever-rising cultivation of rice paddy fields, maintenance of livestock herds, and emissions of CO and NO_x from fossil fuel burning — have apparently begun to significantly rival the natural rates at which atmospheric CH_4, CO, NO_x, and O_3 are produced would cause one to speculate that the levels of these species may be increasing and this in turn would imply a variation in OH as well.

Much stronger evidence suggesting that a significant perturbation in tropospheric chemistry has occurred has been uncovered in the record of CH_4 levels in the atmosphere. In the past few year several investigators have reported that atmospheric CH_4 levels are currently increasing at a rate of about 0.5-2% per year since at least 1965 (c.f. Rasmussen and Khalil, 1981; Ehhalt *et al.*, 1983; Blake *et al.*, 1982; Graedel and McRae, 1980). In an attempt to determine if this CH_4 increase is a short-term fluctuation or part of a long-term trend, Craig and Chou (1982) analyzed air samples from polar ice cores which were trapped in polar ice far back as 27,000 BP. Their results shown in Figure 9 indicate that CH_4 remained fairly constant from 27,000 BP to 1580 AD at 0.7 ppmv (parts per million by volume) — about half the present values of 1.65 ppmv. In 1580 methane levels began to rise, first at a rate of about 0.114 ppmv per century and then, from 1915, much more rapidly, at a rate of 2.5 ppmv

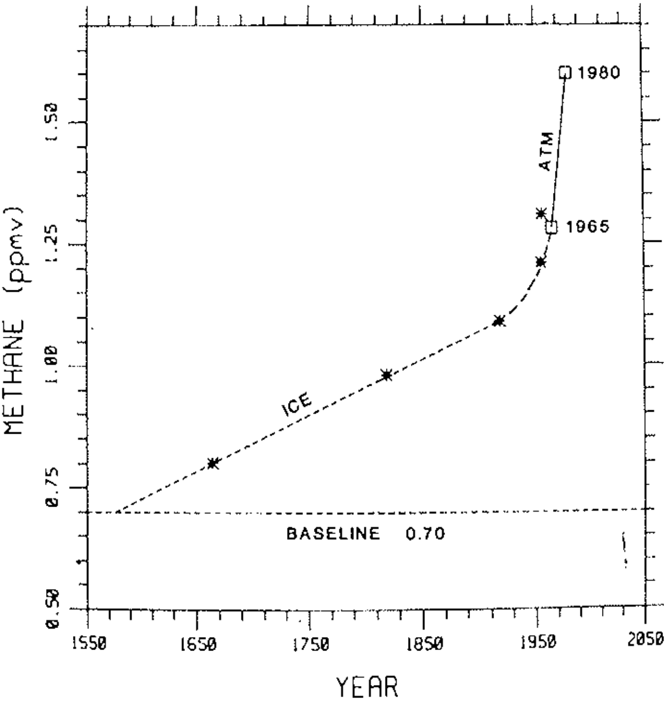

FIG. 9. The temporal variation in atmospheric CH_4 as deduced from analysis of air bubbles trapped in polar ice cores (stars) and analysis of air samples (squares). After Craig and Chou (1983).

per century, roughly equivalent to the rate of 1.7 per cent per year inferred from present day measurements. Should the findings of Craig and Chou prove to be valid then their findings may have significant implications. An increase in methane from 0.7 ppmv to its present value of 1.66 ppmv is estimated to have caused an increase in global temperature of about 0.23°C due to the atmospheric greenhouse effect (Wang *et al.*, 1976). The temperature rise is roughly 38% of the increase calculated to have occurred as a result of the CO_2 increase. Furthermore, since methane interacts with OH the increase in CH_4 may have caused changes in the levels of OH and the myriad of species affected by OH.

There are two processes that could have led to a doubling in CH_4 over the past 400 years. The increasing CH_4 concentrations could be due to increasing biogenic production rates of CH_4. It is known, for instance, that as the world's population demand for food has grown over the past centuries, the population of livestock and the total area of the world under rice paddy cultivation has also grown, implying a corresponding increase in methane production (Ehhalt, 1974). Alternatively increasing emissions of CO from wood and fossil fuel burning could have caused a decrease in OH and a corresponding increase in CH_4 (Sze, 1977; Chameides *et al.*, 1977). In the latter case, the effect of increased CO would be off-set to some extent by enhanced NO_x emissions which would tend to increase OH (Liu, 1977).

What is the magnitude of the increase in CH_4 and/or CO emission rates that would be required to cause a doubling in the atmospheric CH_4 concentration? What does this change in CH_4 imply about the concentrations of OH and O_3? These questions have been explored with the one-dimensional, photochemical model described earlier. For the "Low-NO_x Case" and the "High-NO_x Case" each, four model runs were carried out (i.e. Model O, Model A, Model B, Model C) as well as one additional model run (Model D) for the "High-NO_x Case". Model O corresponds to present-day conditions (i.e. $f(CH_4) = 1.65$ ppmv) and was used to calculate the appropriate present-day OH and O_3 concentrations and the fluxes needed to support the observed levels of CH_4, CO, and NO_x. In the remaining model runs, we project back to the 16th century and assume CH_4 to have a concentration of half its present-day value. In Model A, the concentrations of CO and NO_x were held fixed at their Model O values preventing any feedbacks between the CH_4-H_xO_y and CO-H_xO_y or NO_x-H_xO_y reactive systems. In Model B, these feedbacks are allowed to occur, as the fluxes of CO and NO_x were held fixed but the levels of CO and NO_x were allowed to vary. Model C was like Model B but the CO surface flux was reduced by 1/3, the approximate fraction of the present-day CO emission rate estimated to be due to anthropogenic activities. In model D, run only for the "High-NO_x Case", in addition to reducing the CO surface flux by 1/3, the NO_x surface flux was reduced to the NO_x surface flux used in the "Low-NO_x Case". The "Low-NO_x Case" and "High-NO_x Case" results were then combined in a "Global Average Case" by taking a weighted average with 70% assigned to the "Low-NO_x Case" and 30% to the "High-NO_x Case".

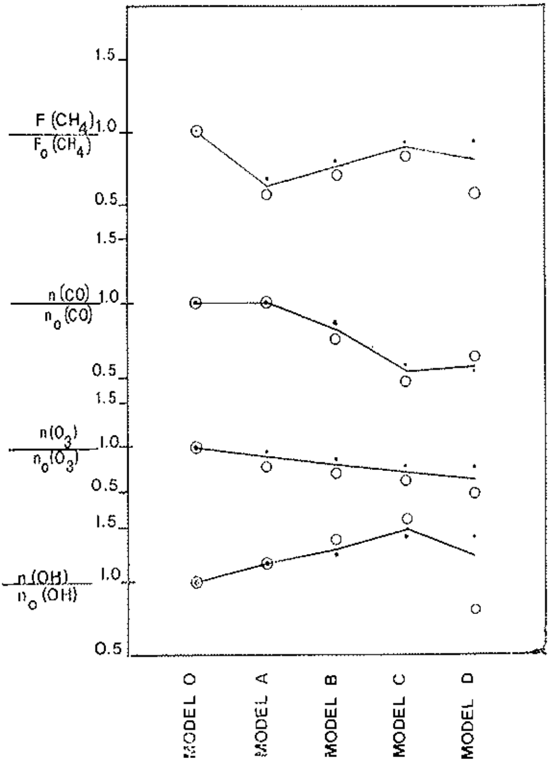

FIG. 10. The calculated relative variations in the CH_4 flux, $F(CH_4)$, and concentrations, n, at the surface in CO, O_3, and OH from present-day conditions. Model O corresponds to present-day conditions; in Model A CH_4 is reduced by 1/2 and CO and NO_x are held fixed; in Model B CH_4 is reduced by 1/2 and CO and NO_x are allowed to vary; Model C is like Model B but the CO emission rate is reduced by 1/3; Model D is like Model C but the NO_x emission rate is reduced to the "Low-NO_x Case" value. The solid points represent the results for the "Low-NO_x Case", the open circles the results for the "High-NO_x Case", and the solid line an average of the two.

The results of the calculations are illustrated in Figure 10. We find that the CH_4-OH system is non-linear; an increase in CH_4 leads to a decrease in OH and a further increase in CH_4. Thus, significantly less than a doubling in the CH_4 emission rate is needed to cause a doubling in CH_4. If CO and NO_x emission rates were constant, the CH_4 flux would have had to increase by only about 40% to have caused a doubling in CH_4 according to the model calculations. Allowing for a corresponding increase in CO emissions in this time period, reduced the required increase in CH_4 emissions to only 25%. However, as the results of Model D show, an increase in NO_x emissions as well as that of CO effectively offsets the impact of CO emission increases.

Another important result of our calculations concerns the concentrations of OH and O_3. It appears that the lower CH_4 levels in the 16th century imply higher OH and lower O_3 concentrations. In the case of OH the variation is predicted to have been quite significant, with about 20-50% more OH in the troposphere in the 16th century as compared to conditions typical of the present-day atmosphere. The change in O_3 levels is predicted to be more modest — only about 10-15%.

Recognizing that the calculations presented here are based on a highly simplified model of tropospheric processes and that the ice core results of Craig and Chou (1982) have yet to be rigorously confirmed by independent investigators we must be cautious to not over-interpret the results of these calculations. Nevertheless, it does now appear quite possible that the troposphere may have undergone a significant chemical perturbation over the past 400 years and that this perturbation continues today. To better understand the character and magnitude of this perturbation a concerted campaign to elucidate the detailed trace gas composition of the troposphere and its temporal variations over the coming decades is needed.

Conclusion

The tropospheric photochemical system consists of a highly complex chemical scheme in which free radical species and especially OH produced in the presence of solar radiation play a central role. The overall trend of this radical system is to oxidize reduced species emitted from earth's surface and cause their eventual return to the biosphere-lithosphere-hydrosphere in an oxidized valence state. This atmospheric chemical cycle is actually one component of a larger set of cycles. In these larger cycles the key biological elements — carbon, oxygen, nitrogen, sulfur, and phosphorus — circulate through the biosphere, lithosphere, and oceans, as well as the atmosphere. By circulating these elements continuously, nature recycles and redistributes the chemicals needed to support life on Earth. And thus it is seen that tropospheric chemistry is closely coupled to biospheric processes.

Recent observations indicating that atmospheric CH_4 is currently increasing and may have been steadily increasing since the 16th century coupled with the fact that anthropogenic activities appear to be a major component in the budgets of tropospheric CH_4, CO, NO_x, and O_3, suggest that the free radical tropospheric system may be undergoing a significant perturbation on a global scale. The implications of such a perturbation have yet to be fully identified.

ACKNOWLEDGEMENT

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DISCUSSION

MARINI-BETTÒLO

Could you give some figures about the CO sink in the soil?

CHAMEIDES

The loss of CO from the atmosphere to soils is roughly one-tenth that of the total CO budget, so it comprises a small fraction of the total. Measurements by Seiler and others show that CO can be emitted as well as absorbed by soils. However the net effect appears to be an uptake of atmospberic CO by soils. Presumably this uptake is being driven by microbial action in the soils.

MALONE

Another question: might it not have been more felicitous if Smith had coined the term "acidic deposition" rather than "acid rain"? What is the aggregate ratio of dry to moist?

CHAMEIDES

That ratio is unfortunately not well-known and it in all likelihood depends on wbere you are located, the closer you are to a source region generally the larger the dry deposition. My best guess right now is that on average the two processes — wet and dry deposition — are roughly of equal importance for acidic species like nitrates and sulfates. I would therefore have to agree with you that a more proper term for the environmental problem most commonly referred to as "acid rain" would be "acid deposition". It is also interesting to note that acid fog looks to be a potentially serious problem in many locations — this being a hybrid form of wet and dry deposition.

ROWLAND

I will comment briefly on the question Tom Malone just asked. I think the budgets for North America show that a number of the order of 20% of the SO_2 going into the atmosphere returns as wet deposition. This leaves 80% some place else. Some of that certainly goes across boundaries out over the ocean as well as across the land boundaries, but the measurements of the dry deposition of the experimental techniques are so far really very much open to question. So that uncertainties of a factor of 3 easily apply there. There was a detailed measurement at Hubbard Brook in New Hampshire, which shows that there the dry deposition was about one-half the wet deposition. But that is a long way from any source, so that probably is sort of the minimum value and the dry deposition close to sources can be probably several times the wet deposition.

WIESENFELD

Two quick questions about aqueous phase oxidation: in addition to oxidation in cloud drops can aqueous phase oxidation in aerosols be important?

CHAMEIDES

Aerosols may be important. The model tabulations I showed for SO_2 oxidation did not include oxidation in aerosols and I am not aware of any calculations carried out by other investigators on this process. One problem is that such a calculation would be loaded with uncertainties. Nevertheless it is an intriguing possibility. For instance, in the marine environment where you have plenty of sea salt aerosol, whenever the humidity is above 78% those aerosols are wet and the humidity is very often above 78% in the marine boundary layer. When these aerosols are wet it is possible for SO_2 to be dissolved in the aerosol along with atmospheric oxidants such as H_2O_2 or NO_3 and the SO_2 can be oxidized to sulfates. Unfortunately because deliquescent aerosols are characterized by extremely high ionic strengths they cannot be treated as an ideal solution and as a result are very difficult to treat theoretically.

WIESENFELD

Can I follow up then with the second question, and that is related to one of your slides, which seemed to imply that it was indeed the free radicals which were undergoing phase transitions from the gas phase to the aqueous phase. There is an unfortunate problem here in nomenclature. People seem to talk about heterogeneous chemistry as occurring in the aqueous phase. In fact it is homogeneous.

CHAMEIDES

You are correct that technically speaking the key reactions occurring in the aqueous phase are homogeneous reactions — meaning aqueous phase homogeneous reactions. If for instance we take the oxidation of SO_2 by H_2O_2 in cloud droplets: there is the gas phase homogeneous reactions which produce H_2O_2; there are the heterogeneous reactions involving the dissolution of SO_2 and H_2O_2; and there are the aqueous-phase homogeneous reactions by which dissolved SO_2 or S_{IV} is oxidized by dissolved H_2O_2. In this particular system even though there is a heterogeneous part to the overall reaction, the rate of oxidation is limited in most cases by the homogeneous aqueous-phase reaction.

WIESENFELD

But of course there can also be homogeneous aqueous phase photochemistry of ozone — that is well known.

CHAMEIDES

Yes there are reactions involving dissolved ozone, even photochemical reactions which can produce free radicals. However given the atmospheric abundance of ozone of about 20-40 ppbv and its very low solubility, it can be easily shown that the ozone concentration in cloudwater is low — about 10^{-10} moles per liter — and hterefore that homogeneous aqueous-phase ozone reactions have a negligible effect on cloud and precipitation chemistry.

CRUTZEN

In your analysis of methane and CO budget you have methane as one of the driving forces in changing the reactions in the atmosphere. However, there is so much more which has been changing in the biosphere. For instance, we know from our work in Brazil that the forests are sources of carbon monoxide, probably through reactive hydrocarbons as intermediates. And so this has to be folded in. I think for the carbon monoxide budget actually methane is not the main source but other hydrocarbons.

CHAMEIDES

In the calculations I presented here methane does not represent a major source of carbon monoxide. Just as you stated, the major sources are non-methane hydrocarbon oxidation and anthropogenic production. And in fact if you accept the Craig and Chou measurements, then 400 years ago when methane was roughly one-half as abundant as it is today, methane oxidation had virtually no effect on the CO budget.

CRUTZEN

I think the whole scheme of reactions which is involved here is not yet well defined, especially if you take into account the possibility of heterogeneous reactions. For instance, the chemistry of methyl peroxide is very uncertain and depending on how you treat this species the methane oxidation chain could enhance OH rahter than decrease it.

CHAMEIDES

Your point is certainly well taken; there are many aspects of tropospheric chemistry that are uncertain, and that involving methyl peroxide is without doubt a prime example. From my own estimation of how the methane system works in the atmosphere, I believe that a significant fraction of the methyl peroxide is removed by heterogeneous reactions before it has a chance to react. This terminates the chain making methane oxidation a net sink for OH regardless of the details of the chemistry of methyl peroxide and its daughter molecules. Nevertheless we certainly need to be aware of the many uncertainties in this chemistry.

REVELLE

What about methane from the ocean?

CHAMEIDES

That source appears to be quite small. While methane is certainly produced by microbes in oxygen-poor and anaerobic regions of the ocean, in order for the methane to escape to the atmosphere it must first pass through an overlying layer in the ocean with abundant oxygen. Probably the methane is oxidized by aerobic microbes in these layers before it can escape.

REVELLE

Is the atmospheric lifetime of CH_4 increasing?

CHAMEIDES

There is no definitive answer to that question. All one can do at this point is speculate. If one accepts the measurements indicating that methane is increasing and one folds in the fact that anthropogenic sources of carbon monoxide are also increasing then the possibility that OH levels are decreasing seems to be a plausible conclusion. And if OH levels are decreasing then the methane lifetime is increasing. However one needs to be cautious since increases in the anthropogenic production of NO tend to cause OH to increase. At the present time a model does not exist that can definitively treat this system by folding in all the effects of pollutants on OH in a global context and determine if OH has in fact decreased over time and if so by how much. My own calculations that I have described here with a very simplistic model indicate that globally averaged OH levels have probably decreased and I would therefore speculate that the methane lifetime is probably increasing. But a good deal more work needs to be done in many different areas before this conclusion can be stated with any confidence.

ROWLAND

I think perhaps this is just a technical quibble on your use of homogeneous for the aqueous phase — there is an implication in the word "homogeneous" that the concentration is the same throughout, and it is my impression that when you are dealing with cloud drops, the concentrations are quite variable depending on how far into the drops you are. It is an inhomogeneous reaction in one phase.

CHAMEIDES

That is a good point; there are certainly large chemical inhomogeneities in the cloud system — inhomogeneities from drop to drop as well as within a single drop. For instance for a species like OH in the aqueous phase, the lifetime is about 10^{-4} seconds. So that OH is destroyed chemically before it has a chance to really mix uniformly throughout most cloud drops. Studies of the effect of this non-uniformity have yet to be carried out, although I do not think it will be overwhelming. Nevertheless the problem of non-uniformity is one that is going to have to be addressed.

WANDIGA

If you look at the distribution of CO along the latitudes, you find quite a big difference, which shows that in the southern and the northern and in the tropics there is a difference in the concentration of CO. However methane is uniformly distributed. What do you attribute this to?

CHAMEIDES

Because methane is long-lived with a lifetime approaching that of 10 years we would expect it to be fairly uniformly mixed in the troposphere even though its sources are not. CO on the other hand has a lifetime of the order of a month and therefore its distribution more closely reflects its source distribution. In this regard there has been an interesting study recently completed by Pinto et al at the Goddard Institute for Space Studies. They used a three-dimensional general circulation model and tried to reproduce the observed latitudinal distribution of CO. In order to do this they needed three sources: one was a well-distributed source and probably is that which arises from methane oxidation; another was a large northern hemispheric source and likely corresponds to the source from anthropogenic activities; and a third was another large source centered in the tropics. Presumably this tropical source of carbon monoxide is from biomass burning and/or oxidation of non-methane hydrocarbons. The important aspect of this work is that a large tropical source such as the one earlier suggested by Crutzen and co-workers is needed to explain the distribution of carbon monoxide.