CHAPTER 4

TROPOSPHERIC CHEMISTRY

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CHAPTER 4

TROPOSPHERIC CHEMISTRY:
PROCESSES CONTROLLING OZONE AND HYDROXYL RADICAL

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4.0 INTRODUCTION

Recent concerns about changes in atmospheric ozone focus not only on the total column of ozone, but also on possible distortion of the vertical profile of ozone. Since approximately 10 percent of the total amount of ozone is present in the troposphere, this assessment includes processes governing tropospheric ozone. There is potential for climate modification resulting from changes in the ozone in both the troposphere and the stratosphere. The trace gases primarily responsible for the solar and long-wave radiative opacity of the present day atmosphere are H_2O, CO_2 and O_3. However, the long-wave opacity of several other radiatively active minor trace gases in the atmosphere, including CH_4 and CH_3CCl_3, contribute significantly to the present day surface temperature. The sources of tropospheric ozone are transport from the stratosphere across the tropopause, and *in situ* photochemical production. Ozone is removed from the troposphere by surface deposition and by photochemical loss processes.

Photolysis of ozone leads to the formation of the hydroxyl radical (HO). Reaction with HO determines the atmospheric lifetime of many important gases in the troposphere, including those that are radiatively important. The troposphere can act as a "chemical filter" for numerous trace gases which are emitted at the earth's surface and transported into the stratosphere. Thus, tropospheric chemistry has an impact on ozone in the stratosphere by controlling HO levels in the troposphere. The tropospheric trace gases that contribute to *in situ* photochemical ozone production, or that influence tropospheric HO levels, include carbon monoxide, methane, oxides of nitrogen and nonmethane hydrocarbons. These gases are emitted at the earth's surface as a result of biogeochemical processes and fossil fuel combustion. There are additional tropospheric sources for NO_x from lightning and aircraft emissions. The source strengths for these trace gases are highly variable on geographic and temporal scales reflecting not only the inhomogeneity of the earth's surface, but also the efficiency of biological processes and the level of human activity.

The planetary boundary layer, PBL, is the initial recipient of substances from ground sources. Because of the dynamic character of the atmosphere, material from the PBL will mix into the free troposphere and can be transported horizontally over great distances. Vertical transport across the PBL is significantly enhanced in the presence of deep convective cloud systems. These dynamic processes provide a transition from high mixing ratios of trace gases near source regions to low mixing ratios in the remote troposphere. These changes in mixing ratios result in changes in chemical reaction paths, thus justifying a chemical classification of the troposphere into the background troposphere, the source region, and a "transition" regime between the two. The chemistry of the background troposphere is discussed in Section 4.1, and that of the source region and the transition region in Section 4.2. The troposphere is governed by heterogeneous chemistry far more so than the stratosphere. Heterogeneous processes of interest here involve scavenging of trace gases by aerosols, cloud and precipitation elements leading to aqueous phase chemical reactions and to temporary and permanent removal of material from the gas phase as discussed further in Section 4.4. They also include exchange of material with the earth's surface, such as dry deposition. Dry deposition is a major removal process for ozone, as well as for other gases of importance in tropospheric photochemistry (e.g., NO_2). These processes are discussed in Section 4.5.

4.1 PHOTOCHEMISTRY OF THE BACKGROUND TROPOSPHERE

The earliest theory of tropospheric ozone held that the gas was supplied by injection from the stratosphere and was removed by surface deposition (e.g., Junge, 1962). Over a decade ago, Crutzen (1973a, 1974) and Chameides and Walker (1973) showed that there are also important chemical sources and sinks for ozone in the troposphere. Recent modelling studies indicate that, averaged over the globe, chemical sources and sinks for ozone are in approximate balance, and are similar in magnitude to the source from the

stratosphere and the sink at the ground (Fishman *et al.*, 1979b; Logan *et al.*, 1981; Chameides and Tan, 1981). Several recent reviews (e.g., Bojkov, 1984; Fishman, 1985) present a detailed account of the debate over chemical versus transport control of tropospheric ozone. They conclude that both mechanisms play important roles, but that the relative importance of the chemical and physical processes controlling ozone in different environments are not well understood. Levy *et al.* (1985) used a general circulation model to investigate the influence of transport processes on tropospheric ozone; the model allowed for downward transport of ozone from the stratosphere and removal at the surface. They compared model simulations with available observations and found that the large scale circulation plays a major role in determining the behavior of ozone, particularly at remote locations. The model results also implied a significant role for chemical sources and sinks for ozone.

4.1.1 The Chemistry of Ozone

Ozone is formed by the association reaction of ground state O atoms with O_2:

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{1}$$

and is removed by photolysis

$$O_3 + h\upsilon \rightarrow O(^1D) + O_2 \tag{2}$$

$$O_3 + h\upsilon \rightarrow O(^3P) + O_2. \tag{3}$$

The metastable $O(^1D)$ is quenched by O_2 and N_2

$$O(^1D) + M \rightarrow O(^3P) + M \tag{4}$$

though it can also react with H_2O to form the hydroxyl radical HO

$$O(^1D) + H_2O \rightarrow HO + HO \tag{5}$$

Nitric oxide reacts with ozone to form NO_2

$$NO + O_3 \rightarrow NO_2 + O_2, \tag{6}$$

with NO_2 removed by photolysis

$$NO_2 + h\upsilon \rightarrow O(^3P) + NO \tag{7}$$

Ozone removed by (6) is reconstituted by (7) followed by (1). It is convenient, because of the cyclic nature of the chemistry, to define a family of species undergoing rapid reactions leading to formation or removal of ozone. We define this family, odd oxygen, as the sum of O_3, $O(^1D)$, $O(^3P)$ and NO_2.

Odd oxygen is conserved in reactions (1)-(4), (6) and (7). It is formed by reactions of NO with HO_2, CH_3O_2, and RO_2.

$$HO_2 + NO \rightarrow HO + NO_2 \tag{8}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{9}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{10}$$

The species RO_2 represents a variety of complex organic peroxy radicals. These reactions occur during the photooxidation of CO, CH_4 and hydrocarbons, for example by

$$HO + CO + O_2 \rightarrow HO_2 + CO_2$$

$$HO_2 + NO \rightarrow NO_2 + HO$$

$$NO_2 + h\upsilon \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$NET: CO + 2O_2 \rightarrow CO_2 + O_3$$

and by

$$HO + CH_4 \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$HO_2 + NO \rightarrow NO_2 + HO$$

$$2 \times (NO_2 + h\upsilon \rightarrow NO + O(^3P)) \quad \lambda < 420nm$$

$$2 \times (O(^3P) + O_2 + M \rightarrow O_3 + M)$$

$$NET: CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3$$
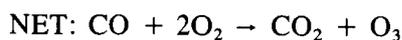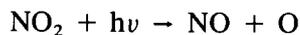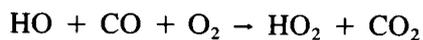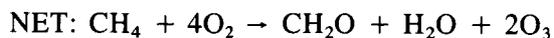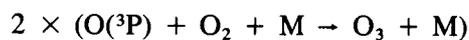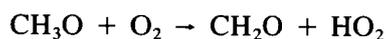
Odd oxygen is removed by reaction of $O(^1D)$ with H_2O, by reaction of O_3 with HO_2 and HO,

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{11}$$

$$HO + O_3 \rightarrow HO_2 + O_2 \tag{12}$$

by formation of nitric acid from NO_2,

$$HO + NO_2 + M \rightarrow HNO_3 \tag{13}$$

and by heterogeneous reactions of O_3 and NO_2 at the earth's surface.

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Oxidation of CO, CH_4 and hydrocarbons leads to net production of odd oxygen in the presence of adequate NO_x. The rate for production of ozone is roughly proportional to the concentration of NO, while the rate of loss is almost independent of NO_x (NO + NO_2) for concentrations below 200 ppt (Fishman et al., 1979). Loss of odd oxygen, primarily by reactions (5) and (11) is balanced by production in reactions (8) and (9) for concentrations of NO near 30 ppt (Fishman et al., 1979; Logan et al., 1981; Crutzen, 1983). Hence, regions of the globe characterized by extremely low concentrations of NO, such as the remote Pacific, are likely to provide a net photochemical sink for odd oxygen (Liu et al., 1983), while the continental boundary layer at midlatitudes, characterized by higher concentrations of NO, is likely to provide a net source. Measurements of NO_x in the troposphere are few, and the lack of data for NO_x contributes significantly to uncertainties in global estimates for the photochemical source of ozone.

Production of ozone in the troposphere is limited ultimately by supply of CO, CH_4, and hydrocarbons, if NO_x is available. One molecule of ozone may be formed for each molecule of CO (Crutzen, 1973b), while the yield of ozone from oxidation of CH_4 could be as large as 3.5 (e.g., Logan et al., 1981). Production of ozone from nonmethane hydrocarbons is discussed in more detail later in this chapter.

4.1.2 The Chemistry of HO

Reaction with HO in the troposphere is the primary removal mechanism for many trace gases which influence the chemical composition and radiative balance of the stratosphere. Consequently, tropospheric and stratospheric chemistry are inextricably linked through the HO radical.

The hydroxyl radical is formed by reaction (2) followed by (5). It is removed by reaction with carbon monoxide and methane,

$$HO + CO + O_2 \rightarrow HO_2 + CO_2 \tag{14}$$

$$HO + CH_4 + O_2 \rightarrow CH_3O_2 + H_2O \tag{15}$$
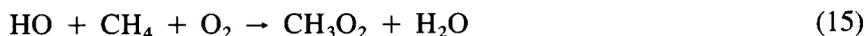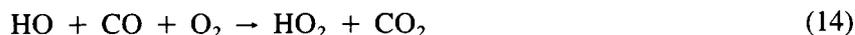
with reaction (14) dominant over (15). HO_2 is removed by reaction (8), and (16)

$$HO_2 + O_3 \rightarrow HO + 2O_2 \tag{16}$$

leading to regeneration of HO, or by

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{17}$$

Hydrogen peroxide is photolysed,

$$H_2O_2 + h\upsilon \rightarrow HO + HO \tag{18}$$

it can react with HO,

$$HO + H_2O_2 \rightarrow H_2O + HO_2 \tag{19}$$

or may be removed by heterogeneous processes such as precipitation scavenging, as discussed below.

$$H_2O_2 + rain \rightarrow removal. \tag{20}$$

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It is convenient, because of the fairly rapid interconversion of H, HO, HO_2 and H_2O_2 to consider these species as a family, odd hydrogen ($=$H $+$ HO $+$ HO_2 $+$ 2 $\times$ H_2O_2). Reaction (5) provides the dominant source for odd hydrogen, while reactions (19) and (20) provide important sinks for odd hydrogen. Reactions (8), (14) and (16)-(18) do not influence the concentration of odd hydrogen.

Atmospheric oxidation of methane (Figure 2-1) may also provide sources and sinks for odd hydrogen, in addition to providing a source for odd oxygen. CH_3O_2, formed in (15), is removed primarily by reaction with NO or HO_2.

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{9}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{21}$$
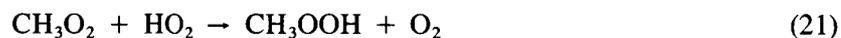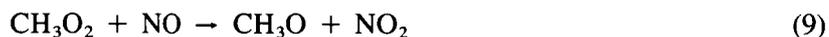
Subsequent reaction of methyl hydroperoxide with HO leads to loss of odd hydrogen.

$$CH_3OOH + HO \rightarrow CH_3O_2 + H_2O \tag{22}$$

$$(21) + (22): \qquad HO_2 + HO \rightarrow H_2O + O_2.$$

Recent measurements of a relatively fast rate for reaction (22) (Niki *et al.*, 1983) indicate that this reaction may provide an important sink for odd hydrogen at low concentrations of NO_x (Logan, 1985, private communication).

The net source of odd hydrogen is determined first by competition between reaction (9) and reaction (21), and second by competition between reactions (22)-(23) which remove odd hydrogen,

$$CH_3OOH + rain \rightarrow removal \tag{23}$$

and reaction (24)

$$CH_3OOH + h\upsilon \rightarrow CH_3O + HO \tag{24}$$

which recycles odd hydrogen. Reaction of the methoxy radical with oxygen yields formaldehyde.

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{25}$$

Photolysis of CH_2O

$$CH_2O + h\upsilon \rightarrow H + HCO \tag{26a}$$

$$CH_2O + h\upsilon \rightarrow H_2 + CO \tag{26b}$$

via path (26a) provides an important source for odd hydrogen in the upper troposphere, while path (26b) and reaction of HO with CH_2O have no net effect on odd hydrogen.

The major pathways in the methane oxidation chain are thought to be understood fairly well. Recent kinetic data for some of the intermediate species have changed the net effect of the cycle on the budget of odd hydrogen. It should be emphasized that the influence of CH_4 chemistry on the budgets of both

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odd hydrogen and odd oxygen depends critically on ambient concentrations of NO_x, because of competition between reactions (9) and (21). A discussion of the chemistry of HO and associated uncertainties may be found in Chameides and Tan (1981), Logan et al. (1981) and NRC (1984). Logan et al. (1981) present a detailed discussion of the potential influence of CH_4 chemistry on odd hydrogen.

4.1.3. The Chemistry of Oxides of Nitrogen

Nitrogen oxides act as catalysts in the photochemical production of ozone. Any reaction which converts NO to NO_2, other than the reaction of NO with ozone, provides a photochemical source of ozone. Present measurements of NO_x are inadequate for definition of its distribution. Preliminary data indicate that ambient concentrations are highly variable in space and time, as discussed in Chapter 3. The lack of data for NO_x precludes accurate quantification of the net global chemical source for ozone.

Nitrogen oxides are produced in the troposphere primarily in the form of NO. Nitric oxide and nitrogen dioxide are rapidly interconverted by reactions (6), (7), (8) and (9) on a time scale of minutes. Nitrogen oxides are removed from the atmosphere by conversion to nitric acid,

$$HO + NO_2 + M \rightarrow HNO_3 \tag{13}$$

followed by heterogeneous processes, i.e., rainout or surface deposition of HNO_3. Surface deposition of NO_2 could provide another important tropospheric sink. There have been few field studies of the rate of uptake of NO_x by surfaces, as discussed later in this chapter, and removal rates of NO_x are not well defined at present.

Current models suggest that NO_x is converted to HNO_3 by reaction (13) within 1-2 days in summer. Nitric acid may be converted to aerosol nitrate, for example by reaction with sea-salt aerosol (Savoie and Prospero, 1982) or by reaction with ammonia (Tang, 1980). Nitric acid and aerosol nitrate are likely to be removed from the atmosphere by precipitation and surface deposition, with mean lifetimes of a few days (Junge, 1963; Levine and Schwartz, 1982). Nitric acid is converted back to NO_x by reactions (20) and (21) more slowly, with a time scale of 2-4 weeks.

$$HNO_3 + HO \rightarrow H_2O + NO_3 \tag{27}$$

$$HNO_3 + h\upsilon \rightarrow HO + NO_2 \tag{28}$$

These processes are significant primarily in the upper troposphere.

Nitric oxide and NO_2 may be converted to HNO_2, HO_2NO_2, NO_3, N_2O_5 and organic nitrates in addition to HNO_3. Most of these molecules decompose thermally or photolytically and therefore provide temporary reservoirs for NO_x. Peroxynitric acid is formed by reaction of HO_2 with NO_2

$$HO_2 + NO_2 + M \rightarrow HO_2 NO_2 + M. \tag{29}$$
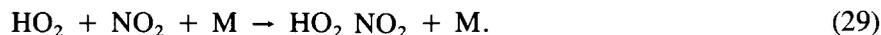
It decomposes rapidly in the lower troposphere,

$$HO_2NO_2 \rightarrow HO_2 + NO_2 \tag{30}$$

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but it is thermally stable in the colder upper troposphere, where it is removed by photolysis and by reaction with HO. Current models suggest that a significant fraction of acidic nitrate may be present in the form of HO_2NO_2 in the upper troposphere, but there are no observational data at present.

Peroxyacetyl nitrate (PAN) is formed during the degradation of hydrocarbons (see below). PAN is more stable than HO_2NO_2 with respect to thermal decomposition, with a lifetime of about a day at 275 °K and several years at temperatures characteristic of the upper troposphere (Cox and Coffey, 1977; Hendry and Kenley, 1979). Recent kinetic data indicate that the lifetime of PAN towards photolysis is about four months (Senum et al., 1984), with a similar value for attack by HO (Wallington et al., 1984). Recent measurements of PAN show that it is an important reservoir for NO_x in clean marine air (Singh and Salas, 1983a, b) and in rural air in North America (Bottenheim et al., 1984; Spicer et al., 1983) and in Europe (Brice et al., 1984).

The nitrate radical (NO_3) is formed by

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{31}$$
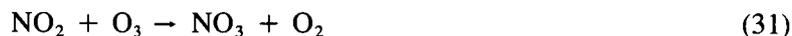
and is photolysed rapidly during the day. At night a steady state should be established between NO_3 and N_2O_5.

$$NO_3 + NO_2 + M \rightleftharpoons NO_2O_5 + M. \tag{32}$$

The nitrate radical has been observed in a variety of "clean-air" locations including Hawaii and rural Colorado. In most cases the concentration of NO_3 at a given level of NO_2 was lower than predicted by model calculations (Noxon et al., 1980; Platt et al., 1980b, 1981, 1984; Platt and Perner, 1980; Noxon, 1983). Some processes, as yet unidentified, appear to be removing NO_3 and/or N_2O_5 from the atmosphere at night. If these processes lead to removal of NO_x, then nighttime removal of NO_x by reactions involving NO_3 could be comparable to daytime by reaction (13). Platt et al. (1981, 1984) speculate that reactions of NO_3, or more likely N_2O_5, on wet aerosols may account for rapid removal of NO_3 under conditions of high humidity, and may provide another sink for NO_x in clouds and fog. A detailed discussion of NO_3 scavenging by cloud droplets, and its possible conversion to NO_3^- by chemical reactions in the liquid phase is given in the section on heterogeneous chemistry. The rate of the homogeneous gas-phase reaction between N_2O_5 and water vapor,

$$N_2O_5 + H_2O \rightarrow HNO_3 + HNO_3 \tag{33}$$
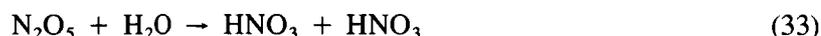
is extremely slow, but this reaction could provide an important source for HNO_3 if it proceeds at the upper limit (k < 1.3 × 10^{-21} cm³ molecule⁻¹ sec⁻¹) given by Tuazon et al. (1983). The role of (33) in nighttime chemistry will remain uncertain until its rate constant is better defined.

4.1.4. The Tropospheric Distribution of HO

Few reliable measurements of hydroxyl radicals have been made so far (e.g., Perner et al., 1976; Huebler et al., 1984; Hoell et al., 1984; Beck et al., personal communication) and these are insufficient to test photochemical theories. Indirect methods have been used, however, to test current models of tropospheric chemistry, and for the determination of average HO concentrations. These methods rely upon mass balance considerations for various trace gases, and they provide a globally averaged estimate for HO. Effective utilization of this approach for determination of HO requires that the tracer species satisfy a number of conditions:

1. Its atmospheric abundance in time and space must be defined accurately.

2. It must be known that removal occurs predominantly by reaction with HO and the rate constant must be determined accurately.

3. The sources and source distribution in time and space must be known accurately.

In recent decades, synthetic organic chemicals have been injected into the atmosphere in such large amounts that measurable background levels are present. Because of the exclusive manmade source of such chemicals, the major uncertainties associated in the source term could, in principle, be eliminated. A preliminary screening led to the selection of methylchloroform CH_3CCl_3 (Singh, 1977: Lovelock, 1977) as the most suitable molecule for the following reasons:

1. Its atmospheric concentration was high enough and could be measured accurately.

2. The usage was such that emissions were similar to production.

3. The HO rate constant was available.

Analysis of data for methylchloroform therefore provides the best current test for global models of the HO distribution. Recent studies of data indicate that the lifetime of CH_3CCl_3 is between 6 and 9 years (Prinn et al., 1983a,b; Khalil and Rasmussen, 1984a). Results from the model for HO described in Logan et al. (1981) using kinetic data given in NASA-JPL (1983) are in good agreement with observations of CH_3CCl_3, in contrast to earlier analyses which underestimated CH_3CCl_3 by about a factor of two (Logan et al., 1981). The improved agreement is due in part to recent revisions in kinetic and solar flux data, which decrease calculated concentrations of HO by 20-30%, and in part to a recalibration of absolute concentrations of CH_3CCl_3 by a factor of 0.8 (Khalil and Rasmussen, 1984a).

The atmospheric lifetime of CH_3CCl_3 can be determined also from its historical emission rates, the observed trends in its atmospheric abundance and the global content. Prinn et al. (1983) estimated an atmospheric removal time of 10.2 years with an uncertainty range of $+5.2$ and -2.6 years from the first three years of data from the ALE network. The corresponding globally averaged HO concentration equals $(5 \pm 2) \times 10^5$ cm^{-3}. The absolute concentration of CH_3CCl_3 has since been revised downward about 20%, as discussed above, yielding revised lifetimes of 6.5 years with an uncertainty range of $+3$ and -2 years.

Other anthropogenic trace gases have been used in a similar manner to estimate HO, for example, dichloromethane, 1,2 dichloroethane and tetrachloroethane (Singh et al., 1983a). A two box model shows that removal rates of these molecules are consistent with average HO concentrations of 4 to 5 $\times 10^5$ molecules cm^{-3}. Because of their relatively short lifetimes compared to methylchloroform, these chemicals can show HO latitudinal gradients with greater sensitivity. However, their source strengths are not as well defined as that of CH_3CCl_3.

Naturally occurring tracers, e.g., ^{14}CO and ^{12}CO, have also been used to estimate HO levels. The ^{12}CO sources however are so poorly defined that such an approach is at best unreliable. Sources of ^{14}CO are somewhat better defined. The dominant source of ^{14}CO is cosmic rays and this source is independent of season and latitude. Compared to the cosmic ray production rate, anthropogenic sources are negligible.

^{14}CO is also produced in significant but uncertain quantities by the oxidation of organic matter. Current atmospheric ^{14}CO data are all taken at ground level; seasonal and latitude gradients have been noted. These limited data have been analysed with the help of a 2-D model to suggest an average tropospheric HO abundance of $7 \pm 3 \times 10^5$ molec cm^{-3} (Volz et al., 1981). These values are a factor of 3 lower than those estimated by Weinstock and Niki (1972) almost a decade ago, largely because of their underestimate of the ^{14}CO abundance. It must be realized, however, that the lifetime of ^{14}CO is short (5 ± 2 months), and a better definition of the organic source term and vertical gradients are needed to improve these estimates.

Recently, Singh et al. (1983b) suggested that simpler and more easily measured molecules such as propane can be used to study the seasonal behavior of HO, provided the source term is characterized adequately. At present, poor characterization of source functions provides the major uncertainty in HO estimates derived from mass balance considerations.

While the budget of CH_3CCl_3 provides one test of global models for HO, significant uncertainties remain in present understanding of tropospheric chemistry. For example, the methane oxidation scheme shown in Figure 2-1 may be an oversimplification of the mechanisms operative in the atmosphere, and the role of larger hydrocarbons in the chemistry of the remote atmosphere remains to be evaluated. Preliminary measurements indicate that nonmethane hydrocarbons (NMHC) may be of some importance for HO chemistry (Rudolph and Ehhalt, 1981; P. Warneck, 1974) even in the background troposphere.

4.1.5. Future Trends

Recent measurements indicate that concentrations of CH_4 and CO may be increasing, as discussed in Chapter 3. It was noted almost a decade ago that increases in these gases could lead to a decrease in HO, since reaction with CO and CH_4 provides the major removal process for HO (Wofsy, 1976: Chameides et al., 1977; Sze, 1977; Hameed et al., 1979). The apparent increase in tropospheric levels of CH_4 and CO over the last 35 years (Rinsland et al., 1985) could have resulted from either an increase in the production rate of CH_4 and/or CO, or a decrease in the destruction rate of these gases, since their concentrations are closely coupled via the methane oxidation chain and the hydroxyl radical. Photochemical model simulations attempting to predict the consequences of these trends are - at best - qualitative. A decrease in HO would imply longer lifetimes and higher concentrations for many chemically reactive and/or radiatively active species resulting in increased transport across the tropopause.

In a recent exploratory study, Levine et al. (1985) used a 1-D photochemical model to simulate present day concentrations of CO and CH_4 at 45 °N and concentrations for 1950 deduced from ground based infrared spectra. They suggest that the global source of CH_4 may have increased by about 11 %, the global surface source of CO may have increased by about 50%, and the tropospheric column of HO decreased by about 25%, from 1950 to the present day. These results should be regarded as extremely preliminary and speculative, however, since it is not clear how to infer changes in global fluxes from the results of a 1-D calculation representing 45 °N in summer. There is a significant latitudinal gradient in CO, and data obtained in recent years suggest that trends in CO in the southern hemisphere are much smaller than at northern midlatitudes, as discussed in Chapter 3.

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4.2 CHEMISTRY OF OZONE FORMATION IN THE POLLUTED TROPOSPHERE

4.2.1 Source Region Chemistry

The discussion on clean tropospheric chemistry indicated that the oxidation of CO, CH_4, and possibly other biogenic hydrocarbons leads to a net production of odd oxygen, if sufficient NO_x is present (i.e., $NO_x > 30$ ppt). In the polluted troposphere, unlike the clean troposphere, the rate of ozone formation is not necessarily proportional to the concentration of NO_x, but varies in a complex way that is dependent upon the ratios and concentrations of the hydrocarbons and NO_x as well as the chemical composition of the hydrocarbons themselves. The chemistry of ozone in the polluted troposphere has been studied for over thirty years. The research emphasis has been predominantly in elucidating the processes for oxidant/ozone formation in urban areas. The focus of interest in urban areas is due mainly to the high emission densities of ozone precursors (hydrocarbons and NO_x) which result typically in very high ozone concentrations under summertime meteorological conditions. In many cases the concentration levels of ozone in urban areas exceed ambient air quality standards which have been set to protect public health and welfare.

Several reviews of the chemistry of polluted atmospheres are available (Leighton, 1961; Stern, 1977; Seinfeld, 1975; Heiklen, 1976), as are detailed discussions of reaction mechanisms (Demerjian et al., 1974; Carter et al., 1979; Baldwin et al., 1977; Falls and Seinfeld, 1978; Whitten et al., 1980) and reaction rate constant reviews (Baulch et al., 1980; Demerjian et al., 1980; Baulch et al., 1982). The discussions which follows provides an overview of the chemistry of the polluted troposphere.

The chemistry that occurs in sunlight-irradiated polluted atmospheres involves the interaction of a host of chemical species. These include: hydrocarbons such as alkanes, alkenes, and aromatics; other organics such as aldehydes and ketones; nitric oxide (NO); nitrogen dioxide (NO_2); ozone (O_3); peroxyacetyl nitrate (PAN); nitric acid (HNO_3); atomic oxygen (O^3P) and its first electronic excited state $O(^1D)$; hydroxy radical (HO); hydroperoxyl radical (HO_2); alkylperoxyl radicals (RO_2); acylperoxyl radicals ($R(O)O_2$); nitrogen trioxide (NO_3); and dinitrogen pentoxide (N_2O_5).

This chemistry explains the rapid conversion of NO to NO_2 observed in the ambient polluted atmosphere (Leighton, 1961; Altshuller and Bufalini, 1965; Demerjian et al., 1974). The key lies in a sequence of reactions involving the same free radical species thought to be important in the chemistry of the clean troposphere and a number of organic radicals derived from the host of more complex hydrocarbon and organic molecules present additionally in the polluted atmosphere.

The most important atmospheric reactions governing the decomposition of alkanes, alkenes, and aromatics involve their reaction with hydroxyl radical. Reaction sequences describing the pathways for their oxidation as a result of HO attack have been studied extensively (Demerjian et al., 1974; Carter et al., 1979; Niki, 1978; Falls and Seinfeld, 1978; Perry et al., 1977; Atkinson et al., 1985; Grosjean, 1984). In a very simplified form this may be represented as follows:

$$HO + Hydrocarbon \rightarrow R + H_2O \tag{34}$$

The alkyl radical (R) produced as a result of the HO attack on the hydrocarbon reacts with an oxygen molecule to form an alkylperoxyl radical (RO_2)

$$R + O_2 \rightarrow RO_2 \tag{35}$$

The alkylperoxyl radical reacts with NO to form NO_2 and an alkoxy radical (RO)

$$RO_2 + NO \rightarrow RO + NO_2 \tag{10}$$

Hydrogen abstraction from the alkoxy radical by molecular oxygen will produce a hydroperoxyl radical (HO_2) and a carbonyl compound $(R(C=O)H)$:

$$RO + O_2 \rightarrow R(C=O)H + HO_2 \tag{36}$$

The aldehydes formed in the RO oxidation, or emitted as such from combustion sources, react with HO or photolyze, introducing another important source of radicals to the atmosphere.

$$R(C=O)H + HO \rightarrow R(C=O) + H_2O \tag{37}$$

$$R(C=O)H + h\nu(\lambda < 400 \text{ nm}) \rightarrow R + H(C=O) \tag{38}$$
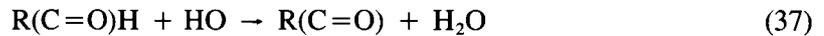
The hydroperoxyl radical can then react with NO to form NO_2 and another hydroxyl radical, which re-enters the cycle.

$$HO_2 + NO \rightarrow \quad HO + NO_2 \tag{8}$$
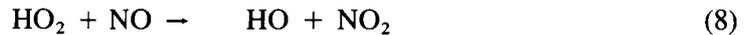
Reactions (8) and (10) taken together provide an efficient mechanism for the rapid conversion of NO to NO_2. This increase in the concentration of "odd oxygen" (previous section) results in an increase of ozone through the perturbation of the chemical steady state relationship (39) derived from the following reactions:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{7}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{1}$$

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{6}$$

The chemical steady state relationship (39) has been shown to be a valid approximation over a considerable range of atmospheric pollutant conditions (Stedman and Jackson, 1975; Calvert, 1976).

$$[O_3] = \frac{J_7[NO_2]}{k_6[NO]} \tag{39}$$

Ratios of NO_2 and NO emitted into the atmosphere by man's activities are typically less than one and would lead to very low ozone steady state concentrations under typical atmospheric solar irradiation conditions. The impact of reactions (8) and (10) is to drive the ratio of NO_2 to NO up by oxidizing the NO to NO_2, in direct competition with the ozone-nitric oxide reaction and thereby allowing ozone to build up in concentration.

Typical observations made in a polluted atmosphere of this phenomenon are shown in Figures 4-1a and b. The diurnal pattern begins with the emission of hydrocarbons, carbon monoxide and NO_x from motor vehicles in the early morning. The NO is converted to NO_2 and ozone accumulation begins when

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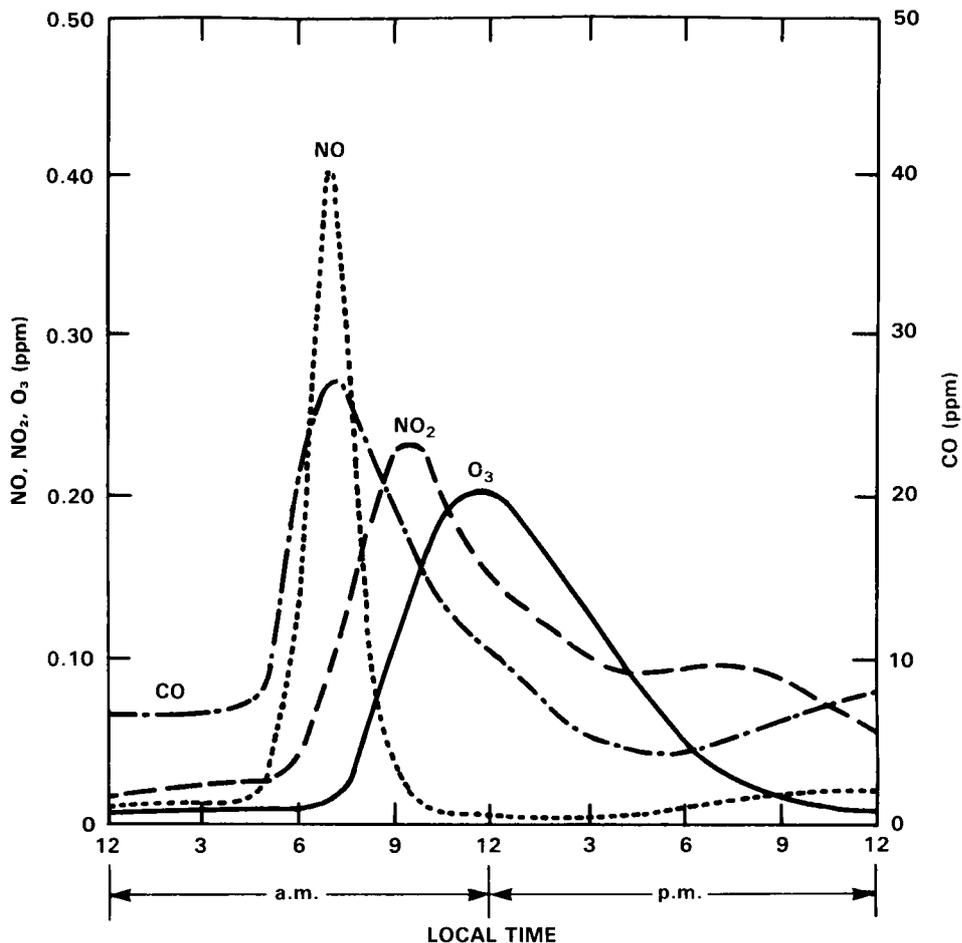
Figure 4-1a. Average daily 1-hour concentrations of selected pollutants in Los Angeles, California, July 19, 1965. From U.S. Department of Health, Education and Welfare.
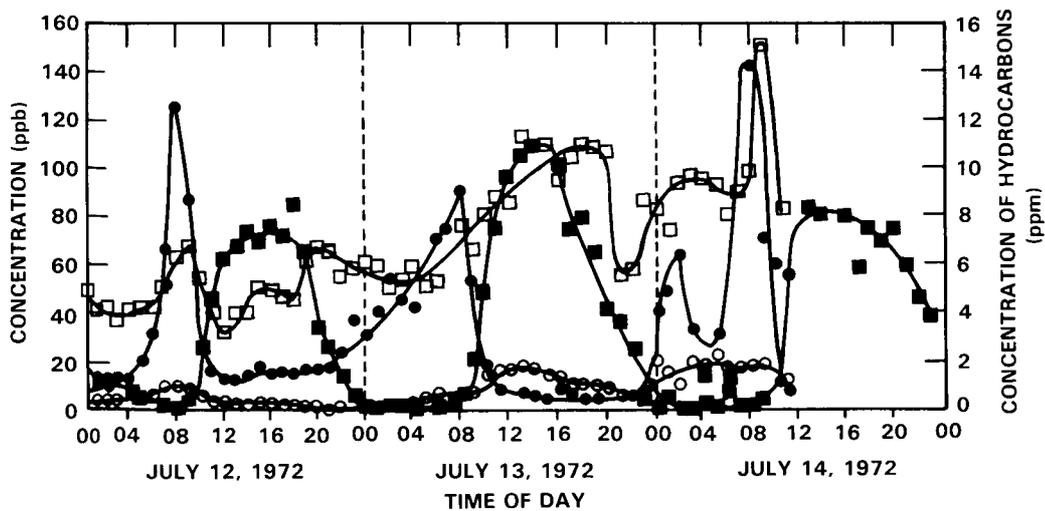
Figure 4-1b. Diurnal variations of air pollutants measured in London from July 12 to July 14, 1972. ■, Ozone ppb; ●, nitric oxide, ppb; □, nitrogen dioxide, ppb; ○, hydrocarbons, ppm. From Derwent and Steward.

most of the NO has been oxidized. The ozone concentration maximizes and then declines either as a result of reaction with additional emissions of NO through the day, dilution due to meteorology, or in the case of extended periods of time and transport, by interaction with the ground surface, which is a major sink for ozone in the atmosphere as will be discussed later in this chapter.

The interaction of organic free radicals produced by hydrocarbon oxidation with NO and NO_2 represents an important aspect of the chemistry of the oxides of nitrogen in the polluted atmosphere. They represent key processes in the conversion of NO to NO_2 and the formation of organic nitrates. It has recently been found that the more complex peroxyalkyl radicals formed during alkane photooxidation can add NO to form alkyl nitrates in non-negligible yields, in competition with reaction (10) (Atkinson $et\ al.$, 1985):

$$RO_2 + NO \rightarrow RONO_2 \tag{40}$$

Also the hydroperoxyl radical formed from hydrocarbon oxidation in reaction (36) supplements that formed in reactions (12) and (14) to create hydrogen peroxide via reaction (17), and aldehydes react with the hydroxy radical to produce peroxyacyl radicals and ultimately peroxyacyl nitrates by reaction with NO_2

$$RCHO + OH \rightarrow RCO + H_2O \tag{41}$$

$$RCO + O_2 \rightarrow R(C=O)O_2 \tag{42}$$

$$R(C=O)O_2 + NO_2 \rightarrow R(C=O)O_2NO_2 \tag{43}$$
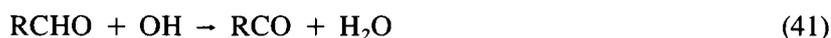
A thermal equilibrium exists between the peroxyacyl nitrate and its components

$$R(C=O)O_2NO_2 \rightleftarrows R(C=O)O_2 + NO_2 \tag{44}$$
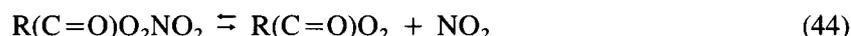
and the peroxyacyl radical is removed from the atmosphere by reaction with NO (Cox and Coffey 1977)

$$R(C=O)O_2 + NO \rightarrow R(C=O)O + NO_2 \tag{45}$$
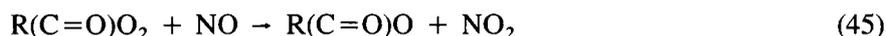
The most commonly occurring peroxyacyl nitrate is peroxyacetyl nitrate or PAN and there is a great similarity between the behavior of PAN and ozone in polluted atmospheres. Their diurnal variations at ground based sites are virtually identical on many occasions (Garland and Penkett 1976) primarily because their formation and removal mechanisms are very similar. PAN is thus an excellent tracer of the photochemical reactivity of the troposphere and since it has no large stratospheric source it can be used in studies designed to investigate the seasonal behavior of tropospheric photochemical activity (Brice $et\ al.$, 1984).

4.2.2 Night-time Chemistry of the Source Region

The nitrate radical NO_3 can be formed by reaction of NO_2 with ozone

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{46}$$

During the day NO_3 is rapidly photolyzed back to its precursors but during the night an equilibrium with N_2O_5 can be established

$$NO_3 + NO_2 \rightleftarrows N_2O_5 \tag{47}$$

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Night-time concentrations of NO_3 as high as 355 pptv have been recorded in the Los Angeles basin (Platt et al., 1980b, 1984). Some NO_3 is converted to HNO_3 by reactions with hydrocarbons and aldehydes,

$$NO_3 + RH \rightarrow R + HNO_3 \tag{48}$$

$$NO_3 + R(C=O)H \rightarrow R(C=O) + HNO_3 \tag{49}$$

but in the absence of NO no chain reactions can be initiated by the peroxy radicals, which will be rapidly lost. The N_2O_5 which is formed will be stable until sunrise or it can be removed either by hydrolysis in deliquescent aerosols or by uptake on ground surfaces.

It is quite possible that heterogeneous chemistry is important in the overall NO_x cycle particularly in the formation of nitrous acid, HONO, which can act as an efficient source of HO radicals in conditions of low light intensity, but this is an area where much more research is required before definite statements can be made.

4.2.3 Ozone in the Non-Urban Troposphere; "The Transition Region"

Anthropogenic emissions of NMHC and NO_x may contribute significantly to photochemical production of ozone and other oxidants on a hemispheric scale, especially in the transition region, where the reactants are removed from their sources but there is still sufficient NO_2 present for the chemistry described above to occur. The state of the science is such that a quantitative understanding of this contribution is not yet possible. Some phenomenological processes which may be important on the larger scales (continental to hemispheric) are: transport of ozone/oxidants formed within the confines of the urban plume followed by dispersal over regional and continental scales; photochemical production of ozone/oxidants from the remnants of aged urban air masses (partially oxidized hydrocarbons and slower reaction hydrocarbon species) which have been transported and dispersed over several days, and photochemical production of ozone/oxidants from low level emissions of non-methane hydrocarbons and NO_x (both natural and anthropogenic) over the continent. It is also possible that emissions of precursors in winter form a reservoir which can influence oxidant chemistry later in the year as photolytic processes become more efficient. Our understanding of the specific sources of ozone/oxidants is somewhat limited, due in part to difficulties in studying the reaction pathways for ozone formation for the less reactive hydrocarbon species, and in part to the lack of data for non-methane hydrocarbons and NO_x in aged polluted air masses and in background air.

The limited data base that exists for hydrocarbons suggests much larger concentrations for many species in the northern hemisphere than in the southern hemisphere. Figure 4-2 shows a latitudinal transect for ethane over the Eastern Pacific Ocean and similar data patterns have been observed over the Atlantic Ocean (Singh and Salas, 1983; Rasmussen and Khalil, 1983; Ehhalt and Rudolf, 1984). Larger differences between the two hemispheres are observed for more reactive hydrocarbons such as propane and butanes which are known to have large anthropogenic emissions. It has also been observed that the northern hemisphere concentrations of these various hydrocarbons vary greatly with season. Table 4-1 shows some average concentrations of hydrocarbons obtained in the vicinity of the Island of Spitzbergen at 79°N in the summer and at the end of the Arctic winter. All show much higher values in the winter than in the summer with the exception of C_2H_4 and C_3H_6 which are believed to have predominantly natural sources (Hov et al., 1984). The decay with time from the spring peak in hydrocarbon concentrations at Point Barrow at 70°N in Alaska has been observed on a day-by-day basis and similar changes in the concentrations of many molecules were observed there (Rasmussen et al., 1983). The variation at high latitudes in the northern hemisphere is also reflected in observations made at 39°N at Point Arena on the Pacific Coast of the U.S.A., particularly for C_3H_8 and C_4H_{10} (Singh and Salas, 1982).
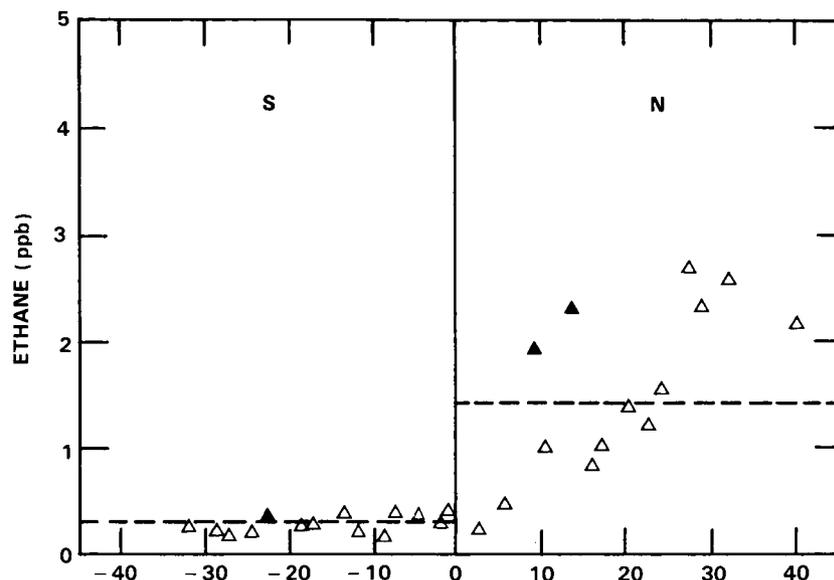
Figure 4-2. Ethane concentrations over eastern Pacific, darkened data points are excluded from the computation of averages for statistical reasons only. Dashed lines show the weighted hemispheric average. Source: Singh and Salas, 1982.

Table 4-1. Average concentrations and standard deviations (in parentheses) in pptv for 9 samples of pressurized air (5 from Bear Island, 2 from Hopen and 2 from Spitzbergen) in July 1982, and for 10 cryogenic samples from Ny-Alesund (Spitzbergen) spring 1983.

Hydrocarbons	July 1982	Spring 1983	Ratio Spring/ Summer
C_2H_6	1195 (27)	3950 (27)	3.3
C_2H_4	255.2 (84.4)	156 (37)	0.6
C_2H_2	66.5 (17.7)	954 (106)	14.3
C_3H_8	87.1 (30.1)	2156 (284)	24.8
C_3H_6	187 (111)	24 (7.7)	0.1
iC_4H_{10}	<20	390 (60)	>20
nC_4H_{10}	<20	805 (141)	>40
2-methyl butane	<20	346 (69)	>17
nC_5H_{12}	<20	339 (93)	>9
2-methyl pentane	<20	182 (34)	>9
3-methyl pentane	<20	160 (20)	>8
nC_6H_{14}	<20	172 (41)	>9
Cyclohexane	<20	54 (14)	>3
C_6H_6	65.6 (23.4)	307 (102)	4.7

Data from Hov *et al.*, 1984.

The extent of this large seasonal effect occurring throughout the northern hemisphere is not known although the studies made over the Atlantic and Pacific Oceans suggest that the largest concentrations of the hydrocarbons are to be found north of 20 °N. It is also quite likely that higher concentrations will be observed over the continents. This would represent a large reservoir of gaseous carbon which would be capable of forming ozone when oxidized in the presence of NO_2.

The NO_x data base is even smaller than that for hydrocarbons and most is probably not directly applicable to the so-called "transitional region" between the truly remote troposphere and the easily identifiable polluted atmosphere adjacent to the source regions. It has been shown for instance that NO concentrations over the Equatorial Pacific Ocean are less than 5 pptv (McFarland *et al.*, 1979) which is less than the theoretical quantity required for ozone production to accompany methane and CO oxidation. Measurements made during the month of June at a coastal site in Ireland however show NO_x concentrations up to 100 pptv (Helas and Warneck, 1981). Median concentrations of NO_x are ~ 280 pptv in winter and ~ 300 pptv in summer at Niwot Ridge, Colorado, perhaps the only site in the transition region for which an extensive climatology for NO_x is available. Measurements of NO_x are discussed in greater detail in Chapter 3.

A further possible source of NO_x is PAN, which is formed in regions of high NO_x and could be carried to regions of low NO_x before decomposing (reaction 44) (Crutzen, 1979). Measurements over the Pacific Ocean have been reported to be in the range of 100 pptv (Singh and Salas, 1983). As yet these are preliminary but they do suggest, along with the Irish data on NO_x, that substantial amounts of NO_2 can be present on occasion. This is important since the only mechanism which can produce ozone on a large scale in the troposphere is photolysis of NO_2 (reaction 7) and possibly lightning.

There is a growing body of evidence to confirm that concentrations of ozone in the non-urban troposphere are influenced by human activity. Concentrations of ozone are larger at mid-latitudes of the northern hemisphere than at corresponding southern latitudes (Pittock, 1977; Fishman and Crutzen, 1978). Regional scale pollution episodes, during which ozone concentrations may exceed 100 ppbv for several days, indicate an extensive anthropogenic influence on ozone near the surface in both Europe and the United States (e.g., Cox *et al.*, 1975; Guicherit and Van Dop, 1977; Wolff and Lioy, 1980). Concentrations of ozone, both at the surface, and in the middle troposphere over Europe and North America, appear to be increasing (Warmbt, 1979; Angell and Korshover, 1983; Logan, 1985) as discussed further in Chapter 14.

In order to test the concepts about processes influencing ozone, and to evaluate future effects of combustion related emissions on tropospheric ozone, it will be necessary to develop rather sophisticated models for chemistry and transport. Such models must allow for the transformation and transport of pollutants from urban source regions to the middle troposphere. Future research is clearly needed into the photochemistry of the complex hydrocarbon/NO_x mix which is found in non-urban air.

4.3 HETEROGENEOUS CHEMISTRY

Heterogeneous chemical reactions are normally defined as ones which occur at the interface between two phases, e.g., gas-liquid, gas-solid, or liquid-solid. In the atmosphere processes are considered to be heterogeneous as long as the overall reaction involves two phases even though specific steps in the reaction may be homogeneous. An example of this is the oxidation of SO_2 in cloudwater, i.e. the dissolution of gaseous SO_2 into a cloud droplet followed by the oxidation of aquated SO_2 by homogeneous aqueous-phase reactions. Because SO_2 is transferred from the gas to the aqueous phase, this process is considered to be heterogeneous even though the actual oxidative reaction is homogeneous.

While heterogeneous reactions are not believed to have a significant direct impact upon the global levels of O_3 and HO, they indirectly impact upon these species by affecting the levels of nitrogen oxide species such as HNO_3, NO_3, and N_2O_5 and hydrogen oxide species such as HO_2, H_2O_2, CH_3OOH, and other organic peroxides. In this section we briefly review the heterogeneous mechanisms that affect nitrogen oxide and hydrogen oxides.

4.3.1 Interactions with Aerosols and Particulates

The presence of particles in the atmosphere raises the possibility that atmospheric gaseous species interact with these particles heterogeneously. In most cases this interaction results in a gas-to-particle conversion; i.e. the transfer of a chemical species from the gas phase to an aerosol or liquid droplet or the formation of a new particle from a gaseous species. Typically gas-to-particle conversion processes are classified into three categories (Kiang *et al.*, 1973; Schryer, 1982):

1) Homogeneous, homomolecular nucleation (the formation of a new stable liquid or solid ultrafine particle from a gas involving one gaseous species only);

2) Homogeneous, heteromolecular nucleation (the formation of a new particle from two or more gaseous species);

3) Heterogeneous, hetermolecular condensation (the growth of pre-existing particles due to deposition of molecules from the gas phase).

Of the above processes, the third, sometimes referred to as "aerosol scavenging", probably has the greatest impact upon the gas-phase levels of nitrogen oxides and hydrogen oxides and thus on the atmospheric abundances of ozone and HO (Turco *et al.*, 1982). Scavenging reactions that are most relevant in this regard are those involving HNO_3, NO_3, N_2O_5, organic nitrates ($RONO_2$), H_2O_2, HO_2, and organic peroxides ($ROOH$). These reactions can be represented by

$$\text{(R1a)} \quad HNO_3 \rightarrow \text{aerosol}$$
$$\text{(R1b)} \quad NO_3 \rightarrow \text{aerosol}$$
$$\text{(R1c)} \quad N_2O_5 \rightarrow \text{aerosol}$$
$$\text{(R1d)} \quad RONO_2 \rightarrow \text{aerosol}$$
$$\text{(R1e)} \quad H_2O_2 \rightarrow \text{aerosol}$$
$$\text{(R1f)} \quad HO_2 \rightarrow \text{aerosol}$$
$$\text{(R1g)} \quad ROOH \rightarrow \text{aerosol}$$
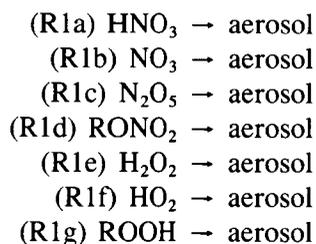
A complete understanding of scavenging reactions such as those listed above requires a thorough description of all the processes occurring at the surface interface and thus a knowledge of the aerosol surface structure and composition and its interaction with the relevant reactants and products. At the present time we have not yet developed this understanding; to do so will require the continued design and application of sophisticated experimental techniques used in conjunction with advanced theoretical studies of surface interactions. As a result present-day descriptions of heterogeneous reactions such as aerosol scavenging are quite rudimentary and involve the use of simple parameterizations to treat many of the complex molecular processes that occur but are not yet understood. One such simple description is described below.

The rate of scavenging of a gaseous species J is normally assumed to be proportional to the species ambient concentration, n_J, so that

$$\text{Rate of aerosol scavenging} = n_J \, k_{part} \tag{1}$$

where the proportionality constant, k_{part}, has units of s^{-1}. The parameter k_{part} can be represented by (Chameides and Davis, 1982; Heikes and Thompson, 1983),

$$k_{part} = \int \phi_J(r) \, n_p(r) \, dr \qquad (2)$$

where $n_p(r)$ is the concentration of aerosol particles having radii between r and $r + dr$ and $\phi_J(r)$ is the rate at which species J diffuses and sticks to an aerosol particle of radius r. $\phi_J(r)$ can be represented by (Schwartz, 1983)

$$\phi_J(r) = \frac{4}{3} \pi \ell r \, V_j \left(1 + \frac{4\ell^{-1}}{3r\alpha}\right) \frac{[n_J - n_J{}^0]}{n_J} \qquad (3)$$

where ℓ is the mean free path, V_J is the species thermal velocity, α is the appropriate sticking or accommodation coefficient for species J impinging upon the aerosol surface, and $n_J{}^0$ is the species' concentration at the surface of the aerosol. Typically, $n_J{}^0$ is assumed to be zero for solid particles and (a_J/H_JRT) for wet particles, where a_J is the activity of J in solution, H_J is the species solubility constant in the appropriate aerosol solution, R is the gas constant, and T is the temperature.

While appearing to be quite straightforward, the application of Equations (1), (2), (3) to determine the rate of aerosol scavenging of a given species J is quite difficult. For one the value of α is highly uncertain. The little data that does exist suggest that α can vary widely depending upon the aerosol composition (i.e. basic or acidic), relative humidity (i.e. for hygroscopic aerosols, solid particles at low humidity and solution droplets at high humidity), and the nature of the impinging gas. For instance while sticking coefficients for species such as HO_2, H_2O_2, NO_3 impinging upon water solutions with pH's above about 5 may approach unity, the α for these species impinging upon H_2SO_4 particles or similar highly acidic dry particles are likely of the order of 10^{-6} to 10^{-4} (cf. Chameides and Davis, 1982).

Another complication arises for hygroscopic aerosol particles which, provided the humidity is high enough, exist as small suspended solution droplets of relatively high ionic strength (i.e. $\mu > 1$). At these ionic strengths, the particle can no longer be treated as an ideal solution as one does for lower ionic strengths. The appropriate values for a_J and H_J are generally not known and can only be accurately determined by detailed experimental studies such as those carried out by Pytkowicz (1984) for seawater.

In spite of these uncertainties, Equation (1), (2), and (3) can be used to obtain a preliminary indication of how important these scavenging reactions may be for a range of possible values for uncertain parameters such as α. As an example, values for k_{part} for NO_3 and N_2O_5 as a function of α and the total number density of aerosol particles (assuming a log-normal distribution) are illustrated in Figure 4-3 for the case when $n_J{}^0 = 0$. (Very similar scavenging coefficients would be obtained for other species such as HNO_3, HO_2, and H_2O_2). The results of Figure 4-3 suggest that for species with sufficiently long lifetimes (i.e. of the order of days or more), aerosol scavenging would represent a significant sink in regions of modest-to-large aerosol loadings if $\alpha \geq 10^{-2}$. Indeed the large levels of NO_3^- found in aerosols in the marine boundary layer would appear to confirm that scavenging of gaseous HNO_3 by sea salt aerosol represents a major sink for this species in the marine atmosphere (Huebert and Lazrus, 1980; Liu $et\ al.$, 1983). At night when NO_3 photochemical lifetimes become large, scavenging by aerosols could also be a significant sink for NO_3; in fact this mechanism has been proposed to explain the low levels of NO_3 observed at night (Noxon $et\ al.$, 1978; Platt $et\ al.$, 1980b; Heickes and Thompson, 1983). It is also interesting to note that in urban locations where aerosol number densities of $10^4 - 10^5$ cm^{-3} are not uncommon, aerosol scavenging could also be an important sink for HO_2, whose photochemical lifetime is about 100s, if $\alpha =$ values near 1 are appropriate.

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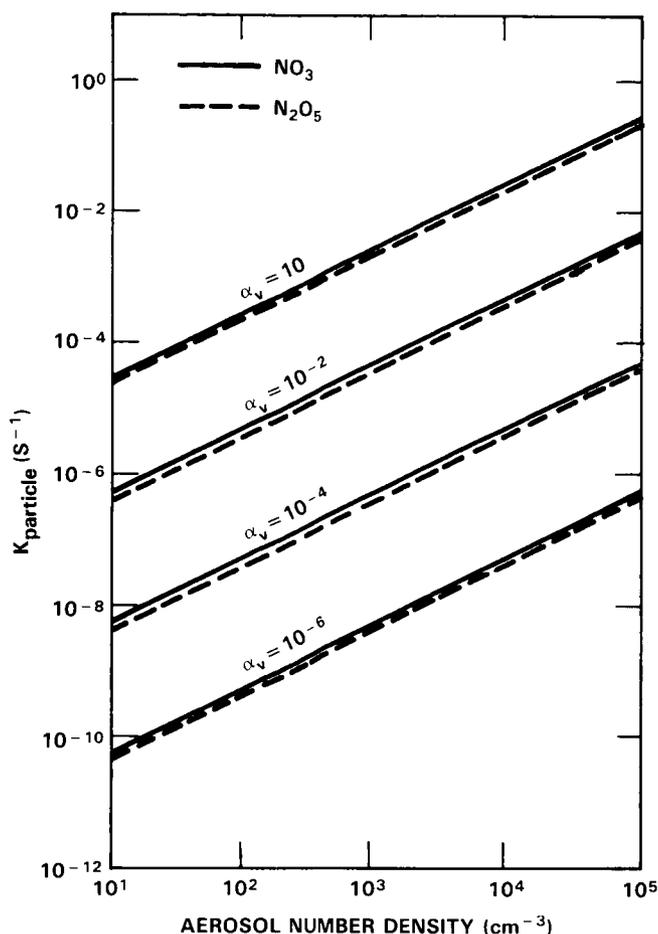
Figure 4-3 Calculated values of aerosol k_{part} for NO_3 and N_2O_5 as a function of aerosol number density and sticking coefficient α_v. After Heikes and Thompson (1983).

Thus these calculations imply that aerosol scavenging can be an important sink for HNO_3 and NO_3, as well as H_2O_2 and possibly HO_2. As such this process would represent a major heterogeneous sink for nitrogen oxides and hydrogen oxides. However, many uncertainties are associated with this assessment. Before a more definitive assessment of aerosol scavenging can be made, experimental studies establishing accurate values for α as well as field measurements characterizing the chemical composition and structure of aerosol surfaces will be needed.

In addition to aerosol scavenging another potentially important heterogeneous sink of nitrogen oxides that needs to be considered is the formation of NH_4NO_3 from gaseous NH_3 and HNO_3, i.e.

$$(R2) \quad (NH_3)_g + (HNO_3)_g \leftrightarrow (NH_4NO_3)_g$$

In regions of high NH_3 levels this process can represent a significant heterogeneous sink for nitrogen oxides. Studies by Stelson and Seinfeld (1982) have indicated that the levels of NH_4NO_3 in the particulate phase relative to that of gas-phase NH_3 and HNO_3 can be accurately described in terms of the thermodynamic equilibrium between the phases. While the condensation of NH_4NO_3 can occur via heteromolecular, homogeneous condensation as well as hetermolecular, heterogeneous condensation, observations indicate that the later process is the dominant one in the atmosphere.

4.3.2 Interactions with Hydrometeors

4.3.2.1 Scavenging

Similar to the interactions of gases with aerosol particles, scavenging or heterogeneous removal is probably the most common process by which hydrometeors affect gas-phase species. This can occur via rainout (removal of gases by cloud droplets) as well as washout (removal of gases by raindrops). Of these two it is generally believed that rainout is more important than washout simply because of the longer lifetime and greater surface area afforded by cloud drops when compared to that of raindrops. With regard to nitrogen oxides and hydrogen oxides, removal of HNO_3, NO_3, H_2O_2, and HO_2 are most relevant because of their high solubility or reactivity in clouds.

The rate of incorporation of a gaseous species J into a cloud droplet can be treated in much the same manner as that for aerosol particles described in the previous section. Thus

$$\text{Rate of cloud droplet scavenging} = n_J \, k_{cloud} \tag{4}$$

where

$$k_{cloud} = \int \phi_J(r) \, n_d(r) \, dr \tag{5}$$

and n_d is the number of cloud droplets with radii between r and r + dr. $\phi_J(r)$ in Equation (5) is essentially the same as that given by Equation (3), except that now $n_J{}^\circ = [J]/HRT$, where [J] is the concentration of J in solution in units of moles (liter)$^{-1}$. (Because ionic strengths in cloudwater are small, the solution can be treated as ideal so that $a_J = [J]$ and H_J is given by the Henry Law constant for J in a pure water solution.) Values for α for cloud drops, while not accurately known, are probably not nearly as uncertain or variable as those for aerosol particles since the water droplet surface is better defined. (On the other hand, the reader should note that the presence of organic films on droplets could further complicate the issue as discussed by Gill et al., 1983). Sticking coefficients for most species of interest impinging on water are probably of the order of 10^{-2} or higher although values as low as 10^{-4} cannot be ruled out at this time (cf., Chameides and Davis, 1982).

Within a cloud, gaseous species are transferred to droplets until equilibrium is attained. Calculations simulating the transfer of gases to droplets indicates that, for reasonable values of α, equilibrium between the two phases is rapidly attained. This fact is illustrated in Table 4-2 where equilibration times, τ_{eq}, are listed for several species of interest as a function of α and r. Because equilibrium does apply the concentration of a species J in solution can be related to its ambient gas-phase concentration in cloud-free regions via

$$[J] \cong [J]^{eq} = n_J/(A \, L \times 10^{-9} + (HRT)^{-1}) \tag{6}$$

where $[J]^{eq}$ is the concentration of J in the cloudwater at equilibrium, A is Avogadro's number, and L is the liquid water content in units of gm^{-3}.

Given Equation (6) as well as statistics for the average cloudiness of the atmosphere, the rate of precipitation from clouds, and the liquid water content of clouds, an expression for the rate of removal of a species via rainout can be obtained. The results of such an analysis are found in Figure 4-4a, where the rainout

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Table 4-2. Values for H_{eff}, $(PF)_{eq.}$ and τ_{eq} as a function of α_w and r for selected soluble species.*

Gas-Phase Species	Heff [M/atm]	(PF)eq	τ_{eq}[sec]			
			$\alpha = 10^{-2}$ $r = 10\mu m$	$\alpha = 1$ $r ^5 10\mu m$	$\alpha = 10^{-4}$ $r = 10\mu m$	$\alpha = 10^{-2}$ $r = 30\mu m$
SO$_2$	4.1×10^3	0.06	2.1	0.93	120	12
HCHO	1.3×10^4	0.16	4.3	1.9	250	24
HO$_2$	3.3×10^4	0.4	10	4.4	580	56
OH	1×10^5	1.1	16	6.9	910	88
HCOOH	1.5×10^5	1.7	33	14	1.9×10^3	180
H$_2$O$_2$	1.9×10^5	2.3	31	14	1.8×10^3	180
NH$_3$	1.6×10^6	19	44	19	2.5×10^3	240
HNO$_3$	7.3×10^{11}	9×10^6	280	120	1.6×10^4	1.6×10^3

*Values calculated for pH $= 5.05$, T $= 291\,°K$, and L $= 0.5g\ m^{-3}$. After Chameides (1984).
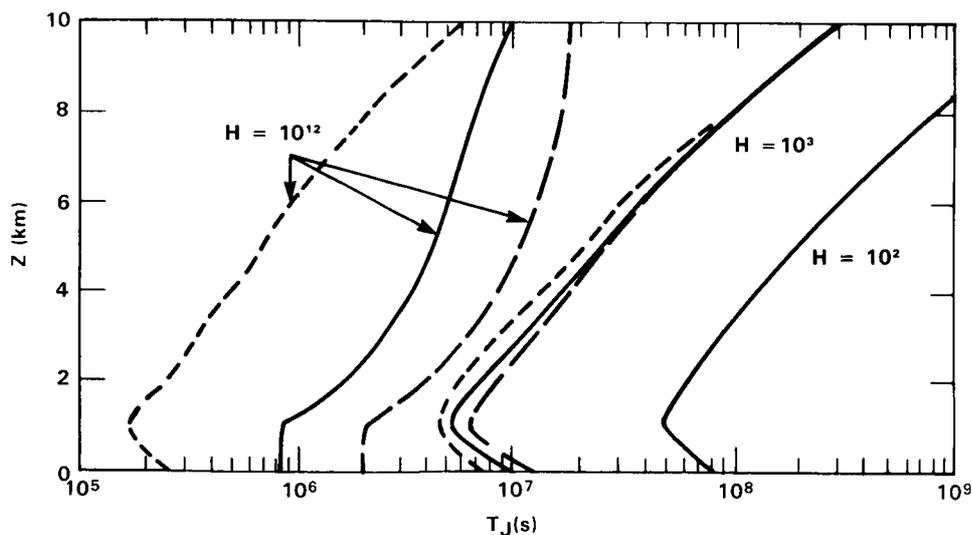
Figure 4-4a Effective rainout lifetimes, $\tau_J°$, for H $= 10^2$, 10^3, and 10^{12} (M atm^{-1}) for different storm cycle periods. The dotted line is for a storm period (i.e. the time for a complete cycle of rain followed by a dry interval to transpire) of 1 day, the solid line is for a storm period of 10 days, and the dashed line is for a storm period of 25 days.

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lifetimes, τ_J, are illustrated as a function of z for different values of H and varying types of storm cycles. For species of low solubility, τ_J is linearly related to H but independent of the length of time between storms. For species of high solubility which are virtually completely removed from the atmosphere during each storm, τ_J is independent of H but linearly related to the time between storms; in this case $\tau_J = T$ where T is the storm period.

Thus in regions of long dry periods between storms, the rainout lifetimes for highly soluble species can become significantly longer than the average 10 day lifetime for water vapor that has been previously assumed to be representative of the lifetime of highly soluble species. It can be seen in Figure 4-4b that for nitrogen oxide species strikingly different profiles can be obtained in model calculations using this parameter for different assumed storm periods even though identical source strengths were assumed in each case. Thus, given the large seasonal and latitudinal variations in the water vapor-cycle, this result would seem to imply that in addition to NO_y sources, NO_y removal rates can also lead to large temporal and spatial variations in NO_y concentrations.
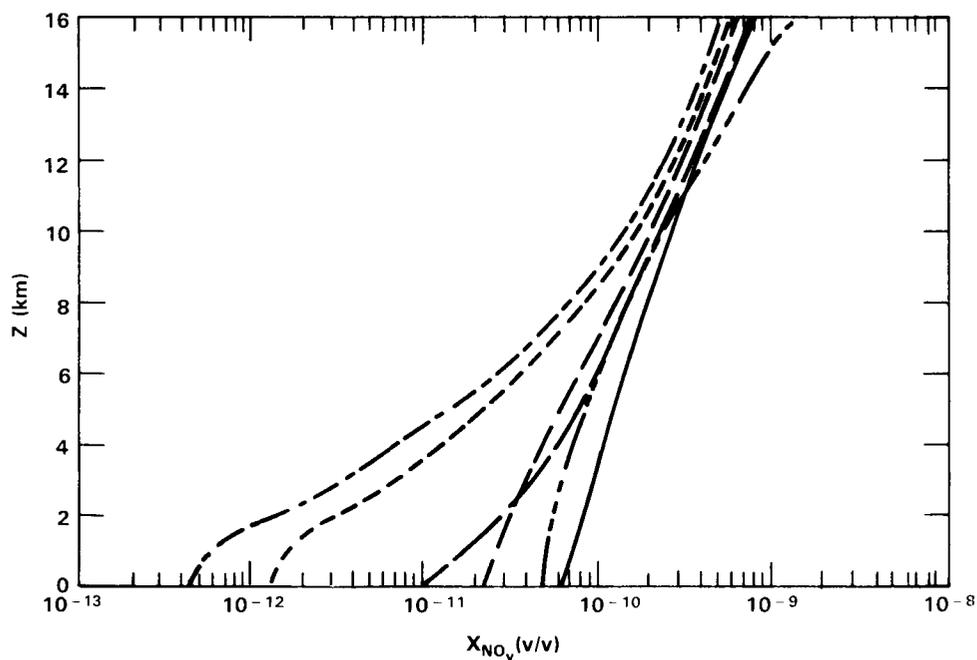
Figure 4-4b Model calculated profiles for "stratospheric NO_y" diffusing down into the troposphere. All profiles adopt a cross-tropopause flux of 3.75×10^8 cm^{-2} s^{-1} and a H $= 10^{12}$ M (atm)$^{-1}$. The dashed-dotted line, dotted line, and solid line adopt a deposition velocity of 0.3 cm s^{-1} and a storm period of 1, 10, and 25 days respectively. The broken line is the same as the solid line except a deposition velocity of 1 cm s^{-1} was used. The circles represent the average NO_y profile calculated by Kley et al. (1984) from the GFDL 3-D tracer-transport model. After Giorgi and Chameides (1985).

4.3.2.2 Chemical Effects

In addition to providing a liquid phase where soluble gases can be dissolved, clouds also offer an active chemical medium where aqueous-phase chemical reactions can occur which affect the removal rate of atmospheric species in general and nitrogen oxide and hydrogen oxide species in particular. For instance while the distribution of gaseous HNO_3

$$\text{(R3)} \quad (HNO_3)_g \rightleftharpoons (H^+)_{aq} + (NO_3^-)_{aq}$$
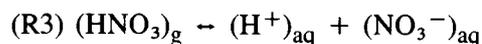
provides a major rainout sink for atmospheric nitrogen oxides and source of dissolved NO_3^- in rainwater, another important sink can arise in regions where $NO_x (= NO + NO_2)$ is large. This sink occurs via the production of gaseous NO_3 radicals in clouds at night. Because NO_3 radicals have long chemical lifetimes at night and can be rapidly scavenged by cloud droplets, their night time production in a cloud is followed by their incorporation into cloudwater. Once in the aqueous-phase, NO_3 is rapidly converted to NO_3^-. A typical reaction sequence leading to NO_3^- production in cloudwater is

$$\text{(R4)} \quad (NO_2)_g + (O_3)_g \rightarrow (NO_3)_g + (O_2)_g$$

$$\text{(R5)} \quad (NO_3)_g \rightleftharpoons (NO_3)_{aq}$$

$$\text{(R6)} \quad (NO_3)_{aq} + (Cl^-)_{aq} \rightarrow (NO_3^-)_{aq} + (Cl)_{aq}$$
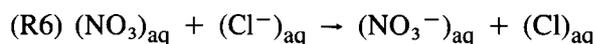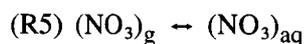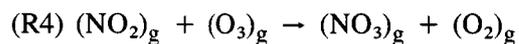
Figure 4-5 taken from a numerical simulation of the coupled gas- and aqueous-phase chemistry of a cloud, illustrates the enhanced levels of NO_3^- that can result from this process at night.
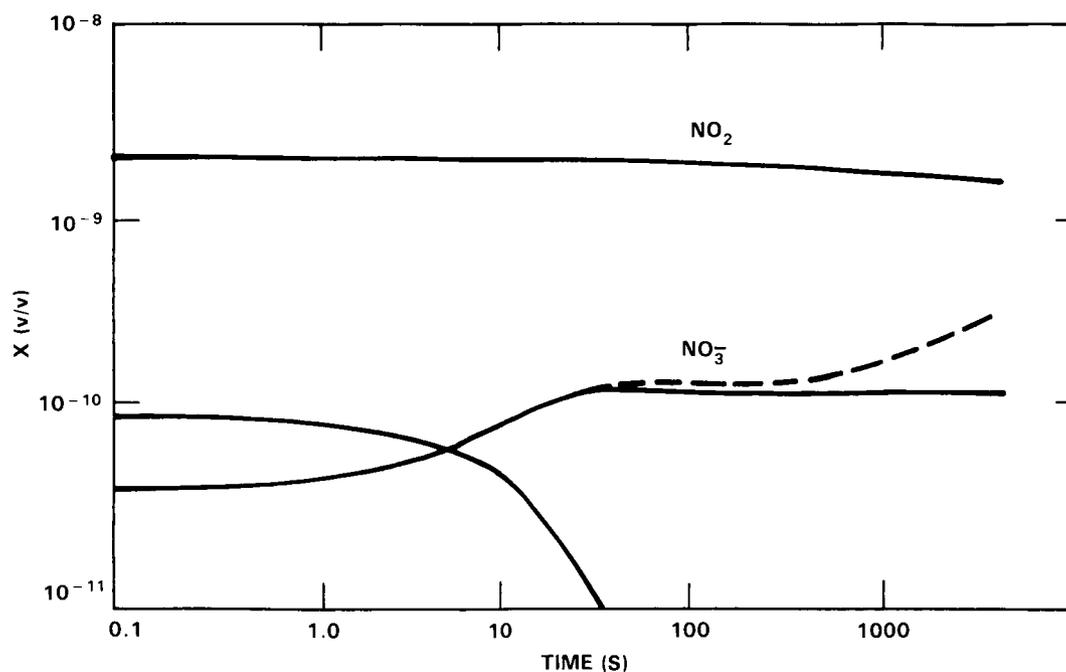
Figure 4-5 The calculated mixing ratios for gaseous NO_2 and HNO_3 and aqueous-phase NO_3^- as a function of time for a stratiform cloud in a "High-NO_x" region. The solid NO_3^- line is without scavenging of gaseous NO_3 and dashed NO_3^- line is with scavenging of gaseous NO_3.

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Whereas chemical processes in clouds can enhance the heterogeneous removal rate of nitrogen oxides, in the case of hydrogen oxides they may result in a net source. While the removal of gaseous H_2O_2 and its incorporation in cloud water via

$$(R7) \quad (H_2O_2)_g \rightarrow (H_2O_2)_{aq}$$
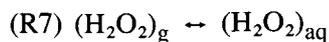
represent a sink for hydrogen oxides, the production of aqueous-phase H_2O_2 via a variety of radical reactions such as

$$(R8) \quad (HO_2)_{aq} + (O_2{}^-)_{aq} \xrightarrow{H^+} (H_2O_2)_{aq}$$
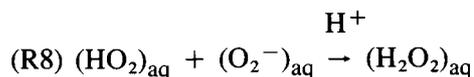
can produce H_2O_2. As illustrated in Figure 4-6, depending on the intensity of these radical sources, significant enhancements in H_2O_2 can result. It is conceivable that clouds with intense H_2O_2 production which evaporate could represent net sources of H_2O_2 to the atmosphere. In order to determine if in fact this does occur it will be necessary to carry out further laboratory studies of radical processes relevant to cloud chemistry and to carry out field experiments which measure gas- and aqueous-phase H_2O_2 levels in and out of a variety of clouds.
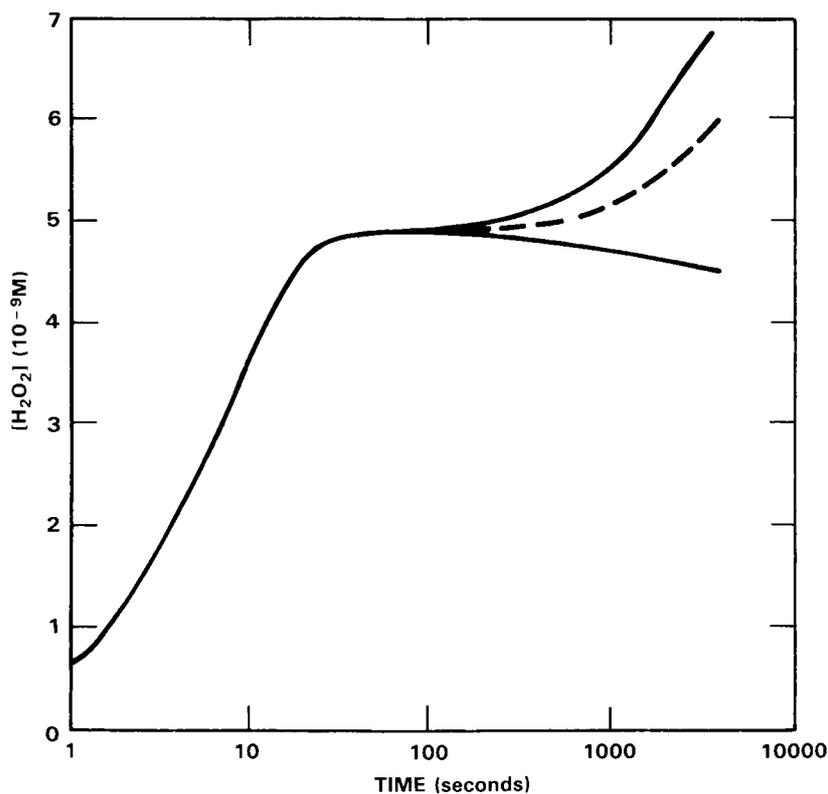
Figure 4-6 Temporal variation in $[H_2O_2]$ for a calculation in which all aqueous-phase sources of (H_2O_2) were neglected (solid line), for the standard model in which the aqueous-phase sources of $(H_2O_2)_{aq}$ were included (dashed line), and for a calculation in which the cloud transmissivity τ was taken to be 1.0 (dotted line). After Chameides (1984).

4.4 SURFACE EXCHANGE AND VERTICAL REDISTRIBUTION

4.4.1 Surface Exchange

Vertical transport in the boundary layer (i.e., the layer of air that is coupled directly to the surface by turbulent exchange processes on a time scale of about an hour or less), and between the boundary layer and the overlying free atmosphere, plays an important role in determining the fate of trace atmospheric species. At the surface, trace species may be both deposited and emitted, so that the flux at the surface is a net balance between the two processes. Deposition at the surface requires transport of the trace species to the surface by turbulent eddies.

Redistribution between the boundary layer and the overlying free atmosphere is mostly a result of highly intermittent cloud processes. Cycling of trace species through clouds can result in chemical transformations and loss through wet deposition (see section 4). The latent heat released by clouds can result in several kilometer ascents of boundary layer air into the free atmosphere within a few minutes. Compensating downward motions can transport air from the free atmosphere into the boundary layer. Eddy diffusivity models are not adequate for describing mixing of trace species over such large vertical displacements. Although some progress has been made in parameterizing these processes, much still remains to be done.

The subsequent sections discuss our current understanding of surface exchange of trace species important in estimating the tropospheric ozone budget, including both dry deposition and surface emission, as well as the exchange of trace species between the boundary layer and the overlying free atmosphere. Both are important in estimating the ozone budget throughout the troposphere.

Dry deposition is the transfer of an atmospheric constituent from the air directly to the earth's surface, regardless of whether the surface is wet or dry, or whether the loss is at the ground or in elements that are attached to, or touching the ground, such as a forest canopy or a snow cover. Because of the complexity of the earth's surface, and the variety of mechanisms for capturing species, precise physical descriptions of how this process takes place are difficult. Instead, the rate of dry deposition is commonly specified with a gross parameter such as a deposition velocity. The deposition velocity is defined as the ratio of the downward flux F_s of a species s to its mean concentration at some reference level s

$$v_d = F_s / \overline{s} \tag{1}$$

Trace constituents are transferred from the atmospheric boundary layer to within a centimeter of the surface (or surface protrusions) by turbulent eddies. Below this, the transfer is predominantly by molecular diffusion. We can, therefore, define the downward flux through a particular level as the averaged product of instantaneous departures of the constituent concentration s' and vertical velocity w' from their means, measured at that level; i.e., $F_s = -\overline{w's'}$, where the overbar denotes an average over a distance or time long enough to ensure a statistically reliable result.

Dry deposition is determined by the efficiency of the turbulence transport process, and the properties of both the constituent and the surface. The constituent may be either adsorbed or absorbed at the surface; that is, the constituent may either be stored on the surface without changing its identity, or it may combine chemically with the surface material. The deposition rate for constituents which are efficiently absorbed at the surface is controlled mainly by the ability of the turbulent eddies to transport the constituents to the surface, while for less reactive constituents, the rate is determined by the efficiency with which the

impinging constituents stick to the surface. As discussed by Wesely (1983) and Wesely and Hicks (1977), a convenient way to express this mathematically is to separate the effects of turbulence transport from constituent and surface properties by considering the reciprocal of the deposition velocity as a "resistance" to deposition, and equating it to the sum of the individual resistances contributed by (1) the turbulence transport process, commonly called the aerodynamic resistance r_a; (2) that contributed by molecular transport through the quasilaminar layer within about a centimeter of the surface and surface elements r_s; and (3) that contributed by how well the constituent sticks to the particular surface r_c:

$$v_d^{-1} = r_a + r_s + r_c \tag{2}$$

In this way, properties of the constituent and surface can, in principle, be separated from aerodynamic properties.

Many species are not only deposited, but are also emitted at the surface. Therefore, in these cases, the surface flux is the net result of both deposition and emission, and the concept of a surface resistance is no longer applicable for estimating surface flux, except when emission is negligible compared to deposition. Nitrogen oxides ($NO_x = NO + NO_2$) for example, are emitted from vegetated surfaces. Depending upon the situation, either deposition or emission may dominate; thus the surface flux may be either positive or negative. Their emissions are mostly the result of the activity of various soil microbes, whose rates of production are governed mainly by soil composition, temperature, moisture and pH, available oxygen, and fertilization practices. Over water, nitrite photolysis is believed to be a source of NO emission (Zafiriou and McFarland, 1981). Surface emissions of O_3 and HNO_3 are considered to be negligible, so that the resistance concept can be used to estimate their surface flux.

The actual process of deposition depends upon many factors. Over vegetated surfaces, the condition of the vegetation can be important, particularly for reactive gas species. Ozone deposition, for example, is much larger when the leaf stomata are open than when they are closed. Thus, ozone deposition is maximized over vegetated areas in the daytime when plants are actively growing. Observations over the ocean indicate a deposition rate several times that predicted on the basis of laboratory studies over pure water. This indicates that trace constituents in the water and on the water surface are important in determining the actual deposition rate.

4.4.1.1 Techniques of Measurement

A variety of techniques have been developed and used for measuring dry deposition. A summary of techniques, and their advantages and disadvantages, is presented by Hicks et al. (1980). The most direct flux measurement technique is the eddy correlation technique. This requires fast response (on the order of 1 Hz bandwidth for ground-based measurements; 10 Hz bandwidth for airplane measurements) high resolution concurrent measurements of concentration and vertical velocity. Ozone sensors have been developed and used for this purpose (Pearson and Stedman, 1980; Eastman and Stedman, 1977; Wesely et al., 1978). Instruments are also under development for measuring fast response nitric oxide fluctuations (e.g., Bradshaw and Davis, 1982). For ground-based sites, the height of measurement is typically a few meters above the ground, and averaging times of at least 20 minutes are required. The measured flux emanates as far as the order of a hundred meters or so upwind of the site; thus the flux is an average over a considerable area.

A common technique for measuring surface deposition and emission of trace species is to place an enclosure over the surface to be considered and measure the change in concentration within the box with time. This can then be related to the surface flux. Problems with this technique include (1) the enclosure modifies the turbulent transport process, and (2) the flux is measured only over the area covered by the enclosure.

Another technique for estimating surface flux is the profile method. The basis for this technique is the existence of a unique relationship between the flux of a species and its gradient near the surface. The eddy diffusivity, which is the negative of the ratio of the flux to the gradient, is a function of the surface roughness, wind speed and hydrodynamic stability. Therefore, additional micrometeorological measurements are required to obtain the flux from gradient or difference measurements. Fast response concentration measurements are not required, but concentration differences between levels need to be measured with an accuracy of about 1% of the mean concentration.

It may also be possible to estimate surface fluxes in some situations by estimating terms in the mean concentration budget. In this technique, the time rate of change of a constituent minus the net amount of a constituent advected into a volume through the top and sides is equated to that contributed by the flux at the surface. This technique cannot be used for constituents which are not conserved on a time scale of less than a day. As pointed out by Williams (1982), this method also requires accurate measurements of concentration differences.

Another factor to consider is that the chemical reactivity of some species is rapid enough that their flux may vary significantly between the measurement level and the ground. As pointed out by Fitzjarrald and Lenschow (1983), this can be the case for O_3, NO, and NO_2, which react rapidly with each other in sunlight. They point out, for example, that for profile or eddy-correlation measurements of NO and NO_2 flux, and also O_3 flux when the mean concentration of NO_x is greater than about 20% of O_3, at least six measurements are needed to accurately estimate the fluxes. These measurements include combinations of the means and fluxes of all three species. The NO_x concentration, however, can be considered a conserved species near the surface.

4.4.1.2 Results of Measurements

In this section, we briefly summarize results of previous studies on surface fluxes of O_3, NO and NO_2, and HNO_3. Compared to these species, very little is known about the surface fluxes of H_2O_2, PAN and particulate nitrates, and thus they are not discussed further. Reviews of dry deposition rates for a variety of species are presented by Sehmel (1980) and McMahon and Denison (1979).

• Ozone

Ozone deposition has been measured over a variety of surfaces by the eddy correlation, profile and box techniques. Reviews of ozone deposition measurements are presented by Galbally and Roy (1980) and Wesely (1983). The results are summarized in the following Section.

Land surfaces

Surface resistance over vegetated areas has strong diurnal, seasonal and climatic variability, mainly due to the size of the leaf stomata. Resistances for water vapor transpiration and ozone uptake in vegetation have been found to be identical when allowance is made for their difference in molecular diffusivity (Turner et al., 1974; Galbally and Roy, 1980). The median value for daytime surface resistance r_c over areas that are photosynthetically active, including both natural vegetation and crop lands, seems to be about 100 s m^{-1}. At the low end of the scale, Wesely (1983) reports values as low as 20 s m^{-1} over soybean fields; Lenschow et al. (1982) measured a value of 50 s m^{-1} over a forest.

At night, or when the vegetation is water stressed, the resistance of both naturally vegetated and cultivated surfaces increases by as much as a factor of two or more as the stomata close. The resistance of the leaves themselves becomes very large, and the deposition occurs mainly at the soil surface. However, even with senescent vegetation, a diurnal variation has been observed (Wesely, 1983). This may be partly due to greater efficiency in daytime for transporting air down to the underlying soil by the turbulence generated by surface heating. Since bare soil not saturated with water has a resistance of 100 s m^{-1} or less (Wesely, 1983; Galbally and Roy, 1980; Turner et al., 1973), its resistance is smaller in daytime over an area with senescent vegetation than at night in an area with actively growing vegetation. Waterlogged bare soil, however, may have a resistance several times that of dry soil. Wesely et al. (1981), for example, measured a resistance of about 1,000 s m^{-1} for water-saturated bare soil just above freezing.

Water

Deposition to water surfaces is observed to be much larger than predicted based on theoretical models of the exchange rate of soluble gases at the sea surface, and laboratory measurements of deposition to distilled water (Garland et al., 1980). The reasons for this are still not completely understood, although it is thought to be the result of reactions of ozone with substances on or near the water surface. Galbally and Roy (1980) suggest an average of 1000 s m^{-1}, and present a summary of values measured by themselves and others using profile and box methods that range from 650 to 4,400 s m^{-1}. Lenschow et al. (1982) obtained a value of 1,800 s m^{-1} from direct eddy correlation measurements from aircraft. Over fresh water, Wesely et al. (1981) made eddy correlation measurements over Lake Michigan that give a surface resistance of about 9,000 s m^{-1}, which is somewhat closer to, but still considerably less than the calculated value for resistance of pure water.

Deposition to snow has been measured by Wesely et al. (1981) to have a resistance of about 3,300 s m^{-1} for crusty snow and snow on the ground for longer than a day, and somewhat less than this for fresh snow. Galbally and Roy (1980), on the other hand, measured a median value of 1,600 s m^{-1} and higher values for fresh snow.

Total ozone surface destruction

Recent estimates of the total ozone destruction at the earth's surface are in the range of 0.5 to 1.5 x 10^{12} kg yr^{-1} (Galbally and Roy, 1980). This is equivalent to an average surface flux of 60 to 180 ng m^{-2} s^{-1} and, assuming a mean ozone concentration of 60 μg m^{-3}, an average deposition velocity of 0.1 to 0.3 cm s^{-1}.

• Nitric acid

The only known published measurements of the deposition of nitric acid were obtained by Huebert (1985). He found that its surface resistance over grassland was virtually zero. Similarly, over water its surface resistance is expected to be negligible compared to the aerodynamic resistance (Levine and Schwartz, 1982). Although further experimental verification is important, it appears that specification of HNO$_3$ deposition is relatively straightforward, with deposition velocities in the range of 0.4 to 2 cm s^{-1}.

• Nitrogen oxides

As discussed previously, NO$_x$ is both emitted and deposited at many surfaces. During daytime over vegetated surfaces, the surface emission is typically larger than at night, and may exceed deposition because

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the higher daytime soil temperature enhances microbial activity. In areas where anthropogenic activities enhance the NO_x concentration, surface deposition may become large enough that emission can be neglected. Because of the diversity of interactions that can occur near the surface, and the reactivity of NO_x, it is often difficult to separate emission and deposition, and parameterization of the surface flux is difficult. The mechanisms of nitrification and denitrification and the involvement of N_2, N_2O, NO and NO_2 in these processes have been studied by, for example, Myers *et al.* (1979). Laboratory studies of soils to investigate the emissions of these gases under various conditions have been carried out by, for example, Lipschultz *et al.* (1981). On a global scale, the net result of these processes can, at present, be only roughly estimated. For example, Ehhalt and Drummond (1982) estimate that between 5 and 17% of the overall NO_x source is due to soil emission, Hahn and Crutzen (1982) estimate 0 to 50%, and Logan (1983) estimates 5 to 15%. Logan (1983) also estimates that dry deposition accounts for about 30% of NO_x removal.

Measurements of NO_x surface deposition are almost nonexistent. Wesely et al. (1982) have made eddy correlation measurements of NO_x flux over a field of soybeans, and found a minimum surface resistance of 130 s m^{-1} in daytime, with NO_2 being the predominant species. At night they measured a resistance of about 1500 s m^{-1}. They estimated that the deposition velocity of NO_x was about 2/3 that of O_3. Over the ocean, there are no known measurements of NO_x surface flux. Thompson and Zafiriou (1981), however, have estimated deposition velocities of 0.00017 cm s^{-1} and 0.0012 cm s^{-1} for NO and NO_2, respectively.

4.4.1.3 Outlook

Instrumentation has been available for measuring ozone surface flux for several years, and our understanding of ozone deposition is now reasonably well understood over crop and range land. Deposition into forests and water is not as well understood, and further measurements would be desirable. In contrast, instruments for measuring NO_x surface flux are just now becoming available, and further technical development is essential—and forthcoming. Furthermore, NO_x surface flux is a combination of deposition and emission,and therefore is more difficult to parameterize. An additional complication in measuring the individual fluxes of NO and NO_2 is their chemical reactivity, which can result in significant variation of their fluxes with height near the surface. As a result, our understanding of their surface fluxes is significantly less than for ozone. Almost nothing is known about surface fluxes of H_2O_2, PAN, and particulate nitrates.

4.4.2. Vertical Redistribution

4.4.2.1 Boundary Layer Transport

Transport in the boundary layer is dominated by turbulent eddies with length scales that extend over several decades. The entire spectrum of motions cannot be explicitly resolved by computer modeling. Therefore, simplifications are made to parameterize the transport process. One of the simplest and most widely used approaches is to assume that the transport occurs by eddy diffusion. This has serious limitations in many situations, since the scales important for transport are comparable to the depth of the boundary layer. Wyngaard (1984) has extended the simple eddy diffusion concept by splitting transport in the convective boundary layer into diffusion from the bottom up and from the top down, and in this way is able to obtain more realistic boundary layer structure. Fiedler (1984) has developed an integral closure model that accounts for exchange of parcels over finite vertical displacements, which again gives more

realistic results than simple eddy diffusion modeling. Another approach is to explicitly model the large eddies in the convective boundary layer, and parameterize only the small eddies which are relatively unimportant for transport. Moeng and Wyngaard (1984) have used this approach to calculate statistics of conservative scalars in the convective boundary layer. In the future, these models will likely be applied to chemically active species.

Parameterizations of the turbulent fluxes in the boundary layer using an eddy diffusion coefficient combined with one-dimensional photochemical models have been used to model trace gas concentrations in the boundary layer. One result of such a simulation, which included diurnal variation of the height of the mixed layer as well as the vertical diffusion coefficient, is that the concentrations of trace species in the troposphere are 20-30% higher than when mixing processes are described by a simple vertical eddy diffusion which is constant with time and height (Fishman and Carney, 1984). Thompson and Lenschow (1984) obtained similar results in the tropical marine boundary layer.

These models also include entrainment at the top of the mixed layer, implying a non-zero flux of the species at that level provided there is a jump in the concentration profile. However, the effects of clouds in intensifying the entrainment rate on top of the mixed layer have not been incorporated satisfactorily in the current one-dimensional models. This effect has been observed to be of importance over convectively active regions from the point of view of the temperature and moisture budgets (Fitzjarrald and Garstang, 1981).

4.4.2.2 Cloud Transport

Vertical motion in the free atmosphere is substantially more complex than a simple advective process at uniform speed. Convective clouds modify this simple view of vertical transport by very localized enhanced vertical transport coupled with heterogeneous removal of water soluble trace species. Vertical motion in a convectively unstable atmosphere cannot be considered as a single upward moving current; the average vertical motion within a certain area is the contribution of the vertical mass flux associated with the convective clouds (updrafts and downdrafts) and the compensating descending motion which occurs within and outside of clouds (Yanai *et al.*, 1976; Gray, 1973). In fact, over convectively active regions in the tropics, it has been shown that the cloud mass flux is about one order of magnitude larger than the average vertical motion at the cloud base (Yanai *et al.*, 1976; Houze, 1982; Nitta, 1977; Betts, 1975). Thus, deep clouds have a tremendous potential for redistributing mass in the troposphere, and transporting trace constituents from the boundary layer to the overlying free atmosphere (Chatfield and Crutzen, 1984).

Considerable progress has been attained in recent years in the development of parameterization schemes to simulate the role of clouds. A more realistic cloud model allows the possibility of taking trace constituents from one level to another where their lifetimes may be different. Individual cloud models with sophisticated microphysics are also available and can be used for vertical transport simulations of trace constituents. These results can then be generalized to provide an estimate of the transport produced by cloud ensembles. Field experiments that estimate heat and moisture budgets also provide observational evidence which can be checked against current results.

It has been also realized in recent years that the most important latent heat sources in the atmosphere are located over tropical land areas and in cloud clusters over the oceanic intertropical convergence zone (Riehl, 1979). Almost half of the earth's surface is in the tropics, and the tropical forests and savannas are important sources of trace constituents that react with or generate O_3. Thus, understanding the vertical

transport of trace constituents is closely associated with understanding the role of deep convective clouds. Trace constituents produced at the surface can be transported vertically and horizontally to long distances, once embedded in the Hadley and Walker circulations. Similarly, cloud transport in mid-latitude cyclones cannot be ignored because these systems also provide enhanced vertical transport depending on the availability of moisture near the surface.

The effect of cloud transports on the O_3 cycle has been addressed from the point of view of the parameterization of the effects of moist convection on the large scale flow. Gidel's (1983) model extrapolates the Arakawa-Schubert (1974) cumulus parameterization theory to trace constituents. He shows that area averaged concentrations of the trace species which participate in the O_3 chemistry are modified by (1) large scale horizontal and vertical advection; (2) detrainment of cloud mass, which can have different concentrations than the environment; (3) detrainment of liquid water which can then evaporate and release droplet constituents into the air; and (4) the compensating subsidence resulting from cloud convection. This simple cloud model captures some of the important physical mechanisms now ascribed to clouds. The main results of the extended Arakawa-Schubert parameterization theory in terms of trace species like O_3 and NO_x are (1) an increasing mixing ratio with height can be obtained for a tracer with only a surface source especially if the photochemical lifetime of the tracer varies with height; (2) the predicted concentrations of some highly reactive lower tropospheric species in the upper troposphere are more realistic than eddy-diffusivity model predictions; and (3) the upper tropospheric distribution of trace species may depend more on surface sources than on upper tropospheric chemistry or stratospheric sources when clouds are present.

However, it is now realized that cumulus transports are considerably more complex than the Arakawa-Schubert parameterization used by Gidel (1983). The effects of cumulus downdrafts and lateral entrainment, the adequacy of the simple cloud model in describing the life cycle of clouds, and mesoscale circulations all have to be considered (Frank, 1983).

The concept of clouds being "vacuum cleaners" of anthropogenic and natural emissions at the surface has also been explored by Chatfield and Crutzen (1984) with a model based on the observed circulation in deep tropical convective systems. Again the role of recycling mass is emphasized but also with restrictions on the realism of the assumed cloud-induced circulation. Perhaps a slightly simpler problem of vertical transport by clouds is the role of small, non-precipitating cumulus clouds which are observed over the marine boundary layer. Carney and Fishman (1984) incorporated a photochemical model of the planetary boundary layer within the structure and mass flow characteristics of a layer of shallow, dispersed cumulus. Their comparisons with conventional flux parameterizations (enhanced eddy diffusivity) and with the available measured data for the remote marine troposphere provide further insight into the vertical distribution of trace gases.

The efficiency of clouds in transporting mass from the mixed layer to the free troposphere can now be estimated with observations. Since ozone is only weakly reactive with water, it is a possible tracer for cloud parcels on the time scale of convective clouds (15–30 min). Weaver and Pearson's (1984) results with ozone agree well with estimates of entrainment rate obtained from standard thermodynamic considerations. However, the available observational evidence is still tentative.

4.5 RESEARCH NEEDS

Several important reports have been published over the past two years focusing on the current status of tropospheric and future research needs. These include the NAS/NRC reports, "A Strategy for Earth

Science from Space in the 1980's and 1990's'' (National Academy Press, Washington, 1985, 149 pp.) and ''Global Tropospheric Chemistry: A Plan for Action'' (National Academy Press, Washington, 1984, 194 pp.). These reports develop recommendations for research in tropospheric chemistry including pro- · cesses controlling ozone and hydroxyl radical, which is the specific focus of this assessment document. The NAS/NRC panel report (NAS 1984) concluded that a major international research program is necessary and feasible. The general scientific goals for this Global Tropospheric Chemistry Program (GTCP), defined by the N.A.S. (1984), are:

1. To understand the basic chemical cycles in the troposphere through field investigations, theory aided by numerical modeling, and laboratory studies.
2. To predict the tropospheric responses to perturbations, both natural and human-induced, to these cycles.
3. To provide the information required for the maintenance and effective future management of the atmospheric component of the global life support system.

Research in the Global Tropospheric Chemistry Program would be undertaken in five major research topics with the following specific research objectives:

1. To evaluate biological sources of chemical substances in the troposphere.
2. To determine the global distribution of tropospheric trace gases and aerosol particles and to assess relevant physical properties.
3. To test photochemical theory through field and laboratory investigations of photochemically driven transformation processes.
4. To investigate wet and dry removal processes for trace gases and aerosol particles.

The primary goal of the GTCP in its first decade is to measure, understand and predict changes in the chemistry of the global troposphere with particular emphasis on changes affecting the oxidizing capacity and radiative properties of the troposphere.

To address this goal the N.A.S. (1984) report has found it convenient to divide the study of tropospheric chemistry into five distinct yet interrelated areas:

- Global Distributions and Trends
- Biological and Surface Exchange Processes
- Gas Phase Photochemistry
- Condensed Phase Processes
- Theoretical Studies and Modeling

These areas were chosen both because they represent a natural breakdown of the overall research effort in tropospheric chemistry and because it was apparent that progress in all five areas would be necessary to achieve the overall GTCP goal.

The essential set of objectives pertinent to ''tropospheric chemistry-processes controlling ozone and hydroxyl radical'' are presented below (NAS 1984):

(a) Gas Phase Photochemistry

The major scientific questions in gas phase photochemistry involve the need to understand better the fundamental oxidizing processes in the troposphere. Current theories point to the hydroxyl radical (HO)

and ozone (O_3) as central players in the oxidizing processes. These theories must be tested and rejected or modified through an extensive field and laboratory measurements program. The essential objectives are:

- To determine through field measurements the tropospheric oxidation rates resulting from short-lived free radicals. The key free radical is HO.
- To understand through field measurements the key processes involved in the production and removal of ozone. The key measurements are of O_3, NO, NO_2, HNO_3, peroxyacetyl nitrate, NH_3, abundant amines, and abundant hydrocarbons.
- To understand through laboratory experiments the mechanisms and kinetics of tropospheric oxidation of abundant alkanes (including CH_4), olefins and terpenoids, and of isoprene.

(b) Heterogeneous Processes (Condensed Phase Processes)

Liquid and solid particles in the atmosphere play important roles in the overall atmospheric oxidation process as sinks and sources for atmospheric gases, in wet and dry deposition, and in the global radiative budget. The essential objectives are:

- To determine through a combination of field and laboratory studies, the mechanisms and kinetics of the major oxidation reactions in cloud and haze droplets.
- To determine through laboratory and field measurements the roles of atmospheric particles in addition, removal and long-range transport of chemically important species.

(c) Biological and Surface Exchange Processes

Emphasis in the study of exchange processes should be on those biological and surface environments and processes involved in determining the atmospheric levels of species important in atmospheric chemistry and radiation and in atmosphere-biota interactions. The essential objectives are:

- To measure the chemical exchanges of key species between the troposphere and dry and wet tropical land regions, certain agricultural regions, oceans, large areas of burning vegetation, and certain subpolar land regions. The key species are CH_4 and other abundant hydrocarbons, CO, CO_2, abundant aldehydes and ketones, NO, NO_2, abundant organic nitrates, nitrites and acids, N_2O, NH_3, dimethyl sulfide and other abundant organosulfur species, H_2S, SO_2, OCS, CS_2, O_3, H_2O_2, abundant organoperoxy compounds, and abundant organohalides.

- To identify the environmental factors controlling the biological emission and uptake of the above key species by tropical forests and savannas, marshlands, rice paddies, boreal forests and peatlands, and wet tundra, and to determine the mechanisms for this control.

(d) Theoretical Studies and Modeling

Theory and models play important complementary roles in many of the experimentally-oriented objectives listed above. In addition, the complexity of the global tropospheric chemical-dynamical system demands the development of global three-dimensional models as essential tools for understanding and predicting changes in the system. The essential objectives are:

- To develop global chemical transport models capable of simulating the chemistry and circulation of atmospheric species on global and regional scales with sufficient spatial and temporal resolution

to include realistic treatment of the smaller-scale processes responsible for the large-scale inhomogeneities. One of these models should be available to and easily utilizable by the broader atmospheric chemistry community.

- To develop theories and models to aid in the interpretation of experimental data. Particular emphasis should be placed on understanding the processes of biological and surface exchange, gas-phase oxidation, and cloud and precipitation chemistry, and on synthesis and interpretation of global distribution and trend data.