CHAPTER 5

Tropospheric Ozone

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CHAPTER 5

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SCIENTIFIC SUMMARY

Although representing only 10 percent of the total ozone column, tropospheric ozone is important because it can influence climate, as it is a greenhouse gas itself, and because its photolysis by UV radiation in the presence of water vapor is the primary source for hydroxyl radicals (OH). Hydroxyl radicals are responsible for the oxidative removal of many trace gases, such as methane (CH_4), hydrofluorocarbons (HFCs), and hydrochlorofluorocarbons (HCFCs), that influence climate and/or are important for the stratospheric ozone layer.

Tropospheric ozone arises from two processes: downward flux from the stratosphere; and *in situ* photochemical production from the oxidation of hydrocarbons and carbon monoxide (CO) in the presence of NO_x ($NO + NO_2$). Ozone is removed from the troposphere by *in situ* chemistry and by uptake at the Earth's surface. The role of photochemistry in the local ozone balance depends strongly on the concentration of NO_x. Human impact on tropospheric ozone and hydroxyl occurs through the emission of precursors, *e.g.*, NO_x, CO, and hydrocarbons. In the case of free tropospheric ozone, this is brought about by the export of both ozone and its precursors, in particular NO_x, from source regions.

While substantial uncertainties remain in assessing the global budget of tropospheric ozone, recent studies have led to significant advances in understanding the local balance of ozone in some regions of the atmosphere.

- Recent measurements of the NO_y/O_3 ratio have basically confirmed earlier estimates of the flux of ozone from the stratosphere to be in the range of 240-820 $Tg(O_3)/yr$, which is in reasonable agreement with results from general circulation models (GCMs).

- The observed correlation between ozone and alkyl nitrates suggests a natural ozone concentration of 20-30 ppb in the upper planetary boundary layer (at about 1 km altitude), which agrees well with the estimate from the few reliable historic data (cf. Figure 1-16, Chapter 1).

- Measurements of the gross ozone production rate yielded values as high as several tens of ppb per hour in the polluted troposphere over populated regions, in good agreement with theoretical predictions. Likewise, the efficiency of NO_x in ozone formation in moderately polluted air masses was found to be in reasonable agreement with theory.

- Direct measurements of hydroxyl and peroxy radicals have become available. While they do not serve to establish a global climatology of OH, they do provide a test of our understanding of the fast photochemistry. To date, theoretical predictions of OH concentrations (from measured trace gas concentrations and photolysis rates) tend to be higher than the measurements by up to a factor of two.

- Measurements of peroxy radical concentrations in the remote free troposphere are in reasonable agreement with theory; however, significant misunderstanding exists with regard to the partitioning of odd nitrogen and the budget of formaldehyde.

- Measurements have shown that export of ozone produced from anthropogenic precursors over North America is a significant source for the North Atlantic region during summer. It has also been shown that biomass burning is a significant source for ozone in the tropics during the dry season. These findings show the influence of human activities on the global ozone balance.

TROPOSPHERIC OZONE PROCESSES

- Photochemical net ozone destruction in the remote atmosphere has been identified in several experiments. It is likely to occur over large parts of the troposphere with rates of up to several ppb per day. Consequently, an increase in UV-B radiation (*e.g.*, from stratospheric ozone loss) is expected to decrease tropospheric ozone in the remote atmosphere but in some cases will increase production of ozone in and transport from the more polluted regions. The integrated effect on hydroxyl concentrations and climate is uncertain.

Uncertainties in the global tropospheric ozone budget, particularly in the free troposphere, are mainly associated with uncertainties in the global distribution of ozone itself and its photochemical precursors, especially CO and NO_x. These distributions are strongly affected by dynamics, by the magnitude and spatial/temporal distribution of sources, particularly those for NO_x to the middle and upper troposphere from the stratosphere, lightning, aircraft, and convective systems, and by the partitioning and removal of NO_y constituents. The role of heterogeneous processes including multiphase chemistry in the troposphere is not well characterized, and the catalytic efficiency of NO_x in catalyzing ozone formation in the free troposphere has not been confirmed by measurements.

5.1 INTRODUCTION

As is outlined in more detail in Chapter 1, there is some, albeit limited, evidence to suggest that ozone concentrations in the troposphere of the Northern Hemisphere have increased by a factor of two or more over the past 100 years, with most of the increase having occurred since 1950. This conclusion is consistent with ozone data gathered continuously since the 1970s at a series of remote and in some cases high altitude stations. It is interesting to note that all stations north of about 20°N exhibit a positive trend in ozone over the past two decades that is significant to the 95% confidence level. During the same time, a statistically significant negative trend of about 0.5%/yr is observed at the South Pole.

For the most part, the trends appear to fall more or less along a straight line that extends from -0.5%/yr at 90°S to +0.8%/yr at 70°N. Somewhat anomalous are the large positive trends observed at the high elevation sites in Southern Germany (1-2%/yr); these large trends perhaps reflect a regional influence above and beyond the smaller global trend (Volz-Thomas, 1993). It should be noted, however, that the average positive trends observed in the Northern Hemisphere are largely due to the relatively rapid ozone increase that occurred in the seventies. Over the last decade, no or little ozone increase has occurred in the free troposphere except over Southern Germany and Switzerland. Indeed, ozone concentrations at some locations in the polluted planetary boundary layer (PBL) over Europe have decreased over the last decade (Guicherit, 1988; Low *et al.*, 1992).

It is important that we understand the causes of the apparent increase in tropospheric ozone concentrations in the Northern Hemisphere because of ozone's central role in global biogeochemistry, its effectiveness as a greenhouse gas, especially in the upper troposphere, and its toxicity to living organisms. It is equally important, however, to understand the causes for the decrease observed at high latitudes in the Southern Hemisphere because of the influence of ozone on the concentration of hydroxyl radicals and, hence, the oxidizing capacity of the atmosphere, which controls the budgets of many long-lived greenhouse gases. This, in turn, requires a quantitative understanding of the chemical and meteorological processes that determine the budget of tropospheric ozone.

5.2 REVIEW OF FACTORS THAT INFLUENCE TROPOSPHERIC OZONE CONCENTRATIONS

The presence of ozone in the troposphere is understood to arise from two basic processes: (1) tropospheric/stratospheric exchange that causes the transport of stratospheric air, rich in ozone, into the troposphere, and (2) production of ozone from photochemical reactions occurring within the troposphere. Similarly, removal of tropospheric ozone is accomplished through two competing processes: (1) transport to and removal at the Earth's surface, and (2) *in situ* chemical destruction. For the past two decades, research on tropospheric ozone has largely focused on understanding the relative roles of these processes in controlling the abundance and distribution of ozone in the troposphere. The basic chemical mechanisms that control the local ozone budget are now reasonably well understood, except for the role of heterogeneous processes. The situation is not as good concerning our quantitative understanding of the natural sources of ozone and its precursors. Transport of ozone and NO_y (see Figure 5-1) from the stratosphere and production of NO_x ($= NO + NO_2$) through lightning must be known to a better degree in order to assess the role of anthropogenic influences, such as air traffic (see Chapter 11). Likewise, a better understanding is needed of the atmospheric transport processes that redistribute ozone and its precursors between the polluted continental regions and the remote atmosphere and between the planetary boundary layer and the free troposphere.

Boundary layer processes, including large-scale eddy mixing and smaller scale turbulence, control the rate at which sources of NO_x and hydrocarbon emissions can combine to begin ozone production chemistry. Because of the nonlinear dependence of photochemical ozone formation on the precursor concentrations, models that assume instantaneous mixing over large spatial grids may significantly overestimate ozone production rates. Vertical transport of ozone and its precursors between the boundary layer and higher altitudes (together with exchange of air with the stratosphere) has a strong influence on ozone distributions in the troposphere due to the longer lifetimes of ozone and precursors in the free troposphere. On the other hand, the upward flow in convective systems must be balanced by downward mesoscale flow, which then carries ozone and odd nitrogen species from the free troposphere into the planetary boundary layer, where they are destroyed more rapidly (see Lelieveld and Crutzen, 1994). Observations of O_3 in convective systems suggest that both mechanisms are in effect (Dickerson *et al.*, 1987; Pickering *et al.*, 1992b), but their relative magnitude has not been evaluated experimentally. Lastly, long-range horizontal advection influences ozone distributions by transport of both ozone and its precursors from source areas into other regions, including the marine environment. This type of long-range transport has been shown to be an important factor in the generation of large regional-scale events of elevated ozone (see, for example, Fishman *et al.,* 1985; Vukovich *et al.,* 1985; Logan, 1989; Sillman *et al.,* 1990).

5.2.1 Stratosphere-Troposphere Exchange

Following the elucidation by Haynes *et al.* (1991) of the control exercised on the diabatic circulation in the stratosphere by waves propagating up from the troposphere (the so-called Downward Control Principle), a clearer picture of stratosphere-troposphere exchange processes has emerged. Trace species such as ozone and NO_y with sources in the middle stratosphere are fed into the lower stratosphere by the diabatic circulation at a rate determined by the dissipation of planetary and gravity wave fields in the stratosphere and mesosphere. The lower stratosphere (especially in midlatitudes) is subject to efficient isentropic mixing, which maintains a close correlation between trace species (Plumb and Ko, 1992). The lower levels of the stratosphere also exchange air with the troposphere.

Estimates of fluxes across the tropopause remain uncertain. For example, the net downward flux of air estimated by Holton (1990) and Rosenlof and Holton (1993), which was based on the concepts described above, is a factor of 2-3 larger than the lower limit of the upward flux derived by Follows (1992) from the growth of CFC-11 in the troposphere. Deriving an analogous estimate for the trace species is even more difficult because their distributions must be accurately known. However, the very close correlation between nitrous oxide (N_2O), NO_y, and ozone in the lower stratosphere (Fahey *et al.,* 1990; Murphy *et al.,* 1993) offers the possibility of deriving the flux of trace gases from the N_2O budget. Murphy and Fahey (1994) used an annual destruction rate of N_2O in the stratosphere of 8-17 Tg(N)/yr to infer a transport of 0.28-0.6 Tg(N)/yr of NO_y and 240-820 Tg/yr of ozone into the troposphere. This corresponds to a flux of $(2\text{-}6)\times10^{10}$ molecules cm^{-2} s^{-1} of ozone, which is slightly less than the earlier estimates made from observations of tropopause folding events (Danielsen and Mohnen, 1977) and is comparable to the fluxes derived from general circulation models (*e.g.*, Gidel and Shapiro, 1980; Levy *et al.*, 1985).

The most active regions of stratosphere-troposphere exchange are in cyclonic regions of the upper troposphere, near jet streams, troughs, and cut-off lows. The contribution of tropopause folds to the exchange has been well documented (*e.g.,* WMO, 1986) and has been confirmed by recent work (Ancellet *et al.,* 1991, 1994; Wakamatsu *et al.*, 1989). Potential vorticity (PV) analyses on isentropic surfaces near the tropopause show long streamers of elevated PV curving anticyclonically from high latitudes, corresponding to narrow streaks and a low tropopause. These streaks are clearly revealed by Meteosat water vapor images (Appenzeller and Davies, 1992), but their contribution to stratosphere-troposphere exchange has yet to be assessed. The contribution of cut-off lows, formed by cyclonically-curving PV streamers (Thorncroft *et al.,* 1993), is better understood. These are preferentially found in particular regions of the world, *e.g.,* Europe (Price and Vaughan, 1992), and can promote exchange by vigorous convective mixing as well as shear instabilities near jet streams (Price and Vaughan, 1993; Lamarque and Hess, 1994). Recently, the contribution of mesoscale convective systems to stratosphere-troposphere exchange was shown to be of potential importance (Poulida, 1993; Alaart *et al.*, 1994).

There have been no studies of trends in stratosphere-troposphere exchange, so the contribution of the stratospheric source to the observed trend in tropospheric ozone remains an open question. A better understanding is also required of transport between the lower stratosphere and the troposphere, and of links between the opposing ozone trends in these two regions of the atmosphere. Decreasing ozone concentrations in the lower stratosphere would, at first approximation, imply a decreasing flux into the troposphere. However, this effect could be offset by changes in the meridional circulation in the stratosphere. Following the Downward Control Principle and assuming the primary source of ozone in the stratosphere to have remained constant, changes in downward flux would have to be forced by changes in gravity wave dissipation. Therefore, changes in climate could well have led to changes in the ozone flux from the stratosphere. As noted by WMO (1992), however, there have not been enough studies of trends in stratospheric temperatures and transport to deduce trends in the ozone flux into the troposphere.

5.2.2 The Photochemical Balance of Ozone in the Troposphere

The production of ozone in the troposphere is accomplished through a complex series of reactions referred to as the "photochemical smog mechanism." The basics of this mechanism were originally identified by Haagen-Smit (1952) as being responsible for the rise of air pollution in Los Angeles in the 1950s. As is outlined in Figure 5-1, this well-known mechanism (see NRC, 1991) involves the photo-oxidation of volatile organic compounds (VOC) and carbon monoxide (CO) in the presence of NO_x (= NO + NO_2). Typical of this mechanism are reactions (R5-1) through (R5-7):

(R5-1) $RH + OH \rightarrow R + H_2O$
(R5-2) $R + O_2 + M \rightarrow RO_2 + M$
(R5-3a) $RO_2 + NO \rightarrow RO + NO_2$
(R5-4) $RO + O_2 \rightarrow HO_2 + R'CHO$
(R5-5) $HO_2 + NO \rightarrow OH + NO_2$
2 × (R5-6) $NO_2 + h\nu \rightarrow NO + O$
2 × (R5-7) $O + O_2 + M \rightarrow O_3 + M$

Net: $RH + 4\,O_2 + 2\,h\nu \rightarrow R'CHO + H_2O + 2O_3$

where an initial reaction between a hydrocarbon (RH) and a hydroxyl radical (OH) results in the production of two O_3 molecules and an aldehyde R'CHO or a ketone. Additional ozone molecules can then be produced from the degradation of R'CHO. In addition to the oxidation of hydrocarbons, ozone can be generated from CO oxidation via (R5-8) and (R5-9) followed by (R5-5), (R5-6), and (R5-7).

(R5-8) $CO + OH \rightarrow CO_2 + H$
(R5-9) $H + O_2 + M \rightarrow HO_2 + M$

Hydrocarbons and CO provide the fuel for the production of tropospheric ozone and are consumed in the process. In remote areas of the troposphere, CO and methane typically provide the fuel for ozone production (Seiler and Fishman, 1981). In urban locations, reactive olefinic and aromatic hydrocarbons (often but not exclusively of anthropogenic origin) are usually the dominant fuel, while in more rural environments reactive biogenic VOC such as isoprene often dominate (Trainer *et al.*, 1987; Chameides *et al.*, 1988).

In contrast to hydrocarbons and CO, NO_x is conserved in the process of ozone production and thus acts as a catalyst in ozone formation. The conversion of NO to NO_2 by peroxy radicals (HO_2 and RO_2) is the crucial step, since the rapid photolysis of NO_2 yields the oxygen atom required to produce ozone (R5-7). Indeed, the *in situ* rate of formation of ozone is given by

$$P(O_3) = [NO] \cdot \{k_5 \cdot [HO_2] + \Sigma k_{3ai} \cdot [RO_2]_i\}$$

As catalysis continues until NO_x is permanently removed by physical processes (deposition) or is transformed to other NO_y compounds that act as temporary or almost permanent reservoirs, the catalytic production efficiency of NO_x can, at first approximation, be defined as the ratio of the rate at which NO molecules are converted to NO_2 by reaction with peroxy radicals to the rate of transformation or removal of NO_x. The lifetime of NO_x varies from a few hours in the boundary layer to at least several days in the upper troposphere. Thus the catalytic production efficiency of NO_x can vary considerably and nonlinearly over the more than three orders of magnitude range of concentrations (see Figure 5-9) typically found between remote and polluted regions of the troposphere (Liu *et al.*, 1987; Lin *et al.*, 1988; Hov, 1989).

As is seen in Figure 5-1, the conversion of NO to NO_2 occurs to a large extent through reaction with O_3 itself:

(R5-10) $NO + O_3 \rightarrow NO_2 + O_2$

This process constitutes only a temporary loss, because O_3 (and NO) are regenerated in the photolysis of NO_2 (R5-6) followed by R5-7. The cycle adjusts the photostationary state between O_3, NO, and NO_2, and therefore, the NO/NO_2 ratio (Leighton, 1961). Through this, reaction R5-10 influences the catalytic efficiency of NO_x in ozone formation since it decreases the fraction of NO_x that is responsible for O_3 production via R5-3a and R5-5 and, at the same time, increases the fraction that is responsible for the loss of NO_x.

Because of the rapid interconversion between NO and NO_2 during daylight, the quantity NO_x = NO + NO_2 was defined. Similarly, it was found to be useful to

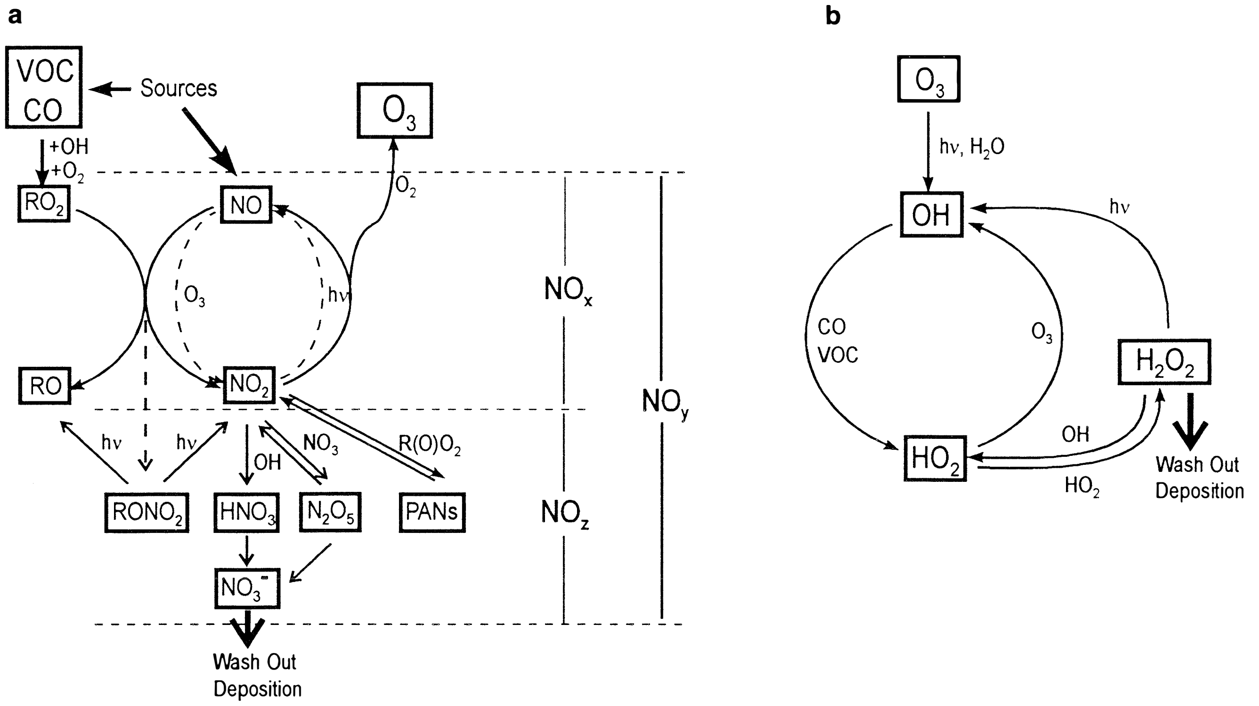


Figure 5-1a. Schematic view of the cycles of NO_x and NO_y and their relation to the chemical ozone balance. The quantity NO_z is defined as NO_y - NO_x and represents the sum of all oxidation products of NO_x.
Figure 5-1b. Primary formation of OH from O_3 photolysis and the HO_x cycle in the absence of NO_x. It leads to formation of hydrogen peroxide and net destruction of ozone.

define the quantity $O_x = O_3 + NO_2$, in order to account for temporary losses of O_3 in highly polluted environments (Guicherit, 1988; Kley *et al.*, 1994). It is a better measure of the time-integrated ozone production than ozone itself (Volz-Thomas *et al.*, 1993a).

Photochemical loss of tropospheric ozone is accomplished through photolysis followed by reaction of the $O(^1D)$ atom with water vapor, (R5-11) and (R5-12). Additional losses occur through reaction of the HO_2 radical formed in (R5-9) with O_3 via (R5-13) and (to a lesser extent) through reaction of OH with O_3 (R5-14):

(R5-11) $O_3 + h\nu \rightarrow O(^1D) + O_2$
(R5-12) $O(^1D) + H_2O \rightarrow 2\,OH$
(R5-13) $HO_2 + O_3 \rightarrow OH + 2\,O_2$
(R5-14) $OH + O_3 \rightarrow HO_2 + O_2$

The photochemical rate of ozone loss is approximated by

$$L(O_3) = [O_3] \cdot \{J_{11} \cdot F_{O^1D} + k_{13} \cdot [HO_2] + k_{14} \cdot [OH]\}$$

where F_{O^1D} is the fraction of excited oxygen atoms that react with water vapor. This expression is only approximate and is more appropriate to the remote free troposphere, since it neglects important loss processes that can occur in the continental boundary layer, such as dry deposition and reactions with unsaturated hydrocarbons. It also neglects potential losses that have been suggested to occur in cloud droplets and nighttime or wintertime losses through nitrate radical (NO_3) chemistry. As such, it is a lower limit for the loss rate.

Ultimately, the budget of ozone in a given region is governed by transport of ozone into or out of the region and the net rate of ozone formation, $P(O_3)$ - $L(O_3)$. Except for urban regions, where NO_2 is the predominant sink for OH radicals and, hence, limits the formation of RO_2 radicals, the rate of O_3 production is most often limited by the availability of NO_x even in the boundary layer over the European and North American continents. In the remote atmosphere, not only is the production rate of O_3 limited by the availability of NO_x, the concentration of NO_x can be so small that $L(O_3)$ exceeds $P(O_3)$. These regions thus act as a buffer against any excess ozone imported from areas having higher production rates or from the stratosphere.

A coarse estimate for the "critical" NO concentration at which local O_3 production and loss rates are equivalent was given by Crutzen (1979) by simply equating the rate of R5-13 to the rate of R5-5. The critical daytime NO concentration thus derived is within a factor of two of 10 ppt, depending on the actual ozone concentration and other factors. However, this is a lower limit because other loss processes have been neglected and the term $J_{11} \cdot F_{O^1D}$ is the dominant contribution to $L(O_3)$ in the remote lower-to-middle troposphere. For example, from experimental observations made at 3.4 km in the mid-North Pacific Ocean region, this term accounted for nearly 50% of the total loss rate when averaged over 24 hours (Ridley *et al.*, 1992).

Nevertheless, any non-zero concentration of NO_x contributes to O_3 production, compensates the loss rate, and increases the lifetime of O_3. Since $P(O_3)$ is so sensitive to the NO_x abundance and $L(O_3)$ is, to first approximation, insensitive to NO_x in the remote atmosphere, possible trends in tropospheric O_3 are intimately dependent upon trends in NO_x concentrations. Clearly, assessing the contribution of photochemical processes to trends in global and regional ozone relies on a good knowledge of the distribution of O_3, the fuels (CO, CH_4, NMHC), and especially the distribution of NO_x. Reactions R5-11 and R5-12 not only constitute an important O_3 loss rate but also initiate the oxidation cycles via OH radicals (see Section 5.4) and therefore link stratospheric O_3 change to tropospheric photochemistry through the sensitive dependence of J_{11} on the overhead column of O_3.

The depletion of stratospheric ozone during the last decade has led to increased ultraviolet radiation of wavelength 290-320 nm penetrating to the troposphere (see Chapter 9). Liu and Trainer (1988) studied the influence of enhanced UV radiation on tropospheric ozone with a simple photochemical model and found that the net effect depended on ambient NO_x levels. To first order, an increase in the ultraviolet flux essentially accelerates the already-existing production and destruction processes. For this reason, a positive trend in UV radiation will, most likely, cause a negative trend in tropospheric ozone in regions where the net photochemical balance is negative, that is, over large areas of the Southern Hemisphere and the remote oceanic regions of the Northern Hemisphere (Section 5.3). The long-term observations at the South Pole (Schnell *et al.*, 1991; Thompson, 1991) indicate that some enhanced net destruction of tropospheric ozone may already be occurring in association with the large stratospheric ozone losses in that region. On the other hand, a long-term increase in UV radiation will likely contribute to an increase in photochemical ozone formation in the NO_x-rich continental regions and possibly in large-scale plumes downwind of these or areas of biomass burning.

Removal or conversion of NO_x to longer-lived reservoirs clearly decreases the local catalytic efficiency of O_3 production. During daytime, losses of NO_x proceed through the reaction of NO_2 with OH radicals (R5-15) and the formation of peroxyacetylnitrate (PAN) and its homologues (R5-16):

(R5-15) $NO_2 + OH + M \rightarrow HNO_3 + M$

(R5-16) $NO_2 + RC(O)O_2 \leftrightarrow RC(O)O_2NO_2$

While nitric acid (HNO_3), at least in the planetary boundary layer, provides an effective sink for NO_x, the thermally unstable compound PAN provides only a temporary reservoir for NO_2. Most important, the lifetime of PAN becomes long enough at the colder temperatures of the middle and upper troposphere that it can be transported over long distances and serve as a carrier of NO_x into remote regions. NO_x is also removed by the formation of alkyl nitrates ($RONO_2$) that are formed in the alternative reaction path of RO_2 with NO (R5-3b) (Atkinson *et al.*, 1982):

(R5-3b) $RO_2 + NO \rightarrow RONO_2$

Similar to PAN, alkyl nitrates could provide a source of NO_x to more remote regions via photolysis or through reaction with OH following transport (Atlas, 1988).

An important loss process for NO_x that was not included in earlier model studies (Liu *et al.,* 1987) is the oxidation of NO_2 by ozone itself. The NO_3 radical formed in reaction (R5-17) is extremely sensitive to photolysis but can build up at night to concentrations of several hundred ppt (Platt *et al.*, 1981; Wayne *et al.*, 1991). Because of the thermal equilibrium (R5-18) that is established between NO_3, NO_2, and N_2O_5, heterogeneous losses of N_2O_5 or NO_3 in addition to reactions of NO_3 with some hydrocarbons provide a sink for NO_x in addition to the reaction with OH (R5-15). For example, (R5-19) constitutes a non-photochemical conversion of active NO_x to long-lived aerosol nitrate (or HNO_3 in case of evaporation of the droplets). According to model calculations, this mechanism could provide a significant sink for NO_x on a global scale (Dentener and Crutzen, 1993). Observations of the chemical lifetime of NO_3 (Platt *et al.*, 1984) indicate that in the boundary layer, the initial reaction R5-17 is often the rate-limiting step for the removal of NO_x by these processes.

(R5-17) $NO_2 + O_3 \rightarrow NO_3 + O_2$
(R5-18) $NO_2 + NO_3 \leftrightarrow N_2O_5$
(R5-19) $N_2O_5 + H_2O_{lq} \rightarrow 2\,H^+ + 2\,NO_3^-$

The occurrence of clouds changes the chemical processing in an air mass significantly (Chameides and Davis, 1982). Although the volume fraction of liquid water in clouds is only of the order of 10^{-6} or less, some gases are so soluble that they largely go into the aqueous phase. This has several consequences: (1) the soluble gases are concentrated in a relatively small volume, which can enhance reaction rates, and (2) soluble gases are separated from insoluble ones, so that some reaction rates are significantly reduced. An important example is reaction R5-5, which almost ceases within clouds because HO_2 is very soluble, whereas NO remains in the interstitial air. Furthermore, the dissociation of dissolved HO_2 yields O_2^-, which destroys O_3 in the aqueous phase. The production of HO_2 in the droplets results to a large extent from the oxidation of dissolved formaldehyde. A radical reaction cycle is thus initiated in which both formaldehyde and O_3 are destroyed.

The estimated effect of cloud chemistry is that the photochemical O_3 production rate in the lower troposphere (where most clouds occur) is reduced by 30-40%, while O_3 destruction reactions are enhanced by up to a factor 2 (Lelieveld and Crutzen, 1990). The net effect of cloud processes on the O_3 burden in the troposphere is estimated to be much smaller, however, since these processes compete with dry deposition (Dentener *et al.*, 1993). Model simulations suggest a 10-30% lower tropospheric ozone burden as compared to a cloud-free atmosphere (Johnson and Isaksen, 1993; Dentener *et al.*, 1993).

5.3 INSIGHTS FROM FIELD OBSERVATIONS: PHOTOCHEMISTRY AND TRANSPORT

During the summer months, elevated and potentially harmful levels of ozone are commonly observed in urban and rural areas of North America and Europe (Cox *et al.*, 1975; Logan, 1985). Slow-moving high pressure systems with predominantly clear skies and elevated temperatures set the stage for the photochemical formation and accumulation of ozone and other oxidants over wide regions during episodes that last several days (Guicherit and van Dop, 1977; Vukovich *et al.*, 1977). There is substantial evidence from field measurements and model calculations that most of this ozone is being produced photochemically from ozone precursors emitted within the region. The export of O_3 and its precursors from the urban to regional and global scales represents the greatest potential impact on trends in global ozone by anthropogenic activities.

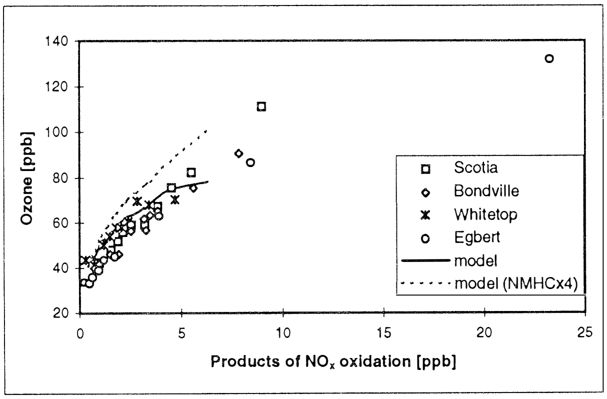
5.3.1 Urban and Near-Urban Regions

High ozone levels in and downwind of urban regions remain an important air quality problem throughout the world. While most industrialized countries have made significant progress in lowering peak ozone concentrations over the last two decades, unhealthy levels of ozone persist in and around many larger cities. In particular, in many developing countries, the absence or ineffectiveness of emissions control efforts can result in extremely high ozone concentrations.

The limited atmospheric chemical measurements from urban areas in developing countries suggest that conditions in many of these areas essentially mimic conditions observed in the Organization for Economic Cooperation and Development (OECD) countries during the 1960s before implementation of large-scale emissions control programs. For example, observations of individual hydrocarbon ratios in Mexico City, Mexico, during 1992 (Seila *et al.*, 1993) were similar to those observed in Los Angeles, California, during the 1960s and are consistent with motor vehicles as the major source of hydrocarbon emissions in this area. Motor vehicle emissions have also been demonstrated to be the major source of hydrocarbons in Athens, Greece; Rio de Janeiro, Brazil; and Beijing, China (see Tang *et al.*, 1993; Xiuli *et al.*, 1994).

The impact of anthropogenic NO_x and VOC emissions on regional and global ozone levels depends on the rate of ozone formation, the amount of ozone that is formed per precursor, and the rate and the pathway of transport out of the source regions. Direct and indirect measurements of peroxy radical concentrations that were made at several rural sites indicate concentrations of up to several hundred ppt at noontime on clear summer days (Parrish *et al.*, 1986; Volz *et al.*, 1988; Mihelcic *et al.*, 1990; Mihelcic and Volz-Thomas, 1993; Cantrell *et al.*, 1993). When combined with concurrent NO measurements, these RO_2 radical concentrations indicate substantial *in situ* ozone production rates of several tens of ppb/h at rural locations in the vicinity of industrialized regions (Volz *et al.*, 1988; Trainer *et al.*, 1991; Cantrell *et al.*, 1993). Such measurements can be used to determine the relative roles of UV radiation, NO_x, and VOC for *in situ* ozone production. The observed ozone increase is usually much smaller than the gross production rate derived from the RO_2 measurements, which indicates that the losses through dry deposition or reactions with unsaturated VOCs such as terpenes and by dilution must be of similar magnitude as the production rate. This indicates that the characteristic lifetime of ozone in polluted air masses is rather small, *e.g.*, less than one day.

In photochemically aged air in summer, O_3 was found to increase with increasing NO_y concentration, from a background value of 30-40 ppb O_3 at NO_y mixing ratios below 1 ppb to values between 70 to 100 ppb at NO_y levels of 10-20 ppb (Fahey *et al.*, 1986). As is expected from photochemical theory, an even better correlation is observed between ozone and the products of the NO_x oxidation (Trainer *et al.*, 1993; Volz-Thomas *et al.*, 1993a). Figure 5-2 shows the results from measurements made during summertime at several rural locations in the U.S. and Canada, and at Schauinsland in Europe. The slope of the correlation provides, at first approximation, experimental information on the ozone production efficiency, *e.g.*, the number of ozone molecules produced by each NO_x molecule before oxidation to more stable products such as HNO_3 and peroxyacetyl nitrate (see Section 5.2.2). The increments in the individual data sets in Figure 5-2 range from 4 to 10 and suggest a somewhat smaller production efficiency than what has been predicted by models for NO_x levels typically encountered in rural regions of the industrialized countries (Liu *et al.*, 1987; Lin *et al.*, 1988; Hov, 1989).



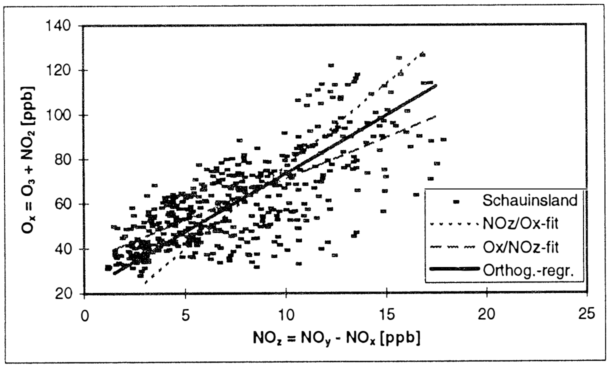


Figure 5-2a. Ozone versus the concentration of NO_x oxidation products (*e.g.*, NO_z in Figure 5-1), as measured at four sites in the eastern United States and Canada during summer 1988 and the results from a model calculation (based upon Trainer *et al.*, 1993).

Figure 5-2b. Same relation as 5-2a measured at Schauinsland, Germany, during summer 1990 in air masses advected from the Rhine Valley (based upon Volz-Thomas *et al.*, 1993a). The quantity O_x = O_3 + NO_2 is used to account for titration of O_3 under high NO_x conditions (R5-10 in Section 5.2.2).

The data also indicate a significantly lower production efficiency for the air masses encountered at Schauinsland in Europe.

The role of hydrocarbons and nitrogen oxides for ozone formation on the urban / sub-urban scale was studied by Hess *et al.*, (1992a, b, c) in an outdoor smog chamber using a synthetic gas blend that closely resembled that of automobile exhaust. The most important finding was that the initial rate of ozone formation depended on the mix of hydrocarbons used and, of course, on the availability of UV light. However, the final amount of O_3 produced during one day depended mainly on the availability of NO_x. To some extent, the latter depends on the hydrocarbon mix, specifically on the existence of NO_x sinks in the chemistry through formation of organic nitrates (Carter and Atkinson, 1989).

Insight into the chemical breakdown of hydrocarbons and their role in ozone formation can be obtained from field measurements of alkyl nitrates ($RONO_2$), since these species are formed as a by-product in reaction (R5-3), which is rate-limiting in ozone formation. From an extensive series of measurements made at Schauinsland, a mountain site in Southern Germany, in summer, a linear relation was found between ozone and alkyl nitrate concentrations, which is shown in Figure 5-3 (Flocke *et al.*, 1991, 1993). The high degree of correlation found in air masses that originate in the Rhine Valley, and thus represent a relatively uniform mix of hydrocarbons, clearly points out that most of the ozone observed at Schauinsland in summer (70 ppb average and peak values of 130 ppb) is formed *in situ* from anthropogenic precursors emitted within the region. By extrapolation to $RONO_2$ concentrations of zero, an estimate of 20-30 ppb is obtained for today's non-photochemical background mixing ratio of ozone in the continental boundary layer in summer (Flocke, 1992; Flocke *et al.*, 1993; Volz-Thomas *et al.*, 1993b). This finding supports the conclusions drawn by Volz and Kley (1988) and by Staehelin *et al.*, (1994) from historic measurements (see Chapter 1) and proves the predominant anthropogenic influence on ozone levels in some rural areas today. Since alkyl nitrates are not removed by rainout, they are better suited for such an extrapolation than either NO_y or NO_z (= NO_y - NO_x), since the latter contain soluble HNO_3 as a major constituent.

The European studies also led to the conclusion that about one ozone molecule per carbon atom is formed from the oxidation of hydrocarbons in these air masses (Flocke, 1992). Furthermore, the relative abundance of the different alkyl nitrates indicates that most of the smaller RO_2 radicals are not formed from the oxidation of the respective parent hydrocarbons but by decomposition of larger alkoxy radicals. This finding is in agreement with results from laboratory studies (Atkinson *et al.*, 1992) and RO_2 production from the decomposition of RO radicals is now a common feature in detailed chemical mechanisms used in urban airshed models (Carter, 1990; Atkinson 1990). The finding is also consistent with the fact that measured ratios of organic peroxy radicals to HO_2 are significantly larger than those predicted by models that do not include this mechanism (Mihelcic and Volz-Thomas, 1993). The conclusion is that the rate of production of RO_2 radicals is greater than originally assumed in these models.

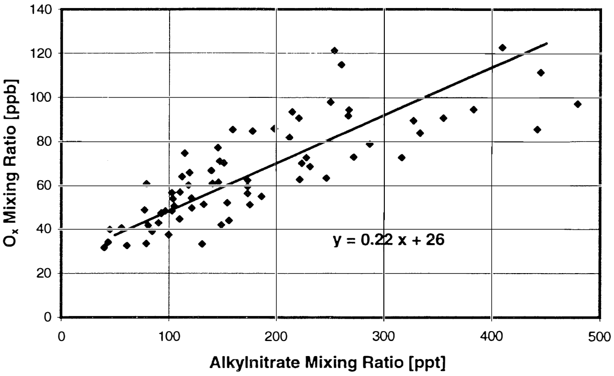


Figure 5-3. Correlation of $O_x = O_3 + NO_2$ concentrations with those of alkyl nitrates ($RONO_2$) as observed at Schauinsland, Germany, in summer under polluted conditions (based upon Flocke *et al.*, 1992). O_x and $RONO_2$ emerge from the same reaction (R5-3).

Carbon monoxide is an anthropogenic pollutant that has a relatively long photochemical lifetime (1 month in summer) and is not affected by rainout. Thus, it is a suitable tracer of anthropogenic pollution on longer time scales (Fishman and Seiler, 1983). Parrish *et al.* (1993) observed a strong correlation between ozone and CO with a consistent slope $\Delta O_3/\Delta CO = 0.3$ at several island sites in eastern Canada (Figure 5-4). The sites were located at approximately 500-km intervals downwind of the northeastern urban corridor of the United States, and covered approximately one-third of the distance from Boston to Ireland. By scaling the observed slope to a CO emission inventory, they inferred a net export of 5 Tg anthropogenic O_3 out of the eastern U.S. in summer. Chin *et al.* (1994) successfully simulated the observed O_3-CO relationship in a continental-scale three-dimensional (3-D) model and concluded that the correlation slope of 0.3 is a general characteristic of aged polluted air in the U.S. The model allowed in particular to correct for the effect of O_3 deposition. From this calculation, Chin *et al.* (1994) estimated that export of eastern North American pollution contributes 7 Tg of O_3

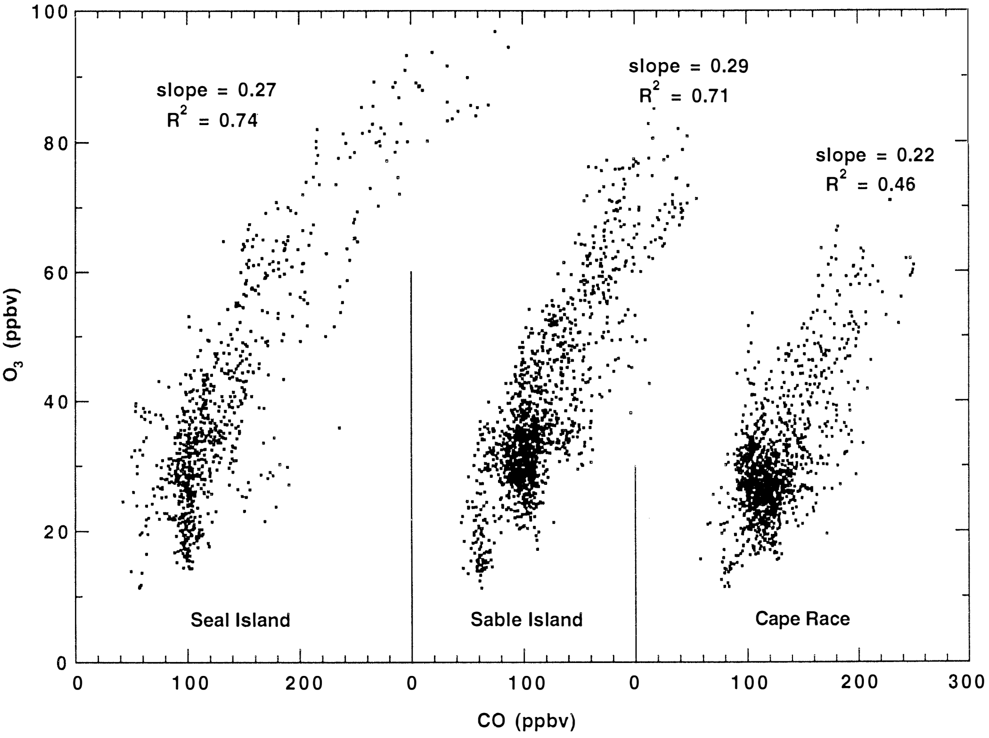


Figure 5-4. Relation between O_3 and CO observed at three island sites in the North Atlantic west of Canada during summer 1992 (based upon Parrish *et al.*, 1993).

in summer. Jacob *et al.* (1993) used the same model to estimate that pollution from all of North America contributes 30 Tg of O_3 to the Northern Hemisphere in summer, of which 15 Tg is due to direct export and 15 Tg is due to export of NO_x leading to O_3 production in the remote troposphere. This anthropogenic source of O_3 is about one-third of the estimated cross-tropopause transport of O_3 in the Northern Hemisphere in summer. Considering that the U.S. accounts for about 30% of fossil fuel NO_x emissions in the Northern Hemisphere, it can be concluded that anthropogenic sources make a major contribution to tropospheric ozone on the hemispheric scale, of magnitude comparable to influx from the stratosphere.

While the summertime measurements show a strong positive correlation of ozone with anthropogenic tracers such as NO_y and CO, a negative correlation was observed during winter. A decrease in the O_3 concentration with increasing CO concentration is observed at a number of locations in North America and Europe (Poulida *et al.*, 1991; Parrish *et al.*, 1993; Scheel *et al.*, 1993; Simmonds, 1993; Derwent *et al.*, 1994). Derwent *et al.* conclude from their analysis of the air masses that arrive at Mace Head, Ireland, that the European continent is a net source of ozone in summer, but is a net sink in winter. This estimate, however, is only valid for the planetary boundary layer and does not include the influence of NO_x export on the net photochemical balance of ozone.

A seasonal trend is also apparent in the correlation of ozone with NO_y and NO_z (Fahey *et al.*, 1986; Volz-Thomas *et al.*, 1993a). The wintertime measurements of O_3, NO_x, and NO_y at Schauinsland indicate a decrease of ozone with increasing concentrations of the products of the NO_x oxidation and, hence, support the importance of nighttime chemistry in the oxidation of NO_x at the expense of ozone in polluted air masses.

Since anthropogenic NO_x emissions do not have a strong seasonal variation, Calvert *et al.* (1985) argued that the absence of a seasonal cycle in nitrate deposition rates provided evidence for the importance of NO_3 chemistry in the removal of NO_x. However, more recent data from the National Acid Deposition Program and

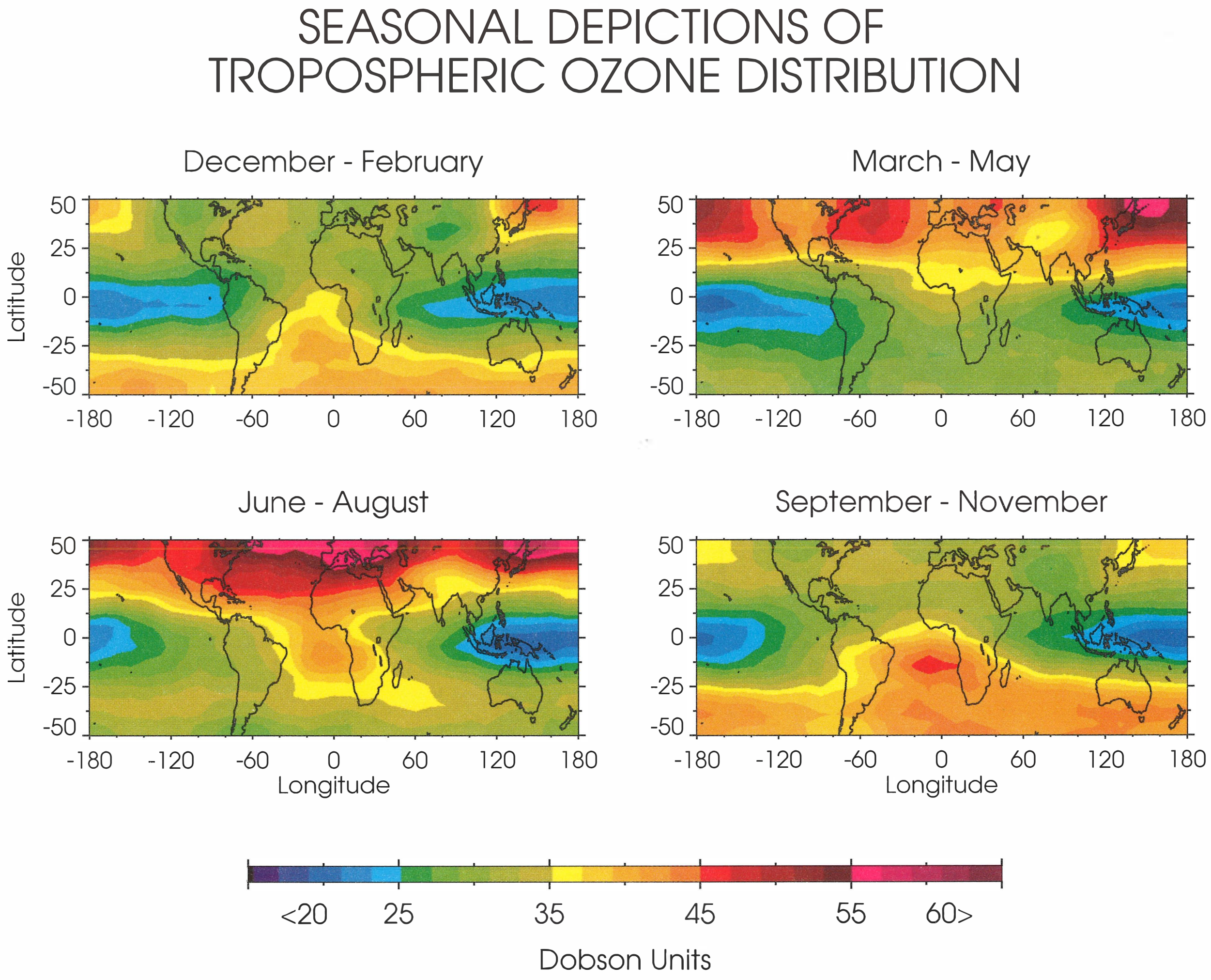


Figure 5-5. Tropospheric ozone column in Dobson units (DU) as derived from satellite observations for different times of the year (based upon Fishman *et al.*, 1991). The red areas of high ozone can be associated with export from North America and Europe and from biomass burning regions in South America and Africa.

other North American sites do indeed show a seasonal cycle in bulk nitrate deposition rates, with larger values in summer (Correll *et al.*, 1987; Doddridge *et al.*, 1992), as would be expected if OH radicals played the dominant role in controlling the NO_x budget. Some further support for the dominance of OH in controlling the removal of NO_x is provided by the observation of larger NO_x levels in the Arctic winter (Dickerson, 1985; Honrath and Jaffe, 1992).

5.3.2 Biomass Burning Regions

Biomass burning takes many forms; among them, forest and savanna fires, burning of agricultural wastes, and the use of biomass fuels as a domestic energy source are the most important. Biomass fires release a mixture of gases containing the same ozone precursors emitted from fossil fuel combustion: NO_x, CO, CH_4, and non-methane hydrocarbons (NMHC), including a large proportion of alkenes. Ozone production in aged biomass-burning plumes has been shown by numerous investigators (Delany *et al.*, 1985; Andreae *et al.*, 1988, 1992; Cros *et al.*, 1988; Kirchhoff *et al.*, 1989, 1992;

Kirchhoff and Marinho, 1994). The global emissions of ozone precursors from biomass burning have been estimated in a recent review by Andreae (1993) to be comparable in magnitude to the emissions from fossil fuel burning. Evidence for the importance of tropospheric ozone production from pyrogenic precursors has been obtained from the analysis of satellite data (Figure 5-5; Fishman *et al.,* 1991), which show a substantial enhancement of tropospheric ozone downwind from the biomass burning regions in South America and Africa. Ozonesonde measurements in Africa and on Ascension Island in the central South Atlantic do indeed confirm the persistence of high ozone levels in the mid-troposphere during the burning season (Cros *et al.*, 1992; Fishman *et al.*, 1992). Aircraft measurements have demonstrated the origin of these ozone-enriched air masses from biomass burning (Marenco *et al.*, 1990; Andreae *et al.*, 1988, 1992, 1994a). Compelling evidence was also collected in more recent aircraft campaigns that documented the distribution of ozone and its pyrogenic precursors in a region extending from South America across the Atlantic Ocean to southern Africa (Andreae *et al.*, 1994b).

Due to the dispersed nature of biomass burning and the relatively small number of field investigations on ozone production from pyrogenic precursors, it is still difficult to provide a quantitative estimate of ozone production from this source. The observed ratio of ozone to CO enhancements in aged burning plumes varies from near zero in some tundra fire emissions (Wofsy *et al.*, 1992) to almost one in some aged savanna fire plumes (Andreae *et al.*, 1994a). As shown in Figure 5-6, these differences appear to be related to the ratio of NO_x to CO (and consequently NMHC) in the emissions. By using an average O_3/CO-ratio of 0.3 and a CO emission of 300 Tg C/yr from biomass burning, Andreae (1993) estimated a global gross O_3 production of ca. 400 Tg O_3/yr from biomass burning, with an uncertainty of at least a factor of two. A recent model study estimated a similar gross rate of 540 Tg/yr; however, the net production of ozone from biomass burning was found to be only 100 Tg/yr (Lelieveld and Crutzen, 1994). This large difference emphasizes, as already discussed for the northern mid-latitudes above, the crucial role of transport processes in distributing the ozone between the PBL, where it is destroyed rapidly, and the free troposphere, where its chemical lifetime is long enough for it to be dispersed hemisphere-wide. The accurate description of these transport processes probably represents the largest difficulty in current global models, as is discussed in more detail in Chapter 7.

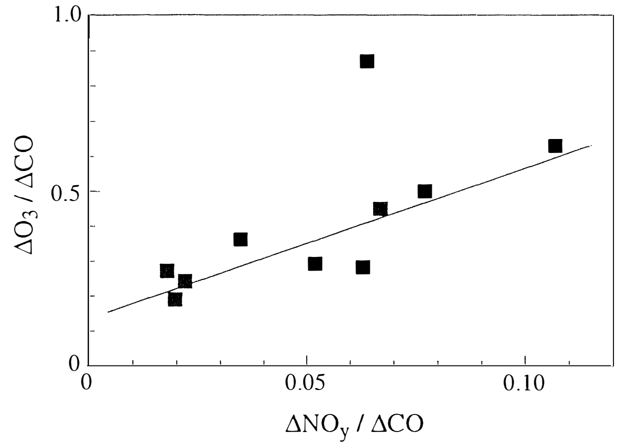


Figure 5-6. Ratio of O_3 to CO in aged biomass burning plumes as a function of the NO_y/CO ratio. The increase seen in the data clearly indicates the important role of NO_x for ozone formation in the plumes (based upon Andreae *et al.*, 1994b). The straight line represents a fit to the majority of the data. It is consistent with an average O_3/NO_y ratio of 4-5, quite similar to the ratios observed in sub-urban air masses over Europe.

The secular trends of biomass burning are highly uncertain. Obviously, fire has been present on Earth since the evolution of land plants, and human activity has resulted in large fires in the savannas of Africa and South America since the advent of human beings. However, other types of biomass burning have clearly been increasing over the last century, especially deforestation fires and domestic biomass fuel use. These types of biomass burning have especially high emission factors for ozone precursors. Andreae (1994) estimated that the release of trace gases from biomass burning has increased by about a factor of two or three since 1850. Semi-quantitative measurements made during the last century, albeit not considered sufficiently reliable for an independent quantitative assessment (Kley *et al.*, 1988), would indeed support a secular increase in tropospheric ozone concentrations in the Southern Hemisphere (Sandroni *et al.*, 1992). No trend is seen in the surface ozone records obtained over the last two decades at Cape Point, South

Africa (Scheel *et al.,* 1990) and American Samoa, Pacific Ocean (Oltmans and Levy, 1994).

5.3.3 Remote Atmosphere and Free Troposphere

While recent work has provided major advances in our understanding of the ozone budget over continental regions relatively close to the centers of precursor emissions and clearly demonstrated the anthropogenic perturbation of tropospheric ozone on a regional scale, the system is still far from being understood on a hemispheric or global scale. Compounding issues are: (1) the strong, if not overriding, influence of transport from both the stratosphere and the continental source regions, transport that is episodic rather than steady; (2) the large difference in chemical time constants between the boundary layer and the free troposphere; (3) the uncertainty in the production rate for NO_x by lightning and its distribution; (4) the extremely low NO_x and NO_y constituent concentrations, which represent a real measurement challenge; and (5) the large volume that must be covered to establish a climatology. Concerns have also been raised about the validity of NO_2 and NO_y measurements in the troposphere obtained by commonly used techniques (see Davis *et al.*, 1993; Crosley, 1994). Nevertheless, the large number of field experiments performed over the last years (see Carroll and Thompson, 1994) has led to a better understanding of the O_3 budget on a global scale. Even greater insight is expected to come out of the recently completed or ongoing experiments that have included direct measurements of OH and RO_2 radicals and the seasonal variations of active nitrogen compounds in the remote atmosphere.

Plumes of "pollution" from biomass burning regions and from the industrialized regions of North America, Europe, and Asia have been identified from satellite observations (Fishman *et al.*, 1990). Being downwind of continental source regions, measurements made in the marine boundary layer at Barbados, West Indies, show that large variations in O_3 concentrations can be associated with changes in long-range transport patterns. There is a pronounced seasonal cycle for O_3 at Barbados (Oltmans and Levy, 1992, 1994). During the winter and spring, daily averaged values are typically in the range of 20-35 ppb, while during the summer, values are typically 10-20 ppb. During the winter-spring period there are often large changes in O_3 concentration; these changes are strongly anticorrelated with a number of aerosol species, including NO_3^- (Savoie *et al.*, 1992). The changes in O_3 are driven by changing transport patterns over the North Atlantic as opposed to chemical reactions involving O_3 and nitrogen species in the atmosphere. Analyses of isentropic trajectories clearly show that high O_3 and low NO_3^- are associated with transport from the middle and high latitudes and from relatively high altitudes in the free troposphere. Conversely, high NO_3^- and relatively low O_3 are associated with transport from Africa. The lack of association of high O_3 with ground-level sources is supported by the strong anticorrelation of O_3 with 210-Pb; conversely, the strong correlation of NO_3^- and 210-Pb (and a weaker correlation with Saharan dust) indicates that NO_3^- is derived principally from continental surface sources, probably in Europe and North Africa. These associations suggest that African biomass burning could be a significant source of NO_3^-, but appears to be a minor source for O_3 at Barbados. Although substantial amounts of O_3 may have been produced as a consequence of the burning, a substantial fraction must have been destroyed in transit in the marine PBL.

The importance of transport processes for the global ozone distribution is also emphasized in studies made at the Spanish Meteorological observatory at Izana, Tenerife. The station is located at an elevation of 2.4 km, above the top of the marine inversion most of the time. At Izana, ozone concentrations have a well-defined seasonal cycle, with monthly means of about 40 ppb in winter, about 55 ppb in spring, and about 50 ppb in July (Schmitt *et al.*, 1988). The concentrations in summer are much higher on average than those observed at Mauna Loa, Hawaii, and exhibit a bimodal distribution. Low mixing ratios of ~20 ppb are advected from the open ocean and the Saharan desert, and high values of up to 100 ppb generally result from relatively rapid transport from northern latitudes (Schmitt and Hanson, 1993). It has been suggested that the persistence of high ozone concentrations in the summer could be due to the transport of ozone from Europe, based on isentropic back-trajectories and the correlation of high ozone episodes with increased concentrations of tracers of anthropogenic origin such as CH_4, PAN, VOC, and CO (Schmitt *et al.*, 1988, 1993; Volz-Thomas *et al.*, 1993c). The seasonal cycle of ozone at Izana is similar to that for

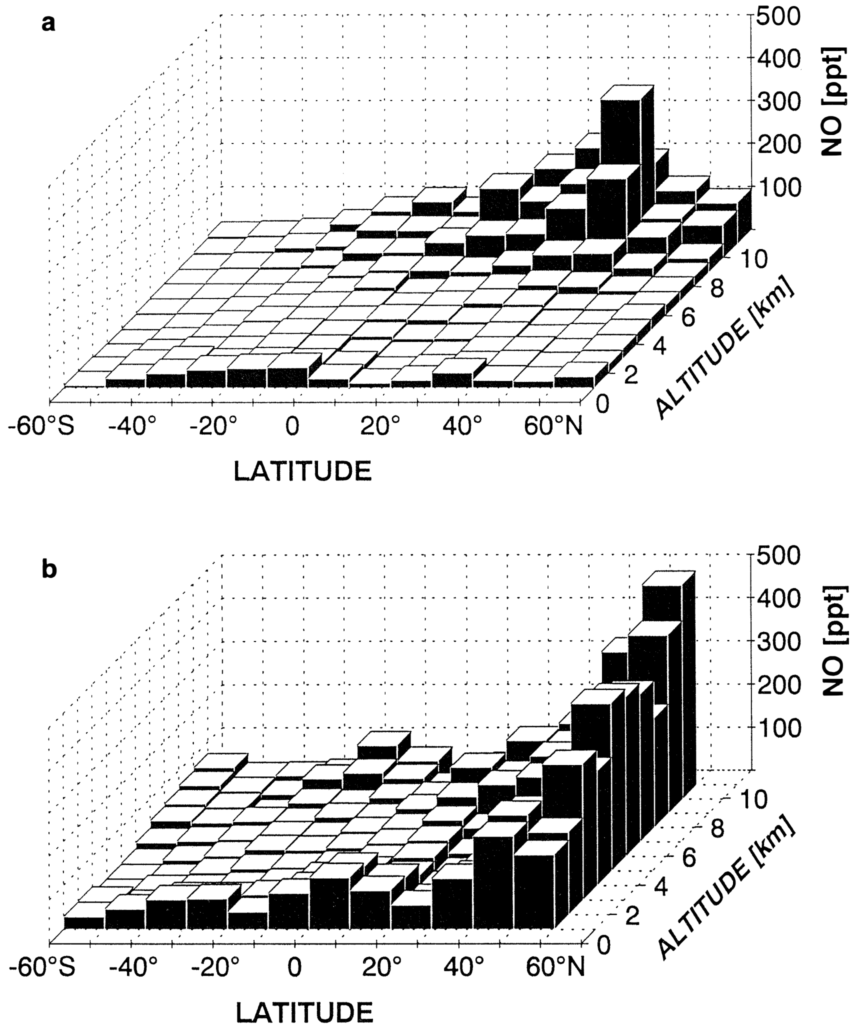


Figure 5-7. NO concentrations measured in the free troposphere during STRATOZ III and TROPOZ II (based upon Ehhalt *et al.*, 1992; Wahner *et al.*, 1994). The flight track was similar in both missions and extended over the North and South Atlantic and the west coast of South America.

non-seasalt sulfate (nss-$SO_4^=$) and NO_3^-, which could be interpreted as supporting an anthropogenic source for ozone. However, on a day-to-day basis, ozone is strongly anticorrelated with aerosol NO_3^- and nss-$SO_4^=$ (Prospero *et al.*, 1993). This and the coherence between ozone and 7-Be, which is produced from cosmic rays in the upper troposphere and lower stratosphere (see Brost *et al.*, 1991), could imply a major contribution of ozone from the stratosphere or effective losses of aerosol nitrate and sulfate during convective transport from the planetary boundary layer into the free troposphere. In this regard, the results obtained at Izana are similar to those obtained in the marine boundary layer at Barbados.

Evidence that stratospheric input is an important component of the upper tropospheric ozone budget, especially in spring and early summer, was presented by Beekmann *et al.* (1994), based on the correlation between ozone mixing ratio and potential vorticity, and by Smit *et al.* (1993), based on a time series of ozonesonde measurements in the upper and lower troposphere. The poleward increase in upper tropospheric ozone suggests

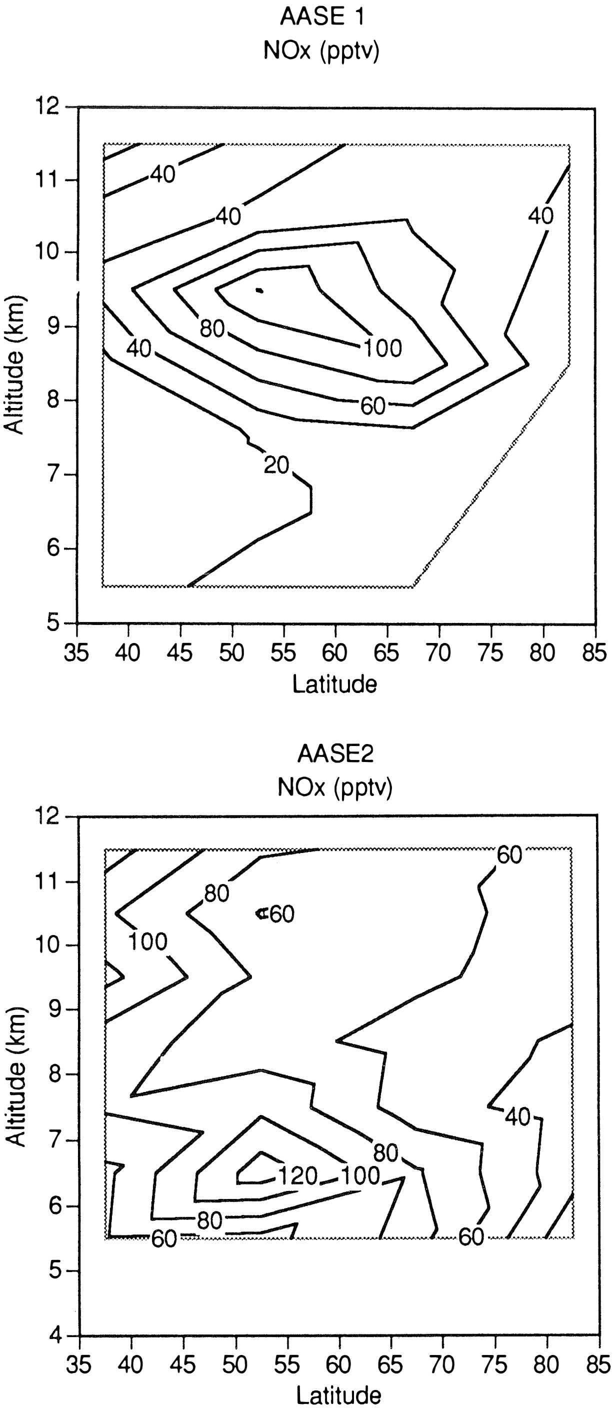


Figure 5-8. Summary of $NO_x = NO + NO_2$ concentrations in the free troposphere measured in the Northern Hemisphere during the AASE I and AASE II missions (based upon Carroll *et al.*, 1990a and Weinheimer *et al.*, 1994).

that this component is even more important at high latitudes. Evidence for stratospheric input to the Arctic troposphere was presented by Shapiro *et al.* (1987) and Oltmans *et al.* (1989). Furthermore, airborne lidar measurements made over the Arctic region in summer found that stratospheric intrusions dominated the ozone budget in the free troposphere (Browell *et al.*, 1992; Gregory *et al.*, 1992). There is also a suggestion in ozonesonde data from the South Pole (Gruzdev and Sitnov, 1993) that ozone depletion in the Antarctic polar vortex extends into the upper troposphere.

An example of progress in determining large-scale reactive nitrogen distributions over the complete tropospheric altitude regime is shown in Figure 5-7, which contrasts the seasonal distribution of NO from aircraft measurements made during the Tropospheric Ozone II (TROPOZ II) mission in January 1991 (Wahner *et al.*, 1994) and the Stratospheric Ozone III (STRATOZ III) mission in June 1984 (Drummond *et al.*, 1988; Ehhalt *et al.*, 1992). The mixing ratios are considerably higher in the Northern Hemisphere, particularly at high latitudes in winter, and at 20-50°N at high altitudes in summer. Vertical gradients are strongest in June north of 20°S. The high mixing ratios of NO at northern midlatitudes are attributed to stratospheric input, aircraft emissions, and convective transport from the "polluted" boundary layer (Ehhalt *et al.*, 1992).

The NO concentrations observed during TROPOZ II are much larger than what has been observed by other investigators at similar latitudes and seasons. Figure 5-8 shows NO_x concentrations observed during the Arctic Airborne Stratospheric Expedition (AASE) I and II missions (Carroll *et al.*, 1990a; Weinheimer *et al.*, 1994). While these flights were made during the same season as TROPOZ II and at overlapping latitudes, they show much lower NO_x ($=NO+NO_2$) concentrations than the NO concentrations alone that were observed during TROPOZ II. The AASE measurements are in general agreement although separated by a three-year period. The difference may be due to the shorter measurement period of the TROPOZ program, and an unusual synoptic event, compared to the longer-term AASE programs. Barring unexpected measurement uncertainty, the differences demonstrate the difficulty in ascertaining a climatology of a short-lived species like NO_x over larger scales.

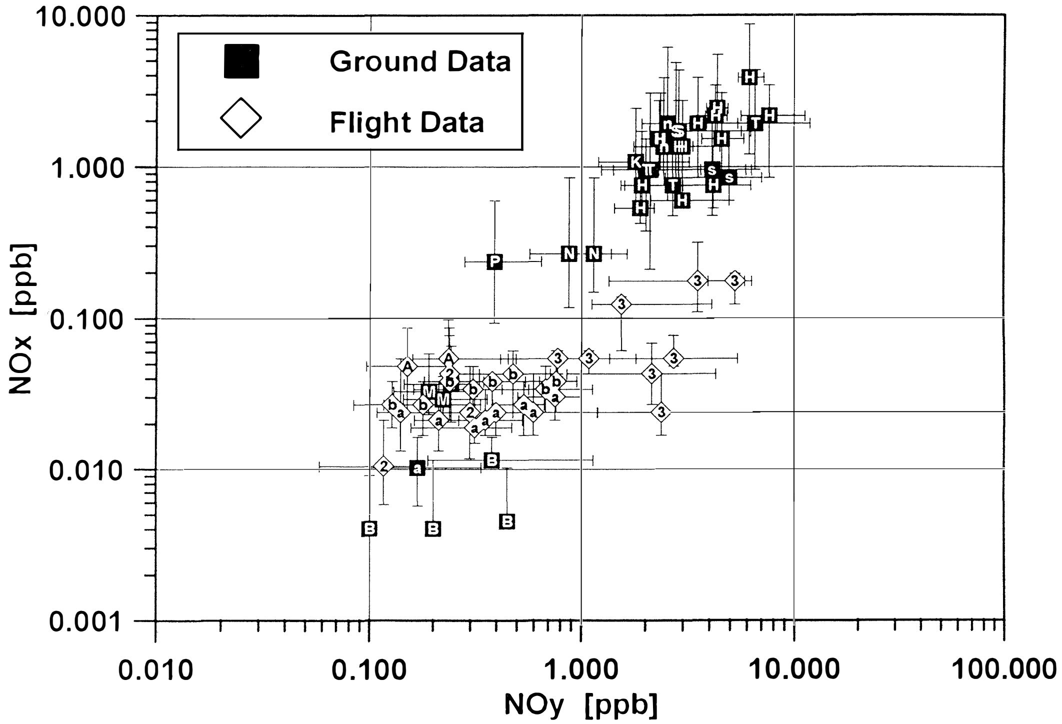


Figure 5-9. Summary of NO_x and NO_y concentrations in the PBL and free troposphere (from Prather *et al.*, 1994, based on Carroll and Thompson, 1994). The majority of the airborne measurements shows NO_x concentrations that are too small to sustain net ozone production. The letters and numbers within the symbols refer to the following measurement campaigns (see Appendix for acronym definitions): a = ABLE3a; A = AASE; b = ABLE3b; B = Barrow, Alaska; H = Harvard Forest; K = Kinterbush, Alabama; M = MLOPEX; n = NACNEMS; N = Niwot Ridge, Colorado; P = Point Arena, California; s = SOS/SONIA, S = Scotia, Pennsylvania; T = TOR; 2 = CITE2; 3 = CITE3.

Murphy *et al.* (1993) have measured vertical distributions of NO_y and O_3 into the stratosphere. Although a strong correlation between NO_y and O_3 was found in the stratosphere, they observed only weak to no correlation between these constituents in the troposphere, *i.e.,* the tropospheric NO_y/O_3 ratio can be larger and more variable, a reflection of the variety of sources, sinks, and transport processes of NO_y and O_3 in the troposphere. In contrast, Wofsy *et al.* (1992) and Hübler *et al.* (1992a, b) reported a significant positive correlation when the data are averaged over a large number of observations. The observed slope was much steeper than that derived from continental boundary layer studies (Section 5.3.2) and approached that found in the stratosphere. The large decrease in the NO_y/O_3 ratio between the continental surface studies and the remote free atmosphere is believed to largely reflect the shorter lifetime of NO_y compared to O_3 in the free troposphere, mixing, and input from the stratosphere.

A summary of tropospheric NO_x and NO_y concentrations from Prather *et al.* (1994) is shown in Figure 5-9. It is based on the compilation of Carroll and Thompson, (1994) of measurements made by various groups in the lower and middle troposphere over the U.S. and Europe. Although very high concentrations from urban areas are excluded, the concentrations of NO_x span a range of three orders of magnitude. On the average, a correlation between NO_x and NO_y is seen. However, the individual data sets clearly show that the shorter-lived NO_x can still vary over an order of magnitude for a given NO_y concentration. From this and the differences in NO_x observations in the upper troposphere at northern latitudes discussed above, it is clear that present measurements are insufficient to reasonably describe a meaningful climatology.

Aircraft programs have continued to strengthen the role of PAN as a reservoir for NO_x, at least in the 3-6 km altitude range over continental regions (Singh *et al.*, 1992, 1994), where PAN decomposition was able to account for much of the observed NO_x, a result that emphasizes the role of transport of odd nitrogen reservoirs. Very high PAN concentrations of up to 200 ppt were also observed in long-range transport events at Izana during spring, whereas PAN concentrations remained below 20 ppt at the higher temperatures of summer (Schmitt and Hanson, 1993). Other studies have shown that the importance of PAN as a NO_x reservoir is not global. Measurements made in the Northern Hemisphere upper troposphere mostly over the Atlantic Ocean have generally shown smaller mixing ratios than observed in the middle troposphere over continental regions, and Southern Hemisphere mixing ratios were very small throughout the troposphere (Rudolph *et al.*, 1987; Perros, 1994). Similarly, during studies at the Mauna Loa Observatory experiment, PAN was not a major constituent. HNO_3 was the dominant reservoir (median of 43% of NO_y), followed by NO_x (14%), particulate nitrate (5%), PAN (5%), and alkyl nitrates (2%) (Atlas *et al.*, 1992).

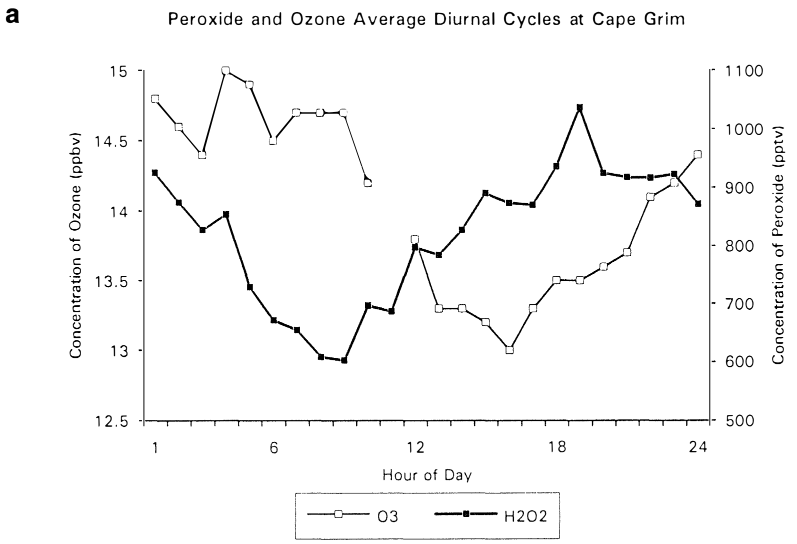
The role of the remote marine PBL as a strong net sink for ozone has been clearly identified in a large number of investigations, a finding first reported by Liu *et al.* (1983). For example, a clear anticorrelation in the diurnal and seasonal variation of O_3 and H_2O_2 was observed by Ayers *et al.* (1992) in marine air at Cape Grim, Tasmania (Figure 5-10). As is seen in Figure 5-1, HO_2 radical recombination leads to formation of H_2O_2, which can thus be utilized as a tracer for photochemical activity. The results are consistent with net photochemical destruction of O_3 in a very low NO_x atmosphere. Net photochemical destruction of O_3 in the tropical PBL of up to 25%/day was also inferred from the data gathered during several ship cruises (Thompson *et al.*, 1993; Smit *et al.*, 1989; Smit and Kley 1993; Harris *et al.*, 1992).

The photochemical buffer regions are not confined to the remote maritime lower atmosphere. Aircraft flights covering Alaska, northern Ontario and Quebec, and Labrador have concluded that the surface layer, especially the boreal forest, was an efficient sink for O_3 and NO_y (Gregory *et al.*, 1992; Jacob *et al.*, 1992; Bakwin *et al.*, 1992). In some regions of these flights, NO_x was nearly independent of altitude up to 6 km with a median mixing ratio of only 25 ppt, insufficient to overcome average net photochemical destruction of O_3 (Sandholm *et al.*, 1992). Earlier studies over the continental U.S. by Carroll *et al.* (1990b) found that air masses between the boundary layer and 5-6 km, were nearly equipartitioned between net loss, approximate balance, and net production of O_3.

An extremely interesting finding that yet awaits complete explanation is the occurrence of nearly complete O_3 depletion in the Arctic surface layer in spring (Barrie *et al.*, 1988; Bottenheim *et al.*, 1990; McConnell *et al.*, 1992; Fan and Jacob, 1992). A recent analysis of the ratios of different hydrocarbons provides evidence for bromine chemistry being responsible for the ozone removal (Jobson *et al.*, 1994), although Platt and Hausmann (1994) argue that the measured BrO concentrations were too small to explain the complete ozone depletion on the short time scales implied by the observations.

Net ozone loss of 0.5 ppb/day, or ~1%/day, was also found in the free troposphere near 3.4 km from observations at the Mauna Loa Observatory (Ridley *et al.*, 1992). The concentrations of peroxy radicals and the rate of ozone formation, $P(O_3)$, were derived from the photostationary state of NO_x (Figure 5-11) and the loss rate, $L(O_3)$, was inferred from model calculations based on the measured concentrations of all relevant parameters. It is noteworthy that both the total concentration of HO_2 and RO_2 determined during this study, as well as the modeled HO_2/RO_2 ratio, are in good agreement with recent direct measurements made by matrix isolation and ESR spectroscopy at Izana, Tenerife (D. Mihelcic, private communication).

The net destruction rate found in spring at Mauna Loa in the free troposphere is slow enough that vertical exchange with the marine boundary layer can overrule *in situ* chemistry. Vertical soundings made from a ship cruise in the Pacific clearly demonstrate the importance of convective transport for the ozone balance of the free troposphere. Extremely low ozone concentrations, that had their origin in the marine boundary layer, were found in the upper troposphere (Smit and Kley, 1993). These observations contrast those made or modeled over continental regions, where an emphasis has been on the role of convection of boundary layer precursors in augmenting O_3 production in the middle and upper troposphere (Dickerson *et al.*, 1987; Pickering *et al.*, 1992a, b; Thompson *et al.*, 1994). As was suggested by



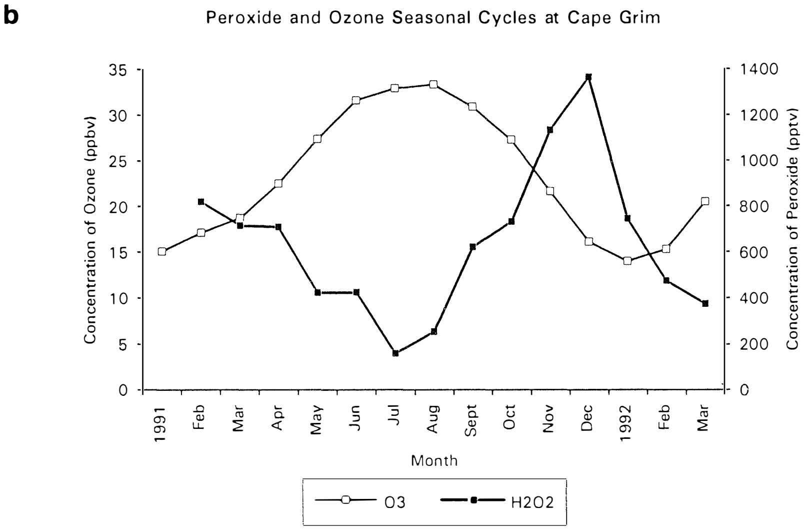


Figure 5-10a. Average diurnal cycles for peroxide and ozone in background air at Cape Grim for January 1992 (based upon Ayers *et al.*, 1992).

Figure 5-10b. Seasonal cycles of peroxide and ozone in background air at Cape Grim (based upon Ayers *et al.*, 1992).

modeling studies (Lelieveld and Crutzen, 1994), downward mesoscale flow in the cloud environment can carry O_3 to the Earth's surface, where it is destroyed more rapidly. Although these model studies yet await confirmation by experimental data, it is likely that deep convection tends to increase free tropospheric ozone levels downwind of continental source areas but may reduce tropospheric O_3 in regions that are removed from polluted areas.

Intensive studies at Mauna Loa have suggested some possible discrepancies in our understanding of the atmospheric oxidizing capacity. Programs completed more recently may help to determine whether these results are more universal in the remote troposphere. First, the abundance of formaldehyde (HCHO) predicted from

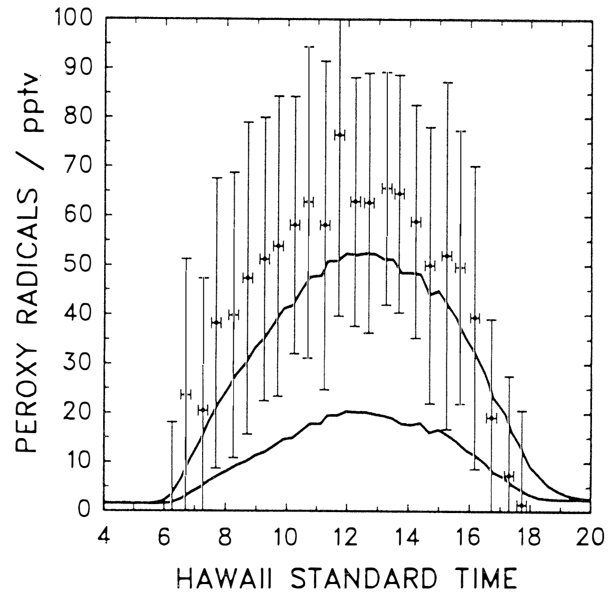


Figure 5-11. Average diurnal variation of peroxy radical mixing ratios derived from measurements of trace gases and photolysis rates during the Mauna Loa Observatory Photochemistry Experiment (Ridley *et al.*, 1992). The bars give the mean and standard deviation of the total peroxy radical mixing ratio estimated from the photostationary state of NO_x. The solid lines are model predictions for the mixing ratios of (HO_2 + CH_3O_2) and of CH_3O_2, respectively.

a model (Liu *et al.,* 1992) was three times larger than the observed median (Heikes, 1992). Since measurements of a variety of hydrocarbons (Greenberg *et al.*, 1992) showed that CH_4 oxidation was the dominant source of HCHO, the results implied that model abundance of OH was too high or, more likely, that other HCHO removal processes not included in the model were important. Second, the observed HNO_3/NO_x ratio was also in poor agreement with the photochemical model, unless the removal rate for HNO_3 was increased equivalent to a 3-5 day lifetime. More limited aircraft measurements have also indicated a smaller-than-expected ratio (Huebert *et al.*, 1990). The model used by Ehhalt *et al.* (1992) to describe the aircraft observations of NO also implied a very short average lifetime of NO_y, on the order of a few days. If the HNO_3 reservoir is indeed removed faster than commonly described in models, the increased efficiency of O_3 production in the remote atmosphere is weakened compared to that modeled previously. However, simply decreasing the model lifetime of HNO_3 will eventually cause significant discrepancies in simulating the mixing ratios of NO_x in the remote atmosphere, since NO_x is ultimately lost through HNO_3 formation. Clearly, more systematic investigations of O_3, NO_x, and other NO_y species and suitable tracers for transport need to be conducted in remote locations in order to better understand the interplay between transport and chemistry in determining the "global" budget of ozone and its potential for future increase.

5.4 FEEDBACK BETWEEN TROPOSPHERIC OZONE AND LONG-LIVED GREENHOUSE GASES

The concentrations of many trace gases that contribute to the greenhouse effect of the atmosphere or are involved in the budget of ozone in the stratosphere or the troposphere, *i.e.*, CH_4, CO, NMHC, NO_x, methyl bromide (CH_3Br), HFCs, and HCFCs, are mediated through oxidation by OH radicals. Reaction R5-11 followed by R5-12 provides the major source for OH in the unpolluted troposphere. Therefore, OH concentrations are strongly linked to the UV flux below 320 nm (UV-B) and the concentrations of water vapor and ozone itself. In addition, OH is affected by other trace gases. For this reason, rising levels of CH_4, CO, and NO_x may lead to changes in the oxidizing capacity of the troposphere (see Thompson and Cicerone, 1986), which in turn influences the concentrations of gases relevant to global warming and/or stratospheric ozone depletion.

On short time scales, increases in UV flux, H_2O, and O_3 lead to increases in OH, as is clearly borne out by the good correlation found between OH concentrations and the photolysis frequency of ozone (Platt *et al.*, 1988). On longer time scales, however, the net effect of enhanced UV radiation and H_2O concentrations on OH depends on the net photochemical balance of ozone $P(O_3) - L(O_3)$ in the particular region of the atmosphere, that is, on the NO_x concentration, and advective transport of ozone from other regions.

Besides being required for ozone maintenance, NO_x increases change the partitioning between OH and HO_2 to favor OH via reaction R5-5. Thus, increasing NO_x will lead to an increase in OH, at least for NO_x concentrations below 1 ppb (Hameed *et al.*, 1979; Logan *et* *al.,* 1981). At higher concentrations, reaction (R5-15) becomes the major loss process for OH (and $HO_x = OH + HO_2$) and a further increase of NO_x will tend to reduce OH concentrations. At very low NO_x levels, *e.g.*, below a few tens of ppt, recycling of OH occurs via reaction (R5-13). In this sense, the dependence of OH on NO_x in the remote atmosphere and on long time scales is much stronger than implied by models that use fixed ozone concentration fields.

The exact concentration of NO_x at which the influence of NO_x upon OH changes sign depends on the concentrations of ozone (see above) and those of other trace gases such as CO, CH_4, and NMHC. The latter gases change the HO_x partitioning in favor of HO_2 (R5-1 to R5-4 and R5-8 to R5-9) and thereby serve to reduce OH. However, this negative influence is not a linear one because of the reduction in HO_x losses that proceed via OH reactions, *i.e.,* R5-15.

Although attempts to measure OH were made in the early seventies (see Wang *et al.*, 1976; Perner *et al.*, 1976), direct measurements are still extremely sparse (Perner *et al.*, 1987; Platt *et al.*, 1988; Felton *et al.*, 1988; Dorn *et al.*, 1988; Mount and Eisele, 1992; Eisele *et al.*, 1994), in particular in the remote atmosphere. One reason for this is the experimental difficulty involved given the extremely low concentrations of OH radicals due to their reactivity. In addition, because of the fast response of OH to changes in the controlling boundary conditions, these measurements will not and cannot produce a global field of OH concentrations. They can, however, lead to improvements in understanding the chemical budget when accompanied by measurements of the controlling factors (Ehhalt *et al.*, 1991) and, hence, help to calibrate the photochemical models used to derive global OH fields (Ehhalt *et al.*, 1991; Poppe *et al.*, 1994), in particular with the recent advances in measurement capability for OH. However, any attempt in modeling the global OH field and, in particular, its secular trend, for example that induced by the increase in methane concentrations (see Chapter 7) or UV radiation, relies on an accurate knowledge of the distribution and trends of ozone, water vapor, and a number of other parameters, but most importantly, on the distribution in space and time of NO_x.

Average figures on global OH concentrations have been derived from the concentrations of tracers that are removed from the atmosphere preferentially by OH. Among these are CH_3CCl_3, with an atmospheric turnover time of about 6 years, and ^{14}CO, with a turnover time of a few months. A detailed discussion of these indirect attempts is given in Chapter 7.

More recently, other potentially important oxidants in the troposphere have been suggested in addition to OH. Among these are chlorine atoms (Pszenny *et al.*, 1993), which may be formed in the marine boundary layer from reactions of N_2O_5 with aerosol chloride (Finlaysen-Pitts *et al.*, 1989; Zetsch and Behnke, 1992). Penkett *et al.* (1993) concluded from the measured ratios of iso- to normal alkanes in the atmosphere that NO_3 radicals could play a significant role in the atmospheric oxidation of NMHC on larger regional scales, in particular at higher latitudes. The importance of these additional oxidizing reagents is, however, still in the hypothesis stage. While it has been suggested that atomic chlorine and bromine could play a role in certain regions of the troposphere, for example during spring in the Arctic (Fan and Jacob, 1992; Jobson *et al.*, 1994), concentrations larger than 1% of the average global OH concentration seem to be inconsistent with the budgets of some trace gases (J. Rudolph, private communication).

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