CHAPTER 8

Tropospheric Ozone and Related Processes

Lead Authors:
J. Lelieveld
A.M. Thompson

Coauthors:
R.D. Diab
Ø. Hov
D. Kley
J.A. Logan
O.J. Nielsen
W.R. Stockwell
X. Zhou

Contributors:
R. Guicherit
D.J. Jacob
M. Kuhn
J.B. Milford
H. Sidebottom
J. Stähelin

CHAPTER 8

TROPOSPHERIC OZONE AND RELATED PROCESSES

Contents

SCIENTIFIC SUMMARY

A concerted effort continues in the deduction of trends in tropospheric ozone from the sparse in situ record. Trends are reported regionally or at stations where monitoring is conducted. Surface ozone increases, typically observed in Northern Hemisphere midlatitudes, have slowed considerably in the past decade. At the South Pole, there continues to be a decrease in surface ozone associated with the Antarctic lower stratospheric ozone depletion.

- Since the 1994 Assessment (WMO, 1995), a thorough evaluation of tropospheric ozone profiles can be summarized as follows:

  - Midlatitude: Three stations over Europe, which have had the greatest increases in free tropospheric ozone since 1970, show a major change in trends since 1980. Only Payerne shows an increase during the period 1980-1996; Uccle shows no change and Hohenpeissenberg a statistically marginal decrease. The two U.S. stations with regular ozonesonde launches (Wallops Island and Boulder) also show no significant change or a slight decrease since 1980. Of three Japanese stations, two show increases of 5-15%/decade, though not all significant; one station shows no trend. Canadian stations show a small decrease in free tropospheric ozone since 1980.

  - Tropics and Southern Hemisphere: There is only one tropical site with sufficient data for trends: Natal, Brazil, shows a 10-20%/decade increase only in the middle troposphere and possibly not significant; the record becomes too sparse for trends after 1992. There is no trend in free tropospheric ozone at Lauder, New Zealand, where the record began in 1986.

- Observations of ozone and other photochemically reactive species during field campaigns have been made with greater focus on understanding the interaction of chemistry and dynamics on local scales. Processes affecting reactive nitrogen species have been elucidated on several intensive campaigns. The free tropospheric nitric oxide (NO) and total reactive nitrogen climatology has been extended in aircraft campaigns in both Northern and Southern Hemispheres. Systematic sampling has extended the NO database along commercial aviation routes. Continental outflow downwind of industrial activity in Northern Hemisphere midlatitudes strongly enhances ozone budgets over large regions of the North Atlantic and North Pacific. Measurement campaigns in the tropics and subtropics show continental influences from long-range transport of biomass-burning emissions, although NO from lightning may also play a significant role in the tropical ozone budget.

  - Reliable instrumentation for hydroxyl radicals (OH), hydroperoxyl radicals (HO_2), and organic peroxyl radicals (RO_2) has been a breakthrough development since the last Assessment. Intercomparisons on the ground, and model interpretation of ground-based and airborne OH and related measurements show that our theoretical understanding of OH is not complete. With the constraint of ancillary measurements, it can be shown that data-model discrepancies tend to be greatest under polluted conditions and that odd hydrogen (HO_x) sinks, rather than sources, are probably not accounted for. In the upper troposphere, under certain conditions, acetone and the recycling of peroxides following deep convective transport appear to be important HO_x sources. On a global scale, inferences about the total OH budget range from no trend in the past decade to a slightly positive trend.

  - Model intercomparisons and uncertainty studies show that photolysis rates, representations of stratospheric-tropospheric exchange, and imprecise pathways in organic oxidation chains continue to limit the reliability of models used in interpretive ozone studies and predictions. Models continue to suggest intriguing possibilities for heterogeneous and multiphase reactions affecting ozone in a major way, but experimental confirmation is lacking for the most part.

- Large-scale ozone distributions calculated in global chemistry-transport models (CTMs) are in fair accord with the sparse measurements and historical ozone data. However, the agreement between models and measurements on regional and smaller scales is more difficult to achieve. The quality of simulations is probably most limited by the treatment of convection and other sub-grid dynamical processes as well as complex chemical pathways near ozone precursor source regions.

8.1 OZONE OVERVIEW

8.1.1 Introduction

In the previous World Meteorological Organization/United Nations Environment Programme (WMO/UNEP) Ozone Assessment (WMO, 1995), it was concluded that tropospheric ozone and several related trace gases have been perturbed significantly, at least over some large regions. These changes are likely to have modified atmospheric oxidizing capacity (Thompson, 1992) in the past century. Changes in low-latitude and summertime free tropospheric ozone may have affected radiative forcing and contributed to climate change (Chapter 10).

Quantitative assessment of tropospheric ozone, ozone precursors, and OH (hydroxyl radical) distributions and trends depends on our ability to self-consistently relate:

- Ozone precursor sources and emissions;
- Mechanisms of ozone and hydroxyl radical formation and loss;
- Observations of ozone, OH, and precursors;
- Model results and observations of ozone.

The purpose of this chapter is to assess recent advances in these areas. This section summarizes the overall picture of tropospheric ozone and is followed by sections on trends (Section 8.2), anthropogenic perturbations of tropospheric ozone (Section 8.3), and key processes affecting ozone (Section 8.4). Models of tropospheric ozone are covered in Section 8.5. Stratospheric ozone depletion is affected by changes in the lifetime of a number of trace gases that are affected by the global OH abundance (Section 8.6) and by the reactivity of CFC substitutes and related species (Section 8.7).

8.1.2 Photochemical Ozone Formation and Precursor Roles

Both regional and global chemistry-transport models are used to estimate exports from the polluted boundary layer in industrialized or biomass-burning regions to more remote environments. Near source regions, ozone is formed from carbon monoxide (CO), methane (CH_4), and nonmethane hydrocarbon (NMHC) chemistry in the presence of nitrogen oxides (NO_x); export of these gases out of the polluted boundary layer by convection and synoptic motions can then perturb the global atmosphere. Results from a 3-D model simulation for North America indicate that 50% of ozone (O_3) produced in the continental boundary layer is exported to the global troposphere on an annual mean basis, and that 20% of anthropogenic NO_x emitted in the United States is exported as NO_x or peroxyacetyl nitrate (PAN) (Horowitz *et al*., 1998; Liang *et al*., 1998). Regional contributions to the ozone budget are discussed further in Section 8.5.

8.1.3 Stratosphere-Troposphere Exchange

Since the last Assessment's review of the role of stratosphere-troposphere exchange (STE) in the tropospheric ozone budget (WMO, 1995), most studies have focused on mass exchanges across the tropopause (Holton *et al*., 1995). The extratropical lowermost stratosphere, a few-kilometer-thick transition layer, is influenced by one-way downward transport across the 400-K level as well as two-way exchange across the tropopause (Dessler *et al*., 1995; Lelieveld *et al*., 1997; Roelofs and Lelieveld, 1997). Observations of STE events, e.g., tropopause folds, cut-off lows, and occasional penetration of the stratosphere by convection, show that these processes are significant, but their episodic nature makes them difficult to assess. Most of the observations are from aircraft although penetration of stratospheric air parcels toward the surface has been detected by measurements at high altitudes (Sunwoo *et al*., 1994; Elbern *et al*., 1997).

Calculations of the contribution by STE to tropospheric O_3 are to a large extent dependent on three-dimensional chemistry-transport models (see Section 8.5.4). Exceptions are the studies by Murphy and Fahey (1994) and Gettelman *et al.* (1997). Murphy and Fahey used observed correlations with nitrous oxide (N_2O) and constrained the STE O_3 flux to 200-900 Tg/yr. This roughly coincides with the range of results obtained with models, although most models indicate an STE O_3 flux exceeding 400 Tg/yr (WMO, 1995). Gettelman *et al.* (1997) combined air mass fluxes, derived from United Kingdom Meteorological Office (UKMO) analyzed meteorological fields, with ozone observations from the Upper Atmosphere Research Satellite (UARS). They obtained a global mean ozone flux to the troposphere of 510 Tg/yr (450-590 Tg/yr). The agreement with recent modeling studies is encouraging. However, this may be fortuitous because these models are applied in relatively

Table 8-1. Estimated emissions of ozone precursors. Best estimates are listed, with ranges given in parentheses.

Sources	CH_4 (Tg/yr)	CO (Tg/yr)	NMHC (Tg C/yr)	NO_x (Tg N/yr)
Energy use	110 (65-155)	500 (300-900)	70 (60-100)	22 (20-24)
Aircraft				0.5 (0.2-1)
Biomass burning	40 (10-70)	500 (400-700)	40 (30-90)	8 (3-13)
Vegetation		100 (60-160)	400 (230-1150)	
Soils				7 (5-12)
Lightning				5 (2-20)
Ruminants	85 (60-105)			
Rice paddies	80 (30-120)			
Animal wastes	30 (15-45)			
Landfills	40 (20-60)			
NH_3 oxidation				0.9 (0-1.6)
N_2O breakdown*				0.6 (0.4-1)
Domestic sewage	25 (20-30)			
Wetlands	145 (115-175)			
Oceans	10 (5-15)	50 (20-200)	50 (20-150)	
Freshwaters	5 (1-10)			
CH_4 hydrates	10 (5-15)			
Termites	20 (1-40)			
Total	**600** (520-680)	**1150** (780-1960)	**560** (340-1490)	**44** (30-73)

* NO_y produced in the stratosphere and transported to the troposphere.

coarse resolution (typically >100 km); Mahlman (1997) suggests that higher resolution models are required.

8.2 OZONE TRENDS

This section is an update on tropospheric ozone trends since the previous Assessment (WMO, 1995, Chapters 5 and 7). It begins with an update on budgets of two ozone precursors, NO_x and NMHC; trends in the other important O_3 precursors, methane and CO, are covered in Chapter 2 (Section 2.5). Because tropospheric ozone is not measured globally by satellite, except in limited regions, the amount of data available for trends analysis is limited to surface monitoring sites and a few stations where ozonesonde launches have been of consistent frequency and quality for deduction of trends.

8.2.1 Ozone Precursor Trends

8.2.1.1 NITROGEN OXIDES

Estimates of nitrogen oxide emissions have recently been assessed by Benkovitz *et al.* (1996) and Lee *et al.* (1997a). Yienger and Levy (1995) estimated soil nitric oxide (NO) emissions and concluded that anthropogenic land-use significantly enhances the natural emissions. It appears that in the tropics, soil emissions (5-12 Tg N/yr) account for more than 50% of the tropospheric NO_x budget. The natural NO_x source from lightning has been reevaluated and is almost certainly less than 20 Tg N/yr and probably less than 10 Tg N/yr (Lawrence *et al.*, 1995; Price *et al.*, 1997). In constructing a global monthly climatology of lightning NO_x, Price *et al.* (1997) found that the main uncertainties in quantifying the lightning NO_x source are related to the energy densities in lightning strokes, the NO_x production per unit energy, and the global extrapolation of these highly variable processes.

Biomass burning constitutes an important anthropogenic NO_x source in the tropics and subtropics of the Americas, Africa, and southern Asia, contributing 3-13 Tg N/yr. The relatively large uncertainty range is mostly due to the limited information available about the amount of biomass burned in forest and savanna fires and the nitrogen content of the fuel. In comparison with fossil fuel combustion, biomass burning occurs at much lower temperatures, so that NO_x production from N_2 and O_2 conversion is much less efficient. Most biomass-burning NO_x results from organic nitrogen transformation while a substantial part of the emissions occur as reduced nitrogen species (Lobert *et al.*, 1991).

The dominant contemporary source of NO_x to the atmosphere is fossil fuel combustion (Table 8-1). However, some national emission inventories have uncertainties as large as 50%. Nevertheless, there is no doubt that in the U.S. (EPA, 1996) and Europe (Veldt, 1985) anthropogenic emissions of NO_x and NMHC in both regions were very much lower in the beginning of this century than at present. Emissions in the U.S. increased from about 0.75 Tg N in 1900 to about 6 Tg N at present. In discussing recent trends in NO_x, it is useful to separate emissions from fossil fuel combustion in the boundary layer ("surface" sources) and from aircraft. Surface emissions of NO_x increased by 20% from 1970 to 1980 in the United States and by 27% in Western Europe, and remained approximately constant up to 1990, as reviewed by Logan (1994). U.S. emissions stayed constant until 1994, then decreased by 9% in 1995 (EPA, 1996). Comparison of the CORINAIR (COre INventories AIR) inventories for 1990 and 1994 indicates that emissions in western Europe (16 countries including eastern Germany in 1990) decreased by 8% from 1990 to 1994. The countries with the largest emissions trends were: Germany, -25%; United Kingdom, -14%; France and Spain, +6%. It is likely that emissions in most of eastern Europe have declined since 1990, because of the decline in fossil fuel consumption, 28% from 1990 to 1994 (Marland and Boden, 1997). The only location with a substantial increase in NO_x emissions in the Northern Hemisphere is Asia, about 4%/yr from 1985 to 1987 (Kato and Akimoto, 1992). The largest contribution to Asian emissions is that of China. Here emissions are unregulated and should parallel growth in fossil fuel combustion, ~7%/yr from 1990 to 1994. Emissions from China increased from 1.5 Tg N/yr in 1980 (Kato and Akimoto, 1992) to 3.1 Tg N/yr in 1994, based on fossil fuel growth statistics given by Marland and Boden (1997). During the same period, U.S. emissions remained constant at 6.3 Tg N/yr (EPA, 1996), and the U.S. contributed 30% to the global emissions of NO_x from fossil fuel combustion in 1985, 21 Tg N, 90% of which are in the Northern Hemisphere (Benkovitz *et al.*, 1996).

Emissions of NO_x from aircraft have increased significantly since 1970 and continue to increase. Emissions of NO_x from aircraft were 0.30 Tg N in 1976, 0.39 Tg in 1984, and 0.51 Tg in 1992, and are projected to be 1.26 Tg in 2015 (S. Baughcum, Boeing Company, U.S., personal communication, 1998). Slightly over half of the aircraft emissions take place between 9 and 13 km in the Northern Hemisphere (Baughcum *et al.*, 1996). There were regional differences in the increase in jet fuel consumption in the 1970s, 17% in the U.S. and 55% in western Europe, while the use increased about 35% in both regions in the 1980s (Logan, 1994). A significant fraction of the emissions are injected into the stratosphere in winter and spring, but in summer almost all emissions take place in the troposphere.

The growth of civil aviation is expected to continue (BAe/Airbus, 1995; Boeing, 1997) as quoted in Brasseur *et al.* (1998), although the rates of growth are slowing with time (15% in the 1970s, 9% in the 1980s, to an estimated 5% from 2000-2015). Growth rates are predicted to vary significantly for the different regions of the world. The differences in the average growth rates between the two forecasts are small compared to actual growth during this period: 225% (Airbus) or 270% (Boeing). Aviation consumes 2.3% of the fossil fuels used worldwide, of which about 80% is consumed by civil aviation. As a consequence of the improvements in engine and aircraft fuel efficiencies, the fuel increase is 70-80% of the traffic increase. Military aircraft have traditionally used about 20% of the aviation fuel. With the reduction in military activity, less aviation fuel is used for this purpose, but it is difficult to predict future consumption levels due to a lack of fixed operational practices and flight patterns and because of national security.

Two comprehensive inventories, Abatement of Nuisance Caused by Air Traffic/European Commission (ANCAT/EC) and National Aeronautics and Space Administration (NASA), have been developed in recent years and are widely used by atmospheric modelers. Both incorporate an extensive air traffic movements database, assumptions about flight operations, and a methodology for prediction of emissions over the entire flight. Comparisons of the fuel and NO_x data, from the initial inventories of the two groups (Gardner *et al.*, 1995; Wuebbles *et al.*, 1993), showed significant differences that have been reported elsewhere (WMO, 1995). Recent revisions result in considerably closer agreement (Gardner *et al.*, 1997; Baughcum *et al.*, 1996; Metwally, 1995).

8.2.1.2 Nonmethane Hydrocarbons

A global source inventory of natural NMHC presented by Guenther *et al.* (1995) on a 0.5 × 0.5 latitude/longitude grid includes contributions from isoprene (44%), monoterpenes (11%), and other reactive (22.5%) and less reactive (22.5%) NMHC. The total terrestrial source flux estimated by Guenther *et al.* (1995) is 1150 Tg C/yr, which is at the upper part of the range of natural NMHC estimates (Table 8-1). Müller and Brasseur (1995) and Houweling *et al.* (1998) have implemented natural and anthropogenic NMHC representations in global models and concluded that such a large emission source would lead to a strong overestimation of the load of reactive carbon gases in the troposphere. This suggests that either the natural NMHC emissions have been overestimated or that a large fraction of these compounds and their oxidation products do not appear in the atmosphere as reactive carbon.

NMHC emissions appear to be decreasing. Industrial NMHC emissions (especially process emissions) are thought to have declined since the beginning of the 1970s. From 1970 to 1980, reductions of NMHC emissions ranging from 15% to more than 30% have been reported for northwest European countries. The decrease in industrial NMHC emissions was, however, (over)compensated by an increase in NMHC emissions by traffic. This is the reason why net NMHC emissions in Europe were still increasing in the 1970s. Between the beginning and middle of the 1980s, NMHC emissions have leveled off. During the 1990s NMHC emissions have been slowly declining as is the case for NO_x emissions. According to the European Monitoring and Evaluation Programme (EMEP) emission inventory, from 1989 to 1994, NMHC emissions decreased by 2-5%/yr in many northern and western European countries. It should be pointed out that for Europe as a whole reductions were less, because in many European countries pollution control measures were less stringent than in the northwest countries of Europe.

8.2.2 Surface Ozone Trends

The previous UNEP/WMO Assessment reviewed historical and contemporary measurements of ozone at remote surface sites. That material is updated here. Tropospheric ozone trends vary regionally, with largest trends reported for Europe (Table 8-2). Current background monitoring sites are given in Table 8-3.

Marenco *et al.* (1994) analyzed Schoenbein measurements from Pic du Midi, France, from 1874 and 1909. Ozone concentrations were stable, about 10 ppb, for the first 20 years, followed by an increase of 1.6%/yr for the next 15 years. Values of 10 ppb were reported also for a Paris suburb (Montsouris) for 1876-1911 using a more quantitative method (Volz and Kley, 1988), raising the question of the apparent lack of vertical gradient between the two datasets (Pic du Midi is located at 3000 m). Marenco *et al.* (1994) showed also that the Montsouris data, together with recent observations at Pic du Midi and observations from a few high-altitude European sites measured sporadically between 1933 and 1980, imply that ozone has increased by 1.6%/yr for over 100 years. The recent measurements from Pic du Midi show that ozone was approximately constant for 1990 to 1993.

Oltmans *et al.* (1998) reported trends for remote sites and for selected ozonesonde stations that have used consistent measurement techniques (see Figure 8-1 and Table 8-2). The largest increase has occurred at Zugspitze, Germany (3000 m), with a mean rate of about 1.5%/yr. Most of the increase took place in the late 1970s and early 1980s, and the trend for the first half of the period is nearly 5 times as large as that for the second half, 3.06%/yr and 0.63%/yr, respectively. A similar pattern is seen at the nearby sonde station of Hohenpeissenberg in the lower and middle troposphere, with an increase in the late 1970s and early 1980s, and an insignificant increase in ozone in the 1980s and 1990s (Figure 8-1b). At Whiteface Mountain, New York, the ozone increase is 0.45%/yr, with a smaller increase in the later part of the record. Most non-urban monitoring stations for ozone in the United States show no significant trend in ozone for 1980-1995 (Fiore *et al.*, 1998), and the sonde stations in the U.S show no increase in ozone since 1980 (see below). Of the other remote surface sites in the Northern Hemisphere, only Mauna Loa, Hawaii, shows a significant increase, 0.35%/yr, most of which seems to have taken place prior to the early 1980s. There are small increases at Cape Point and at Cape Grim, in the Southern Hemisphere, but not at Samoa (Table 8-2).

Ozone has decreased at the South Pole, with a trend of -0.70%/yr since 1975. The decline is largest in the spring, during the period of the Antarctic ozone hole (Chapter 4), and is likely influenced by the greater penetration of UV to the surface.

Table 8-2. Trends in surface ozone mixing ratios in percent per year. The 95% confidence interval is based on Student-*t* tests (Oltmans *et al.*, 1998; S. Oltmans, National Oceanic and Atmospheric Administration, U.S., personal communication, 1998).

Station	Period	Annual Trend (%/yr)
Barrow (70°N)	1973-1997	0.30 ± 0.22
	1980-1997	-0.06 ± 0.34
Zugspitze (47°N)	1978-1995	1.48 ± 0.51
Whiteface Mountain (44°N)	1974-1995	0.45 ± 0.22
Mauna Loa (20°N)	1973-1997	0.36 ± 0.11
	1980-1997	0.01 ± 0.28
Samoa (14°S)	1976-1994	-0.26 ± 0.38
Cape Point (34°S)	1983-1995	0.53 ± 0.34
Cape Grim (41°S)	1982-1995	0.18 ± 0.14
South Pole (90°S)	1975-1997	-0.70 ± 0.17
	1980-1997	-0.83 ± 0.24

Table 8-3. Location, elevation, and period of observation of surface ozone measurement stations.

Station	Elevation (m)	Latitude	Longitude	Period of Observation	Present-Day O_3 (ppbv)*
Zeppelin Mountain, Spitzbergen	474	79°N	12°E		32
Barrow, Alaska	11	71°N	157°W	1973-present	27
Areskutan, Sweden	1240	63.4°N	13°E		37
Hohenpeissenberg, Germany	975	48°N	11°E	1970-present	45
Zugspitze, Germany	2937	47°N	11°E	1978-present	49
Sonnblick, Austria	3106	47°N	13°E		47.5
Pic du Midi, France	2877	43°N	0°E	1982-present	48.5
Niwot Ridge, Colorado	3000	40°N	106°W	1990-present	
Bermuda	40	32°N	64°W	1988-present	
Izaña, Canary Islands	2360	28°N	16°W	1987-present	45
Mauna Loa, Hawaii	3397	20°N	156°W	1973-present	41
Barbados	45	13°N	59°W	1989-present	20
Samoa	82	14°S	171°W	1976-present	13
Cape Point, South Africa	75	34°S	18°E	1983-present	22
Cape Grim, Australia	94	41°S	145°E	1982-present	25
Syowa, Antarctica	21	69°S	40°E	1989-present	20
South Pole, Antarctica	2835	90°S	—	1975-present	26

* Mean O_3 mixing ratio. In areas with relatively high NO_x concentrations, O_3 is partly destroyed by reaction with NO. This NO titration effect may be accounted for by regarding O_x (Oxidant = $O_3 + NO_2$) instead of O_3 (Guicherit, 1988; Kley *et al.*, 1994). This means that the "real" ozone concentrations at some of the measuring sites may be somewhat higher. Data from Hov (1997) and Oltmans *et al.* (1998).

8.2.3 Ozone Trends above the Surface

Measurements of the vertical distribution of ozone have been made with ozonesondes for about 30 years. The majority of sonde stations are located at middle and high latitudes of the Northern Hemisphere. Shorter time series are available for a few stations in the subtropics, tropics, and Southern Hemisphere. The primary source of results used here is analysis of ozone trends (WMO, 1998) sponsored by SPARC (Stratospheric Processes and Their Role in Climate) and the IOC (International Ozone Commission), discussed in Chapter 4. The latter report gives a detailed discussion of the quality of ozonesonde data. As part of the SPARC/IOC study, ozonesonde data were reevaluated and reprocessed by those responsible for the individual programs for the stations for which trends were analyzed, with the exception of the data for Wallops Island and Canada. The latter data were obtained from the World Ozone and Ultraviolet Data Centre (WOUDC), and the Canadian data are described by Tarasick *et al.* (1995).

Two groups carried out independent trend analyses of the sonde data, Logan and Megretskaia of Harvard University (LM), and Taio, Choi, and Zhang of the

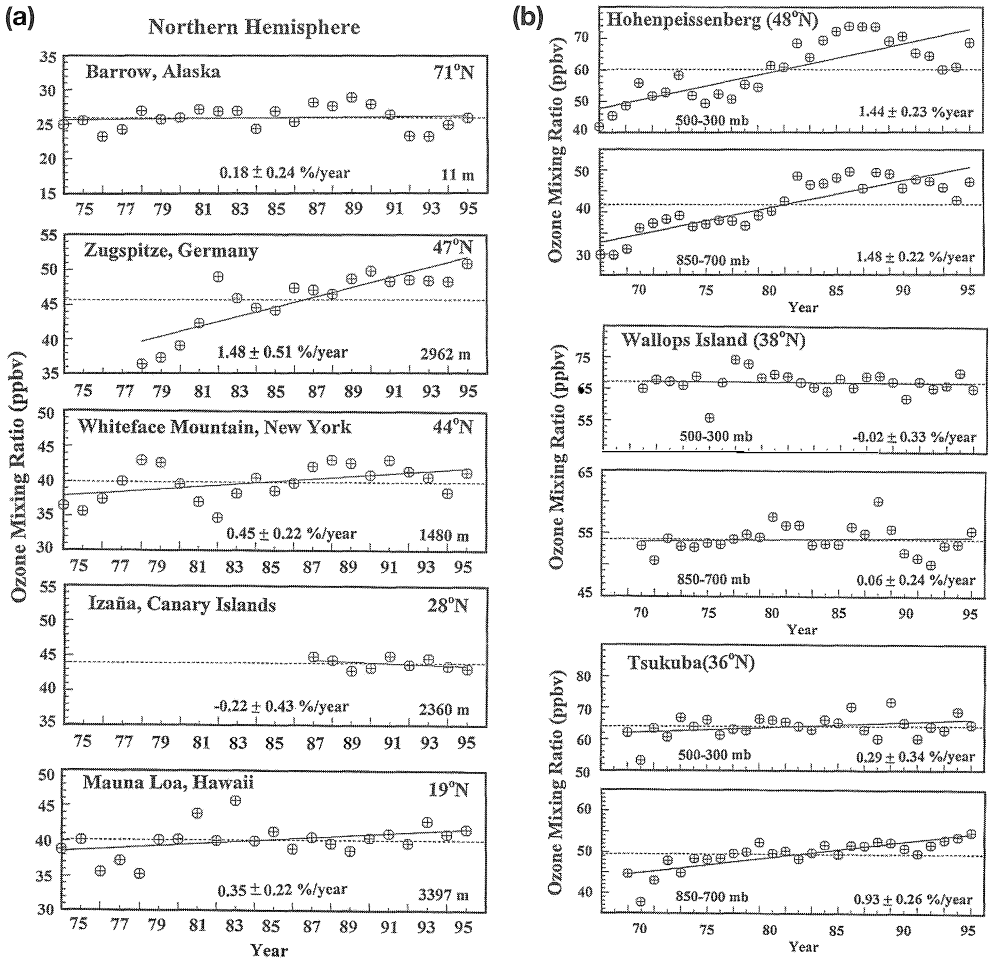

Figure 8-1. Panel (a): Annual average ozone mixing ratios (ppbv) for surface ozone measuring sites. The dashed line is the long-term average. The solid line is the linear least squares fit to the monthly anomalies. The linear trend and 95% confidence interval in percent per year is given with the plot for each location. (From Oltmans *et al.*, 1998.) Panel (b): Annual average ozone mixing ratios and trends from ozonesonde data for two layers in the troposphere (850-700 hPa and 500-300 hPa) at Hohenpeissenberg, Tsukuba (Tateno), and Wallops Island. (From Oltmans *et al.*, 1998.)

University of Chicago (TCZ). Trends were calculated by both groups for the period 1970-1996 and by one group (LM) also for 1980-1996. The two groups used different data selection criteria and different statistical models, as discussed in WMO (1998). They derive similar trends, however, and most of the differences are ascribed to the data selection criteria rather than to the statistical models. The trends are generally in reasonable agreement with results published earlier for somewhat shorter time periods by Logan (1994), Miller *et al.* (1995), Tarasick *et al.* (1995), Akimoto *et al.* (1994), Harris *et al.* (1997), Bojkov and Fioletov (1997), and Oltmans *et al.* (1998).

Trends in tropospheric ozone derived by the two groups are shown in Figure 4-36 of Chapter 4 of this Assessment. The most obvious feature of this figure is that there are significant spatial variations in the magnitude and sign of the tropospheric trends. The largest increases, 5-25%/decade for 1970-1996, are found over Europe (Hohenpeissenberg, Payerne, and Uccle) and extend from the surface to 300 mb. Bojkov and Fioletov (1997) analyzed trends relative to the tropopause location and found that the increase at Hohenpeissenberg is significant up to 1 km below the tropopause (which is located between 200 and 250 mb). Data from Japan show increases in ozone for 1970-1996 of 5-15%/decade, primarily below 500 mb; only Kagoshima shows an increase at 300 mb (Figure 8-2), which is well below the tropopause at this sub-tropical station. There is no evidence for such large increases over North America, as emphasized in WMO (1995). In the eastern U.S. (Wallops Island), the increase is less than 5%/decade. There has been no increase in ozone over Canada for 1970-1996, with some evidence for a decrease; however, the Canadian data prior to 1980 is of low quality (WMO, 1998). The trends shown in Figure 4-36 derived by TCZ are less negative for the Canadian stations, more positive for the European stations and Wallops Island, and about the same for the Japanese stations, compared to those derived by LM. Part of this difference is caused by TCZ referencing the trend to ozone in 1970, and LM referencing the trend to the mean of the time series. Results from both groups for the tropospheric column trends in Dobson units (DU)/decade are in close agreement (WMO, 1998). Oltmans *et al.* (1998) report an increase of 15%/decade for Hohenpeissenberg for 1968-1995. They also find no trend at Wallops Island and results very similar to those in Figure 4-36 for Tateno (called Tsukuba in Figure 8-1). They analyzed only these three stations, selected for the consistency of their record, and used the data at WOUDC.

There is a major change in trends for the period 1980-1996 compared to 1970-1996 in Europe, as shown in Figure 8-2. There is no significant trend for Uccle and a marginally significant decrease for Hohenpeissenberg in the middle troposphere for 1980-1996: only Payerne shows an increase, of about 10%/decade. There are concerns about the consistency of the tropospheric data for Payerne in the 1980s (WMO, 1998). The trends for the later period are smaller because the increases in ozone occurred primarily before 1985, and ozone values have not increased significantly since then, as shown in Figure 8-2. Two of the Japanese stations have increases of 5-15%/decade, not all of which are significant, while Tateno, with the best data record of the three stations, shows no trend in ozone. The Canadian stations show decreases of 2 to 8%/decade, and these are more reliable than the results for 1970-1996 because electrochemical concentration cell (ECC) sondes were used exclusively after 1980. Previous analyses of the Canadian ECC data also showed decreases (Logan, 1994; Tarasick *et al.*, 1995; Oltmans *et al.*, 1998). In the U.S., Wallops Island shows no significant trend, and Boulder shows a decrease of 5% /decade in the mid-troposphere since 1980. There is no significant trend in the middle troposphere at Hilo, Hawaii, since 1982, or in Lauder, New Zealand, since 1986. Oltmans *et al.* (1998) find no significant trend in ozone for Hohenpeissenberg, Boulder, Wallops Island, Tateno, and Hilo for 1979-1995 in the middle troposphere, in agreement with the results in Figure 8-2, while Bodeker *et al.* (1998) find no significant trend for Lauder.

Trend data for tropical ozone are sparse. Limited sonde data from Natal, Brazil, suggest an increase of 10-20%/decade in the middle and upper troposphere for 1978-1991, but the trends are significant only for 400-600 mb (Logan, 1994). Few sondes were flown in 1993-1996 (V.W.J.H. Kirchhoff, Instituto Nacional de Pesquisas Espaciais, Brazil, personal communication, 1997), so that reliable trends cannot be determined for recent years. TOMS data have been used to infer the column of ozone in the lower troposphere off the west coast of South America (Jiang and Yung, 1996; Kim and Newchurch, 1996). Jiang and Yung (1996) find an increase in ozone in a very small region at 25°S west of South America to be 5-15%/decade for 1979-1993. The same technique applied to the New Guinea area indicates a 1%/yr increase in lower tropospheric ozone (Kim and

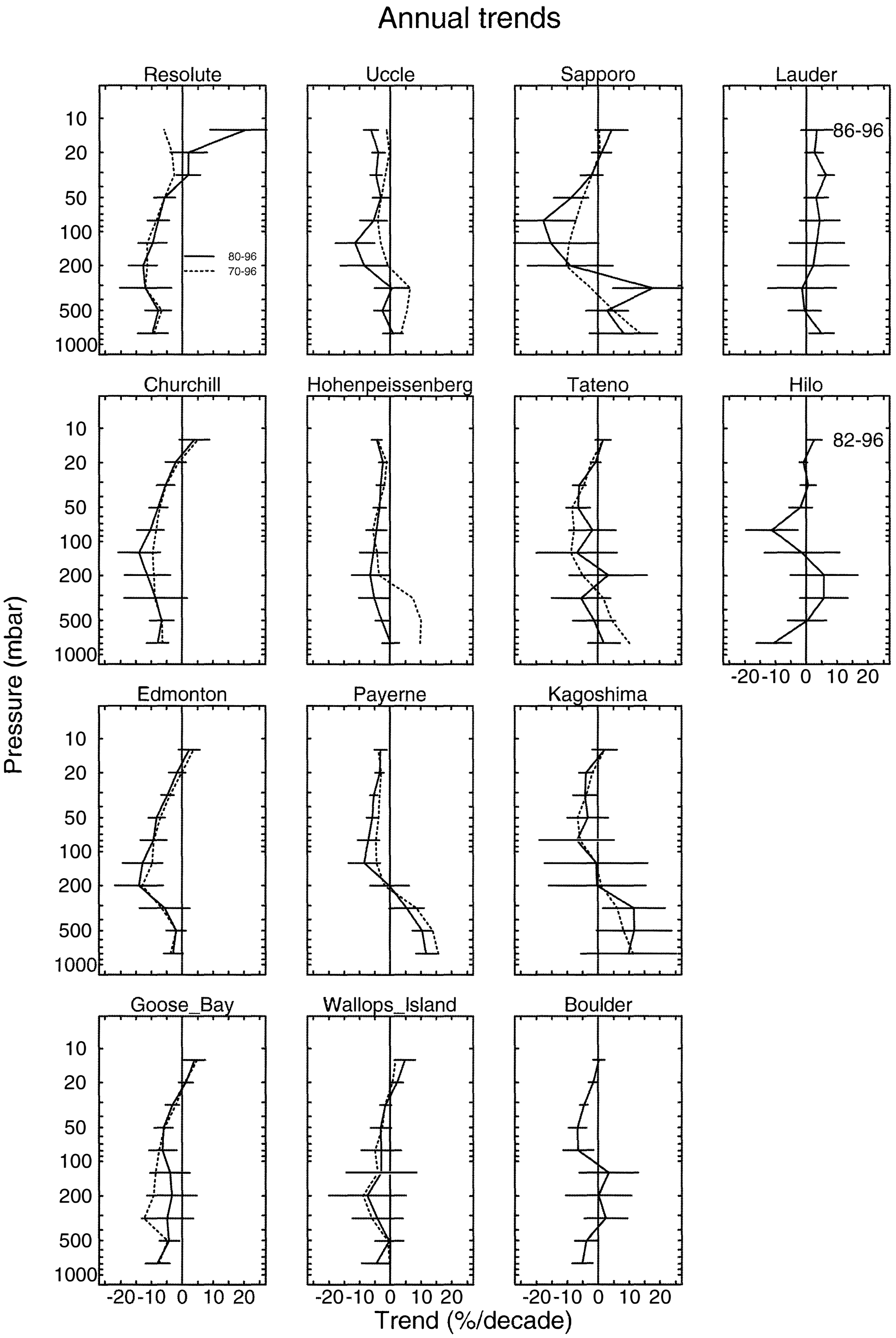

Figure 8-2. Annual trends for 1980-1996 (solid lines) compared to trends for 1970-1996 (dashed lines) where available. The Lauder trends are for 1986-1996, and the Hilo trends are for 1982-1996.

Newchurch, 1998). The indirect methods used in these studies are subject to errors associated with retrieval efficiencies of the backscatter ultraviolet method at low altitudes (Hudson *et al.*, 1995; Kim *et al.*, 1996).

Data for southern midlatitudes are sparse. Sonde data from Australia suggest no trend in ozone from 1970 to 1990 (Logan, 1994). These data are presently under revision (R. Atkinson, Cooperative Research Centre for Southern Hemisphere Meteorology, Australia, personal communication, 1998) and were not included therefore in the SPARC/IOC study.

8.2.4 Are Recent Ozone Trends Consistent with Precursor Trends?

Much of the focus of recent modeling of tropospheric ozone perturbations since 1970 has been on the influence of aircraft emissions (IPCC Assessment in preparation, 1999). Predicted effects of aircraft on ozone are small, increases of a few ppbv (or ~5%) in upper tropospheric ozone, for 0.5 Tg N from aircraft. Assuming that 0.5 Tg N cause a 5% increase in ozone, the increase in aircraft emissions from 1976 to 1992 implies an increase in upper tropospheric ozone of less than 2%/decade. This is smaller than the observed trends over Europe for 1970 to 1996, i.e., 5-25%/decade, and is not inconsistent with the lack of ozone trend observed in the upper troposphere over Japan and eastern North America, given the natural variability in ozone.

Given that surface emissions of NO_x have changed little since 1980, and that the predicted effects of aircraft on ozone are relatively small, it is not surprising that several locations in the Northern Hemisphere show no significant trend in ozone since 1980. Several features of the trend are more difficult to explain, namely, the magnitude of the increase in Europe since the late 1960s, the decrease over Canada, and the lack of a recent increase over Japan. From 1970 to the mid-1980s, ozone increased about 30% over Europe. The increase in ozone is larger than the increase in NO_x emissions, as noted by Logan (1994). To date there have been no 3-D model simulations to address this issue, but model studies of the boundary layer over North America suggest that the fractional response of ozone is about one-third the fractional change in NO_x emissions (McKeen *et al.*, 1991; Jacob *et al.*, 1993). The observed change over Europe was not seen over the United States, while there appears to have been increases in ozone over Japan, although the data are rather sparse. Reasons for the ozone decrease over Canada since 1980 are also unclear. The decrease in stratospheric ozone could contribute, both in terms of providing a smaller stratospheric source and in terms of allowing higher photochemical loss of ozone because of the reduced ozone column. Again, a quantitative model assessment is lacking. The Japanese sonde station with the best record, Tateno, shows no trend in ozone since 1980. This station might be influenced by the rapidly growing NO_x emissions in Asia, but so far no effect on ozone is apparent.

Three-dimensional model simulations are required to explore the causes of regional trends in ozone, and these have not been carried out (see Section 8.5). Any trend in ozone caused by changes in precursors is superimposed on the interannual variability of ozone driven by dynamical factors, including stratosphere-troposphere exchange. These types of simulations should be possible in the next few years, with models driven by assimilated data.

The likely cause of any increase in tropical ozone is an increase in biomass burning. At present, there are few datasets to address this issue, for ozone, or for trends in the number of fires. Herman *et al.* (1997), using TOMS aerosol data as a proxy for fire emissions of ozone precursors over the 1980s, show a small increase over eastern Brazil, and none over southern Africa; a similar inference with TOMS aerosol data over Brazil is shown by Gleason *et al.* (1998). Brazil is the only country for which Advanced Very High Resolution Radiometer (AVHRR) fire count data are available for several years, but intra-seasonal changes in sampling characteristics and uncertainties in detection algorithms have precluded compilation of a consistent dataset from which trends could be derived. Any increase in biomass burning is expected to be accompanied by an increase in gases such as CO that are directly emitted by fires, but calibrated time series extending back to 1980 are generally lacking. Surface data for the southern tropics and midlatitudes for 1990-1996 show a decrease in CO (Novelli *et al.*, 1998).

In summary, the picture that emerges with respect to ozone precursor emissions seems to be consistent with the observed ozone trends, i.e., a sharp increase in the 1970s and a less significant ozone increase during the 1980s and 1990s. At present, ozone growth rates seem to be close to zero or are slightly negative (Scheel *et al.*, 1997). Major urban areas of the U.S. show a decline in surface ozone (Fiore *et al.*, 1998).

Table 8-4. Summary of major findings from campaigns in the Northern Hemisphere.

Campaign	Location	Key Findings	Authors
PEM-West A	East Asia/northern Pacific Ocean	Well-aged marine air maintains continental signature up to ~10 days. Asian plumes with 60-80 ppbv O_3 in the low troposphere over the Pacific. Sources of tropospheric NO_x cannot yet be accurately defined. Continental sources important for O_3 in western Pacific troposphere. NMHC of minor importance for O_3 in N. Pacific troposphere.	Gregory *et al.* (1996); Browell *et al.* (1996a); Singh *et al.* (1996); Kondo *et al.* (1996); Davis *et al.* (1996)
MLOPEX 2	Mauna Loa Observatory	Free tropospheric net O_3 formation ~1.5 ppbv/day (24 hr average).	Cantrell *et al.* (1996a,b)
NARE	North Atlantic Ocean	In low troposphere anthropogenic O_3 exceeds O_3 transported by STE. Anthropogenic influence supported by alkyl nitrate measurements. Summertime pollution transports from N. America mostly confined to boundary layer. Pollutant plumes travel hundreds of km over N. Atlantic; strong H_2O_2 formation can occur (>4 ppbv).	Fehsenfeld *et al.* (1996); Roberts *et al.* (1996); Buhr *et al.* (1996); Daum *et al.* (1996)
POLINAT	North Atlantic flight corridor	Major aircraft exhaust signatures detected. Small fraction of NO_x is oxidized to HNO_3 in plumes.	Schlager *et al.* (1997)
NOXAR	Tropopause region at 10°-70°N	Background NO_x ~20-200 pptv. Extended areas with NO_x >1 ppbv.	Brunner (1998)
STRAT	Sub-tropical upper troposphere	Photolysis of acetone and peroxides from convective transports major OH source.	Jaeglé *et al.* (1997)
SUCCESS	Upper troposphere central U.S.	NO_x mostly from surface sources. Rapid uptake of HNO_3 by ice clouds.	Jaeglé *et al.* (1998); Weinheimer *et al.* (1998)
TOHPE	Colorado	Measured NO_x/OH relation in agreement with theory. Model calculations overpredict OH by ~50%, possibly due to heterogeneous chemistry.	Eisele *et al.* (1997); Mount and Williams (1997); McKeen *et al.* (1997)
PEM-West B	East Asia/northern Pacific Ocean	Troposphere throughout the Pacific Rim is influenced by Asian outflow. Confirmation that convection over land *is* and marine convection *is not* accompanied by significant lightning NO_x production. Upper tropospheric NO_y significantly influenced by lightning and aircraft exhausts. Measured NO_y partitioning can be reproduced by photochemical model.	Gregory *et al.* (1997); Kawakami *et al.* (1997); Koike *et al.* (1997); Thompson *et al.* (1997a)

8.3 ANTHROPOGENIC PERTURBATIONS TO TROPOSPHERIC OZONE

Much effort has been devoted to field campaigns to determine anthropogenic effects of the North American and Asian continents on the Atlantic and Pacific Oceans, respectively. Major field campaigns are listed in Tables 8-4 and 8-5. Regional campaigns have also been conducted to assess urban influences on rural tropospheric ozone and reactive nitrogen, NMHC, OH, hydroperoxy radicals (HO_2), peroxy radicals (RO_2), and other photochemically active species.

8.3.1 Northern Hemisphere

Whereas ozone is a major focus of major field experiments, precursor species have been measured with improved accuracy and precision, thus increasing confidence in calculation of ozone-forming tendencies and regional budgets. This section summarizes advances and gaps related to assessing global ozone in two areas: (1) long-range transport and regional studies; (2) advances in the understanding of NMHC and reactive nitrogen chemistry and climatologies. Assessment of progress in measuring and interpreting OH, HO_2, and RO_2 is covered in Section 8.6.

8.3.1.1 TROPOSPHERIC OZONE AND TRANSPORT

In the 1993 North Atlantic Regional Experiment (NARE) summertime intensive (Table 8-4), much of the ozone northeast of the American continent is attributed to North American emissions (Fehsenfeld *et al.*, 1996). Although elevated CO is a tracer for the anthropogenic origin of the ozone, the sum of C1-C4 hydrocarbons may be an even stronger indicator of the human input to photochemical ozone formation (Roberts *et al.*, 1996). In some cases well-defined pollution plumes leave the North American continent at altitudes below about 2 km (Daum *et al.*, 1996; Kleinman *et al.*, 1996). Such plumes can travel hundreds of km over the North Atlantic, with up to 20 ppbv NO_y, 480 ppbv CO, and 150 ppbv ozone. Hydrogen peroxide (H_2O_2) levels of 4 ppbv were encountered during NARE, with excursions to over 11 ppbv (Weinstein-Lloyd *et al.*, 1996). In the relatively cleaner free troposphere, H_2O_2 appeared to correlate strongly with the product of ozone and water vapor, consistent with our understanding of gas-phase H_2O_2 formation under relatively NO_x-poor conditions. Note that from surface sampling of ozone at Mace Head (Ireland, 53°N, 9°W), it is deduced that surface destruction of ozone is effective. The seasonal ozone maximum occurs in spring, not during the summer North American maximum.

Similar conclusions about transport of ozone downwind from a major continental source can be drawn from the trace gas measurements that were part of the APARE (East Asian-North Pacific Regional Experiment) NASA DC-8 PEM-West A (Pacific Exploratory Mission, September-October 1991) and PEM-West B (February-March 1994) experiments. Typical profiles from the airborne lidar and in situ ozone instruments for the PEM-West A campaign appear in Figure 8-3. Westerly winds transported pollutant plumes with ozone mixing ratios of about 60-80 ppbv to the Pacific. These plumes were not always industrial in origin, but were sometimes of biomass-burning origin. Most Asian pollution was transported below 2 km altitude toward the North Pacific (Talbot *et al.*, 1996), but significant transport also occurred at 8-12 km (Gregory *et al.*, 1997). Hydrocarbon tracers confirm that most of the upper-level ozone originates from convectively transported pollution from Asia (Blake *et al.*, 1996). However, acetylene/CO ratios indicate some contributions from larger distances farther away (Smyth *et al.*, 1996).

Stratosphere-troposphere exchange (STE) played a role in enriching tropospheric ozone levels during PEM-West A; even at low latitudes ozone reached 40-60 ppbv as a result of this transport. However, at low latitudes and low altitudes in the western Pacific region during late summer and fall, easterly winds prevailed, carrying clean ozone-poor air (<10 ppbv) to the continent. This clean air is comparable to the low O_3 concentrations recorded by balloonborne ozonesondes over the equatorial central Pacific by Kley *et al.* (1996).

Mauna Loa, Hawaii (20°N, 156°W, at 3.4 km elevation), is a ground station in the free troposphere that gives the chemical composition in a northeasterly trade wind regime (Atlas and Ridley, 1996). A 20-year surface ozone record has been obtained for Mauna Loa (Oltmans *et al.*, 1996), showing that ozone is relatively abundant in the winter-spring half year, with a maximum reached in March through May. Trajectories show that this coincides with large-scale descending motion and, therefore, it is assumed that stratospheric intrusions have a large influence on the mean ozone concentration. Model calculations are in agreement with this assumption (Roelofs and Lelieveld, 1997). Polluted Asian air masses are indicated as contributors to the springtime maximum

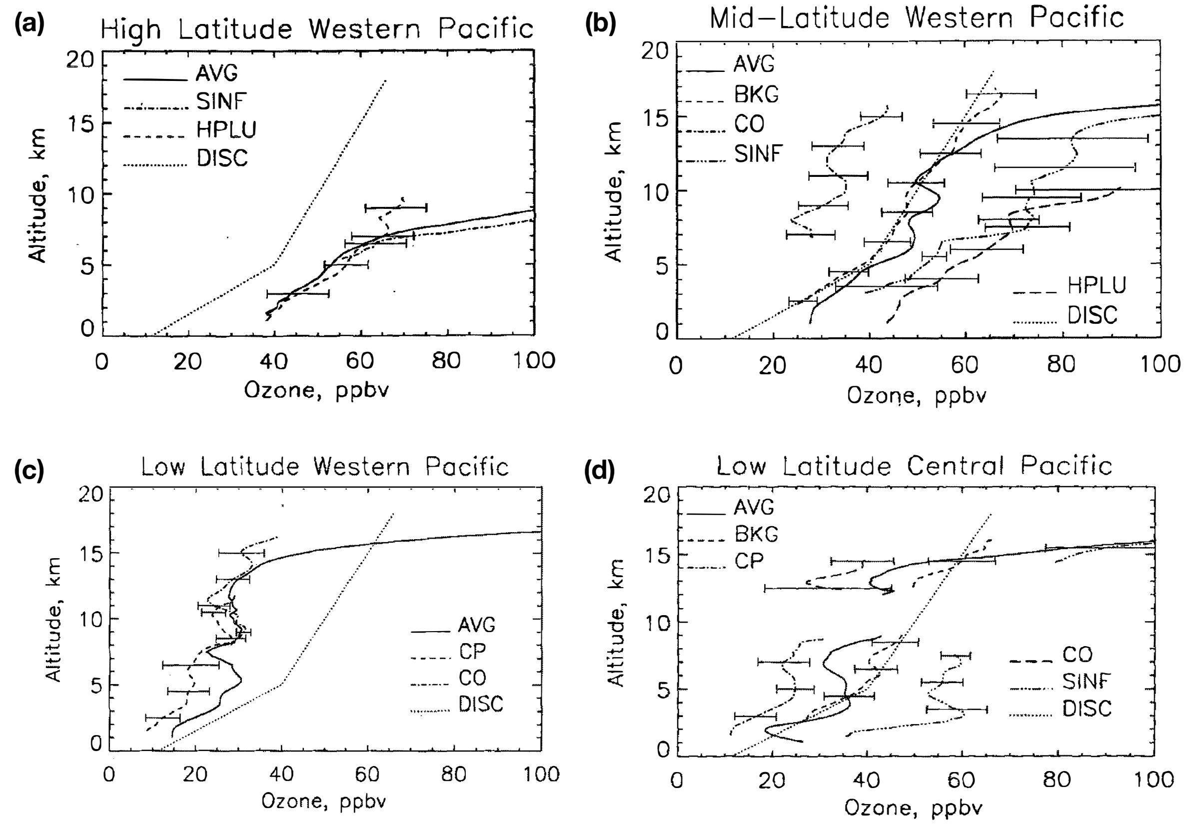

Figure 8-3. Panel (a): Overall average O_3 profile (AVG) for Pacific high-latitude region (40°-60°N, 150°E-160°W), average O_3 profile for STE-influenced air (SINF), and plumes with enhanced O_3 (HPLU), shown relative to a reference profile (DISC = discriminator), i.e., the average of O_3 profiles in air relatively unaffected by recent sources. Horizontal bars represent the 1-sigma standard deviation (Browell *et al.*, 1996a). Panel (b): Overall average O_3 profile (AVG) for western Pacific midlatitude region (20°-40°N, 110°-150°E), for background air (BKG), convective outflow (CO), STE influenced (SINF) and high O_3 plume (HPLU). Panel (c): Ozone profiles for western Pacific low latitude air (0°-20°N, 110°-150°E), including clean Pacific O_3 profile (CP). Panel (d): Ozone profiles for low-latitude central Pacific region (0°-20°N, 150°E-160°W).

(Oltmans *et al.*, 1996); ambient ozone precursors, CO and NMHC, are highest at this time (Greenberg *et al.*, 1996). Periods of high NO_y (~2 ppbv) can persist for several days, which are traceable to Asia (Ridley *et al.*, 1997).

8.3.1.2 Hydrocarbons and Reactive Nitrogen

The combined influence of anthropogenic and biogenic NMHC affects photochemical ozone formation in remote regions. These impacts have been evaluated in recent experiments; the following examples show that the influences can be detected near urban regions in midlatitude continental areas, as well as at sparsely populated high latitudes.

Measurements in the southeastern U.S. during summer show that isoprene contributes more than half the hydrocarbon reactivity (Lawrimore *et al.*, 1995), with a large impact on ozone formation. Measurements by O'Brien *et al.* (1995) suggest that isoprene nitrate formation may be important. If nitrates formed in isoprene and terpene chemistry efficiently partition in the aerosol phase (Hoffmann *et al.*, 1997), these processes would sequester NO_x and suppress ozone formation.

Solberg *et al.* (1996) present several years of measurements of C2-C5 NMHC and carbonyl compounds at a number of European rural monitoring stations from the Arctic to the Mediterranean (79°-42°N latitude). They conclude that releases of natural gas and

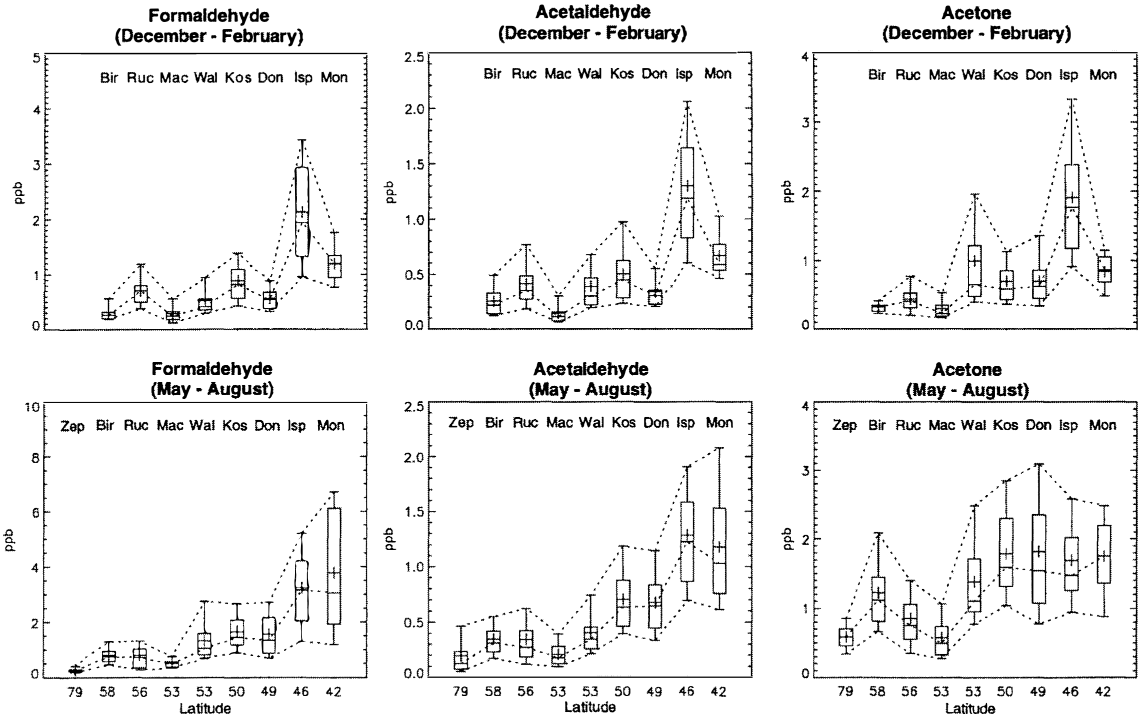

Figure 8-4. Percentiles and mean concentrations of observed carbonyl compounds during winter (3 months) and summer (4 months) at a number of European locations from the Arctic to the Mediterranean: Zeppelin Mountain (79°N, 12E°), Birkenes (58°N, 8°E), Rucava (56°N, 21°E), Mace Head (53°N, 9°W), Waldhof (53°N, 11°E), Kosetice (50°N, 15°E), Donon (48°N, 7°E), Ispra (46°N, 9°E), and Montelibretti (42°N, 13°E) (Solberg *et al.*, 1996).

fuel evaporation are among the main sources of light hydrocarbons in Europe (Figure 8-4). During winter the fraction of carbonyls compared to C2-C5 NMHC is about 5-15%; in summer this is close to 50%, consistent with the expected higher yield from NMHC oxidation.

Recent measurements under semi-polluted conditions confirm earlier speculations that nighttime peroxy radical formation may be important (Carslaw *et al.*, 1997). This could contribute to significant OH formation, although at least an order of magnitude less than during daytime. Relatively high levels of nitrate radicals (NO_3) (~10 pptv) play an important role in nighttime chemistry under these conditions (Heintz *et al.*, 1996).

Measurements in the marine upper troposphere are not always consistent in providing evidence for anthropogenic influences on NO_x and ozone. Reactive nitrogen measurements over the western North Pacific during PEM-West A indicate that a significant fraction of NO_y cannot be accounted for by the sum of NO_x+HNO_3+PAN (Smyth *et al.*, 1996; Singh *et al.*, 1996). However, for PEM-West B, 85% of the total reactive nitrogen in the upper troposphere was accounted for by these constituents; model calculations showed that the remainder could be explained by pernitric acid (HNO_4), methyl peroxy nitrate ($CH_3O_2NO_2$), and alkyl nitrates (Thompson *et al.*, 1997a).

Measurements of nitrogen oxides close to the tropopause are important to assess the role of aircraft emissions and their contribution to ozone formation and radiative forcing of climate. Liu *et al.* (1996) estimate that stratospheric N_2O destruction was the source of 25% of reactive nitrogen in the upper troposphere on PEM-West A, lightning and convective transport of surface emissions contributed another 25%, and subsonic aircraft contributed about 50%. The climatology of NO and NO_x prepared by Emmons *et al.* (1997) has been augmented by the NOXAR (Nitrogen OXide and ozone concentration measurements along Air Routes) experiment. A B-747 aircraft equipped with instruments

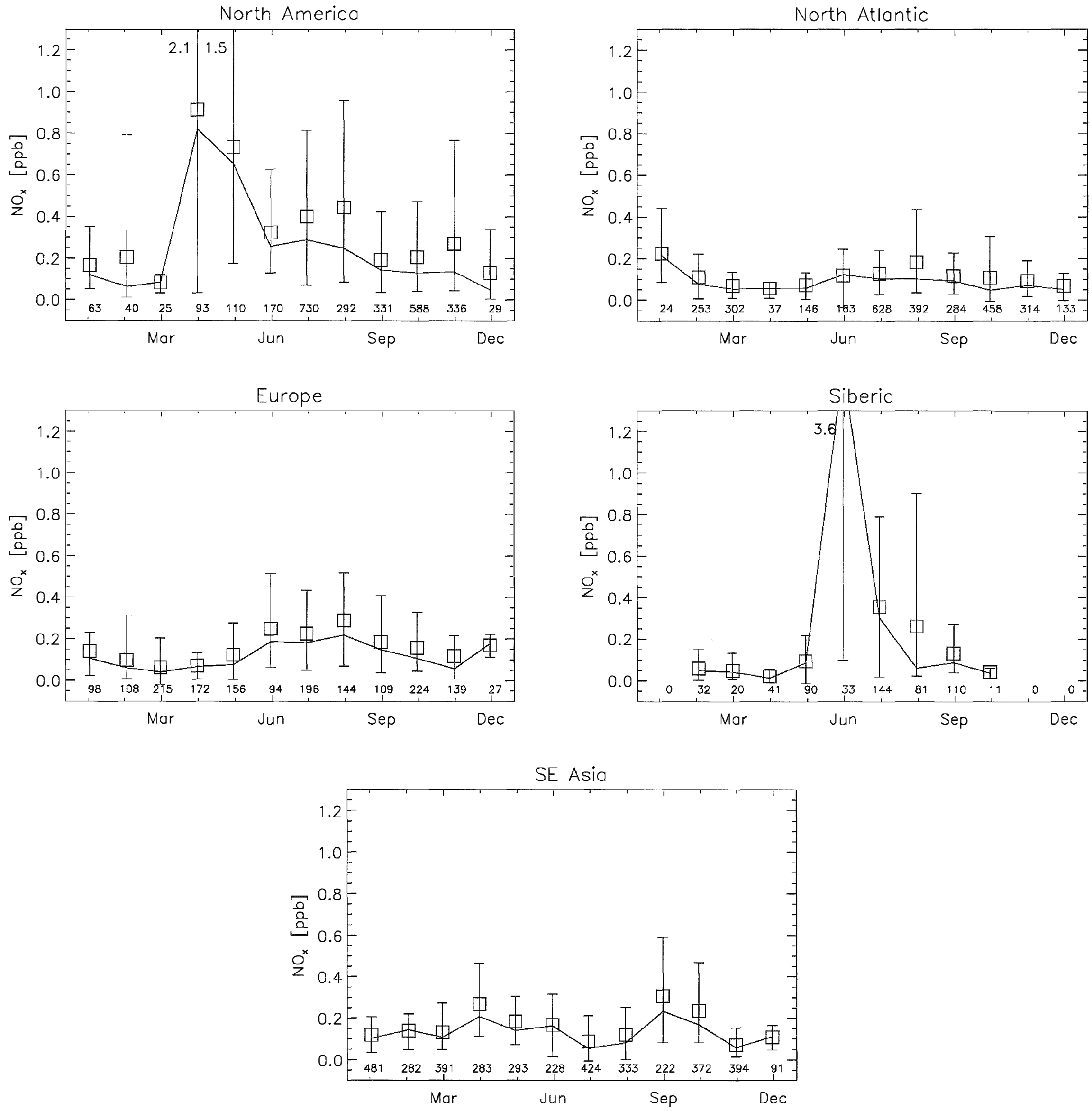

Figure 8-5. Seasonal variation of the monthly mean NO$_x$ concentrations of the upper troposphere from the NOXAR (Nitrogen OXide and ozone concentration measurements along Air Routes) programme. The tropopause altitude was calculated by using the 2-PVU (potential vorticity unit) surface from European Centre for Medium-Range Weather Forecasts (ECMWF) analyses. Median values are connected by solid lines. Squares denote monthly mean values and the vertical bars represent the range between the 10% and 90% quantiles of the monthly distributions. Numbers at the bottom denote the sample size (2-minute averages). Latitude and longitude range of the four selected regions: North America: 30-60°N, 60-90°W (90% quantiles for April and May: 2.1 and 1.5 ppbv); North Atlantic: 40-60°N, 10-40°W; Europe: 40-60°N, 0-30°E; Siberia: 50-70°N, 60-90°E; Southeast Asia, 10-30°N, 70-120°E (June: mean 1.7 ppbv, median: 1.5 ppbv) (Brunner, 1998).

for NO, nitrogen dioxide (NO_2), and O_3 measurements (Brunner, 1998) operated from Zürich to destinations in the U.S. and the Far East. Large NO_x plumes with concentrations of several ppbv were frequently observed in the vicinity of aircraft. Further, NO_x concentrations up to more than 1 ppbv were observed over extended areas (100-1500 km); these were ascribed to continental pollution. The results of upper tropospheric NO_x measurements from more than 500 flights for regions sampled between spring 1995 and spring 1996 are depicted in Figure 8-5. It is difficult to generalize about NO_x sources. Jaeglé *et al.* (1998) infer from the springtime SUCCESS experiment (SUbsonic aircraft: Contrail and Cloud Effects Special Study) that over the central U.S., convectively transported surface NO_x was the predominant upper tropospheric NO_x source.

The high latitude lower troposphere in the Northern Hemisphere has been studied for many years because pollutants accumulate in this region during winter. Measurements in Svalbard (79°N, 12°E) and Poker Flat, Alaska (65°N, 147°W), of O_3, PAN, and several important ozone precursors by Beine *et al.* (1997) and Herring *et al.* (1997) show that PAN decomposition at these locations in spring appears to be a significant NO_x source. Whereas the NO_x is probably mostly of anthropogenic origin, transported to the region as PAN, much of the NMHC may be natural.

8.3.2 Southern Hemisphere: Effects of Biomass Burning on Ozone

The striking feature of the Southern Hemisphere is the large-scale tropospheric ozone enhancement observed over the tropical Atlantic in the austral spring. High column ozone (50 Dobson units (DU) or more) extends from South America across the Atlantic, over Africa and at subtropical latitudes, to the Indian Ocean (Fishman *et al.*, 1990). Since the last Assessment (WMO, 1995), the contribution of biomass burning on the African and South American continents during the dry season to this maximum (Browell *et al.*, 1996a; Fishman *et al.*, 1996; Thompson *et al.*, 1996a,b) was confirmed by observations during the TRACE-A (Transport and Atmospheric Chemistry near the Equator-Atlantic) and SAFARI (Southern African Fire-Atmosphere Research Initiative) campaigns. Key findings of these campaigns and other Southern Hemisphere experiments appear in Table 8-5.

Several issues not yet resolved during the SAFARI/TRACE-A campaigns are: (1) fire emissions of trace gases over the southern African continent, based on remotely sensed fire counts and emissions factors (Scholes *et al.*, 1996b; Justice *et al.*, 1996), were much lower than previously thought; for example, they were too low to support CO calculated by global models; (2) African savanna soils appear to be a greater source of biogenic NO_x than previously estimated; (3) lightning NO_x played a significant role in upper tropospheric ozone formation, but this is not yet quantified (Thompson *et al.*, 1996a,b); (4) in southern Africa south of 20°S, an in situ, non-biomass-burning source may have dominated the local ozone budget (Tyson *et al.*, 1997).

During SAFARI/TRACE-A, the role of transport was clarified by a trajectory climatology (Garstang *et al.*, 1996) and a global circulation model study (Krishnamurti *et al.*, 1996). Surface emissions are trapped in the lower atmosphere in a large-scale anticyclonic recirculation extending over hundreds to thousands of kilometers, leading to the accumulation of ozone and ozone precursors (Tyson *et al.*, 1996; Thompson *et al.*, 1996a). Elevation to the upper levels can only occur during periodic synoptic-scale disturbances or at the beginning of the wet season, when convective activity commences. Exit from the African subcontinent occurs both to the west, where the dominant pathway is in the semi-permanent easterly wave and occurs below the 3 km stable layer, and to the east, as a rising plume below the 5-km stable layer. South of 20°S, transport to the Indian Ocean is dominant, accounting for over 90% of the trajectory pathways, which explains high ozone concentrations observed over the Indian Ocean. Ozone downwind from African burning was detected over the western subtropical Pacific during the PEM-Tropics A field mission in September 1996 (Schultz *et al.*, 1998).

In Brazil, the presence of enhanced tropospheric ozone at the ozonesonde station of Natal has long been ascribed to biomass burning in the dry season (August-October) (Logan and Kirchhoff, 1986). Observations (Kirchhoff *et al.*, 1996) have shown that the difference between sites close to the biomass burn source region and a control site is greater in the lower 2 km than in the upper troposphere. The role of convective transport in contributing to elevated ozone over South America and the Atlantic, which had been predicted in earlier modeling studies (Thompson *et al.*, 1997b), was confirmed from observations taken during the TRACE-A experiment. Following deep convection, downwind ozone production

Table 8-5. Summary of major findings from campaigns in the Southern Hemisphere.

Campaign	Location	Key Findings	Authors
CITE 3	Western Atlantic Ocean	Substantially greater lower tropospheric ozone (0-3.3 km) in SH (13.5 DU) than NH (5 DU), due to long-range transport of biomass burn products and subsidence in South Atlantic anticyclone.	Anderson *et al.* (1993)
R/V *Polarstern* meridional transects	Central Atlantic Ocean	Lower tropospheric ozone greater in NH than SH. Free tropospheric ozone (4-8 km) ~120 ppbv in SH and ~50 ppbv in NH. Unable to distinguish between biomass burning and O_3 of stratospheric origin.	Weller *et al.* (1996)
SAFARI	Southern Africa	Total tropospheric ozone 40-56 DU, compared with background of 28 DU. Co-incidence with high CO, CH_4, CO_2 confirms O_3 source as biomass burning. Trace gas emissions from savanna fires less than previous findings (14.9 Tg CO and 1.06 Tg NO_x). African savanna soils are a significant source of biogenic emissions.	Browell *et al.* (1996b); Thompson *et al.* (1996a); Scholes *et al.* (1996a,b); Parsons *et al.* (1996); Levine *et al.* (1996)
SOAPEX	Tasmania	Baseline photochemistry in cloud-free clean boundary layer well characterized.	Penkett *et al.* (1997)
ACE-1	Tasmania, marine boundary layer	Direct airborne OH measurements show very high OH above cloud; chemical OH sink in clouds is confirmed.	Mauldin *et al.* (1997)
SCATE	Antarctic marine boundary layer	DMS lifetime due to OH reaction confirmed. DMS oxidation by OH mostly in buffer layer, i.e., above boundary layer.	Berresheim and Eisele (1998); Davis *et al.* (1998)
PACE-I aircraft transects	Western Pacific Ocean	Low ozone (<20 ppbv) at equator due to photochemical destruction. Higher ozone (>50 ppbv) between 12-20°S where air originated over Australia.	Tsutsumi *et al.* (1996)
TRACE-A	Brazil and Atlantic Ocean	High-level outflow from Brazil contributes 20-30% of excess tropospheric ozone in South Atlantic. Low-level African outflow accounts for 70%. South Atlantic ozone maximum due to biomass burning plus long residence times in the atmosphere, deep convective activity, lightning and biogenic sources. Convective storms are responsible for redistribution of trace gases. Ozone production in cloud outflow region ~7-8 ppbv/d.	Thompson *et al.* (1996a); Pickering *et al.* (1996)

(7-8 ppbv/day) was detected by ozonesonde measurements in Natal and Ascension Island (Pickering *et al.*, 1996).

Ozone soundings taken at Cuiabá during the 1995 SCAR-B (Smoke, Clouds and Radiation-Brazil) (Kaufman *et al.*, 1998) experiment showed much higher ozone concentrations in the boundary layer than the Cuiabá soundings during TRACE-A. The reasons were both the amount of biomass burning (much higher in 1995 than in 1992), as well as less deep convection and a stable boundary layer during SCAR-B. Trajectory analysis and smoke aerosol, used as a tracer with ozone, showed some urban as well as biomass burning contributions.

Marked contrasts between the Northern and Southern Hemisphere tropospheric ozone over the Atlantic Ocean are noted by Anderson *et al.* (1993) and Weller *et al.* (1996), who reported on the CITE 3 (Chemical Instrument Test and Evaluation) and R/V *Polarstern* experiments, respectively. Substantially more lower tropospheric ozone is present in the southern tropics (13.5 DU between the surface and 3.3 km) compared with the northern tropics (5.0 DU) (Anderson *et al.*, 1993). Weller *et al.* (1996) noted that in the Northern Hemisphere free troposphere, ozone mixing ratios seldom exceed 80 ppbv, whereas in the Southern Hemisphere there is a strong ozone summer and spring maximum (values up to 120 ppbv) situated between 4 and 8 km in the tropics (0-20°S).

Tropospheric ozone enhancement in the Indian Ocean, downwind of biomass burning, is noted in the ozonesonde observations on Réunion Island (21°S, 55°E). Middle tropospheric ozone enhancements (>80 ppbv) in the September to November period, are linked through trajectory analysis to regions of active biomass burning over continental areas to the west of Réunion (Baldy *et al.*, 1996; Diab *et al.*, 1996). A similar seasonal behavior may occur over Indonesia, but there are fewer in situ observations to confirm this (Komala *et al.*, 1996).

8.4 KEY PROCESSES IN THE TROPOSPHERE

8.4.1 Gas-Phase Processes

In order to assess tropospheric ozone perturbations, mechanisms of formation and loss must be well defined. The basic steps have been known for some time and were described in the previous Assessment (WMO, 1995; Chapter 7). This section summarizes updates in processes affecting tropospheric ozone and OH.

The temperature dependence of ozone photolysis (Talukdar *et al.*, 1998) leads to $O(^1D)$ formation rates being larger than previously believed; this means more rapid photochemical loss and greater OH formation, up to a factor of 3 times greater in the free troposphere during the fall and spring.

In the lower troposphere the formation of nitric acid (HNO_3) is a major sink of NO_x, competing with cycling of NO_x that leads to ozone formation. A laboratory study by Donahue *et al.* (1997) measured the room-temperature rate constant of the reaction $OH + NO_2\ (+M) \rightarrow HNO_3\ (+M)$ to be 10-30% lower than determined by previous studies.

The dominant fate of organic peroxy radicals is to produce alkoxy radicals (RO); RO formation is critical in OH-HO_2 cycling and ozone yields. However, RO can also decompose or isomerize, implying uncertainties in ozone formation. It is possible that during the oxidation of complex hydrocarbon molecules, more than one alkyl radical and, subsequently, several peroxy radicals and ozone molecules are generated.

Donahue *et al.* (1998) reported the direct observation of OH formation in the flow tube reaction of a series of olefins with ozone. However, experimental work at atmospheric pressure in air by Schäfer *et al.* (1997) gives evidence that OH radicals are not directly produced from the olefin-ozone reaction in the troposphere. In view of these conflicting results, the issue must be considered unresolved for the time being.

Another significant update to OH and ozone mechanisms has been the finding that acetone (CH_3COCH_3) is ubiquitous at concentrations up to several ppbv (Arnold *et al.*, 1997) that render it a potentially important OH source in the free troposphere (Singh *et al.*, 1995). Acetone sources include biomass burning, direct biogenic emissions, and atmospheric NMHC breakdown. Acetone photodissociation yields CH_3O_2 and peroxyacetyl radicals, from which HO_x and PAN are formed, respectively, with the latter a NO_x source in the upper troposphere. With OH measurements in the upper troposphere now available from aircraft (Section 8.6), modeling studies are better constrained in determining the significance of acetone photodissociation as an OH source. Under conditions of the Stratospheric Tracers of Atmospheric Transport (STRAT) and SUCCESS experiments, acetone was a more important OH source than $O(^1D) + H_2O$ due to the low ambient water vapor pressure (Jaeglé *et al.*, 1997). Model calculations by Prather and Jacob (1997) suggest that photolysis of peroxides, notably CH_3OOH, that have been transported from the boundary layer by deep convection, contribute to OH formation as well.

8.4.2 Uncertainties in Gas-Phase Processes

Section 8.5.3 describes the propagation of kinetics inaccuracies in model calculations. Although uncertainties in many processes can be now be assessed, the chemistry of organic compounds remains a major source of uncertainty in chemical mechanisms affecting ozone and OH. Even the predictions of highly detailed explicit mechanisms derived completely from first principles are uncertain because, in spite of extensive recent research (DeMore *et al.*, 1997; Le Bras, 1997; Atkinson *et al.*, 1998), there continues to be a dearth of laboratory kinetics data. Although the rate constants for the primary reactions of OH, O_3, and NO_3 with many organic compounds have been measured, there have been relatively few product yield studies or studies aimed at understanding the chemistry of reaction products.

There is little available data on the chemistry of compounds with carbon numbers greater than 3 or 4 and most of the chemistry of these compounds is based upon extrapolating experimental studies of the reactions of lower molecular weight compounds. The chemistry of intermediate oxidation products, including aldehydes, ketones, alcohols, and ethers, is particularly significant for biogenics like isoprene and terpenes (Stockwell *et al.*, 1997). The most recent detailed mechanism for isoprene underpredicts PAN by about 40% for isoprene/NO_x experiments even though PAN is predicted well for methylvinyl ketone/NO_x and methacrolein/NO_x experiments (Carter and Atkinson, 1997).

The reactions of peroxy radicals (RO_2) can be important under nighttime conditions when nitric oxide concentrations are low. The RO_2-RO_2 reactions and NO_3-RO_2 reactions lower PAN concentrations by about 40% and increase organic peroxide concentrations by about 25% through their impact on nighttime chemistry (Stockwell *et al.*, 1995; Kirchner and Stockwell, 1996, 1997).

8.4.3 Heterogeneous and Multiphase Processes

Heterogeneous reactions are defined as those reactions that occur on the surfaces of aerosol particles and droplets, whereas multiphase reactions are those that occur in a bulk liquid such as cloud water or deliquesced aerosol particles. It has been proposed, and in some cases, demonstrated through model sensitivity studies, that these processes have a significant effect on tropospheric constituents. An evaluation of some of these processes is given in Ravishankara (1997).

Particles may affect gas-phase tropospheric concentrations through both chemical and physical processes. Reactions occurring on aerosol particles or in cloud water droplets may have a significant effect on tropospheric constituents either directly, or indirectly through a perturbed radiation field (Baker, 1997; Andreae and Crutzen, 1997). Sedimentation of aerosol particles or rainout removes soluble species from the gas phase, leaving behind relatively insoluble species. The following is a summary of heterogeneous processes for which calculations or observations suggest some significance, but for which a complete assessment is still lacking:

(a) Formation of ozone is suppressed by the removal of HO_2 radicals and highly reactive stable species such as formaldehyde (HCHO) (Lelieveld and Crutzen, 1991). This process is thought to be most effective under clean conditions; Jonson and Isaksen (1993) calculated an ozone reduction between 10 and 30% globally for NO_x-poor conditions. (Section 8.6.2 describes observations of HO_2 loss in clouds.) A study by Liang and Jacob (1997), however, derives an effect of merely about 3% globally on tropospheric ozone through cloud removal of HO_x. Zhang *et al.* (1998) derive much larger effects, for example, in-cloud O_3-formation reductions up to 100%. Hence uncertainties remain large.

(b) Dissolved transition metals such as copper, iron, and manganese may counteract ozone reduction effects by clouds. Calculations show that the ozone destruction rate by clouds is decreased by 45 to 70% for clean conditions (Matthijsen *et al.*, 1995; Walcek *et al.*, 1997). In polluted areas with high NO_x concentrations, the photochemical formation rate of ozone is also decreased (Lelieveld and Crutzen, 1991). Matthijsen *et al.* (1995) concluded that the reaction between Fe(II) and ozone increases the ozone destruction rate in polluted areas by a factor of 2 to 20 depending on the iron concentration. PAN may be converted to NO_x through the scavenging of acetyl peroxy radicals by cloud water, even though PAN itself is not very soluble (Villalta *et al.*, 1996). This process tends to increase ozone concentrations.

(c) The most important multiphase reactant is often water, and many hydrolysis reactions have a somewhat heterogeneous character because the reactions are so fast that they are completed at or very near to the water surface (Hanson *et al.*, 1994). N_2O_5 rapidly hydrolyzes in the presence of liquid water, whereas its reaction with H_2O is extremely slow in the gas phase (DeMore *et al.*, 1997).

(d) Organic-containing aerosols formed from emissions of organic compounds from biogenic and anthropogenic sources may be important (Mazurek *et al.*, 1991; Odum *et al.*, 1997). There is increasing evidence that the organic fraction of aerosols is considerable (Smyth *et al.*, 1996).

(e) The marine boundary layer contains sea-salt aerosols that contain high concentrations of halides. Halides and their reaction products may be released from the sea-salt aerosols through the scavenging and reactions of compounds such as NO_3, N_2O_5, and HOBr (Vogt *et al.*, 1996; Sander and Crutzen, 1996). The water content of the sea-salt aerosol may be an important variable for characterizing the chemistry of these aerosols (Rood *et al.*, 1987; Ravishankara, 1997).

(f) Heterogeneous reactions occurring on ice, wind-blown dust, fly ash, and soot may be important (Dentener *et al.*, 1996). Heterogeneous reactions on cirrus clouds involving ice, N_2O_5, and other species may be important in removing reactive nitrogen from the upper troposphere. Borrmann *et al.* (1997) detected reactive chlorine within upper tropospheric cirrus clouds, which may contribute to in situ ozone loss. Weinheimer *et al.* (1998) obtained observational evidence for HNO_3 removal on wave cloud particles and concluded that all the ambient nitric acid (25-75 pptv) was depleted within a couple of minutes after ice cloud formation. Soot may reduce HNO_3 to NO_x (Hauglustaine *et al.*, 1996a; Rogaski *et al.*, 1997; Lary *et al.*, 1997).

Incorporation of nitric acid and other solubles in ice clouds may contribute to their vertical redistribution. Gravitational settling and evaporation of cloud droplets and ice particles can induce a significant downward flux of HNO_3 and H_2O_2, and affect related trace gases such as OH and NO_x (Lawrence and Crutzen, 1998). This finding may help explain why many models tend to overestimate HNO_3 in the upper troposphere.

8.5 GLOBAL MODELING OF TROPOSPHERIC OZONE AND RELATED SPECIES

Since the previous Assessment (WMO, 1995), many studies have been published in which global 3-D models are used to represent the complex interactions among the ozone precursors, e.g., NO_x and CO, loss processes, and physical and chemical variability determined by meteorological conditions in the troposphere. Table 8-6 lists results from several global CTMs (chemistry-transport models) now in use. Both dynamical (Section 8.5.1) and chemical mechanisms (Section 8.5.2) of these models have been intercompared. Models have been evaluated through comparisons with observations (Section 8.5.4), although comprehensive data are limited to intensive field campaigns, which are sparse in spatial and temporal coverage. This picture should change as more satellites with tropospheric sampling capabilities become available.

8.5.1 Intercomparison of Model Transport Schemes

Transport properties are evaluated through tracer tests. Radon-222 (^{222}Rn), which is emitted from soils and has a radioactive lifetime of 5.5 days, is used for evaluation of model simulation of small-scale meteorological processes, such as boundary layer venting by convection and frontal activity. Jacob *et al.* (1997) summarized a study of 20 global models for which comparison with ^{222}Rn was made to intercompare parameterizations of sub-grid convection. Although models tended to capture the location and timing of synoptic weather systems, ^{222}Rn concentrations in the upper troposphere were often ill-simulated, indicating that deep convection is not well represented. Upper tropospheric simulations are highly sensitive to the treatment of moist convection (Mahowald *et al.*, 1995) and to the spatial scale of deep convection (Lelieveld and Crutzen, 1994; Pickering *et al.*, 1995).

The limitations of present-day treatments of transport in global 3-D models are a major source of uncertainty in the global model assessment of tropospheric ozone. For example, Allen *et al.* (1996) used a model that simulates transport based on data assimilation for a multi-year simulation. They found that transport of the ozone precursor CO may explain up to 90% of the CO interannual variability at coastal

Table 8-6. Processes affecting tropospheric O_3 in global chemistry-transport models (Tg O_3/yr).

Model Reference	Stratospheric Input	Dry Deposition	Photochemical Production	Photochemical Loss	Net Effect Photochemistry
Müller and Brasseur (1995)	550	1100	4550	4000	550
Berntsen and Isaksen (1997)	846	1178			295
Levy *et al.* (1997)	696	825			128
Roelofs *et al.* (1997)	459	534	3415	3340	75
Houweling *et al.* (1998)	768	681	3979	4065	-86
Wang *et al.* (1998a)	400	820	4100	3680	420
Range	**400-846**	**534-1178**	**3425-4550**	**3350-4065**	**-86-550**

monitoring stations and at least 50% of the CO variability at some remote marine locations. This complicates assessment of ozone impacts of source changes in global models over time scales of only a few years (Novelli *et al.*, 1998).

8.5.2 Intercomparison of Gas-Phase Chemical Mechanisms

Assessments with 3-D global models are limited by unknowns in the chemical schemes used. Further uncertainties in results come from the fact that a range of values is obtained by a set of models due to variations in photodissociation schemes. In describing an intercomparison activity undertaken for the 1995 Intergovernmental Panel on Climate Change assessment (IPCC, 1996), Olson *et al.* (1997) showed that with 24 models, using their own photolysis schemes, many differences could be attributed to differences in calculated photolysis frequencies, especially for O_3, NO_2, HCHO, and H_2O_2.

Kuhn *et al.* (1998) extended the IPCC exercise to scenarios that are more typical for relatively polluted air on a regional scale; cases were selected to represent atmospheric conditions for Europe. By prescribing photolysis frequencies, Kuhn *et al.* (1998) ensured that differences in results from different mechanisms were due to gas-phase chemistry representations. Similar ozone concentrations resulted for the lower troposphere, but deviations among ozone-forming tendencies were considerable: 15 to 38% depending upon the conditions. For the OH radical, noontime differences among mechanisms ranged from 10 to 19%; for the NO_3 radical, a regionally important nighttime oxidant, differences were up to 40%. Calculated concentrations of other species like H_2O_2 and PAN differed considerably between the mechanisms. For H_2O_2 the root mean square errors of the tendencies ranged from 30 to 76%; some of this variability was explained by the incorrect use of the HO_2 + HO_2 reaction rate constant (Stockwell, 1995) and by differences in the treatment of peroxy radical interactions.

8.5.3 Uncertainties in Chemical Mechanisms

Increasing effort has been given to uncertainty analysis of model reaction schemes as well as to intercomparison of models. These are based on recommendations for the uncertainties associated with kinetic data by review panels, e.g., the International Union of Pure and Applied Chemistry (IUPAC) (Atkinson *et al.*, 1998) and NASA (DeMore *et al.*, 1997), that evaluate rate coefficients for use in atmospheric chemistry models.

Several methods of analyzing how rate coefficient uncertainties propagate into model-computed mixing ratios have been used. The sensitivity of chemical concentrations to small variations in rate parameters, as in the direct decoupled method (Dunker, 1984;

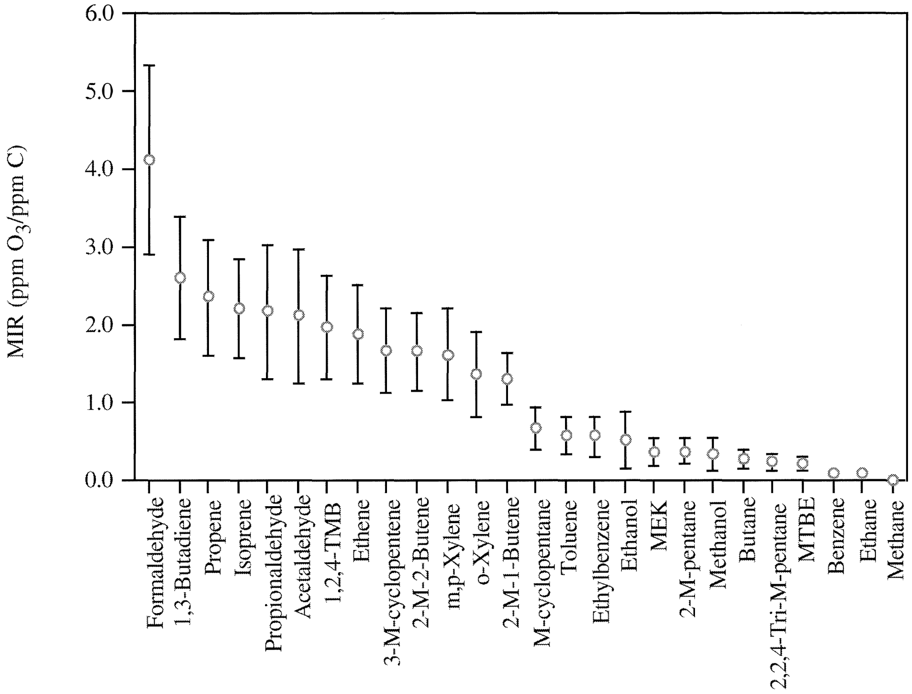

Figure 8-6. Mean values and 1-σ uncertainties of maximum incremental reactivity (MIR) values for selected hydrocarbons determined from Monte Carlo simulations (Yang *et al.*, 1995).

McCroskey and McRae, 1987), is one method that has been used for lower tropospheric studies. Ozone concentrations are particularly sensitive to the photolysis rates of NO_2 and O_3 and the formation and decomposition rates of PAN. The same conclusion was reached by a random variation of rate coefficients in a Monte Carlo approach (Stewart and Thompson, 1996; Thompson *et al.*, 1997a). The calculated ozone concentration is also sensitive to coefficients of reactions of peroxy radicals with NO, OH + CO, and OH + organic compounds, which are important sources of peroxy radicals (Stockwell *et al.*, 1995).

Refinements to lower tropospheric Monte Carlo studies made by Gao *et al.* (1996) with Latin hypercube sampling showed that the rate parameter for the reaction $OH + NO_2 \rightarrow HNO_3$ is highly influential due to its role in removing NO_x and radicals. Ozone photolysis and the rate parameter for the reaction $HCHO + h\nu \rightarrow 2HO_2 + CO$ strongly influence radical sources. For urban-influenced conditions, Gao *et al.* (1996) showed that uncertainties in peak ozone concentrations over a 12-hour simulation vary from ~20 to 50%.

Monte Carlo analysis has also been applied to ozone-forming potentials for evaluation of maximum incremental reactivities (MIR) due to variations in assumed organic composition (Figure 8-6) (Yang *et al.*, 1995). Relatively unreactive compounds tended to lead to greater ozone uncertainties than more reactive compounds because the latter reacted completely over the 10-hour simulation period.

Monte Carlo calculations addressing inaccuracies in temperature-dependent rate coefficients yielded uncertainties of ~20% and 40% for calculated ozone and H_2O_2 concentrations, respectively, in the upper troposphere (Stewart and Thompson, 1996). Although NMHC complicate calculation of ozone and OH in the lower troposphere, addition of more complex NMHC chemistry to a methane and ethane-only kinetics scheme showed only small changes in computed mixing ratios in the upper troposphere (Thompson *et al.*, 1997a).

8.5.4 Global and Regional Ozone Budgets

Recent global 3-D model studies suggest that the amount of ozone that is photochemically produced in the troposphere amounts to about 3500-4500 Tg/yr, which is largely balanced by chemical loss (e.g., Müller and Brasseur, 1995; Berntsen and Isaksen, 1997; Levy

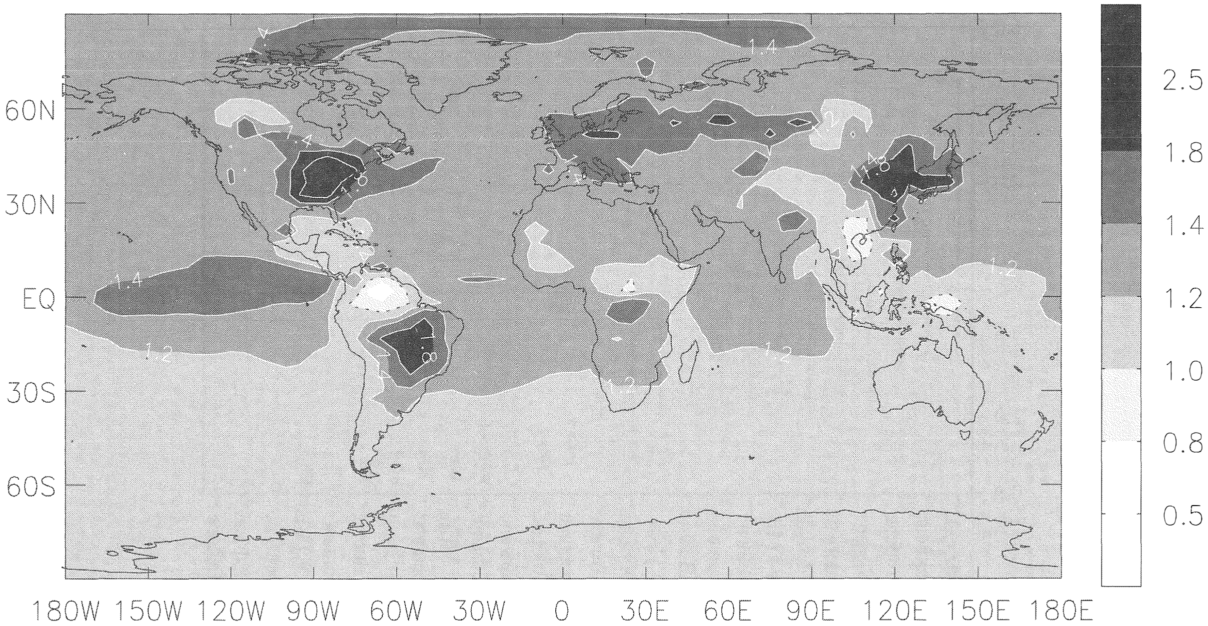

Figure 8-7. Model calculation of surface ozone for the year 1993, comparing a simulation that accounts for NMHC-CH_4-CO emissions and chemistry, and one that only accounts for CH_4-CO chemistry (Houweling *et al.*, 1998). These ratios are relatively high in areas of strong anthropogenic NMHC emissions (darkest), indicating that large-scale O_3 levels are enhanced by up to a factor of 2-3 by natural and anthropogenic NMHC emissions (e.g., in the eastern U.S.). The black dashed lines indicate the 1.0 contour. Note that, e.g., over the Amazon basin, natural NMHC cause an ozone reduction.

et al., 1997; Roelofs and Lelieveld, 1997; Wang *et al.*, 1998a,b). Thus, net photochemical formation of ozone is the difference between two large numbers (Table 8-6). Net transport into and out of the troposphere, signified by the difference between stratospheric input and dry deposition, is also the difference between two numbers of comparable magnitude.

Individual models give insight into mechanistic complexities. For example, close balance between chemical production and chemical loss of ozone in the tropospheric column appears to be maintained at all latitudes except at high latitudes in winter (Wang *et al.*, 1998c). This balance implies in particular that ozone in the tropical troposphere, which plays a key role in the global oxidizing capacity of the atmosphere, is sustained largely by tropical sources of NO_x (Jacob *et al.*, 1996). Nonmethane hydrocarbon chemistry increases the global tropospheric ozone inventory by 10-20% (Figure 8-7); this relatively small perturbation reflects compensating effects from increases and decreases in ozone production in different regions of the troposphere (Wang *et al.*, 1998c). The latter study shows that most of the NMHC effect on ozone takes place via perturbation to the NO_x budget, involving the formation of PAN as a reservoir for long-range transport of NO_x.

Export of PAN from polluted boundary layers can provide a major reservoir of NO_x for remote regions of the atmosphere (Moxim *et al.*, 1996). Most of the PAN production over the United States appears to be driven by interaction of anthropogenic NO_x with biogenic isoprene (Horowitz *et al.*, 1998). In the boundary layer, strong horizontal PAN gradients occur between the continents and oceans, with maxima in polluted environments, whereas in the free troposphere PAN is distributed relatively zonally. In the Northern Hemisphere PAN reaches maximum levels in the cold high latitudes. In the Southern Hemisphere PAN maxima occur at latitudes north of 30°S, in association with biomass burning.

In summary, it appears that the influence of PAN on NO_x in remote locations (and presumably on ozone) is mostly exerted in the lower troposphere. In the upper troposphere PAN releases of NO_x at relatively low temperatures do not strongly affect ozone distributions.

This is confirmed by the Lamarque *et al.* (1996) NO_x "labeling" study, which showed that photochemical ozone formation in the Southern Hemisphere free troposphere is mostly controlled by the natural lightning NO_x source, except in the dry season, when biomass-burning emissions augment ozone formation (Thompson *et al.*, 1996a,b). In the Northern Hemisphere the calculated free tropospheric NO_x is largely determined by fossil fuel combustion, aircraft emissions, and lightning (Lamarque *et al.*, 1996).

Both regional and global chemistry-transport models are being employed to estimate exports from the polluted boundary layer in industrialized regions to the global environment. Ozone is formed over these areas from NMHC chemistry in the presence of NO_x. With NMHC chemistry added to global models (Müller and Brasseur, 1995; Berntsen and Isaksen, 1997), it appears that NMHC deplete OH in the vicinity of sources, in particular near natural sources that do not co-emit NO_x (Houweling *et al.*, 1998). On the other hand, NMHC breakdown leads to intermediate species, such as acetone, that can release OH at greater distance from the sources (Singh *et al.*, 1995). This affects the global distribution of OH, for example, by increasing the OH gradients between continental and marine environments (Houweling *et al.*, 1998). The global 3-D model study of Wang *et al.* (1998c) indicates that NMHC chemistry decreases the global abundance of tropospheric OH by 15%, whereas Houweling *et al.* (1998) conclude that the net effect on OH (and thus, e.g., on methyl chloroform and methane) is only small. Hence this issue remains associated with important uncertainty.

Although significant amounts of ozone are transported from North America toward the western North-Atlantic region, this ozone mixes with natural ozone from the stratosphere in synoptic weather systems (Moody *et al.*, 1996). Nevertheless, especially over the western Atlantic Ocean, ozone, CO, and NO_y show strong positive correlations, a clear signature of pollutant outflow from the U.S. (Parrish *et al.*, 1993; Chin *et al.*, 1994; Atherton *et al.*, 1996). Model simulations by Kasibhatla *et al.* (1996) suggest that the summertime North Atlantic mid-troposphere contains at least 50% more ozone compared to natural levels, even though during summer net ozone destruction prevails in the marine boundary layer. Most net ozone production appears to take place during the period April-June in this area, with cross-Atlantic transport of pollutant ozone reaching a maximum during spring (Roelofs and Lelieveld, 1997).

An important region of emerging pollutant emissions is the rapidly developing southeastern part of Asia. Strong indications of significant photochemical pollution have, for example, been reported by Liu *et al.* (1990), Sunwoo *et al.* (1994), Chao *et al.* (1996), Akimoto *et al.* (1996), and Kok *et al.* (1997). Industrial growth in rapidly developing countries, such as China and India, will perturb the atmosphere regionally in the next few decades (Elliot *et al.*, 1997). The degree to which this has global consequences depends on dynamics as well as sources. For example, the monsoon circulation may enhance pollutant transports toward the free troposphere in (Northern Hemisphere) summer by convection and towards the Indian and Pacific Oceans during winter. If anthropogenic emissions from southern Asia are transported toward the Inter-Tropical Convergence Zone (ITCZ), direct injection of ozone into the tropical upper troposphere could take place, leading to significant radiative forcing of climate.

Berntsen and Isaksen (1997) have calculated the contributions of several regions to the global tropospheric ozone budget. Europe is the largest source of photochemically formed ozone with a net contribution of nearly 97 Tg/yr, followed by North America with 77 Tg/yr. Asia appears to be developing strongly with a current net ozone flux of almost 65 Tg/yr. Berntsen and Isaksen (1997) calculate that the troposphere in the Northern Hemisphere, over the Atlantic and Pacific Oceans, is a region of strong net photochemical ozone destruction, mostly in the mid-troposphere.

8.6 TROPOSPHERIC OH: MEASUREMENTS, MODELING, OXIDIZING CAPACITY

8.6.1 Surface OH Measurements

A breakthrough in the ability to evaluate the tropospheric oxidizing capacity and photochemical mechanisms has been the development of reliable instrumentation for in situ measurements of OH and other oxidizing free radicals. In situ OH measurements and associated detailed studies of chemical OH production and destruction processes have been conducted in several ground-based campaigns, including a major intercomparison effort. During the Tropospheric OH Photochemistry Experiment (TOHPE) campaign in Colorado, it was confirmed that, especially under relatively clean conditions, OH is mostly controlled by

O_3 photolysis and the subsequent reaction of $O(^1D)$ with water vapor (e.g., Mount and Williams, 1997; Eisele *et al.*, 1997).

Under more polluted conditions, sufficient NO_x is available to enhance OH levels through HO_2 recycling and increased ozone production. On the other hand, natural and anthropogenic NMHCs deplete OH in the vicinity of sources (Goldan *et al.*, 1997). In the Northern Hemisphere, typical RO_2 levels ($RO_2 = HO_2 + CH_3O_2$ + higher peroxy radicals) in relatively clean continental air during the summer half-year are a few tens of pptv, while in more polluted air masses these levels can increase by more than a factor of 2 (Cantrell *et al.*, 1997). Hydroxyl measurements in the POPCORN (Photo-Oxidant formation by Plant emitted Compounds and OH Radicals in North-Eastern Germany) field campaign in Germany confirmed that ozone photolysis is the primary OH formation pathway under most conditions, except during morning and evening hours when other HO_x production pathways must be important (Brandenburger *et al.*, 1998). Likely important OH precursor gases under these conditions are nitrous acid (HONO) and formaldehyde (HCHO) (Holland *et al.*, 1998).

The comparison by Poppe *et al.* (1994) of model simulations with OH measurements for rural and moderately polluted sites in Germany showed good correlation in rural environments, with the model overpredicting OH by about 20%. Under more polluted conditions the correlation coefficient between experimental and modeled data is significantly smaller ($r = 0.61$) and the model overpredicts OH by about 15%. Poppe *et al.* (1994) conclude that the deviations between model simulations and measurements are well within the systematic uncertainties of the measured and calculated OH due to uncertain rate constants.

Penkett *et al.* (1997) performed RO_2 measurements in clean marine air at Cape Grim, Tasmania, within the SOAPEX campaign (Southern Ocean Atmospheric Photochemistry EXperiment). The average RO_2 levels encountered during summer were about 5-10 pptv. Penkett *et al.* (1997) derive simple relationships between RO_2 and $J(O^1D)$, in line with predictions from photochemical theory, which offers credence to our knowledge of baseline processes. Also measurements of peroxides in this unpolluted marine location could be explained with a simple photochemical model, indicating that ozone destruction under NO_x-poor conditions is consistent with modeled and measured levels of peroxy radicals and peroxides (Ayers *et al.*, 1996).

8.6.2 Free Tropospheric OH

Hydroxyl radical and hydroperoxy and organic peroxy radicals in the free troposphere at Mauna Loa were measured during several periods of the year during Mauna Loa Observatory Photochemistry Experiment-2 (MLOPEX-2) (Eisele *et al.*, 1996; Helmig *et al.*, 1996; Cantrell *et al.*, 1996a,b). The mean mid-day clear-sky values of $RO_2 + HO_2$ were 20-25 pptv, much lower than expected from models (Hauglustaine *et al.*, 1996b). Heterogeneous loss of peroxy radicals on aerosols may account for part of the discrepancy (Cantrell *et al.*, 1996b). Measurements and calculations of free tropospheric OH during spring and summer show relatively good agreement, whereas air masses from the boundary layer (upslope wind conditions) show lower OH concentration than the model (Eisele *et al.*, 1996). An unidentified vegetative emittant may be the sink. Hydrogen peroxide measured at Mauna Loa is also lower than expected from theory (Heikes *et al.*, 1996; Staffelbach *et al.*, 1996).

The ER-2 STRAT (Stratospheric Tracers of Atmospheric Transport) experiment over the Pacific included a number of tropospheric flight legs during which upper tropospheric OH and HO_2 measurements were performed (Wennberg *et al.*, 1998). Comparison with theory showed measured concentrations nearly always greater than expected from typical gas-phase photochemical mechanisms in most models. One possible explanation is the photodissociation of acetone (Jaeglé *et al.*, 1997), a constituent for which upper tropospheric mixing ratios at northern midlatitudes are consistently about 0.5 to 1 ppbv (Singh *et al.*, 1995; Arnold *et al.*, 1997). Peroxides, injected from the surface by convection, may be another HO_x source (Wennberg *et al.*, 1998). The OH and HO_2, along with ambient NO measured during STRAT (typically 50-200 pptv), suggest an upper tropospheric ozone source of about 1 ppbv/day, which is significant in a region where the ozone lifetime is relatively long. This rate is comparable to upper tropospheric ozone formation in regions in which NO_x is enhanced due to biomass burning and lightning (Thompson *et al.*, 1996a,b).

Intermediate products of NMHC breakdown, such as acetone, can play an important role as OH-producing agents (Singh *et al.*, 1995). A similar role is expected from formaldehyde and, to a smaller extent, from hydrogen peroxide. In particular, the oxidation of natural and anthropogenic NMHC can yield copious amounts of formaldehyde that, through its photolysis, could also play a role as an early morning source of free radicals (Fried *et al.*, 1997). Further, direct release of formaldehyde and hydrogen peroxides from biomass fires in the tropics may constitute an important source of free radicals (Lee *et al.*, 1997b; Folkins *et al.*, 1997).

Mauldin *et al.* (1997) performed in situ airborne OH measurements in the lower marine troposphere during the first Aerosol Characterization Experiment campaign (ACE-1) from October-December 1995. Significantly enhanced OH levels were measured above clouds, i.e., (8-15) × 10^6 molecules cm^{-3}, compared to (3-5) × 10^6 molecules cm^{-3} in cloud-free air. In-cloud OH levels were substantial, ~7.5 × 10^6 molecules cm^{-3}, due to enhanced photolysis rates from multiple reflections. However, these in-cloud OH levels could only be explained by assuming a significant aqueous chemical radical sink, consistent with predictions from modeling studies (Section 8.4.3.).

8.6.3 Global OH—Changes in Oxidizing Capacity

Model-calculated global OH distributions are tested by simulating the emissions and distribution of methyl chloroform (MCF = CH_3CCl_3). MCF is also largely removed from the atmosphere by OH and its sources are relatively well quantified. On the basis of MCF simulations, a global mean OH concentration of about 10^6 molecules cm^{-3} has been inferred (Prinn *et al.*, 1995; Krol *et al.*, 1998).

A recent study by Krol *et al.* (1998) has reassessed global OH changes based on MCF data. Prinn *et al.* (1995) showed that MCF measurements at five background stations (both hemispheres) during the period 1978-1993, combined with accurate estimates of MCF emissions, can be used to determine a global OH trend. Although Prinn *et al.* (1995) inferred that the global average OH trend over this period was close to zero, Krol *et al.* (1998) use an alternative statistical technique and a more detailed model to show that the 15-year OH trend may be positive. For all five monitoring stations they derive an OH trend of 0.4-0.5%/yr (7% over the whole period). Possible explanations for a positive trend include enhanced UV radiation penetration into the troposphere due to stratospheric O_3 loss, increasing tropospheric O_3 formation, e.g., from NO_x emissions, and recent reductions of tropospheric CO (in particular in the Northern Hemisphere) (Granier *et al.*, 1996). These effects are opposed by the observed methane increase over this time period (Chapter 2).

Hence, although tropospheric OH levels have probably decreased since preindustrial times (Crutzen and Zimmermann, 1991; Thompson, 1992) the recent OH trend may be zero or positive. Some of these recent atmospheric changes, if correct, may be temporary. For example, it can be anticipated that stratospheric O_3 decreases will diminish in the next 10-15 years. Furthermore, it appears that CO and NO_x emissions have recently decreased or stabilized in some countries, e.g., in northern middle latitudes, whereas emerging emissions from developing countries may continue to increase.

8.7 DEGRADATION OF CFC SUBSTITUTES

A large body of data pertaining to the atmospheric behavior of chlorofluorocarbon (CFC) substitutes is now available and has been extensively reviewed (e.g., WMO, 1995). Since the last Assessment (WMO, 1995), further insight into the detailed mechanisms for the tropospheric degradation of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) has been obtained. In particular, it has been shown that the reactions of fluorinated peroxy radicals with NO can involve a direct carbon-carbon bond cleavage channel. Another class of compounds, namely hydrofluoroethers (HFEs), has recently been considered as possible CFC replacements, and the kinetics and mechanisms for the tropospheric degradation of a number of these compounds have been reported.

The potential environmental impact of CFC substitutes is determined mainly by the tropospheric lifetimes of the parent compounds and the halogenated carbonyl species formed as oxidation products. The general scheme for the tropospheric degradation of CFC substitutes to halogenated carbonyl compounds is outlined below with the main emphasis placed on research carried out since the WMO (1995) report.

8.7.1 Degradation Pathways

Degradation of CFC substitutes is mainly initiated by the gas-phase reaction with hydroxyl (OH) radicals. This process, which involves either H-atom abstraction or addition to an unsaturated compound, is the slowest step in the conversion of the CFC substitutes into the eventual oxidation products (such as CO_2, hydrogen fluoride (HF), hydrogen chloride (HCl), and halogenated organic acids). There now exists a large database of rate coefficients for the reactions of OH radicals with CFC alternatives that is continuously evaluated (DeMore *et al.*, 1997) and provides a means of calculating consistent tropospheric lifetimes for these compounds. Moreover, this database allows rate coefficients to be estimated within a factor of about 2 for compounds for which there are no experimental data available.

The reaction of halocarbons with OH radicals in air leads to rapid formation of haloalkyl peroxy radicals that react with three important tropospheric trace gases: NO_2, HO_2, and NO. The relative importance of these reactions is dictated by the rate coefficients for reactions with the peroxy (CX_3CYZOO) radicals and their ambient concentrations (X, Y, Z = H, Br, Cl, or F). Reaction of haloalkyl peroxy radicals with NO_2 and HO_2 leads to the formation of the corresponding peroxynitrates ($CX_3CYZOONO_2$) and hydroperoxides ($CX_3CYZOOH$). These species appear to be rather short-lived and undergo photolysis, thermal decomposition, or reaction with OH radicals, leading to the regeneration of peroxy (CX_3CYZOO) or the formation of alkoxy (CX_3CYZO) radicals (WMO, 1995).

The reactions of haloalkyl peroxy radicals with NO have generally been assumed to result in quantitative formation of NO_2 and the corresponding haloalkoxy radicals (WMO, 1995). However, studies on one of the most important CFC substitutes, CF_3CH_2F (HFC-134a) have called into question this basic premise (Wallington *et al.*, 1996). This important question pertains to the fate of the alkoxy radical, CF_3CFHO. The alkoxy radical, assumed to be formed with a yield close to 100%, may either decompose via carbon-carbon bond cleavage to give CHFO or react with molecular oxygen. Reaction with O_2 forms CF_3CFO, which, following uptake in clouds or surface water, is hydrolyzed to CF_3COOH. The estimated atmospheric yield of CF_3COOH due to emission of CF_3CH_2F thus depends critically on laboratory measurements of the relative importance of the reaction with O_2 and the decomposition.

Experimental studies on the reactions of CF_3CHFO radicals have generally employed the self-reaction of the corresponding peroxy radical as the alkoxy radical source. However, the study of the oxidation of HFC-134a by Wallington *et al.* (1996) also employed the reaction of CF_3CHFO_2 radicals with NO as the alkoxy radical source. The experimental results showed a reduced yield of CF_3CFO, thereby implying that the decomposition of CF_3CHFO radicals is more favorable when they are generated from reaction of the peroxy radical with NO rather than from self-reaction of CF_3CHFOO radicals.

From the above considerations, it is evident that calculations of the yield of CF_3CFO, and hence CF_3COOH, from the atmospheric oxidation of CF_3CH_2F, based on experiments in which CF_3CHFO radicals were generated from the self-reaction of CF_3CHFOO, are likely to overestimate the yield of CF_3COOH. Previously, the yield of CF_3COOH obtained from the atmospheric degradation of HFC-134a was calculated to be 29-36%. Incorporation of the results of Wallington *et al.* (1996) into the model revises the yield down to 7-20%.

There has been further support (Møgelberg *et al.* 1997; Manning and Sidebottom, 1997) for the conclusions drawn by Wallington *et al.* (1996). These findings appear to be particularly relevant for systems where haloalkoxy radicals may react by both C-C bond fission and reaction with O_2.

8.7.2 Reactions of Haloalkoxy Radicals

The reaction pathways for haloalkoxy radicals ultimately determine the primary degradation products and depend on the number and chemical identity of the halogen atoms in the parent molecule. A number of new studies on the reaction of haloalkoxy radicals, including C3 and C4 compounds, have been carried out since the last WMO report (1995) and have increased the understanding of haloalkoxy radical chemistry (Nielsen *et al.*, 1994; Møgelberg *et al.*, 1995a,b,c,d; Giessing *et al.*, 1996; Møgelberg *et al.*, 1996; Chen *et al.*, 1997; Barry *et al.*, 1997). A number of general conclusions concerning the relative importance of the possible reaction pathways for haloalkoxy radicals may be drawn from the experimental data:

(a) CX_2ClO and CX_2BrO radicals eliminate a Cl or Br atom to produce CX_2O, except for CH_2ClO and CH_2BrO, where reaction with O_2 to give CHClO and CHBrO is the dominant reaction.

(b) CH_2FO and CHF_2O radicals react with O_2 to form CHFO and CF_2O. Loss of CF_3O is largely determined by reaction with CH_4 or NO to generate CF_2O.

(c) RCH_2O and RCHOR radicals (R = haloalkyl group) react with O_2 to form the corresponding aldehydes and ketones, respectively.

(d) $RCCl_2O$ and RCClFO radicals react predominantly by Cl atom elimination to give the corresponding acyl chlorides and fluorides rather than by C-C bond fission.

(e) RCF_2O radicals undergo C-C bond cleavage to form CF_2O.

(f) RCHYO radicals (Y = Cl or F) have three important reaction channels: C-C bond fission (producing CHYO), HCl elimination (giving haloacyl radicals), and reaction with O_2 (to form acyl halides). The relative importance of these three reaction pathways is a function of temperature, O_2 pressure, and total pressure and will therefore vary considerably with altitude.

8.7.3 Halogenated Carbonyl Compounds

Halogenated carbonyl compounds are generated in the troposphere from the degradation of all CFC substitutes and undergo significant chemical or physical transformation in the troposphere.

The final tropospheric degradation products of the CFC substitutes are thus HCl, HF, oxides of carbon, and halogenated carboxylic acids. Although atmospheric chloride and fluoride production from CFC substitutes is insignificant compared to natural sources, some concern has been expressed about the environmental impact of halogenated carboxylic acids, particularly trifluoroacetic acid (TFA) (AFEAS, 1994a,b). Trifluoroacetic acid is chemically very stable and has no known abiotic sinks in the environment. It has been suggested that the acid could accumulate in seasonal wetlands (AFEAS, 1994a,b). However, at the levels predicted to arise from the use of CFC substitutes, trifluoroacetic acid is unlikely to have any impact on micro-organisms, plants, or animals.

8.7.4 Hydrofluoroethers (HFEs)

Kinetic studies on the reaction of OH radicals with a variety of HFEs have been reported in the literature (Zhang *et al.*, 1992; Garland *et al.*, 1993; Orkin *et al.*, 1994; Hsu and DeMore, 1995; O'Sullivan *et al.*, 1997; Wallington *et al.*, 1997, 1998). The experimental results indicate that hydrofluoroethers are significantly less reactive than the parent (fully hydrogenated) ethers and that, as for HFCs, their reactivity depends to a large extent on the number and positions of fluorine atoms in the molecule. This large variation in reactivity yields tropospheric lifetimes for removal by OH radicals that are as short as 45 days ($CF_3CH_2OCH_3$) and as long as 75 years (CF_3OCHF_2). Nevertheless, the activating effect of the oxygen atom in HFEs means that, in general, the tropospheric lifetimes for HFEs are considerably shorter than the structurally analogous HFCs.

There have also been several investigations on the oxidation of HFEs (O'Sullivan *et al.*, 1997; Wallington *et al.*, 1997, 1998). The experimental evidence to date suggests that the behavior of the alkoxy radicals formed in the oxidation of hydrofluoroethers is entirely analogous to the alkoxy radicals generated from the oxidation of non-fluorinated ethers. For example, the alkoxy radicals $CF_3CH_2OCHOCF_3$ and $C_4F_9OCH_2O$, generated from $CF_3CH_2OCH_2CF_3$ and $C_4F_9OCH_3$ respectively, react to produce the formates CF_3CH_2OCHO and C_4F_9OCHO. Unfortunately, there is no data available concerning the reaction rates of these products with OH radicals or their photolysis rates. However, since formates are considerably less reactive towards OH radicals than their parent ethers, one can assume that these fluorinated formates are likely to be similarly unreactive. On this basis, it seems that reaction with OH radicals is not likely to be a significant loss process for fluorinated formates. Uptake by clouds and rainwater followed by hydrolysis to produce fluorinated organic acids is the most likely scenario.

8.8 AVIATION AND THE GLOBAL ATMOSPHERE

Air traffic in the upper troposphere and lower stratosphere has reached a volume where the emissions of gases and particles may be affecting the physical and chemical properties of the atmosphere in a major way (Schumann, 1997; Derwent *et al.*, 1998; Friedl, 1997; Brasseur *et al.*, 1998). An update of the atmospheric impact of subsonic aircraft since the last ozone Assessment (Chapter 11 in WMO, 1995) will appear in a dedicated IPCC-sponsored Assessment (IPCC, 1999), to which the reader is referred.

8.9 CONCLUSIONS

The reader is referred to the Scientific Summary in the beginning of this chapter for a recapitulation of the Chapter's major points. The following paragraphs discuss some uncertainties and areas for which the next Assessment may show advances.

Ozone trends continue to be difficult to establish on a global basis due to the unevenness of monitoring sites and inconsistencies among instrumentation used. A recent balloonsonde intercomparison has shed some light on the latter issue. Tropical ozonesonde sites are gradually coming on line, but the midlatitude Southern Hemisphere remains undersampled.

The capability for measuring a large number of relevant trace gases with the required sensitivity and accuracy in field campaigns has improved greatly. However, extending free tropospheric measurements from aircraft, mountain sites, or balloons to larger regions requires an increased interaction with models. Recent and near-term developments in remote sensing of tropospheric ozone and ozone precursors are showing great promise.

Measurement campaigns in the North Atlantic and North Pacific have demonstrated the strong impact of anthropogenic emissions throughout the troposphere. Aircraft measurements have shown that pollution plumes from eastern Asia and North America travel large distances over these oceans, especially in the lower troposphere. The complexity of upper tropospheric NO_x sources has been elucidated in a number of experiments. Sources from aircraft, the stratosphere, surface pollution, and lightning have all been identified. Global models have constrained the total lightning source to 20 Tg N/yr, probably less than 10 Tg N/yr. Still, it is not possible to assign the fractional budget of NO_x sources within a given region with a high degree of certainty.

REFERENCES

AFEAS (Alternative Fluorocarbons Environmental Acceptability Study), Workshop on decomposition of TFA in the environment, Washington D.C., February, 1994a.

AFEAS (Alternative Fluorocarbons Environmental Acceptability Study), Workshop on the environmental fate of trifluoroacetic acid, Washington D.C., March, 1994b.

Akimoto, H., H. Nakame, and Y. Matsumoto, The chemistry of oxidant generation: Tropospheric ozone increase in Japan, in *The Chemistry of the Atmosphere: Its Impact on Global Change*, edited by J. Calvert, pp. 261-273, Blackwell Sci., Cambridge, Mass., 1994.

Akimoto, H., H. Mukai, M. Nishikawa, K. Murano, S. Hatakeyama, C.M. Liu, M. Buhr, K.J. Hsu, D.A. Jaffe, L. Zhang, R. Honrath, J.T. Merrill, and R.E. Newell, Long-range transport of ozone in the East Asian Pacific rim region, *J. Geophys. Res.*, *101*, 1999-2010, 1996.

Allen, D.J., P. Kasibhatla, A.M. Thompson, R.B. Rood, B.G. Doddridge, K.E. Pickering, R.D. Hudson, and S.-J. Lin, Transport induced interannual variability of carbon monoxide determined using a chemistry and transport model, *J. Geophys. Res.*, *101*, 28655-28669, 1996.

Anderson, B.E., G.L Gregory, J.D.W. Barrick, J.E. Collins, G.W. Sachse, C.H. Hudgins, J.D. Bradshaw, and S.T. Sandholm, Factors influencing dry season ozone distributions over the tropical South Atlantic, *J. Geophys. Res.*, *98*, 23491-23500, 1993.

Andreae, M.O., and P.J. Crutzen, Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, *Science*, *276*, 1052-1058, 1997.

Arnold, F., V. Bürger, B. Droste-fanke, F. Gimm, A. Krieger, J. Schneider, and T. Stilp, Acetone in the upper troposphere and lower stratosphere: Impact on trace gases and aerosols, *Geophys. Res. Lett.*, *24*, 3017-3020, 1997.

Atherton, C.S., S. Sillman, and J. Walton, Three-dimensional global modeling studies of the transport and photochemistry over the North Atlantic Ocean, *J. Geophys. Res.*, *101*, 29289-29304, 1996.

Atkinson, R., D.L. Baulch, R.A. Cox, R.F. Hampson, J.A. Kerr, M.J. Rossi, and J. Troe, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry Supplement-V-IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, *J. Phys. Chem. Ref. Data*, *25*, in press, 1998.

Atlas, E.L., and B.A. Ridley, The Mauna Loa Observatory Photochemical Experiment: Introduction, *J. Geophys. Res.*, *101*, 14531-14541, 1996.

Ayers, G.P., S.A. Penkett, R.W. Gillett, B. Bandy, I.E. Galbally, C.P. Meyer, C.M. Elsworth, S.T. Bentley, and B.W. Forgan, The annual cycle of peroxides and ozone in marine air at Cape Grim, Tasmania, *J. Atmos. Chem.*, *23*, 221-252, 1996.

BAe/Airbus, *World Civil Jet Market Forecast*, Airbus Industrie, pp. 1995-2014, Bristol, U.K., 1995.

Baker, M.B., Cloud microphysics and climate, *Science*, *276*, 1072-1078, 1997.

Baldy, S., G. Ancellet, M. Bessafi, A. Badr, and D. Lan Sun Luk, Field observations of the vertical distribution of tropospheric ozone at the island of Réunion (southern tropics), *J. Geophys. Res.*, *101*, 23835-23850, 1996.

Barry, J., G. Locke, D. Scollard, H. Sidebottom, J. Treacy, C. Clerbaux, R. Colin, and J. Franklin, 1,1,1,3,3-pentafluorobutane (HFC-365mfc): Atmospheric degradation and contribution to radiative forcing, *Int. J. Chem. Kinet.*, *29*, 607-617, 1997.

Baughcum, S.L., T.G. Tritz, S.C. Henderson, and D.C. Pickett, *Scheduled Civil Aircraft Emissions Inventories for 1992: Database Development and Analysis*, NASA Contractor Report 4700, U.S. National Aeronautics and Space Administration, Washington, D.C., 1996.

Beine, H.J., D.A. Jaffe, J.A. Herring, J.A. Kelley, T. Krognes, and F. Stordal, High-latitude springtime photochemistry: Part 1, NO_x, PAN and ozone relationships, *J. Atmos. Chem.*, *27*, 127-153, 1997.

Benkovitz, C.M., T.M. Scholtz, J. Pacyna, L. Rarrason, J. Dignon, E.C. Voldner, P.A. Spiro, J.A. Logan, and T.E. Graedel, Global gridded inventories of anthropogenic emissions of sulfur and nitrogen, *J. Geophys. Res.*, *101*, 29239-29253, 1996.

Berntsen, T.K., and I.S.A. Isaksen, A global three-dimensional chemical transport model for the troposphere: 1, Model description and CO and ozone results, *J. Geophys. Res.*, *102*, 21239-21280, 1997.

Berresheim, H., and F.L. Eisele, Sulfur Chemistry in the Antarctic Troposphere Experiment: An overview of project SCATE, *J. Geophys. Res.*, *103*, 1619-1628, 1998.

Blake, D.R., T.Y. Chen, T.Y. Smith, C.J.L. Wang, O.W. Wingenter, N.J. Blake, F.S. Rowland, and E.W. Mayer, Three-dimensional distribution of non-methane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.*, *101*, 1763-1778, 1996.

Bodeker, G.E., I.S. Boyd, and W.A. Matthews, Trends and variability in vertical ozone and temperature profiles measured by ozonesondes at Lauder, New Zealand, *J. Geophys. Res.*, submitted, 1998.

Boeing, Current market outlook, *World Air Travel Demand and Aeroplane Supply Requirements*, Boeing Commercial Airplane Group, pp. 3-8, Seattle, Wash., 1997.

Bojkov, R.D., and V.E. Fioletov, Changes of the lower stratospheric ozone over Europe and Canada, *J. Geophys. Res.*, *102*, 1337-1347, 1997.

Borrmann, S., S. Solomon, L. Avallone, D. Toohey, and D. Baumgardner, On the occurrence of ClO in cirrus clouds and volcanic aerosol in the tropopause region, *Geophys. Res. Lett.*, *24*, 2011-2014, 1997.

Brandenburger, U., T. Brauers, H.-P. Dorn, M. Hausmann, and D.H. Ehhalt, In-situ measurements of tropospheric hydroxyl radicals by folded long-path laser absorption during the field campaign POPCORN, *J. Atmos. Chem.*, in press, 1998.

Brasseur, G.P., R.A. Cox, D. Hauglustaine, I. Isaksen, J. Lelieveld, D.H. Lister, R. Sausen, U. Schumann, and A. Wahner, European Scientific Assessment of the Atmospheric Effects of Aircraft Emissions, *Atmos. Environ.*, *32*, 2329-2416, 1998.

Browell, E.V., M.A. Fenn, C.F. Butler, W.B. Grant, J.T. Merrill, R.E. Newell, J.D. Bradshaw, S.T. Sandholm, B.E. Anderson, A.R. Bandy, A.S. Bachmeier, D.R. Blake, D.D. Davis, G.L. Gregory, B.G. Heikes, Y. Kondo, S.C. Liu, F.S. Rowland, G.W. Sachse, H.B. Singh, R.W. Talbot, and D.C. Thornton, Large-scale air mass characteristics observed over western Pacific during summertime, *J. Geophys. Res.*, *101*, 1691-1712, 1996a.

Browell, E.V., M.A. Fenn, C.F. Butler, W.B. Grant, M.B. Clayton, J. Fishman, A.S. Bachmeier, B.E. Anderson, G.L. Gregory, H.E. Fuelberg, J.D. Bradshaw, S.T. Sandholm, D.R. Blake, B.G. Heikes, G.W. Sachse, H.B. Singh, and R.W. Talbot, Ozone and aerosol distributions and air mass characteristics over the South Atlantic basin during the burning season, *J. Geophys. Res.*, *101*, 24043-24068, 1996b.

Brunner, D., Climatology of NO_x and O_3 from measurements from a Swissair airliner B-747, Ph.D. Dissertation, ETH-Zürich, 1998.

Buhr, M., D. Sueper, M. Trainer, P. Goldan, B. Kuster, F. Fehsenfeld, G. Kok, R. Shillawski, and A. Schanot, Trace gas and aerosol measurements using aircraft data from the North Atlantic Regional Experiment (NARE 1993), *J. Geophys. Res.*, *101*, 29013-29027, 1996.

Cantrell, C.A., R.E. Shetter, T.M. Gilpin, J.G. Calvert, F.L. Eisele, and D.J. Tanner, Peroxy radicals measured and calculated from trace gas measurements in the Mauna Loa Observatory Photochemistry Experiment 2, *J. Geophys. Res.*, *101*, 14653-14664, 1996a.

Cantrell, C.A., R.E. Shetter, T.M. Gilpin, and J.G. Calvert, Peroxy radicals measured during Mauna Loa Observatory Photochemistry Experiment 2: The data and first analysis, *J. Geophys. Res.*, *101*, 14643-14652, 1996b.

Cantrell, C.A., R.E. Shetter, J.G. Calvert, F.L. Eisele, E. Williams, K. Baumann, W.H. Brune, P.S. Stevens, and J.H. Mather, Peroxy radicals from photostationary state deviations and steady state calculations during the tropospheric OH experiment at Idaho Hill, Colorado, 1993, *J. Geophys. Res.*, *102*, 6396-6378, 1997.

Carslaw, N., L.J. Carpenter, J.M.C. Plane, B.J. Allan, R.A. Burgess, K.C. Clemitshaw, H. Coe, and S.A. Penkett, Simultaneous observations of nitrate and peroxy radicals in the marine boundary layer, *J. Geophys. Res.*, *102*, 18917-18933, 1997.

Carter, W.P.L., and R. Atkinson, Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x, *Int. J. Chem. Kinet.*, *28*, 497-530, 1997.

Chao, L., T. Jie, and Z. Xiuji, Measurements and model simulations of surface ozone variations at different background concentrations of the precursors, *Acta Meteor. Sinica*, *10*, 215-221, 1996.

Chen, J., V. Young, H. Niki, and H. Magid, Kinetic and mechanistic studies for reactions of $CF_3CH_2CHF_2$ (HFC-245fa) initiated by H-atom abstraction using atomic chlorine, *J. Phys. Chem.*, *101*, 2648-2653, 1997.

Chin, M., D.J. Jacob, J.W. Munger, D.D. Parrish, and B.G. Doddridge, Relationship of ozone and carbon monoxide over North America, *J. Geophys. Res.*, *99*, 14565-14573, 1994.

Crutzen, P.J., and P.H. Zimmermann, The changing chemistry of the troposphere, *Tellus*, *43AB*, 136-151, 1991.

Daum, P.H., L.I. Kleinman, L. Newman, W.T. Luke, J. Weinstein-Lloyd, C.M. Berkowitz, and K.M. Busness, Chemical and physical properties of plumes of anthropogenic pollutants transported over the North Atlantic during the North Atlantic Regional Experiment, *J. Geophys. Res.*, *101*, 29029-29042, 1996.

Davis, D.D., J. Crawford, G. Chen, W. Chameides, S. Liu, J. Bradshaw, S. Sandholm, G. Sachse, G. Gregory, B. Anderson, J. Barrick, A. Bachmeier, J. Collins, E. Browell, D. Blacke, S. Rowland, Y. Kondo, H. Singh, R. Talbot, B. Heikes, J. Merrill, J. Rodriguez, and R.E. Newell, Assessment of ozone photochemistry in the western North-Pacific as inferred from PEM-West A observations during the fall 1991, *J. Geophys. Res.*, *101*, 2111-2134, 1996.

Davis, D.D., G. Chen, P. Kasibhatla, A. Jefferson, D. Tanner, F. Eisele, D. Lenschow, W. Neff, and H. Berresheim, DMS oxidation in the Antarctic marine boundary layer: Comparison of model simulations and field observations of DMS, DMSO, $DMSO_2$, H_2SO_4(g), MSA(g), and MSA(p), *J. Geophys. Res.*, *103*, 1657-1678, 1998.

DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 12*, U.S. National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., 1997.

Dentener, F.J., G.R. Carmichael, Y. Zhang, J. Lelieveld, and P.J. Crutzen, The role of mineral aerosol as a reactive surface in the global troposphere, *J. Geophys. Res.*, *101*, 22869-22889, 1996.

Derwent, R.G., R.R. Friedl, I.L. Karol, H. Kelder, V.W.J.H. Kirchhoff, T. Ogawa, M.J. Rossi, and P. Wennberg, Impacts of aircraft emissions on atmospheric ozone, Provisional draft of Chapter 2, in *Aviation and the Global Atmosphere*, Intergovernmental Panel on Climate Change, in preparation, 1998.

Dessler, A.E., E.J. Hintsa, E.M. Weinstock, J.G. Anderson, and K.R. Chan, Mechanisms controlling water vapor in the lower stratosphere: "A tale of two stratospheres", *J. Geophys. Res.*, *100*, 23167-23172, 1995.

Diab, R.D., A.M. Thompson, M. Zunckel, G.J.R. Coetzee, J. Combrink, G.E. Bodeker, J. Fishman, F. Sokolic, D.P. McNamara, C.B. Archer, and D. Nganga, Vertical ozone distribution over southern Africa and adjacent oceans during SAFARI-92, *J. Geophys. Res.*, *101*, 23823-23834, 1996.

Donahue, N.M., M.K. Dubey, R. Mohrschladt, K.L. Demerjian, and J.G. Anderson, High-pressure flow study of the reactions $OH+NO_x \rightarrow HONO_x$: Errors in the falloff region, *J. Geophys. Res.*, *102*, 6159-6168, 1997.

Donahue, N.M., J.H. Kroll, J.G. Anderson, and K.L. Demerjian, Direct observation of OH production from the ozonolysis of olefins, *Geophys. Res. Lett.*, *25*, 59-62, 1998.

Dunker, A.M., The decoupled direct method for calculated sensitivity coefficients in chemical kinetics, *J. Chem. Phys.*, *81*, 2385-2393, 1984.

Eisele, F.L., D.J. Tanner, C.A. Cantrell, and J.G. Calvert, Measurements and steady state calculations of OH concentrations at Mauna Loa Observatory, *J. Geophys. Res.*, *101*, 14665-14679, 1996.

Eisele, F.L., G.H. Mount, D. Tanner, A. Jefferson, R. Shetter, J.W. Harder, and E.J. Williams, Understanding the production and interconversion of the hydroxyl radical during the Tropospheric OH Photochemistry Experiment, *J. Geophys. Res.*, *102*, 6457-6465, 1997.

Elbern, H., J. Kowol, R. Sladkovic, and A. Ebel, Deep stratospheric intrusions: A statistical assessment with model guided analysis, *Atmos. Environ.*, *31*, 3207-3226, 1997.

Elliot, S., M. Shen, D.R. Blake, R. Lu, A.G. Russell, C.Y.J. Kao, G.E. Streit, X.P. Zhao, E.I. McCreary, F.S. Rowland, M.J. Brown, and R.P. Turco, Atmospheric effects of the emerging mainland Chinese transportation system at and beyond the regional scale, *J. Atmos. Chem.*, *27*, 31-70, 1997.

Emmons, L.K., M.A. Carroll, D.A. Hauglustaine, G.P. Brasseur, C. Atherton, J. Penner, S. Sillman, H. Levy, F. Rohrer, W.M.F. Wauben, P.F.J. VanVelthoven, Y. Wang, D. Jacob, P. Bakwin, R. Dickerson, B. Doddridge, C. Gerbig, R. Honrath, G. Hübler, D. Jaffe, Y. Kondo, J.W. Munger, A. Torres, and A. Volz-Thomas, Climatologies of NO_x and NO_y: A comparison of data and models, *Atmos. Environ.*, *31*, 1851-1904, 1997.

EPA (U.S. Environmental Protection Agency), *National Air Pollutant Emissions Trends, 1900-1995*, EPA-454/R-96-007, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1996.

Fehsenfeld, F.C., P. Daum, W.R. Leaitch, M. Trainer, D.D. Parrish, and G. Hübler, Transport and processing of O_3 and O_3 precursors over the North Atlantic: An overview of the 1993 North Atlantic Regional Experiment (NARE) summer intensive, *J. Geophys. Res.*, *101*, 28877-28891, 1996.

Fiore, A.M., D.J. Jacob, J.A. Logan, and J.H. Yin, Long-term trends in ground level ozone over the contiguous United States: 1980-1995, *J. Geophys. Res.*, *103*, 1471-1480, 1998.

Fishman, J., C.E. Watson, J.C. Larsen, and J.A. Logan, The distribution of tropospheric ozone determined from satellite data, *J. Geophys. Res.*, *95*, 3599-3617, 1990.

Fishman, J., J.M. Hoell Jr., R.D. Bendura, R.J. McNeal, and V.W.J.H. Kirchhoff, NASA GTE TRACE A Experiment (September-October 1992): Overview, *J. Geophys. Res.*, *101*, 23865-23879, 1996.

Folkins, I., P.O. Wennberg, T.F. Hanisco, J.G. Anderson, and R.J. Salawitch, OH, HO_2, and NO in two biomass burning plumes: Sources of HO_x and implications for ozone production, *Geophys. Res. Lett.*, *24*, 3185-3188, 1997.

Fried, A., S. McKeen, S. Sewell, J. Harder, B. Henry, P. Goldan, W. Kuster, E. Williams, K. Baumann, R. Shetter, and C. Cantrell, Photochemistry of formaldehyde during the 1993 Tropospheric OH Photochemistry Experiment, *J. Geophys. Res.*, *102*, 6283-6296, 1997.

Friedl, R. (ed.), *Atmospheric Effects of Subsonic Aircraft: Interim Assessment Report of the Advanced Subsonic Technology Program*, U.S. National Aeronatics and Space Administration, Goddard Space Flight Center, Greenbelt, Md., 1997.

Gao, D., W.R. Stockwell, and J.B. Milford, Global uncertainty analysis of a regional scale gas-phase chemical mechanism, *J. Geophys. Res.*, *101*, 9107-9119, 1996.

Gardner, R.M., M. Williams, C. Shoreman, I. Piper, P. Newton, M. Leech, B. Stonehouse, R. Flak, D. Lee, C.J. Hume, T. Cook, M. Metcalfe, C. Walker, B. Massé, S. Korolitski, C. Baudoin, H. Wieting, D. Lenormand, A. Depitre, E. Herms, J. Pavaux, S. Dumont, M. O'Hanrahan, A. Schmitt, M. Lecht, M. Dameris, F. Deidewig, D. Wurzel, J. Peper, W. Fransen, S. Ernedal, W. Bula, E. Fleuti, B.O. Näs, K. Morris, H.P. Roth, W. Förtsch, A. Rowland, J.K. Adams, R. Dunker, H. Neuman, J.P. Desgranges, P. Wiederkehr, C. Vandenberghe, R. Harman, R. Stewart, D. Lister, N. Louisnard, R. Sausen, and C. Johnson, A global inventory of aircraft NO_x emissions, in *AERONOX Impact of NO_x Emissions from Aircraft upon the Atmosphere at Flight Altitudes 8-15 km*, edited by U. Schumann, pp. 129-194, European Commission, Directorate - General XII for Science and Development, Publication on Research Related to Aeronautics and Environment, Brussels, 1995.

Gardner, R.M., K. Adams, T. Cook, F. Deidewig, S. Ernedal, R. Falk, E. Fleuti, E. Herms, C.E. Johnson, M. Lecht, D.S. Lee, M. Leech, D. Lister, B. Massé, M. Metcalfe, P. Newton, A. Schmitt, C. Vandenbergh, R. VanDrimmelen, ANCAT/EC (The Abatement of Nuisances Caused by Air Transport/ European Commission) global inventory of NOx emissions from aircraft, *Atmos. Environ.*, *31*, 1751-1766, 1997.

Garland, N.L., L.J. Medhurst, and H.H. Nelson, Potential chlorofluorocarbon replacements: OH reaction rate constants between 250 and 315 K and infrared absorption spectra, *J. Geophys. Res.*, *98*, 23107-23111, 1993.

Garstang, M., P.D Tyson, R. Swap, M. Edwards, P. Kollberg, and J.A. Lindesay, Horizontal and vertical transport of air over southern Africa, *J. Geophys. Res.*, *101*, 23721-23736, 1996.

Gettelman, A., J.R. Holton, and K.H. Rosenlof, Mass fluxes of O_3, CH_4, N_2O and CF_2Cl_2 in the lower stratosphere calculated from observational data, *J. Geophys. Res.*, *102*, 19149-19159, 1997.

Giessing, A.M.B., A. Freilberg, T. Møgelberg, J. Sehested, M. Bilde, T.J. Wallington, and O.J. Nielsen, Atmospheric chemistry of HFC-227ca: Spectrokinetic investigation of the $CF_3CF_2CF_2O_2$ radical, its reaction with NO and NO_2, and the atmospheric fate of the $CF_3CF_2CF_2O$ radical, *J. Phys. Chem.*, *100*, 6572-6576, 1996.

Gleason, J.F., N.C. Hsu, and O. Torres, Biomass burning smoke measured using backscattered ultraviolet radiation: SCAR-B and Brazilian smoke interannual variability, *J. Geophys. Res.*, in press, 1998.

Goldan, P.D., W.C. Kuster, and F.C. Fehsenfeld, Nonmethane hydrocarbon measurements during the Tropospheric OH Photochemistry Experiment, *J. Geophys. Res.*, *102*, 6315-6324, 1997.

Granier, C., J.F. Müller, S. Madronich, and G.P. Brasseur, Possible causes for the 1990-1993 decrease in the global tropospheric CO abundances: A three-dimensional sensitivity study, *Atmos. Environ.*, *30*, 1673-1682, 1996.

Greenberg, J.P., D. Helmig, and P.R. Zimmerman, Seasonal measurements of nonmethane hydrocarbons and carbon monoxide at the Mauna Loa Observatory during the Mauna Loa Observatory Photochemistry Experiment 2, *J. Geophys. Res.*, *101*, 14581-14598, 1996.

Gregory, G.L., B.E. Anderson, and E.V. Browell, Influence of lower tropospheric ozone on total column ozone as observed over the Pacific Ocean during the 1991 PEM-West A expedition, *J. Geophys. Res.*, *101*, 1919-1930, 1996.

Gregory, G.L., J.T. Merrill, M.C. Shipham, D.R. Blake, G.W. Sachse, and H.B. Singh, Chemical characteristics of tropospheric air over the Pacific Ocean as measured during PEM-West-B: Relationship to Asian outflow and trajectory history, *J. Geophys. Res.*, *102*, 28275-28285, 1997.

Guenther, A., C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P. Zimmerman, A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, *100*, 8873-8892, 1995.

Guicherit, R., Ozone on an urban and regional scale-with special reference to the situation in the Netherlands, in *Tropospheric Ozone-Regional and Global Scale Interactions*, edited by I.S.A. Isaksen, *NATO series C, Vol. 227*, pp. 49-62, Reidel Publ., Dordrecht, The Netherlands, 1988.

Hanson, D.R., A.R. Ravishankara, and S. Solomon, Heterogeneous reactions in sulfuric acid aerosols: A framework for model calculations, *J. Geophys. Res.*, *99*, 3615-3629, 1994.

Harris, N.R.P., G. Ancellet, L. Bishop, D.J. Hofmann, J.B. Kerr, R.D. McPeters, M. Prendez, W.J. Randel, J. Staehelin, B.H. Subbaraya, A. Volz-Thomas, J. Zawodny, and C.S. Zerefos, Trends in stratospheric and free tropospheric ozone, *J. Geophys. Res.*, *102*, 1571-1590, 1997.

Hauglustaine, D.A., B.A. Ridley, S. Solomon, P.G. Hess, and S. Madronich, HNO_3/NO_x ratio in the remote troposphere during MLOPEX2: Evidence for nitric acid reduction on carbonaceous aerosols? *Geophys. Res. Lett.*, *23*, 2609-2612, 1996a.

Hauglustaine, D.A., S. Madronich, B.A. Ridley, J.G. Walega, C.A. Cantrell, and R.E. Shetter, Observed and model calculated photostationary state at Mauna Loa Observatory during MLOPEX 2, *J. Geophys. Res.*, *101*, 14681-14696, 1996b.

Heikes, B.G., M. Lee, J. Bradshaw, S. Sandholm, D.D. Davis, J. Crawford, J. Rodriguez, S. Liu, S. McKeen, D. Thornton, A. Bandy, G. Gregory, R. Talbot, and D. Blake, Hydrogen peroxide and methylhydroperoxide distributions related to ozone and odd hydrogen over the North Pacific in the fall of 1991, *J. Geophys. Res.*, *101*, 1891-1905, 1996.

Heintz, F., U. Platt, H. Flentje, and R. Dubois, Long-term observation of nitrate radicals at the Tor station, Kap Arkona (Rügen), *J. Geophys. Res.*, *101*, 22891-22910, 1996.

Helmig, D., W. Pollock, J. Greenberg, and P. Zimmerman, Gas chromatography and mass spectrometry analysis of volatile organic trace gases at Mauna Loa Observatory, Hawaii, *J. Geophys. Res.*, *101*, 14697-14710, 1996.

Herman, J.R., P.K. Bhartia, O. Torres, C. Hsu, C. Seftor, and E. Celarier, Global distribution of UV-absorbing aerosols from Nimbus 7/TOMS data, *J. Geophys. Res.*, *102*, 16911-16922, 1997.

Herring, J.A., D.A. Jaffe, H.J. Beine, S. Madronich, and D.R. Blake, High-latitude springtime photochemistry: Part II, Sensitivity studies of ozone production, *J. Atmos. Chem.*, *27*, 155-178, 1997.

Hoffmann, T., J.R. Odum, F. Bowman, D. Collins, D. Klokow, R.C. Flagan, and J.H. Seinfeld, Formation of organic aerosols from the oxidation of biogenic hydrocarbons, *J. Atmos. Chem.*, *26*, 189-222, 1997.

Holland, F., U. Aschmutat, M. Hessling, A. Hofzumahaus, and D.H. Ehhalt, Highly time resolved measurements of OH during POPCORN using laser-induced fluorescence spectroscopy, *J. Atmos. Chem.*, in press, 1998.

Holton, J.R., P.H. Haynes, M.E. McIntyre, A.R. Douglass, R.B. Rood, and L. Pfister, Stratosphere-troposphere exchange, *Rev. Geophys.*, *33*, 403-439, 1995.

Horowitz, L.W., J. Liang, G.M. Gardner, and D.J. Jacob, Export of reactive nitrogen from North America during summertime, *J. Geophys. Res.*, *103*, 13451-13476, 1998.

Houweling, S., F. Dentener, and J. Lelieveld, The impact of non-methane hydrocarbon compounds on tropospheric photochemistry, *J. Geophys. Res.*, *103*, 10673-10696, 1998.

Hov, Ø. (ed.), *Tropospheric Ozone Research: Tropospheric Ozone in the Regional and Sub-Regional Context*, Springer-Verlag, Berlin, Germany, 1997.

Hsu, K.J., and W.B. DeMore, Temperature-dependent rate constants and substituent effects for the reactions of hydroxyl radicals with three partially fluorinated ethers, *J. Phys. Chem.*, *99*, 11141-11146, 1995.

Hudson, R.D., J.-H. Kim, and A.M. Thompson, On the derivation of tropospheric column ozone from radiances measured by the total ozone mapping spectrometer, *J. Geophys. Res.*, *100*, 11137-11145, 1995.

IPCC (Intergovernmental Panel on Climate Change), *Climate Change 1995: The Science of Climate Change*, edited by J.T. Houghton, L.G. Meira Filho, B.A. Callander, N. Harris, A. Kattenberg, and K. Maskell, Cambridge University Press, Cambridge, U.K., 1996.

IPCC (Intergovernmental Panel on Climate Change), *Aviation and the Global Atmosphere: A Special Report of IPCC Working Groups I and III*, edited by J.T. Houghton, D. Lister, J. Penner, M. McFarland, D. Griggs, and D. Dokken, Cambridge University Press, Cambridge, U.K., in preparation, 1999.

Jacob, D.J., J.A. Logan, G.M. Gardner, R.M. Yevich, C.M. Spivakovsky, and S.C. Wofsy, Factors regulating ozone over the United States and its export to the global atmosphere, *J. Geophys. Res.*, *98*, 14817-14826, 1993.

Jacob, D.J., B.G. Heikes, S.M. Fan, J.A. Logan, D.L. Mauzerall, J.D. Bradshaw, H.B. Singh, G.L. Gregory, R.W. Talbot, D.R. Blake, and G.W. Sachse, Origin of ozone and NO_x in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic basin, *J. Geophys. Res.*, *101*, 24235-24250, 1996.

Jacob, D.J., M.J. Prather, P.J. Rasch, R.L. Shia, Y.J. Balkanski, S.R. Beagley, D.J. Bergmann, W.T. Blackshear, M. Brown, M. Chiba, M.P. Chipperfield, J. deGrandpre, J.E. Dignon, J. Feichter, C. Genthon, W.L. Grose, P.S. Kasibhatla, I. Kohler, M.A. Kritz, K. Law, J.E. Penner, M. Ramonet, C.E. Reeves, D.A. Rotman, D.Z. Stockwell, P.F.J. VanVelthoven, G. Verver, O. Wild, H. Yang, and P. Zimmerman, Evaluation and intercomparison of global atmospheric transport models using ^{222}Rn and other short-lived tracers, *J. Geophys. Res*, *101*, 5953-5970, 1997.

Jaeglé, L., D.J. Jacob, P.O. Wennberg, C.M. Spivakovsky, T.F. Hanisco, E.J. Lanzendorf, E.J. Hintsa, D.W. Fahey, E.R. Keim, M.H. Proffitt, E.L. Atlas, F. Flocke, S. Schauffler, C.T. McElroy, C. Midwinter, L. Pfister, and J.C. Wilson, Observed OH and HO_2 in the upper troposphere suggests a major source from convective injection of peroxides, *Geophys. Res. Lett.*, *24*, 3181-3184, 1997.

Jaeglé, L., D.J. Jacob, W.H. Brune, D. Tan, I.C. Faloona, A.J. Weinheimer, B.A. Ridley, T.L. Campos, and G.W. Sachse, Sources of HO_x and production of ozone in the upper troposphere over the United States, *Geophys. Res. Lett.*, *25*, 1709-1712, 1998.

Jiang, Y., and Y.L. Yung, Concentrations of tropospheric ozone from 1979 to 1992 over tropical Pacific South America from TOMS data, *Science*, *272*, 714-716, 1996.

Jonson, J.E., and I.S.A. Isaksen, Tropospheric ozone chemistry: The impact of cloud chemistry, *J. Atmos. Chem.*, *16*, 99-122, 1993.

Justice, C.O., J.D. Kendall, P.R. Dowty, and R.J. Scholes, Satellite remote sensing of fires during the SAFARI campaign using NOAA Advanced Very High Resolution Radiometer data, *J. Geophys. Res.*, *101*, 23851-23863, 1996.

Kasibhatla, P., H. Levy II, A. Klonecki, and W.L. Chameides, Three-dimensional view of the large-scale tropospheric ozone distribution over the North-Atlantic Ocean during summer, *J. Geophys. Res.*, *101*, 29305-29316, 1996.

Kato, N., and H. Akimoto, Anthropogenic emissions of SO_2 and NO_x in Asia: Emissions inventory, *Atmos. Environ.*, *26A*, 2997-3017, 1992.

Kaufman, Y.J. , R. Kleidman, M.D. King, and D.E. Ward, SCAR-B Fires in the tropics: Properties and their remote sensing from EOS-MODIS, *J. Geophys. Res.*, SCAR-B Special Issue, in press, 1998.

Kawakami, S., Y. Kondo, M. Koike, H. Nakajima, G.L. Gregory, G.W. Sachse, R.E. Newell, E.V. Browell, D.R. Blake, J.M. Rodriguez, and J.T. Merrill, Impact of lightning and convection on reactive nitrogen in the tropical free troposphere, *J. Geophys. Res.*, *102*, 28367-28384, 1997.

Kim, J.H., and M.J. Newchurch, Biomass-burning influence on tropospheric ozone over the eastern Pacific Ocean: The influences of biomass burning and tropospheric dynamics, *Geophys. Res. Lett.*, *23*, 3723-3726, 1996.

Kim, J.H., and M.J. Newchurch, Biomass-burning influence on tropospheric ozone over New Guinea and South America, *J. Geophys. Res.*, *103*, 1455-1462, 1998.

Kim, J.H., R.D. Hudson, and A.M. Thompson, A new method of deriving time-averaged tropospheric column ozone over the tropics using Total Ozone Mapping Spectrometer (TOMS) radiances: Intercomparison and analysis using TRACE A data, *J. Geophys. Res.*, *101*, 24317-24330, 1996.

Kirchhoff, V.W.J.H., J.R. Alves, F.R. da Silva, and J. Fishman, Observations of ozone concentrations in the Brazilian cerrado during the TRACE A field expedition, *J. Geophys. Res.*, *101*, 24029-24042, 1996.

Kirchner, F., and W.R. Stockwell, Effect of peroxy radical reactions on the predicted concentrations of ozone, nitrogenous compounds and radicals, *J. Geophys. Res.*, *101*, 21007-21022, 1996.

Kirchner, F., and W.R. Stockwell, Correction to "Effect of peroxy radical reactions on the predicted concentrations of ozone, nitrogenous compounds and radicals" by F. Kirchner and W.R. Stockwell, *J. Geophys. Res.*, *102*, 10871, 1997.

Kleinman, L.I., P.H. Daum, Y.-N. Lee, S.R. Springston, L. Newman, W.R. Leaitch, C.M. Banic, G.A. Isaac, and J.I. MacPherson, Measurement of O_3 and related compounds over southern Nova Scotia: 1, Vertical distributions, *J. Geophys. Res.*, *101*, 29043-29060, 1996.

Kley, D., H. Geiss, and V.A. Mohnen, Concentrations and trends of tropospheric ozone precursor emissions in the USA and Europe, in *The Chemistry of the Atmosphere: Its Impact on Global Change*, edited by J.G. Calvert, pp. 245-259, Blackwell Sci., Cambridge, Mass., 1994.

Kley, D., P.J. Crutzen, H.G.J. Smit, H. Vömel, S.J. Oltmans, H. Grassl, and V. Ramanathan, Observations of near-zero ozone concentrations over the convective Pacific: Effects on air chemistry, *Science*, *274*, 230-233, 1996.

Koike, M., Y. Kondo, S. Kawakami, H. Nakajima, G.L. Gregory, G.W. Sachse, H.B. Singh, E.V. Browell, J.T. Merrill, and R.E. Newell, Reactive nitrogen and its correlation with O_3 and CO over the Pacific in winter and early spring, *J. Geophys. Res.*, *102*, 28385-28404, 1997.

Kok, G.L., J.A. Lind, and M. Fang, An airborne study of the air quality around the Hong Kong territory, *J. Geophys. Res.*, *102*, 19043-19057, 1997.

Komala, N., S. Saraspriya, K. Kita, and T. Ogawa, Tropospheric ozone behaviour observed in Indonesia, *Atmos. Environ.*, *30*, 1851-1856, 1996.

Kondo, Y., H. Ziereis, M. Koike, S. Kawakami, G.L. Gregory, G.W. Sachse, H.B. Singh, D.D. Davis, and J.T. Merrill, Reactive nitrogen over the Pacific Ocean during PEM-West A, *J. Geophys. Res.*, *101*, 1809-1828, 1996.

Krishnamurti, T.N., M.C. Sinha, M. Kanamitsu, D. Oosterhof, H. Fuelberg, R. Chatfield, D.J. Jacob, and J. Logan, Passive tracer transport relevant to the TRACE A experiment, *J. Geophys. Res.*, *101*, 23889-23907, 1996.

Krol, M., P.J. van Leeuwen, and J. Lelieveld, Global OH trend inferred from methylchloroform measurements, *J. Geophys. Res.*, *103*, 10697-10711, 1998.

Kuhn, M., P.J.H. Builtjes, D. Poppe, D. Simpson, W.R. Stockwell, Y. Andersson-Sköld, A. Baart, M. Das, F. Fiedler, Ø. Hov, F. Kirchner, P.A. Makar, J.B. Milford, M.G.M. Roemer, R. Ruhnke, A. Strand, B. Vogel, and H. Vogel, Intercomparison of the gas-phase chemistry in several chemistry and transport models, *Atmos. Environ.*, *32*, 693-709, 1998.

Lamarque, J.-F., G.P. Brasseur, P.G. Hess, and J.-F. Müller, Three-dimensional study of the relative contributions of the different nitrogen sources in the troposphere, *J. Geophys. Res.*, *101*, 22955-22968, 1996.

Lary, D.J., A.M. Lee, R. Toumi, M.J. Newchurch, M. Pirre, and J.B. Renard, Carbon aerosols and atmospheric photochemistry, *J. Geophys. Res.*, *102*, 3671-3682, 1997.

Lawrence, M.G., and P.J. Crutzen, The impact of cloud particle gravitational settling on soluble trace gas distributions, *Tellus*, submitted, 1998.

Lawrence, M.G., W.L. Chameides, P.S. Kasibhatla, H. Levy, and W. Moxim, Lightning and atmospheric chemistry: The rate of atmospheric NO production, in *Handbook of Atmospheric Electrodynamics*, *Vol. 1*, edited by H. Volland, CRC Press, Boca Raton, Fla., 1995.

Lawrimore, J.H., M. Das, and V.P. Aneja, Vertical sampling and analysis of nonmethane hydrocarbons for ozone control in urban North Carolina, *J. Geophys. Res.*, *100*, 22785-22793, 1995.

Le Bras, G. (ed.), *Chemical Processes in Atmospheric Oxidation*, Springer-Verlag, Berlin, Germany, 1997.

Lee, D.S., I. Köhler, E. Grobler, F. Rohrer, R. Sausen, L. Gallardo-Klenner, J.G.J. Olivier, F.J. Dentener, and A.F. Bouwman, Estimations of global NO_x emissions and their uncertainties, *Atmos. Environ.*, *31*, 1735-1749, 1997a.

Lee, M., B.G. Heikes, D.J. Jacob, G. Sachse, and B. Anderson, Hydrogen peroxide, organic hydroperoxide, and formaldehyde as primary pollutants from biomass burning, *J. Geophys. Res.*, *102*, 1301-1309, 1997b.

Lelieveld, J., and P.J. Crutzen, The role of clouds in tropospheric photochemistry, *J. Atmos. Chem.*, *12*, 229-267, 1991.

Lelieveld, J., and P.J. Crutzen, Role of deep cloud convection in the ozone budget of the troposphere, *Science*, *264*, 1759-1761, 1994.

Lelieveld, J., F. Arnold, B. Bregman, V. Bürger, P. Crutzen, H. Fischer, P. Siegmund, P. van Velthoven, and A. Waibel, Chemical perturbation of the lowermost stratosphere through exchange with the troposphere, *Geophys. Res. Lett.*, *24*, 603-606, 1997.

Levine, J.S., E.L. Winstead, D.A.B Parsons, M.C. Scholes, R.J. Scholes, W.R. Cofer III, D.R. Cahoon Jr., and D.I. Sebacher, Biogenic soil emissions of nitric oxide (NO) and nitrous oxide (N_2O) from savannas in South Africa: The impact of wetting and burning, *J. Geophys. Res.*, *101*, 23689-23697, 1996.

Levy, H. II, P.S. Kasibhatla, W.J. Moxim, A.A. Klonecki, A.I. Hirsch, S.J. Oltmans, and W.L. Chameides, The global impact of human activity on tropospheric ozone, *Geophys. Res. Lett.*, *24*, 791-794, 1997.

Liang, J., and D.J. Jacob, Effect of aqueous phase cloud chemistry on tropospheric ozone, *J. Geophys. Res.*, *102*, 5993-6001, 1997.

Liang, J., L.W. Horowitz, D.J. Jacob, Y. Wang, A.M. Fiore, J.A. Logan, G.M. Gardner, and J.W. Munger, Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere, *J. Geophys. Res.*, *103*, 13435-13450, 1998.

Liu, C.-M., S.C. Liu, and S.-H. Shen, A study of Taipei ozone problem, *Atmos. Environ.*, *24A*, 1461-1472, 1990.

Liu, S.C., S.A. McKeen, E.Y. Hsie, X. Lin, K.K. Kelly, J.D. Bradshaw, S.T. Sandholm, E.V. Browell, G.L. Gregory, G.W. Sachse, A.R. Bandy, D.C. Thornton, D.R. Blacke, F.S. Rowland, R. Newell, B.G. Heikes, H. Singh, and R.W. Talbot, Model study of tropospheric trace species distribution during PEM-West A, *J. Geophys. Res.*, *101*, 2073-2085, 1996.

Lobert, J.M., D.H. Scharffe, W.M. Hao, T.A. Kuhlbush, R. Sewen, P. Warneck, and P.J. Crutzen, Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning: Atmospheric Climatic and Biospheric Implications*, edited by J.S. Levine, pp. 289-304, MIT Press, Cambridge Mass., 1991.

Logan, J.A., Trends in the vertical distribution of ozone: An analysis of ozone sonde data, *J. Geophys. Res.*, *99*, 25553-25585, 1994.

Logan, J.A., and V.W.J.H Kirchhoff, Seasonal variations of tropospheric ozone at Natal, Brazil, *J. Geophys. Res.*, *91*, 7875-7881, 1986.

Mahlman, J.D., Dynamics of transport processes in the upper troposphere, *Science*, *276*, 1079-1983, 1997.

Mahowald, N.M., P.J. Rasch, and R.G. Prinn, Cumulus parameterizations in chemical transport models, *J. Geophys. Res.*, *100*, 26173-26189, 1995.

Manning, M., and H. Sidebottom, On the role of activated haloalkoxy radicals in the degradation of HCFC and HFC molecules, in *The Proceedings of the AFEAS Workshop*, Washington D.C., 1997.

Marenco, A., H. Gouget, P. Nedelec, J.P. Pages, and F. Karcher, Evidence of a long-term increase in tropospheric ozone from Pic du Midi data series, Consequences: Positive radiative forcing, *J. Geophys. Res.*, *99*, 16617-16632, 1994.

Marland, G., and T. Boden, Global, Regional, and National CO_2 Emissions, in *Trends: A Compendium of Data on Global Change*, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1997.

Matthijsen, J., P.J.H. Builtjes, and D.L. Sedlak, Cloud model experiments of the effect of iron and copper on tropospheric ozone under marine and continental conditions, *Meteorol. Atmos. Phys.*, *57*, 43-60, 1995.

Mauldin, R.L. III, S. Madronich, S.J. Flocke, F.L. Eisele, G.J. Frost, and A.S.H. Prevot, New insights on OH: Measurements around and in clouds, *Geophys. Res. Lett.*, *24*, 3033-3036, 1997.

Mazurek, M.A., G.R. Cass, and B.R.T. Simoneit, Biological input to visibility-reducing aerosol particles in the remote arid southwestern United States, *Environ. Sci. Technol.*, *25*, 684-694, 1991.

McCroskey, P.S., and G.J. McRae, *Documentation for the Direct Decoupled Sensitivity Analysis Method—DDM*, *Report*, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Penn., 1987.

McKeen, S.A., E.-Y. Hsie, and S.C. Liu, A study of the dependence of rural ozone on ozone precursors in the eastern United States, *J. Geophys. Res.*, *96*, 15377-15394, 1991.

McKeen, S.A., G. Mount, F. Eisele, E. Williams, J. Harder, P. Goldan, W. Kuster, S.C. Liu, K. Baumann, D. Tanner, A. Fried, S. Sewell, C. Cantrell, and R. Shetter, Photochemical modeling of hydroxyl and its relationship to other species during the Tropospheric OH Photochemistry Experiment, *J. Geophys. Res.*, *102*, 6467-6493, 1997.

Metwally, M., *Jet Aircraft Engine Emissions Database Development, 1992 Military, Charter and Non-scheduled Traffic*, NASA Contractor Report 4686, National Aeronautics and Space Administration, Washington, D.C., 1995.

Miller, A.J., G.C. Tiao, G.C. Reinsel, D. Wuebbles, L. Bishop, J. Kerr, M. Nagatani, J.J. DeLuisi, and C.L Mateer, Comparisons of the observed ozone trends in the stratosphere through examination of Umkehr and balloon sonde data, *J. Geophys. Res.*, *100*, 11209-11217, 1995.

Møgelberg, T., O.J. Nielsen, J. Sehested, T.J. Wallington, and M.D. Hurley, Atmospheric chemistry of HFC-272ca: Spectrokinetic investigation of the $CF_3CF_2CH_2O_2$ radical, its reactions with NO and NO_2, and the fate of the $CF_3CF_2CH_2O$ radical, *J. Phys. Chem.*, *99*, 1995-2001, 1995a.

Møgelberg, T., J. Platz, O.J. Nielsen, J. Sehested, and T.J. Wallington, Atmospheric chemistry of HFC-236fa: Spectrokinetic investigation of the $CF_3CHO_2(\cdot)CF_3$ radical, its reaction with NO and the fate of the $CF_3CHO(\cdot)CF_3$ radical, *J. Phys. Chem.*, *99*, 5373-5378, 1995b.

Møgelberg, T., O.J. Nielsen, J. Sehested, and T.J. Wallington, Atmospheric chemistry of HCFC-133a: The UV absorption spectra of CF_3CClH and CF_3CClHO_2 radicals, reactions of CF_3CClHO_2 with NO and NO_2, and fate of CF_3CClHO radical, *J. Phys. Chem.*, *99*, 13437-13444, 1995c.

Møgelberg, T., A. Freilberg, A.M.B. Giessing, J. Sehested, M. Bilde, T.J. Wallington, and O.J. Nielsen, Atmospheric chemistry of HFC-236cb: Spectrokinetic investigation of the $CF_3CF_2CFHO_2$ radical, its reaction with NO and NO_2, and the fate of the CF_3CF_2CFHO radical, *J. Phys. Chem.*, *99*, 17386-17393, 1995d.

Møgelberg, T., J. Sehested, M. Bilde, T.J. Wallington, and O.J. Nielsen, Atmospheric chemistry of CF_3CFHCF_3 (HFC-227ea): Spectrokinetic investigation of the $CF_3CFO_2(\cdot)CF_3$ radical, its reaction with NO and NO_2, and the fate of the $CF_3CFO(\cdot)CF_3$ radical, *J. Phys. Chem.*, *21*, 8882-8889, 1996.

Møgelberg, T., J. Sehested, G.S. Tyndall, J.J. Orlando, J.M. Fracheboud, and T.J. Wallington, Atmospheric chemistry of HFC-236cb: Fate of the alkoxy radical CF_3CF_2CFHO, *J. Phys. Chem.*, *101*, 2828-2832, 1997.

Moody, J.L., J.C. Davenport, J.T. Merrill, S.J. Oltmans, D.D. Parrish, J.S. Holloway, H. Levy II, G.L. Forbes, M. Trainer, and M. Buhr, Meteorological mechanisms for transporting O_3 over the western North Atlantic Ocean: A case study for August 24-29, 1993, *J. Geophys. Res.*, *101*, 29213-29227, 1996.

Mount, G.H., and E.J. Williams, An overview of the Tropospheric OH Photochemistry Experiment, Fritz Peak/Idaho Hill, Colorado, Fall 1993, *J. Geophys. Res.*, *102*, 6171-6186, 1997.

Moxim, W.J., H. Levy II, and P.S. Kasibhatla, Simulated global tropospheric PAN: Its transport and impact on NO_x, *J. Geophys. Res.*, *101*, 12621-12638, 1996.

Müller, J.-F., and G. Brasseur, IMAGES: A three-dimensional chemical transport model of the global troposphere, *J. Geophys. Res.*, *100*, 16445-16490, 1995.

Murphy, D.M., and D.W. Fahey, An estimate of the flux of stratospheric reactive nitrogen and ozone into the troposphere, *J. Geophys. Res.*, *99*, 5325-5332, 1994.

Nielsen, O.J., E. Gamborg, J. Sehested, T.J. Wallington, and M.D. Hurley, Atmospheric chemistry of HFC-143a: Spectrokinetic investigation of the $CF_3CH_2O_2$ radical, its reactions with NO and NO_2, and fate of CF_3CH_2O, *J. Phys. Chem.*, *98*, 9518-9525, 1994.

Novelli, P.C., K.A. Maserie, and P.M. Lang, Distribution and trends of carbon monoxide in the lower troposphere, *J. Geophys. Res.*, *103*, 19015-19033, 1998.

O'Brien, J.M., P.B. Shepson, K. Muthuramu, C. Hao, H. Niki, D.R. Hastie, R. Taylor, and P.B. Roussel, Measurements of alkyl and multifunctional organic nitrates at a rural site in Ontario, *J. Geophys. Res.*, *100*, 22795-22804, 1995.

Odum, J.R., T.P.W. Jungkamp, R.J. Griffin, R.C. Flagan, and J.H. Seinfeld, The atmospheric aerosol-forming potential of whole gasoline vapor, *Science*, *276*, 96-99, 1997.

Olson, J., M. Prather, T. Berntsen, G. Carmichael, R. Chatfield, P. Connell, R. Derwent, L. Horowitz, S.X. Jin, M. Kanakidou, P. Kasibhatla, R. Kotamarthi, M. Kuhn, K. Law, J. Penner, L. Perliski, S. Sillman, F. Stordal, A. Thompson, and O. Wild, Results from the Intergovernmental Panel on Climatic Change photochemical model intercomparison (Photocomp), *J. Geophys. Res.*, *102*, 5979-5991, 1997.

Oltmans, S.J., D.J. Hofmann, J.A. Lathrop, J.M. Harris, W.D. Komhyr, and D. Kuniyuki, Tropospheric ozone during Mauna Loa Observatory Photochemistry Experiment 2 compared to long-term measurements from surface and ozonesonde observations, *J. Geophys. Res.*, *101*, 14569-14580, 1996.

Oltmans, S.J., A.S. Lefohn, H.E. Scheel, J.M. Harris, H. Levy, I.E. Galbally, E.G. Brunke, C.P. Meyer, J.A. Lathrop, B.J. Johnson, D.S. Shadwick, E. Cuevas, F.J. Schmidlin, D.W. Tarasick, H. Claude, J.B. Kerr, O. Uchino, and V. Mohnen, Trends of ozone in the troposphere, *Geophys. Res. Lett.*, *25*, 139-142, 1998.

Orkin, V.L., V.G. Khamaganov, A.G. Guschin, B. Laszlo, R.E. Huie, and M.J. Kurylo, Rate constants for the reactions of OH with hydrofluorocarbons, *Abstracts of Papers of The American Chemical Society*, *208:* 240-ENVR, Part 1, 1994.

O'Sullivan, N., J. Wenger, and H. Sidebottom, Kinetics and mechanisms of the OH radical initiated degradation of fluorinated ethers, in *Proceedings of the 7th European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants: The Oxidizing Capacity of the Troposphere*, pp. 77-84, Office for Official Publications of the European Communities, Luxembourg (EUR 17482) ISBN 92-828-0158-6, 1997.

Parrish, D.D., J.S. Holloway, M. Trainer, P.C. Murphy, L.G. Forbes, and F.C. Fehsenfeld, Export of North-American ozone pollution to the North-Atlantic Ocean, *Science*, *259*, 1436-1439, 1993.

Parsons, D.A.B., M.C. Scholes, R.J. Scholes, and J.S. Levine, Biogenic NO emissions from savanna soils as a function of fire regime, soil type, soil nitrogen, and water status, *J. Geophys. Res.*, *101*, 23683-23688, 1996.

Penkett, S.A., P.S. Monks, L.J. Carpenter, K.C. Clemitshaw, G.P. Ayers, R.W. Gillett, I.E. Galbally, and C.P. Meyer, Relationships between ozone photolysis rates and peroxy radical concentrations in clean marine air over the Southern Ocean, *J. Geophys. Res.*, *101*, 12805-12817, 1997.

Pickering, K.E., A.M. Thompson, D.P. McNamara, W.-K. Tao, A.M. Molod, and R.B. Rood, Vertical transport by convective clouds: Comparisons between cloud-scale and global-scale models, *Geophys. Res. Lett.*, *22*, 1089-1092, 1995.

Pickering, K.E., A.M. Thompson, Y.S. Wang, W.K. Tao, D.P. McNamara, V.W.J.H. Kirchhoff, B.G. Heikes, G.W. Sachse, J.D. Bradshaw, G.L. Gregory, and D.R. Blake, Convective transport of biomass burning emissions over Brazil during TRACE A, *J. Geophys. Res.*, *101*, 23993-24012, 1996.

Poppe, D., J. Zimmermann, R. Bauer, T. Brauers, D. Bruning, J. Callies, H.P. Dorn, A. Hofzumahaus, F.J. Johnen, A. Khedim, H. Koch, R. Koppmann, H. London, K.P. Muller, R. Neuroth, C. Plassdulmer, U. Platt, F. Rohrer, E.P. Roth, J. Rudolph, U. Schmidt, M. Wallasch, and D.H. Ehhalt, Comparison of measured OH concentrations with model calculations, *J. Geophys. Res.*, *99*, 16633-16642, 1994.

Prather, M.J., and D.J. Jacob, A persistent inbalance between HO_x and NO_x photochemistry of the upper troposphere driven by deep tropical convection, *Geophys. Res. Lett.*, *24*, 3189-3192, 1997.

Price, C., J. Penner, and M. Prather, NO_x from lightning: 1, Global distribution based on lightning physics, *J. Geophys. Res.*, *102*, 5929-5941, 1997.

Prinn, R.G., R.F. Weiss, B.R. Miller, J. Huang, F.N. Alyea, D.M. Cunnold, P.J. Fraser, D.E. Hartley, and P.G. Simmons, Atmospheric trend and lifetime of CH_3CCl_3 and global OH concentrations, *Science*, *269*, 187-192, 1995.

Ravishankara, A.R., Heterogeneous and multiphase chemistry in the troposphere, *Science*, *276*, 1058-1065, 1997.

Ridley, B.A., E.L. Atlas, J.G. Walega, G.L. Kok, T.A. Staffelbach, J.P. Greenberg, F.E. Grahek, P.G. Hess, and D.D. Montzka, Aircraft measurements made during the spring maximum of ozone over Hawaii: Peroxides, CO, O_3, NO_y, condensation nuclei, selected hydrocarbons, halocarbons, and alkyl nitrates between 0.5 and 9 km altitude, *J. Geophys. Res.*, *102*, 18935-18961, 1997.

Roberts, J.M., D.D. Parrish, R.B. Norton, S.B. Bertman, J.S. Holloway, M. Trainer, F.C. Fehsenfeld, M.A. Carroll, G.M. Albercook, T. Wang, and G. Forbes, Episodic removal of NO_y species from the marine boundary layer over the North Atlantic, *J. Geophys. Res.*, *101*, 28947-28960, 1996.

Roelofs, G.-J., and J. Lelieveld, Model study of the influence of cross-tropopause O_3 transports on tropospheric O_3 levels, *Tellus*, *49B*, 38-55, 1997.

Roelofs, G.-J., J. Lelieveld, and R. van Dorland, A three-dimensional chemistry general circulation model simulation of anthropogenically derived ozone in the troposphere and its radiative climate forcing, *J. Geophys. Res.*, *102*, 23389-23401, 1997.

Rogaski, C.A., D.M. Golden, and L.R. Williams, Reactive uptake and hydration experiments on amorphous carbon treated with NO_2, SO_2, O_3, HNO_3 and H_2SO_4, *Geophys. Res. Lett.*, *24*, 381-384, 1997.

Rood, M.J., D.S. Covert, and T.V. Larson, Hygroscopic properties of atmospheric aerosol in Riverside, California, *Tellus*, *39B*, 383-397, 1987.

Sander, R., and P.J. Crutzen, Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea, *J. Geophys. Res.*, *101*, 9121-9138, 1996.

Schäfer, C., O. Horie, J.M. Crowley, and G.K. Moortgat, Is the hydroxyl radical formed in the gas-phase ozonolysis of alkenes? *Geophys. Res. Lett.*, *24*, 1611-1614, 1997.

Scheel, H.E., G. Ancellet, H. Areskoug, J. Beck, J. Bèsenberg, D. De Muer, A.L. Dutot, A.H. Egelov, P. Esser, A. Etienne, Z. Ferenczi, H. Geiβ, G. Grabbe, K. Granby, B. Gomišcek, L. Haszpra, N. Kezele, L. Klasinc, T. Laurila, A. Lindskog, J. Mowrer, T. Nielsen, P. Perros, M. Roemer, R. Schmitt, P. Simmonds, R. Sladkovic, H. Smit, S. Solberg, G. Toupance, C. Varotsos, and L. de Waal, Spatial and temporal variability of tropospheric ozone over Europe, in *Transport and Chemical Transformation of Pollutants in the Troposphere, Tropospheric Ozone Research, Vol 6.*, edited by Ø. Hov, Springer-Verlag, Berlin, Germany, 1997.

Schlager, H., P. Konopka, P. Schulte, U. Schumann, H. Ziereis, F. Arnold, M. Klemm, D.E. Hagen, P.D. Whitefield, and J. Ovarlez, In situ observations of air traffic emission signatures in the North Atlantic flight corridor, *J. Geophys. Res.*, *102*, 10739-10750, 1997.

Scholes, R.J., D.E. Ward, and C.O. Justice, Emissions of trace gases and aerosol particles due to vegetation burning in southern hemisphere Africa, *J. Geophys. Res.*, *101*, 23677-23682, 1996a.

Scholes, R.J., J. Kendall, and C.O. Justice, The quantity of biomass burned in southern Africa, *J.Geophys. Res.*, *101*, 23667-23676, 1996b.

Schultz, M.G., D.J. Jacob, Y. Wang, J.A. Logan, E. Atlas, D.R. Blake, N.J. Blake, J.D. Bradshaw, E.V. Browell, M.A. Fenn, F. Flocke, G.L. Gregory, B.G. Heikes, G.W. Sachse, S.T. Sandholm, R.E. Shetter, H.B. Singh, and R.W. Talbot, On the origin of tropospheric ozone and NO_x over the tropical Pacific, *J. Geophys. Res.*, in press, 1998.

Schumann, U., The impact of nitrogen oxides emissions from aircraft upon the atmosphere at flight altitudes: Results from the AERONOX project, *Atmos. Environ.*, *31*, 1723-1733, 1997.

Singh, H.B., M. Kanakidou, P.J. Crutzen, and D.J. Jacob, High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature*, *378*, 50-54, 1995.

Singh, H.B., D. Herlth, R. Kolyer, L. Salas, J.D. Bradshaw, S.T. Sandholm, D.D. Davis, J. Crawford, Y. Kondo, M. Koike, R. Talbot, G.L. Gregory, G.W. Sachse, E. Browell, D.R. Blake, F.S. Rowland, R. Newell, J. Merrill, B. Heikes, S.C. Liu, P.J. Crutzen, and M. Kanakidou, Reactive nitrogen and ozone over the western Pacific: Distribution, partitioning, and sources, *J. Geophys. Res.*, *101*, 1793-1808, 1996.

Smyth, S., J. Bradshaw, S. Sandholm, S. Liu, S. McKeen, G. Gregory, B. Anderson, R. Talbot, D. Blake, S. Rowland, E. Browell, M. Fenn, J. Merrill, S. Bachmeier, G. Sachse, J. Collins, D. Thornton, D. Davis, and H. Singh, Comparison of free tropospheric western Pacific air mass classification schemes for the PEM-West A experiment, *J. Geophys. Res.*, *101*, 1743-1762, 1996.

Solberg, S., C. Dye, N. Schmidbauer, A. Herzog, and R. Gehrig, Carbonyl and nonmethane hydrocarbons at rural European sites from the Mediterranean to the Arctic, *J. Atmos. Chem.*, *25*, 33-66, 1996.

Staffelbach, T.A., G.L. Kok, B.G. Heikes, B. McCully, G.I. Mackay, D.R. Karecki, and H.I. Schiff, Comparison of hydroperoxide measurements made during the Mauna Loa Observatory Photochemistry Experiment 2, *J. Geophys. Res.*, *101*, 14729-14739, 1996.

Stewart, R.W., and A.M. Thompson, Kinetic data imprecisions in photochemical rate calculations: Means, medians and temperature dependence, *J. Geophys. Res.*, *101*, 20953-20964, 1996.

Stockwell, W.R., On the $HO_2 + HO_2$ reaction: Its misapplication in atmospheric chemistry models, *J. Geophys. Res.*, *100*, 11695-11698, 1995.

Stockwell, W.R., J.B. Milford, D. Gao, and Y-J. Yang, The effect of acetyl peroxy—peroxy radical reactions on peroxyacetyl nitrate and ozone concentrations, *Atmos. Environ.*, *29*, 1591-1599, 1995.

Stockwell, W.R., F. Kirchner, M. Kuhn, and S. Seefeld, A new mechanism for regional atmospheric chemistry modeling, *J. Geophys. Res.*, *102*, 25847-25879, 1997.

Sunwoo, Y., G.R. Carmichael, and H. Ueda, Characteristics of background surface ozone in Japan, *Atmos. Environ.*, *28*, 25-37, 1994.

Talbot, R.W., J.E. Dibb, K.I. Klemm, J.D. Bradshaw, S.T. Sandholm, D.R. Blake, G.W. Sachse, J. Collins, B.G. Heikes, G.L. Gregory, B.E. Anderson, H.B. Singh, D.C. Thornton, and J.T. Merrill, Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during September-October 1991: Results from PEM-West A, *J. Geophys. Res.*, *101*, 1713-1725, 1996.

Talukdar, R.K., C.A. Longfellow, M.K. Gilles, and A.R. Ravishankara, Quantum yields of $O(^1D)$ in the photolysis of ozone between 289 and 329 nm as a function of temperature, *Geophys. Res. Lett.*, *25*, 143-146, 1998.

Tarasick, D.W., D.I. Wardle, J.B. Kerr, J.J. Bellefleur, and J. Davis, Tropospheric ozone trends over Canada: 1980-1993, *Geophys. Res. Lett.*, *22*, 409-412, 1995.

Thompson, A.M., The oxidizing capacity of the Earth's atmosphere: Probable past and future changes, *Science*, *256*, 1157-1165, 1992.

Thompson, A.M., R.D. Diab, G.E. Bodeker, M. Zunckel, G.J.R. Coetzee, C.B. Archer, D.P. McNamara, K.E. Pickering, J. Combrink, J. Fishman, and D. Nganga, Ozone over southern Africa during SAFARI-92/TRACE A, *J. Geophys. Res.*, *101*, 23793-23807, 1996a.

Thompson, A.M., K.E. Pickering, D.P. McNamara, M.R. Schoeberl, R.D. Hudson, J.H. Kim, E.V. Browell, V.W.J.H. Kirchhoff, and D. Nganga, Where did tropospheric ozone over southern Africa come from in October 1992? Insights from TOMS, GTE TRACE A and SAFARI 1992, *J. Geophys. Res.*, *101*, 24251-24278, 1996b.

Thompson, A.M., H.B. Singh, R.W. Stewart, T.L. Kucsera, and Y. Kondo, A Monte Carlo study of upper tropospheric reactive nitrogen during the Pacific Exploratory Mission in the Western Pacific Ocean (PEM-West B), *J. Geophys. Res.*, *102*, 28437-28446, 1997a.

Thompson, A.M., W.-K. Tao, K.E. Pickering, J.R. Scala, and J. Simpson, Tropical deep convection and ozone formation, *Bull. Amer. Met. Soc.*, *78*, 1043-1054, 1997b.

Tsutsumi, Y., Y. Makino, and J. Jensen, Aircraft measurements of tropospheric ozone over the western Pacific Ocean, *Atmos. Environ.*, *30*, 1763-1772, 1996.

Tyson, P.D., M. Garstang, R. Swap, P. Kollberg, and M. Edwards, An air transport climatology for subtropical southern Africa, *Int. J. Clim.*, *16*, 265-291, 1996.

Tyson, P.D., M. Garstang, A.M. Thompson, P. D'Abreton, R.D. Diab, and E.V. Browell, Atmospheric transport and photochemistry of ozone over south central southern Africa during SAFARI, *J. Geophys. Res.*, *102*, 10623-10635, 1997.

Veldt, C., Hydrocarbons and air quality, in *Calculating Air Pollution*, edited by K.D. van den Hout, R.M. van Aalst, A.C. Besemer, P.J.H. Builtjes and F.A.A.M. de Leeuw, TNO Report CMP 85/03, Delft, 1985.

Villalta, P.W., E.R. Lovejoy, and D.R. Hanson, Reaction probability of peroxyacetyl radical on aqueous surfaces, *Geophys. Res. Lett.*, *23*, 1765-1768, 1996.

Vogt, R., P.J. Crutzen, and R. Sander, A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature*, *383*, 327-330, 1996.

Volz, A., and D. Kley, Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, *Nature*, *332*, 240-242, 1988.

Walcek, C.J., H.-H. Yuan, and W.R. Stockwell, The influence of in-cloud chemical reactions on ozone formation in polluted and nonpolluted areas, *Atmos. Environ.*, *31*, 1221-1237, 1997.

Wallington, T.J., M.D. Hurley, J.M. Fracheboud, J.J. Orlando, G.S. Tyndall, J. Sehested, T. Møgelberg, and O.J. Nielsen, Role of excited CF_3CFHO radicals in the atmospheric chemistry of HFC-134a, *J. Phys. Chem.*, *100*, 18116-18122, 1996.

Wallington, T.J., W.F. Schneider, J. Sehested, M. Bilde, J. Platz, O.J. Nielsen, L.K. Christensen, M.J. Molina, L.T. Molina, and P.W. Wooldridge, Atmospheric chemistry of HFE-7100 ($C_4F_9OCH_3$): Reaction with OH radicals, UV spectra and kinetic data for $C_4F_9OCH_2\cdot$ and $C_4F_9OCH_2O_2\cdot$ radicals, and the atmospheric fate of $C_4F_9OCH_2O\cdot$ radicals, *J. Phys. Chem.*, *101*, 8264-8274, 1997.

Wallington, T.J., A. Guschin, T.N.N. Stein, J. Platz, J. Sehested, L.K. Christensen, and O.J. Nielsen, Atmospheric chemistry of $CF_3CH_2OCH_2CF_3$: UV spectra and kinetic data for $CF_3CH(\cdot)OCH_2CF_3$ and $CF_3CH(OO\cdot)OCH_2CF_3$ radicals, and the atmospheric fate of $CF_3CH(O\cdot)OCH_2CF_3$ radicals, *J. Phys. Chem.*, in press, 1998.

Wang, Y.H., D.J. Jacob, and J.A. Logan, Global simulation of tropospheric O_3-NO_x-hydrocarbon chemistry: 1, Model formulation, *J. Geophys. Res.*, *103*, 10713-10726, 1998a.

Wang, Y.H., J.A. Logan, and D.J. Jacob, Global simulation of tropospheric O_3-NO_x-hydrocarbon chemistry: 2, Model evaluation, *J. Geophys. Res.*, *103*, 10727-10756, 1998b.

Wang, Y.H., D.J. Jacob, and J.A. Logan, Global simulation of tropospheric O_3-NO_x-hydrocarbon chemistry: 3, Origin of tropospheric ozone and effects of non-methane hydrocarbons, *J. Geophys. Res.*, *103*, 10757-10768, 1998c.

Weinheimer, A.J., T.L. Campos, J.G. Walega, F.E. Grahek, B.A. Ridley, D. Baumgardner, C.H. Twohy, and B. Gandrud, Uptake of NO_y on wave-cloud particles, *Geophys. Res. Lett.*, in press, 1998.

Weinstein-Lloyd, J.B., P.H. Daum, L.J. Nunnermacker, J.H. Lee, and L.I. Kleinman, Measurement of peroxides and related species in the 1993 North Atlantic Regional Experiment, *J. Geophys. Res.*, *101*, 29081-29090, 1996.

Weller, R., R. Lilischkis, O. Schrems, R. Neuber, and S. Wessel, Vertical ozone distribution in the marine atmosphere over the central Atlantic Ocean (56S-50N), *J. Geophys. Res.*, *101*, 1387-1399, 1996.

Wennberg, P.O., T.F. Hanisco, L. Jaeglé, D.J. Jacob, E.J. Hintsa, E.J. Lanzendorf, J.G. Anderson, R.S. Gao, E.R. Keim, S.G. Donnelly, L.A. Del Negro, D.W. Fahey, S.A. McKeen, R.J. Salawitch, C.R. Webster, R.D. May, R.L. Herman, M.H. Proffitt, J.J. Margitan, E.L. Atlas, S.M. Schauffler, F. Flocke, C.T. McElroy, and T.P. Bui, Hydrogen radicals, nitrogen radicals, and the production of O_3 in the upper troposphere, *Science*, *279*, 49-53, 1998.

WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 1994*, Global Ozone Research and Monitoring Project—Report 37, Geneva, 1995.

WMO (World Meteorological Organization), *SPARC/IOC/GAW Assessment of Trends in the Vertical Distribution of Ozone*, edited by N. Harris, R. Hudson, and C. Phillips, SPARC Report No. 1, World Meteorological Organization Global Ozone Research and Monitoring Project – Report No. 43, Geneva, 1998.

Wuebbles, D.J., D. Maiden, R.K. Seals Jr., S.L. Baugchum, M. Metwally, and A. Mortlock, Emissions scenarios development: Report of the Emissions Scenarios Committee, in *The Atmospheric Effects of Stratospheric Aircraft*, edited by R. Stolarski and H.L. Wesoky, NASA Ref. Publ. 1313, pp. 63-208, U.S. National Aeronautics and Space Administration, Washington, D.C., 1993.

Yang, Y-J., W.R. Stockwell, and J.B. Milford, Uncertainties in incremental reactivities of volatile organic compounds, *Environ. Sci. Technol.*, *29*, 1336-1345, 1995.

Yienger, J.J., and H. Levy II, Empirical model of global soil-biogenic NO_x emissions, *J. Geophys. Res.*, *100*, 11447-11464, 1995.

Zhang, Z., R.D Saini, M.J Kurylo, and R.E Huie, Rate constants for the reactions of the hydroxyl radical with several partially fluorinated ethers, *J. Phys. Chem.*, *96*, 9301-9304, 1992.

Zhang, Y., C.B. Bischof, R.C. Easter, and P.-T. Wu, Sensitivity analysis of a mixed-phase chemical mechanism using automatic differentiation, *J. Geophys. Res.*, *103*, 18953-18979, 1998.