CHAPTER 4

Tropical and Midlatitude Ozone

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CHAPTER 4

TROPICAL AND MIDLATITUDE OZONE
Contents

SCIENTIFIC SUMMARY

Since the last Assessment, much new information has been obtained about the photochemical and dynamical processes that influence ozone concentrations at middle latitudes. Measurements in the lower stratosphere have significantly increased our confidence in the basic gas phase and heterogeneous processes affecting ozone at middle latitudes, although some discrepancies still exist. Laboratory studies have provided data that have led to an improved quantification of the photochemical processes that affect ozone at middle latitudes. Understanding of the dynamical factors influencing middle latitudes has improved, although significant uncertainties remain. The relative contributions of these different processes to the ozone trends observed middle latitude are still poorly understood and important uncertainties are still outstanding.

The major new findings are:

Photochemical Processes

• Observations, coupled with photochemical model calculations, have established with little doubt the role of the heterogeneous hydrolysis of N_2O_5 on the sulfate aerosol layer. However, there are instances where discrepancies still arise, and it is unclear whether these reflect deficiencies in modeling known chemistry (*e.g.*, imperfect knowledge of aerosol surface areas, photolysis rates, etc.) or, more profoundly, missing chemical processes.

• Measurements of radical species in the low stratosphere have provided direct confirmation that *in situ* photochemical ozone loss in the lower stratosphere at midlatitudes is dominated by HO_x and (man-made) halogen chemistry, and not by (largely natural) NO_x chemistry. Nevertheless, NO_x chemistry exerts an important control on the effectiveness of the halogen loss cycles. Current photochemical models can reproduce observed radical concentration changes and coupling between different chemical families, provided that heterogeneous reactions are incorporated and that the source gases are suitably constrained by observations.

• Satellite and *in situ* measurements of chlorine monoxide (ClO) concentrations in the low stratosphere at middle latitudes in both hemispheres show the existence of a seasonal cycle with maximum ClO during winter months. This variation appears to be broadly consistent with changes in NO_x due to *in situ* heterogeneous processes but does not appear consistent with the timing of springtime vortex dilution or wintertime flow through the vortex.

• There is evidence that the hydrolysis of chlorine nitrate ($ClONO_2$) on sulfate aerosols can occur at low temperatures and may be important in middle latitudes under high aerosol loading conditions.

• There are unresolved discrepancies between models and observations regarding the partitioning between reservoir and reactive species, notably the ratio of ClO_x to HCl. Even when constrained by observed source gas fields and radical species, photochemical models in the low stratosphere significantly overestimate observed HCl amounts. In the upper stratosphere models overestimate the ClO/HCl ratio.

Laboratory Studies

• Recent studies have confirmed that N_2O_5 hydrolysis on sulfate aerosol surfaces is fast and occurs readily under most stratospheric conditions, while reactions that lead directly to chlorine activation depend strongly on atmospheric temperature and humidity.

• The rate of the reaction of BrO with HO_2 has been revised upwards by a factor of 6, implying a much larger bromine-catalyzed ozone loss in the low stratosphere.

TROPICAL/MIDLATITUDE PROCESSES

- Quenching rates for vibrationally excited O_2 appear to be faster than previously thought, reducing the likely importance of the photolysis of vibrationally excited O_2 as a source of ozone in the upper stratosphere. The discrepancy between observed and modeled ozone in this region still persists.

Dynamical Processes

- The transport of air from polar regions has the potential to influence ozone concentrations at middle latitudes. While there are uncertainties about the relative contributions of transport and *in situ* chemistry for midlatitude ozone loss, both processes directly involve ozone destruction by bromine- and chlorine-catalyzed reactions.

- Observations and models indicate that, above about 16 km in winter, air at midlatitudes is mixed relatively efficiently and that influx of air from the tropics and from the interior of the polar vortex is weak. However, the importance of the erosion of air from the edge of the polar vortex relative to *in situ* chemical effects for midlatitude ozone loss is poorly known.

- Below 16 km, air is more readily transported between polar regions and midlatitudes. The influence of this transport on midlatitude ozone loss has not been quantified.

Eruption of the Mt. Pinatubo Volcano

- The eruption of Mt. Pinatubo in 1991 led to a massive increase in sulfate aerosol in the lower stratosphere. There is compelling evidence that this led to significant, but temporary, changes in the partitioning of NO_x, reactive halogen compounds, and abundances of HO_x in the low and mid-stratosphere at middle latitudes in such a way as to accelerate photochemical ozone loss. However, there is also evidence that circulation changes associated with heating on Mt. Pinatubo aerosols led to significant changes in the distribution of ozone in the tropics and middle latitudes. Changes in photolysis rates arising directly from the presence of volcanic aerosols are also thought to have affected ozone amounts.

4.1 GENERAL INTRODUCTION

In the light of the observed trends in ozone away from polar regions, a wide range of observational and modeling studies have been focused on the midlatitude lower stratosphere. A large number of dynamical and photochemical mechanisms that can influence the concentrations of stratospheric ozone have been identified. Those processes that are now thought to be the more important for midlatitude ozone loss are shown schematically in Figure 4-1. Assessments of the importance of chemical and dynamical processes are given in Sections I and II respectively.

I. CHEMICAL PROCESSES INFLUENCING MIDDLE LATITUDE AND TROPICAL OZONE

4.2 INTRODUCTION

The main photochemical processes that are thought to be important in midlatitude ozone photochemistry are shown schematically in Figure 4-1. The diagram is intended to show the winter months when the polar vortex is well established.

Ozone is produced by the photolysis of O_2 at wavelengths shorter than 242 nm to give oxygen atoms, followed by recombination (1). Variations in the solar output, for example during the 11-year solar cycle, lead directly to small changes in the photolysis of O_2 and thus to a correlated change in ozone amounts (2). Catalytic ozone loss occurs through a range of gas phase chemical cycles (3), those currently thought to be most important in the low stratosphere at midlatitudes being shown in the figure. It is known that at middle latitudes the hydrolysis of N_2O_5 (4) can proceed effectively on sulfate aerosols, reducing the available NO_x and indirectly increasing the degree of chlorine activation. At the lower temperatures present at higher latitudes, the hydrolysis of chlorine nitrate ($ClONO_2$) can occur (5), leading directly to increased chlorine activation. In the colder polar regions, chlorine activation on polar stratospheric clouds may also occur (6). Processes (4) and (5) are dependent on the aerosol loading in the stratosphere, and thus on the level of volcanic activity.

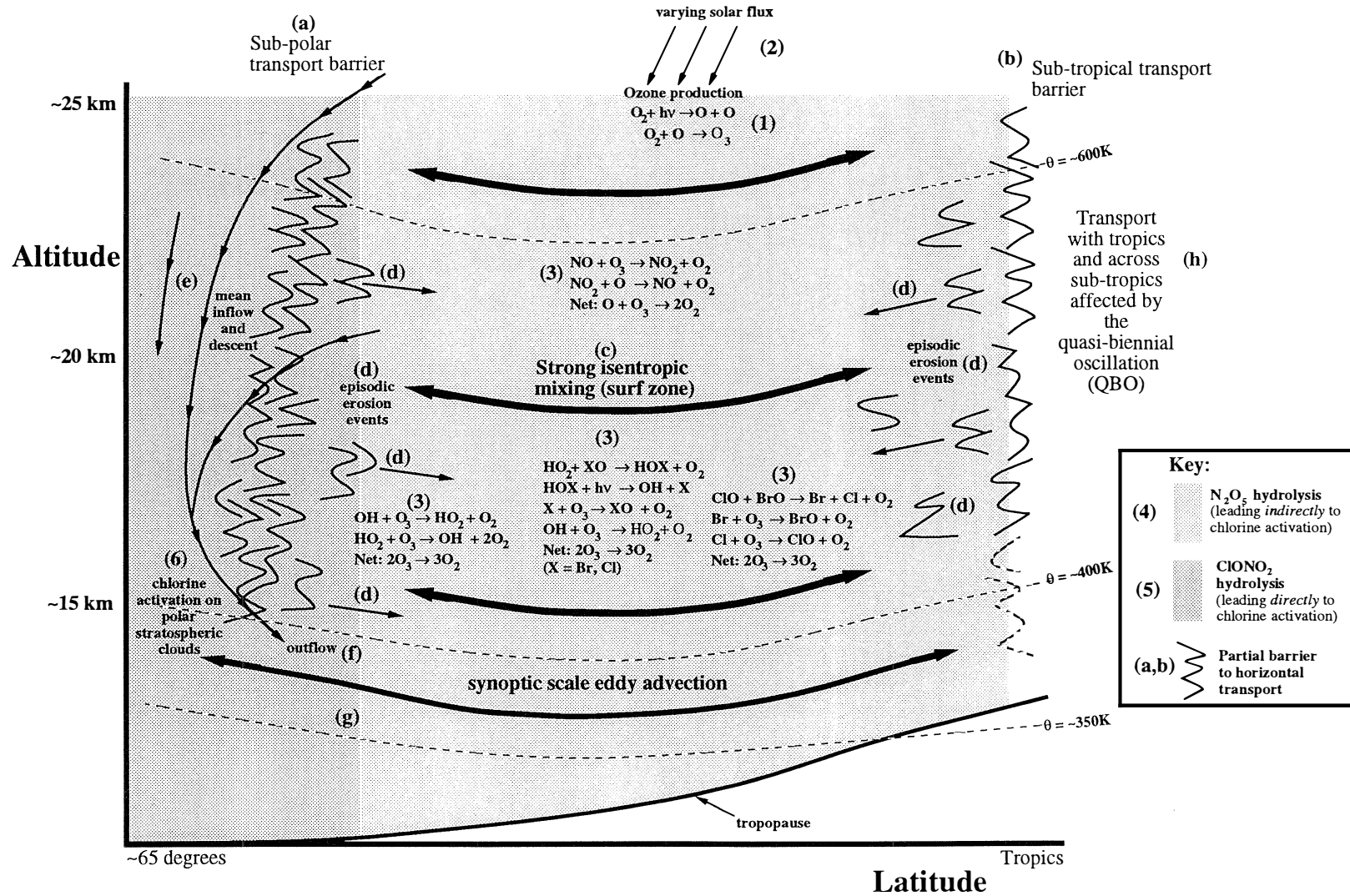Processes (4) and (5) have the effect of altering the balance of photochemical ozone loss by the different chemical cycles shown, reducing the effectiveness of the NO_x-only cycles in the low stratosphere in favor of the HO_x-only and coupled HO_x-halogen cycles. Information leading to this picture is discussed below.

4.2.1 Laboratory Studies of Photochemistry and Gas Phase Kinetics

Several new laboratory measurements of rate parameters and absorption cross sections (DeMore et al., 1992) are of direct consequence for understanding ozone loss in the tropics and midlatitudes.

The photolysis of nitric acid (HNO_3) in the atmosphere is important because it affects NO_x concentrations and thus, indirectly, ClO_x amounts. The temperature dependence of the HNO_3 absorption cross section (Rattigan et al., 1992; Burkholder et al., 1993) and the wavelength dependence of the hydroxyl radical (OH) quantum yield from HNO_3 photolysis (Turnipseed et al., 1992; Schiffman et al., 1993) have now been measured. The OH yield was confirmed to be nearly unity at long wavelengths, but other products, such as HONO, become more important at wavelengths shorter than 250 nm. The absorption cross section shows a temperature dependence (smaller at lower temperatures) that is strongest at wavelengths longer than 300 nm. As a result, the greatest effect on the calculated photolysis rate occurs at altitudes below about 28 km (Burkholder et al., 1993). These new data will yield more accurate calculations of the HNO_3 photolysis rate in photochemical models, but the magnitude of the effect will depend on the prior formulation used by each model.

The product yield from $ClONO_2$ photolysis at 193 and 248 nm has also been investigated (Minton et al., 1992), indicating that the products are split roughly evenly between $ClO + NO_2$ and $Cl + NO_3$. In contrast to prior measurements, no evidence was found for O-atom formation. However, it must be recognized that most $ClONO_2$ photolysis takes place at wavelengths longer than ~280 nm, where different products may form. If a similar effect were to be present at longer wavelengths, the result would be a reduction in the efficiency of ozone destruction from $ClONO_2$ photolysis (Toumi et al., 1993c). In addition, the quantum yields for NO_3 photolysis between 570 and 635 nm have recently been remeasured (Orlando et al., 1993) and give photolysis rates in reasonable agreement with the currently recom-

(a)
Sub-polar
transport barrier

varying solar flux

(2)

(b) Sub-tropical transport
barrier

~25 km

Ozone production
$O_2 + h\nu \rightarrow O + O$
$O_2 + O \rightarrow O_3$ (1)

~θ = ~600K

Altitude

Transport
with tropics
and across (h)
sub-tropics
affected by
the
quasi-biennial
oscillation
(QBO)

(e)

(d)

mean
inflow
and
descent

(3)
$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$
Net: $O + O_3 \rightarrow 2O_2$

(d)

~20 km

(d)
episodic
erosion
events

(c)
**Strong isentropic
mixing (surf zone)**

episodic
erosion (d)
events

(d)

(3)

(d)
$HO_2 + XO \rightarrow HOX + O_2$
$HOX + h\nu \rightarrow OH + X$
$X + O_3 \rightarrow XO + O_2$
$OH + O_3 \rightarrow HO_2 + O_2$
Net: $2O_3 \rightarrow 3O_2$
(X = Br, Cl)

(3)
$ClO + BrO \rightarrow Br + Cl + O_2$
$Br + O_3 \rightarrow BrO + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
Net: $2O_3 \rightarrow 3O_2$

(d)

(3)
$OH + O_3 \rightarrow HO_2 + O_2$
$HO_2 + O_3 \rightarrow OH + 2O_2$
Net: $2O_3 \rightarrow 3O_2$

(6)
chlorine
activation on
polar
stratospheric
clouds

(d)

~15 km

θ = ~400K

outflow (f)

synoptic scale eddy advection

(g)

θ = ~350K

tropopause

~65 degrees

Tropics

Latitude

Key:

(4) N_2O_5 hydrolysis
(leading *indirectly* to
chlorine activation)

(5) ClONO₂
hydrolysis
(leading *directly* to
chlorine activation)

(a,b) Partial barrier
to horizontal
transport

Figure 4-1. A schematic illustrating the dynamical and photochemical processes thought to play roles in controlling midlatitude ozone amounts. The various processes are discussed in the text (see Section 4.2 and following for a discussion of processes **1 - 6**, and Section 4.6 for a discussion of processes **a - h**).

mended values (DeMore *et al.*, 1992) but that are probably temperature dependent.

Increases in calculated photolysis rates and, hence, reductions in calculated lifetimes for species such as chlorofluorocarbons (CFCs) and nitrous oxide (N_2O) may be expected following adoption of more accurate cross sections for oxygen in the Schumann-Runge bands calculated using line-by-line methods (Minschwaner *et al.*, 1992; Toumi and Bekki, 1994). Recent estimates for N_2O, CF_2Cl_2 (CFC-12), and $CFCl_3$ (CFC-11) are 123, 116, and 44 years, respectively (Minschwaner *et al.*, 1993).

A recent measurement has shown that the room-temperature rate constant for the reaction of BrO with HO_2 is a factor of 6 larger than previously determined (Poulet *et al.*, 1992). Combined with an estimated temperature dependence based on the HO_2 + ClO reaction (DeMore *et al.*, 1992), this new determination dramatically increases the importance of bromine-catalyzed ozone loss, particularly in the 15 to 20 km region. The magnitude of possible HBr production from this reaction is currently under scrutiny. However, atmospheric HBr observations by Traub *et al.* (1992) suggest that only 2 ± 2 pptv of HBr is present at 32 km, implying that this channel must be slow.

Some unresolved discrepancies between observations and models exist for the partitioning of inorganic chlorine species in the stratosphere that could impact model predictions of ozone trends.
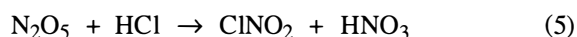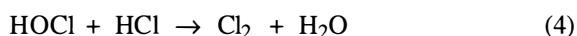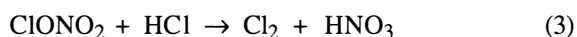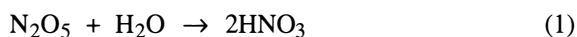
In the upper stratosphere there are uncertainties regarding the ClO/HCl ratio. The first simultaneous measurements of these species were reported by Stachnik *et al.* (1992) and supported the earlier assertion (McElroy and Salawitch, 1989) that models overestimate this ratio in the upper stratosphere. Calculations of the ClO/HCl ratio can be considerably improved by including a minor channel (approximately 5%) for the reaction of OH with ClO to give HCl. This reaction channel is unobserved to date, however, a channel of this magnitude would be within the upper limit suggested by laboratory studies (DeMore *et al.*, 1992). Addition of this channel to photochemical model calculations improves agreement with Atmospheric Trace Molecule Spectroscopy (ATMOS) data (Natarajan and Callis, 1991), with the annual amplitude of O_3 changes (Chandra *et al.*, 1993), and with the ozone trend in the upper stratosphere (Toumi and Bekki, 1993a).

In the lower stratosphere, there are indications of outstanding problems in the ratio of HCl to Cl_y (see Section 4.2.3.2).

The underestimation of upper stratospheric ozone remains unresolved (Minschwaner *et al.*, 1993), although the deficit now appears to be less than 20%. Calculations that incorporate the photolysis of vibrationally excited oxygen as a potential additional source of ozone gave promising results (Toumi *et al.*, 1991; Toumi, 1992; Minschwaner *et al.*, 1993; Eluszkiewicz and Allen, 1993), but recent laboratory measurements of the quenching rates for vibrationally excited O_2 imply they are more rapid than previously thought (Price *et al.*, 1993), suggesting that this mechanism is unlikely to be important.

4.2.2 Heterogeneous Processes

Five heterogeneous reactions on stratospheric sulfuric acid aerosols have been identified that could play important roles in the midlatitude ozone balance:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{1}$$
$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \tag{2}$$
$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{3}$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O \tag{4}$$
$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \tag{5}$$

These reactions all activate chlorine, either directly by converting reservoir species to photochemically active forms (2-5), or indirectly by reducing NO_x, which regulates ClO via formation of $ClONO_2$ (reaction 1).

Recent laboratory results suggest that the rates of heterogeneous reactions (1-5) on stratospheric sulfuric acid aerosol particles (SSAs) depend strongly on the chemical composition and phase of the aerosols. SSAs are thought to be composed primarily of sulfuric acid and water, but at temperatures lower than about 205 K they may take up significant amounts of HNO_3 (Molina *et al.*, 1993; Zhang *et al.*, 1993; Tabazadeh *et al.*, 1993) and may eventually freeze, with uncertain effects on the rates of heterogeneous reactions.

The hydrolysis of N_2O_5 (reaction 1) occurs rapidly on all liquid SSAs, with very little temperature dependence (see Tolbert, 1993, for a review of these results). In contrast, the hydrolysis of $ClONO_2$ (reaction 2) is a strong function of aerosol composition, occurring faster

for more dilute aerosols (Hanson *et al.*, 1994, and references therein). In the stratosphere, this property manifests itself as a strong temperature dependence, with an increasing reaction rate at low temperatures at which SSAs are most dilute.

At present, it is difficult to assess the importance of reactions 3-5, as there are few relevant measurements; values for HCl solubility vary by an order of magnitude (Zhang *et al.*, 1993; Williams and Golden, 1993; Hanson and Ravishankara, 1993b; Luo *et al.*, 1994). There are no direct measurements of diffusion coefficients and very few second-order rate constants have been determined. In general, however, these reactions appear to be limited by the availability of HCl in solution. Because HCl solubility increases rapidly with decreasing temperature and decreasing H_2SO_4 concentration, the rates of reactions 3-5 should behave similarly with temperature to that of reaction 2.

A reactive uptake model has been used to investigate the differences between reaction probabilities in small particles and in the bulk liquid (Hanson *et al.*, 1994). The differences are illustrated in Figure 4-2, which shows calculated reaction probabilities (γ) as functions of weight percent sulfuric acid (and temperature) for reactions 2 and 3 on 0.5 μm particles, together with the measured bulk rate for reaction 2.

At very low temperatures, possibly after the formation of polar stratospheric clouds (PSCs), sulfuric acid aerosol particles are likely to freeze as sulfuric acid tetrahydrate (SAT). Once frozen, SAT are expected to remain solid until they warm to above 210 to 215 K (Middlebrook *et al.*, 1993). Although there are relatively few studies of heterogeneous reactions on frozen SSAs, some results are available. Reaction 1, fast on all liquid SSAs, appears to be quite slow on SAT, even at high relative humidity (Hanson and Ravishankara, 1993a). Reaction 2 also appears to be slower on SAT than on liquid SSAs, although there is uncertainty in the measured value of γ (Hanson and Ravishankara, 1993a; Zhang *et al.*, 1994). In contrast, reaction 3 occurs readily on SAT surfaces at high relative humidity. Like its counterpart on type I PSCs, the rate of reaction 3 on SAT decreases as the relative humidity decreases. Reactions 4 and 5 have not yet been studied on SAT surfaces.

Laboratory work also shows that several species in the HO_x family, for example, OH and HO_2 (Hanson *et al.*, 1992) and CH_2O (Tolbert *et al.*, 1993), are readily
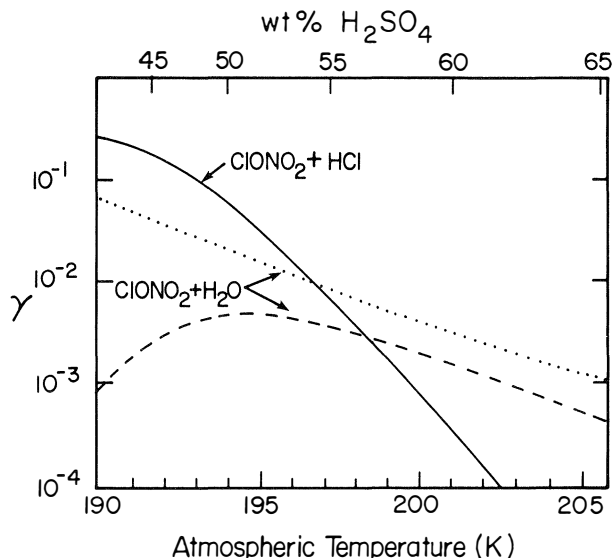
Figure 4-2. The uptake coefficients (γ) for $ClONO_2$ onto small liquid sulfuric acid droplets due to reaction with HCl (solid curve) and with H_2O (dashed curve) are shown here. These values are calculated with parameters obtained from laboratory measurements over bulk liquid surfaces using the methodology presented in Hanson *et al.* (1994). The calculation was made for a partial pressure of water equal to 2×10^{-4} mTorr, equivalent to 5 ppmv at 50 hpa. The approximate H_2SO_4 content of the droplets is shown at the top of the figure. The dotted curve is the laboratory measured γ for $ClONO_2$ with H_2O in the absence of HCl. The reaction probability for HOCl + HCl is similar to that for $ClONO_2$ + HCl. The reactive loss coefficient for N_2O_5 on 60 wt% H_2SO_4 at low temperatures is ~0.1, and probably does not vary greatly from this value over the range of acid content shown in this figure. (Adapted from Hanson *et al.*, 1994.)

taken up by SSAs. The competing gas phase reactions of OH and HO_2 are so rapid that heterogeneous loss does not significantly perturb the HO_x budget or partitioning (Hanson *et al.*, 1994). However, condensed phase reactions of OH or HO_2 and uptake of HO_x reservoirs such as CH_2O may impact the chemistry of other radical families.

A number of studies (Abbatt, 1994; Hanson and Ravishankara, 1994) have shown that heterogeneous reactions of bromine compounds (HBr, HOBr, and $BrONO_2$) occur on sulfate aerosol and may be important sources of halogen atoms.

Finally it should be noted that heterogeneous reactions also occur very readily on polar stratospheric clouds. These processes, which may have an impact on midlatitude chemistry (see Section 4.7), are discussed in Chapter 3.

4.2.3 Atmospheric Observations

Since the last Assessment, measurements from a variety of sources including the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) and the second Airborne Arctic Stratospheric Expedition (AASE II) campaigns, from the Upper Atmosphere Research Satellite (UARS) and ATMOS instruments, and from ground-based instruments have all provided new information that bears directly on the issue of midlatitude ozone loss. Details of these advances are given below.

4.2.3.1 NO_x/NO_y RATIO

Many new measurements indicate that incorporation of reaction 1 (see above) into photochemical models results in better agreement between theory and measurements. A variety of observations of nitrogen oxide species show a lower-than-gas-phase NO_x/NO_y ratio including *in situ* (Fahey *et al.*, 1993; Webster *et al.*, 1994a), column measurements (Keys *et al.*, 1993; Koike *et al.*, 1993), and ATMOS data (McElroy *et al.*, 1992; Toumi *et al.*, 1993b). Indirect measurements (*e.g.*, the balloon-borne ClO profiles measured by Avallone *et al.*, 1993a) also support inclusion of N_2O_5 hydrolysis in models, in order to more accurately reproduce observations. Figure 4-3 illustrates a comparison between data and models from that study.

Observations obtained during the SPADE campaign showed that models that neglect heterogeneous chemistry provide a completely inadequate description of the observed radicals, but that inclusion of the heterogeneous hydrolysis of N_2O_5 and $ClONO_2$ at the recommended rates resulted in better agreement between observation and theory. The modeled partitioning between NO_x and NO_y generally shows good (30 percent) agreement with the measured ratio when the hydrolysis of N_2O_5 and the temperature dependence of the nitric acid cross sections (Burkholder *et al.*, 1993) are used (*e.g.*, Salawitch *et al.*, 1994a, b; Wennberg *et al.*, 1994).
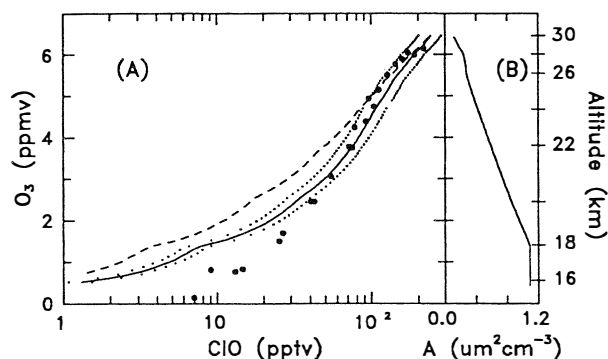
Figure 4-3. Curve A: A 0.5-km average of measured ClO, shown as solid circles. The dashed line represents gas-phase-only model results and the heavy solid line shows the calculation with addition of N_2O_5 hydrolysis. The dotted lines depict the range of uncertainty in calculated ClO for the heterogeneous model resulting from the reported uncertainty in ozone, which was used to initialize the trace gases in the model. The model is unable to reproduce ClO at the lowest altitudes, possibly due to inaccurate partitioning of HCl and $ClONO_2$. **Curve B:** Surface area density used for the heterogeneous model calculations. (From Avallone *et al.*, 1993a.)

Systematic differences between model and observations suggest, however, that our knowledge of N_2O_5 chemistry may still be incomplete. For example, Toumi *et al.* (1993c) conclude that the currently recommended γ for N_2O_5 hydrolysis is too fast to be consistent with the ATMOS observations. Other specific anomalies remain, for example anomalous NO_x/NO_y ratios (Fahey *et al.*, 1994). However, it is unclear whether these reflect deficiencies in modeling known chemistry (*e.g.*, imperfect knowledge of aerosol surface areas, photolysis rates, etc.), or more profoundly, missing chemical or transport processes.

4.2.3.2 PARTITIONING OF RADICAL SPECIES

During the SPADE campaign (November 1992 to April/May 1993), measurements of the concentrations of the free radicals NO_2, NO, ClO, HO_2, and OH were obtained, together with those of ozone and a number of tracers and reservoir species (CO_2, H_2O, N_2O, CH_4, HCl). The main results from this campaign that have implications for ozone photochemistry are summarized in the following paragraphs.

Modeled OH and HO_2 concentrations are in reasonable agreement with the measurements, although usually systematically lower by 10-20% (Salawitch et al., 1994a, b; Wennberg et al., 1994). While this is well within the uncertainty of the measurements, there were at times more serious discrepancies: OH and HO_2 concentrations at high solar zenith angles are much higher (as much as 10 times at 90° SZA) than expected. This is most pronounced in the sunrise data (Wennberg et al., 1994). It is unclear what process is responsible for this HO_x production (Michelsen et al., 1994), although, since there is a simultaneous increase in NO, the photolysis of HONO formed by the heterogeneous decomposition of HNO_4 has been suggested (Wennberg et al., 1994).

The partitioning between OH and HO_2 agrees well (15 percent) with that expected based on a simple steady state model using the measured concentrations of NO and O_3 (Cohen et al., 1994). This result is a confirmation of our understanding of the coupling between the HO_x and NO_x families and the ozone reaction chemistry with OH and HO_2.

The measured partitioning between NO_2 and NO is usually in reasonable (30%) agreement with the expected steady-state relationship:

$$NO_2/NO = \{k_{NO+O_3}(O_3) + k_{NO+ClO}(ClO)\} / J_{NO_2}$$

although disagreements of more than a factor of two are occasionally observed (Jaeglé et al., 1994).

In combination with the earlier AASE II observations (King et al., 1991; Avallone et al., 1993b), the SPADE measurements demonstrate the role that aerosols play in enhancing ClO (Salawitch et al., 1994a, b). The ratio of ClO to the available inorganic chlorine was observed to be strongly anticorrelated with the available NO_x (Wennberg et al., 1994; Stimpfle et al., 1994), and it was observed that ClO concentrations dropped between the fall and spring flights, consistent with a direct response to observed NO_x enhancements.

However, balancing the chlorine budget in the lower stratosphere remains problematic. Calculations of the ClO/HCl ratio from ER-2-based measurements (Webster et al., 1993) show that this ratio is not accurately represented by a model that includes the heterogeneous hydrolysis of N_2O_5, as shown in Figure 4-4. This conclusion was also drawn in the work of Avallone et al. (1993a), in which the model was unable

to reproduce the measured values of ClO below about 18 km altitude. However, as discussed below, provided the ratio of NO_x to NO_y is modeled correctly, accurate simulations of observed ClO are obtained, implying that the modeled HCl concentrations are in error, but not the modeled ClO concentrations. Models predict much higher (1.5 to 3 times) HCl than was measured (Webster et al. 1994b; Salawitch et al., 1994b). While the disagreement observed during SPADE was smaller than that during the AASE II campaign, large differences remain.

If, however, the inorganic chlorine unaccounted for is taken to be chlorine nitrate, the observed ClO and NO concentrations would imply that the photolysis rate of chlorine nitrate must be approximately 1/3 of the recommended value (Webster et al., 1994b). While simultaneous measurements of chlorine nitrate are a prerequisite to resolving this problem, the reasons for this discrepancy, and the implication for ozone loss, remain unclear.

Figure 4-5 shows measurements of the diurnal dependencies of stratospheric free radicals obtained on the flights of May 11 (sunrise) and May 12 (sunset) at 37°N and 63 hPa (18.8 km). Making certain assumptions (see caption), Salawitch et al. (1994a), using a data-assimilation photochemical model constrained by the observed source gas fields, obtained very good agreement with the observations (see Figure 4-5), implying a good understanding of the basic controlling processes.

Further confirmation of our generally good understanding of fast photochemistry over a range of conditions in the low stratosphere was provided by the SPADE survey flights, which were made from 15-60°N with altitude profiles (15-21 km) made approximately every 10 degrees of latitude. Figure 4-6 shows data obtained during the SPADE ER-2 flights of May 14 and May 18, 1993, compared with the data-assimilation model of Salawitch et al. (1994b) constrained by observed source gas fields. Observed changes in aerosol surface area along the flight track of between ~5 and ~15 $\mu m^2 cm^{-3}$ are also included in the calculations. Details of the model calculations are given in the figure caption. Salawitch et al. conclude that inclusion of heterogeneous processes is essential if radical concentrations are to be modeled correctly, although discrepancies remain, notably in the modeled OH/HO_2 and NO/NO_2 ratios.

OCTOBER 1991 → MARCH 1992
LATITUDES 26 → 90°N
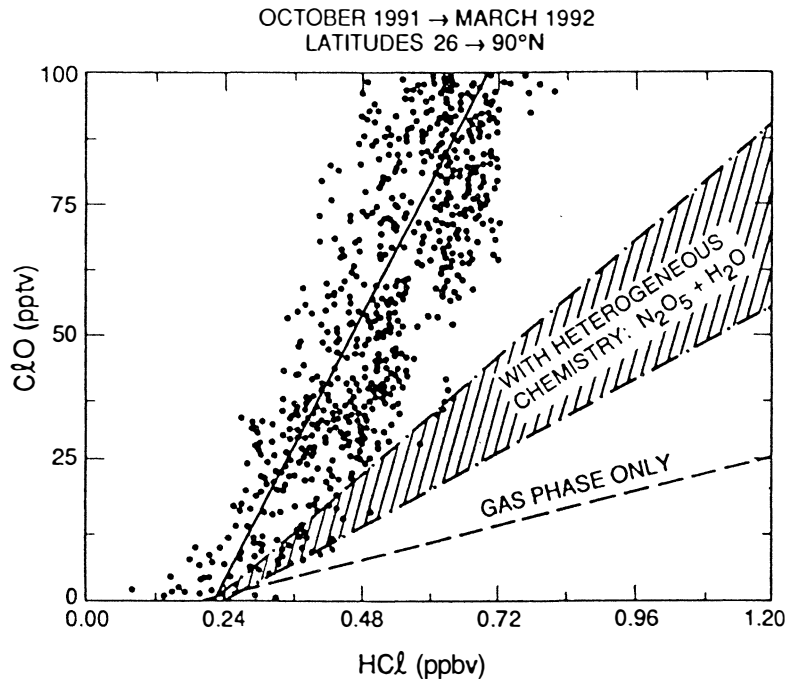
Figure 4-4. Scatter plot of ClO versus HCl data from instruments aboard the NASA ER-2, taken on the flights of Oct. 14, 1991, Feb. 13, 1992, and Mar. 15 and 22, 1992, covering latitudes between 26° and 90°N. The data included are limited to ClO mixing ratios less than 100 pptv, and to solar zenith angles less than or equal to 80°. Also plotted are results from the 2-D model of Solomon and Garcia using either gas-phase-only photochemistry, or including the heterogeneous hydrolysis of N_2O_5 on two levels of sulfate aerosol surface area that bracketed the ER-2 observations. The figure illustrates that observed HCl concentrations for a given ClO amount are approximately a factor of 2 lower than model calculations including heterogeneous chemistry would imply. (From Webster et al., 1993.)

These discrepancies can be reduced, but not eliminated, with further refinements.

Measurements from the Microwave Limb Sounder (MLS) have allowed the global behavior of ClO concentrations in the low stratosphere to be determined. In Figures 4-7 (left and right panels) (Froidevaux et al., 1994) are shown monthly mean zonal average ClO mixing ratios at 22 hPa, 46 hPa, and 100 hPa averaged over 30°N-50°N and 30°S-50°S, respectively. The data extend from September 1991 through to the end of 1993.

The MLS data reveal a distinct seasonal cycle in both hemispheres, with maximum ClO mixing ratios seen during midwinter months. This variation appears to be qualitatively consistent with expected changes in NO_x as discussed above. In agreement with studies mentioned above, lower stratospheric midlatitude ClO values of 0.1 to 0.2 ppbv, as measured by MLS, cannot

be explained with gas phase chemistry alone (Froidevaux et al., 1994). The MLS data show that ClO mixing ratios at 46 hPa and 22 hPa are closely comparable in the respective seasons in the two hemispheres.

Differences would be expected in the extent of air exposed to heterogeneous processes in the polar regions of the Southern and Northern Hemispheres, and indeed interannual differences would be present, particularly in the North (Jones and Kilbane-Dawe, 1994). Thus, the consistent phasing of the observed ClO maxima and, after adjustment for season, the comparable ClO amounts in the two hemispheres, suggest that *in situ* chemistry rather than the processing of air from the polar vortex is the main factor controlling these midlatitude ClO concentrations (Froidevaux et al., 1994). However, it should be noted that the MLS instrument has very limited sensitivity in the lowest region of the strato-
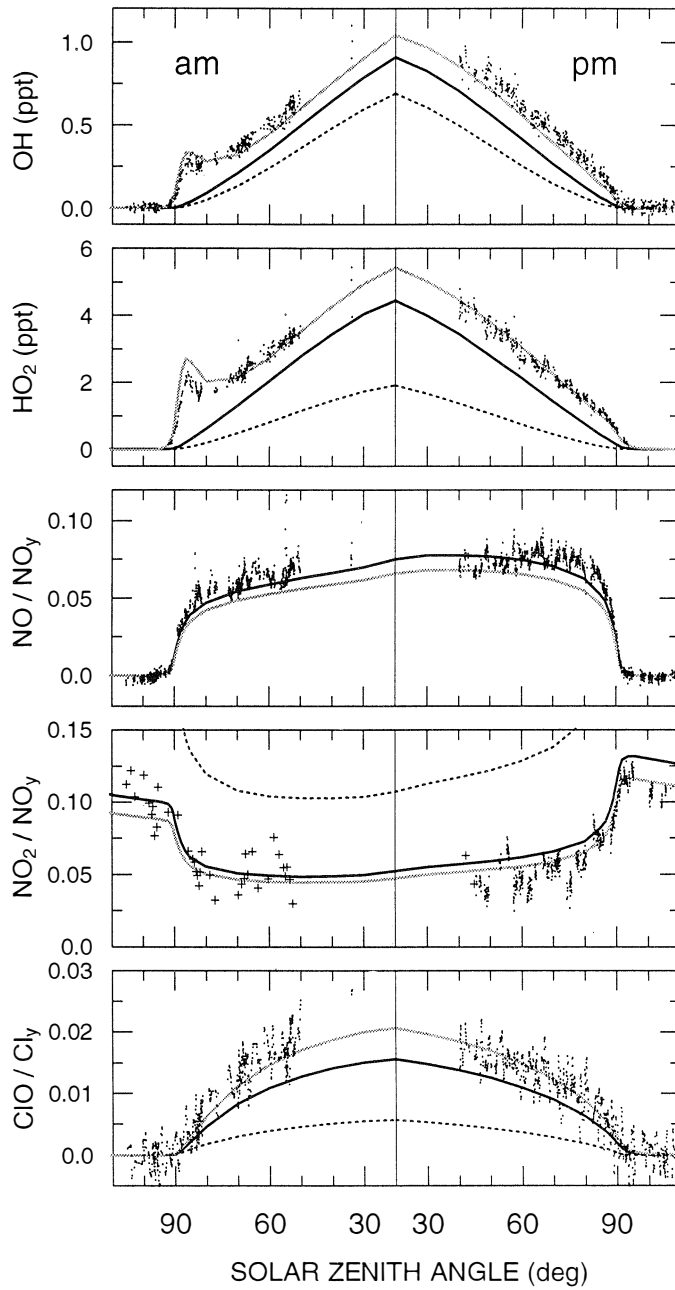
Figure 4-5. Measurements (dots) of the diurnal variations of stratospheric free radicals NO_2, NO, HO_2, OH (crosses and dots represent data from the JPL and NOAA instruments, respectively), and ClO from two ER-2 flights of May 11 (sunrise) and May 12 (sunset), both near 37°N and 63 hPa and [N_2O] between 240 and 260 ppbv, plotted as a function of solar zenith angle. Also shown are results from a constrained data assimilation model (Salawitch *et al.*, 1994a). Three calculations are shown. Dark dotted curve: gas phase reactions only, using rate constants and cross sections of DeMore *et al.* (1992). Curve 1, dark solid line: as for above, except including also the heterogeneous hydrolysis of N_2O_5 and $ClONO_2$. Curve 2, gray line: as for curve 1, except including the heterogeneous decomposition of HNO_4 to form HONO, the $O(^1D)$ quantum yield of Michelsen *et al.* (1994), and the temperature-dependent cross sections of HNO_3 from Burkholder *et al.* (1993). (From Salawitch *et al.*, 1994a.)
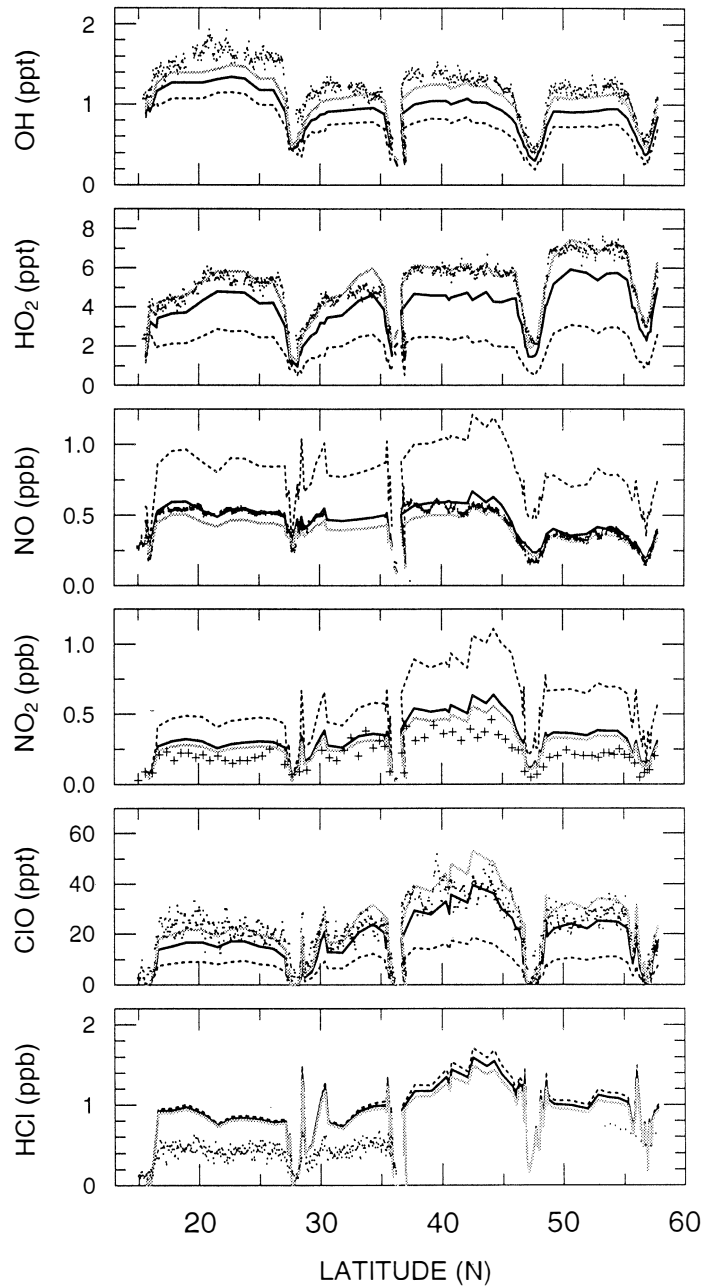
Figure 4-6. Measurements (points) of NO_2, NO, ClO, HO_2, OH, and HCl obtained on May 14 and 18, 1993, during which the ER-2 flew from 15 - 55°N. Also shown are calculations from the data assimilation model of Salawitch *et al.,* 1994b. The individual calculations are as for Figure 4-5. As can be seen, all three calculations significantly overestimate HCl concentrations. (From Salawitch *et al.*, 1994b.)
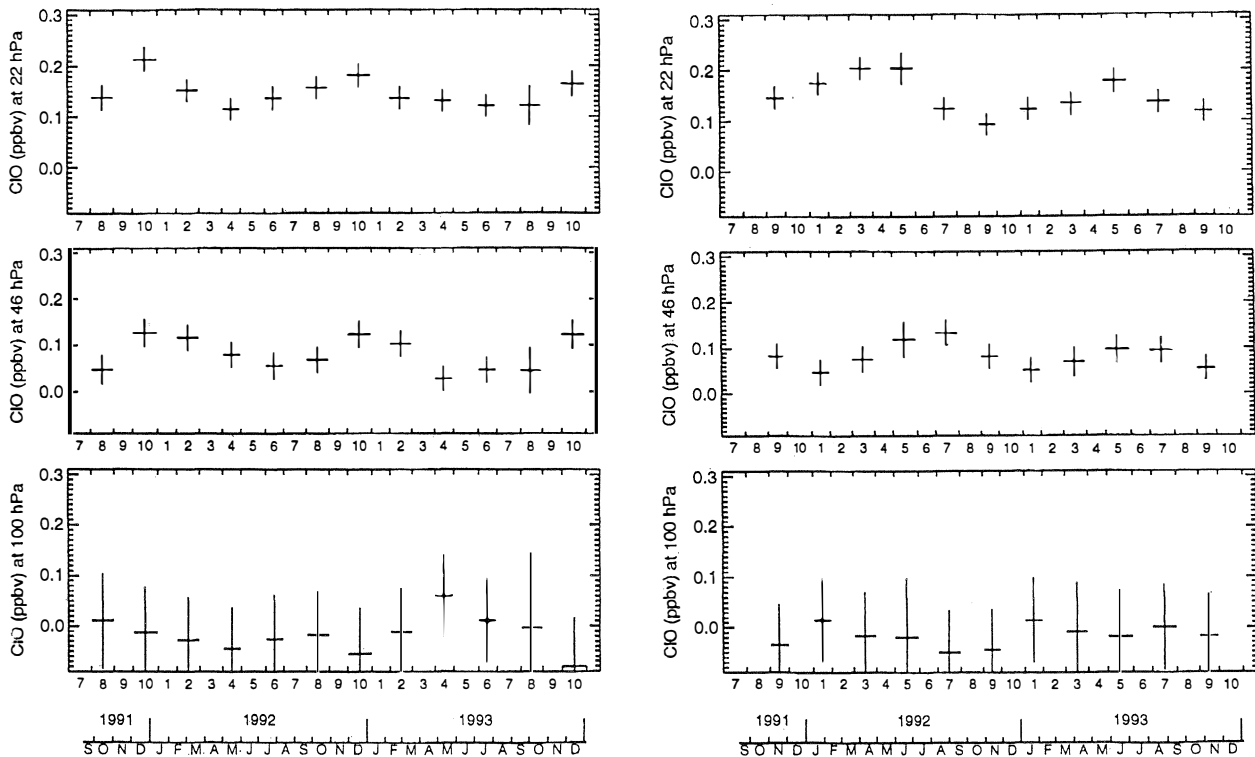
Figure 4-7. (left panels) Monthly zonal mean lower stratospheric ClO mixing ratio from 30°N - 50°N from the UARS MLS instrument. The figure shows monthly zonal mean ClO between September 1991 and December 1993. Results are given for pressures of 22 hPa (approximately 25 km, upper), 46 hPa (approximately 20 km, center) and 100 hPa (approximately 15 km, lower). In order to remove small biases, day (solar zenith angles < 90°) minus night (SZA > 95°) differences have been taken. Error bars are ± 2.8 σ. (Adapted from Froidevaux *et al.*, 1994.) **(right panels)** As Figure 4-7a) except for 30°S - 50°S. (Adapted from Froidevaux *et al.*, 1994.)

sphere (~100 hPa). This is an important limitation because the bulk of the ozone column at midlatitudes resides in this region, and any hemispheric differences in ClO at these low altitudes might not be detected.

Detailed comparisons of HCl data from the NASA ER-2 instrument of Webster *et al.* (*e.g.,* 1993) and the Halogen Occultation Experiment (HALOE) (Russell *et al.*, 1993b) are ongoing. ClONO$_2$ measurements from the Cryogenic Array Etalon Spectrometer (CLAES) (Roche *et al.*, 1993) will also augment this data set to provide a nearly complete inorganic chlorine budget for the lower stratosphere.

4.3 ERUPTION OF MT. PINATUBO

The eruption of Mt. Pinatubo, located in the Philippines (15°N, 120°E), culminated in an enormous explosion on June 14-15, 1991. The plume reached altitudes in excess of 30 km, depositing 15 to 20 Mt of sulfur dioxide (SO$_2$) into the stratosphere (Bluth *et al.*, 1992; McPeters, 1993; Read *et al.*, 1993), nearly 3 times as much as the El Chichón eruption in 1982. Conversion of SO$_2$ into sulfuric acid (H$_2$SO$_4$) occurred rapidly, resulting in sulfate aerosol surface areas as large as 85 $\mu m^2 cm^{-3}$ over Northern midlatitudes (Deshler *et al.*, 1992, 1993) at some altitudes. This huge perturbation has allowed a test of many aspects of our understanding of heterogeneous chemical processes in the stratosphere, building on the earlier work of Hofmann and Solomon (1989).

4.12

4.3.1 Effects on Chemical Composition

In the first few months following the Mt. Pinatubo eruption, low ozone amounts were detected in the tropics, roughly coincident with the region of largest aerosol loading (*e.g.*, Grant *et al.*, 1992, 1994; Schoeberl *et al.*, 1993a). On a longer time scale, ozone reductions were observed at midlatitudes by satellite (Gleason *et al.*, 1993; Waters *et al.*, 1993), ground-based (Bojkov *et al.*, 1993; Kerr *et al.*, 1993), and *in situ* instrumentation (Weaver *et al.*, 1993; Hofmann *et al.*, 1994). Details of this anomalous ozone behavior are given in Chapter 1.

The short-term tropical ozone decline has been attributed both to dynamical effects (see Section 4.6.3), and to a reduction of O_2 photolysis, and hence ozone production, due to absorption of solar ultraviolet radiation by SO_2 (Bekki *et al.*, 1993). SO_2 has also been shown to be capable of catalyzing ozone production via the following mechanism (Crutzen and Schmailzl, 1983; Bekki *et al.*, 1993):

$$SO_2 + h\nu \rightarrow SO + O \; (\lambda > 220 \text{ nm})$$

$$SO + O_2 \rightarrow SO_2 + O$$

$$2(O + O_2 + M \rightarrow O_3 + M)$$

$$\text{net: } 3O_2 \rightarrow 2O_3$$
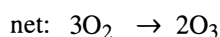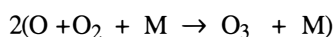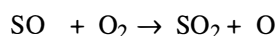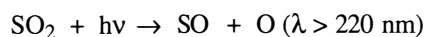
The longer-term ozone decrease is likely to be the result of a combination of enhanced heterogeneous chemistry resulting from the large increase in sulfate aerosol surface area, changes in the radiation field, and altered stratospheric dynamics (see, for example, Brasseur and Granier, 1992; Michelangeli *et al.*, 1992; Pitari and Rizi, 1993; Tie *et al.*, 1994).

Once the initial SO_2 plume is converted to aerosol particles, enhanced absorption of terrestrial emission and backscattering of solar radiation is expected especially in the tropics, leading to changed photolysis rates. The enhanced backscatter reduces the photolysis of all molecules below the cloud, but for molecules that absorb radiation at wavelengths longer than 300 nm, which can penetrate to the low stratosphere (for example, O_3 and NO_2), photolysis rates are enhanced above the cloud-top. The net effect is to accelerate photochemical ozone loss, leading to reductions in column ozone of several percent in the vicinity of the cloud (Pitari and Rizi, 1993; Tie *et al.*, 1994).
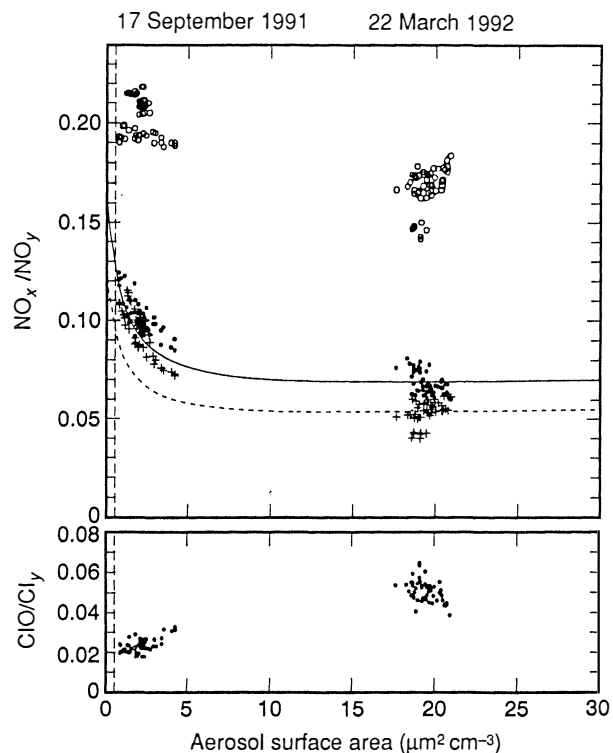
Figure 4-8. Scatter plot of NO_x/NO_y and ClO/Cl_y data from the NASA ER-2 with observed aerosol surface area (solid circles) in high and low aerosol conditions. Gas phase only (open circles) and heterogeneous case (crosses) model calculations are included (using observed aerosol surface areas with reaction 1). The surface area scale has no meaning for the gas phase case, except to separate data from the two flights. The vertical dashed line represents background aerosol surface area. The curved lines represent the dependence on surface area in the model heterogeneous case for the average conditions in September (solid) and March (dashed) data sets. Also shown are the corresponding ClO/Cl_y observations. (From Fahey *et al.*, 1993.)

A variety of chemical changes thought to be the results of heterogeneous reactions on the Mt. Pinatubo aerosol cloud have been observed. Fahey *et al.* (1993) and Kawa *et al.* (1993) showed dramatic reductions in the NO_x/NO_y ratio as sulfate surface area increased (see Figure 4-8). In response to this change, the amount of active chlorine (ClO/Cl_y) was observed to increase, as expected (Wilson *et al.*, 1993; Avallone *et al.*, 1993b;
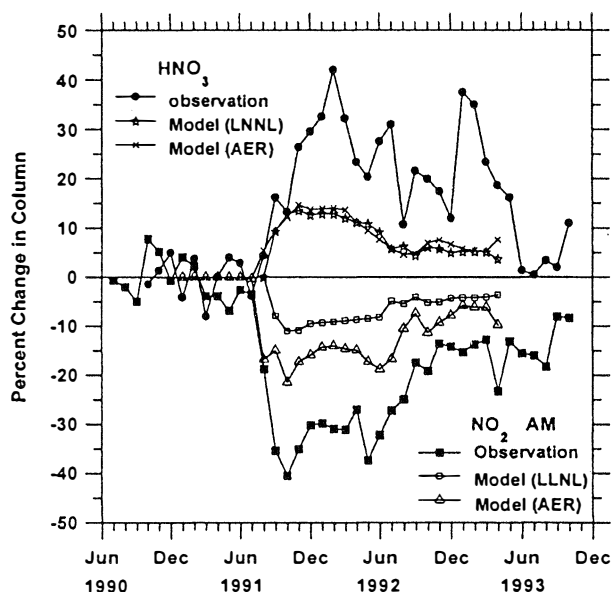
Figure 4-9. Percentage changes in HNO_3 and NO_2 column amounts above Lauder, New Zealand, (45°S) following the arrival of the Mt. Pinatubo aerosol. The Lawrence Livermore National Laboratory (LLNL) results are for 42.5°S and the Atmospheric Environmental Research, Inc. (AER) results are for 47°S. Heterogeneous chemistry is included in the calculations based on the observed aerosol field from SAGE II. (From Koike *et al.*, 1994.)

and Wennberg *et al.*, 1994). In addition, several measurements of column NO_2 at middle and high latitudes showed substantial decreases (25 to 50%) in comparison to previous years (Johnston *et al.*, 1992; Koike *et al.*, 1994; Mills *et al.*, 1993; Coffey and Mankin, 1993; Solomon *et al.*, 1994a).

The hydrolysis of N_2O_5 is expected to saturate at moderate values of surface area (Prather, 1992), but the hydrolysis of $ClONO_2$ may become increasingly important as surface area grows, as in the case of the Mt. Pinatubo aerosol. This saturation effect is evident in the NO_x/NO_y measurements of Fahey *et al.* (1993) (Figure 4-8) and further confirmed by the lack of major ClO enhancements at mid- to high Northern latitudes (Avallone *et al.*, 1993a; Dessler *et al.*, 1993) and seen in the MLS data shown in Figure 4-7. Further qualitative support for N_2O_5 hydrolysis comes from Koike *et al.* (1994), who have observed the effects of Mt. Pinatubo aerosol on NO_2 and HNO_3 over New Zealand. In Figure 4-9 are

shown percent changes in HNO_3 and NO_2 columns over Lauder (45°S) from June 1990 to December 1993. The data show a reduction in NO_2 columns as the Mt. Pinatubo cloud reached Lauder, and a simultaneous increase in column HNO_3. Model calculations using the observed aerosol field from SAGE II (Stratospheric Aerosol and Gas Experiment II) (Kent and McCormick, 1993) as input show good qualitative agreement with the observations, although the magnitude of the changes is underestimated in the models.

A number of studies have provided evidence for the heterogeneous hydrolysis of $ClONO_2$ on sulfate aerosols, particularly during periods of volcanic activity. Solomon *et al.* (1993) argue that the observation of enhancements to the OClO column in the austral fall of 1992 are due to the hydrolysis of $ClONO_2$ on sulfate aerosols. The formation of substantial OClO amounts requires enhanced ClO in addition to moderate BrO concentrations, and had in the past only been detected following the appearance of PSCs. However, in 1992, OClO was detected earlier and in larger quantities than in previous years, suggesting that chlorine had been activated to some degree on sulfate aerosols. This conclusion is predicated on the absence of PSC processing prior to the observation of OClO.

Column reductions of $ClONO_2$, HCl, and HNO_3 were also observed from the NASA DC-8 during transit below a very cold region of volcanically enhanced aerosol (O. Toon *et al.*, 1993). The heterogeneous reaction probability γ for $ClONO_2$ hydrolysis calculated from these observations, taking into account the history of the air parcels, is very close to laboratory values. Dessler *et al.* (1993) attempt a similar calculation based on balloon observations of ClO and NO and determine a value of γ again consistent with laboratory experiments. However, the possible influence of PSC processing at some earlier time cannot be entirely ruled out as influencing the observed concentrations of ClO and OClO.

Calculations using 2- and 3-dimensional models suggest that once the aerosol cloud is dispersed from the tropics and the aerosol loading begins to increase at mid- and high latitudes, significant (several percent) column ozone reductions arising from accelerated heterogeneous chemistry are likely to be widespread, with maximum reductions (up to ~10%) at midlatitudes in winter where the photolysis of HNO_3 is slow (Pitari and Rizi, 1993; Tie *et al.*, 1994). This is discussed further in

Section 4.6.3. However, there are several outstanding anomalies. For example, despite the more rapid movement of the Mt. Pinatubo aerosol cloud to the Southern Hemisphere (Trepte *et al.*, 1993), ozone trends were apparently smaller in the South compared to the North following the Mt. Pinatubo eruption. This is discussed further in Section 4.4.

4.3.2 Implications for the Normal State of the Atmosphere

Observations of chemical constituents in the presence of enhanced sulfate aerosol surface area and over a wide temperature range have shown that the heterogeneous hydrolysis of $ClONO_2$ should be considered in addition to the hydrolysis of N_2O_5 to more accurately simulate ozone loss in the stratosphere. The area of largest debate regarding heterogeneous chemistry is an accurate quantification of the actual rates of reaction in the stratosphere. Laboratory determination of rate parameters and uptake coefficients for a variety of species is essential, but improved understanding of the composition and physical characteristics of the stratospheric aerosol layer at temperatures less than about 210 K when ternary ($H_2O/HNO_3/H_2SO_4$) solutions may exist is equally important. Understanding of the potential role of heterogeneous processes other than the hydrolysis of N_2O_5 and $ClONO_2$ is expected to improve as a result of measurements made during periods of highly perturbed surface area, as reaction rates are expected to be large enough to cause an observable effect (Hanson *et al.*, 1994). It is unlikely that all of these processes will be important under "background" surface area conditions, but the possible continued emission of sulfur from current subsonic aircraft and a proposed supersonic fleet may significantly increase the sulfate aerosol loading of the stratosphere (Bekki and Pyle, 1992). Under such a scenario, heterogeneous reduction of NO_x and subsequent enhancement of active chlorine may have a serious effect on the ozone balance in the tropical and midlatitude stratosphere.

4.4 PHOTOCHEMICAL OZONE LOSS PROCESSES AT MIDLATITUDES

There is now a much clearer understanding of the relative importance of different photochemical destruction cycles to ozone loss in the low stratosphere, supported, as discussed above, by a comprehensive range of atmospheric measurements, laboratory studies, and model calculations. However, knowledge of the absolute rate of photochemical ozone loss still remains uncertain, primarily because of limitations in our ability to model accurately the distributions of source gases, but also because of uncertainties in heterogeneous chemistry.

A number of recent studies have provided a relatively consistent picture of the relative importance of different ozone destruction cycles (*e.g.,* Avallone *et al.*, 1993a; Rodriguez *et al.*, 1994; Garcia and Solomon, 1994; Wennberg *et al.*, 1994). In Figure 4-10 are shown calculations of the contributions of different photochemical cycles to ozone loss between 13 and 23 km, for 32°-63°N (from Rodriguez *et al.*, 1994). Panels show: a) background aerosol conditions, b) volcanically enhanced aerosol with hydrolysis of N_2O_5 only, and c) volcanically enhanced aerosol with hydrolysis of both N_2O_5 and $ClONO_2$. The broad picture is of reactions involving HO_2 being responsible for over half the photochemical destruction of ozone in the low stratosphere, while halogen (chlorine and bromine) chemistry accounts for a further third. Although catalytic destruction by NO_x accounts for less than 20% of the photochemical ozone loss, NO and NO_2 are vital in regulating the abundance of hydrogen and halogen radicals and thus the total photochemical ozone destruction rate. The effect of increased aerosol loading is to enhance the HO_x and halogen destruction cycles at the expense of the NO_x, with a net increase of ~20% in the ozone loss rate at peak aerosol loading. Figure 4-11 shows loss rates as a function of altitude from the model of Garcia and Solomon (1994) for 40°N in March for background aerosol loading. Below 22 km, reactions involving HO_x dominate, while between 23 and 40 km, NO_x cycles dominate. Bromine and chlorine loss cycles are important in the low stratosphere and chlorine becomes dominant near 40 km. Reductions in NO_x above about 22 km, where it represents the dominant photochemical loss mechanism, would therefore result in local ozone increases (Tie *et al.*, 1994).

This provides a possible explanation of the apparent absence of an ozone reduction in the Southern Hemisphere following Mt. Pinatubo (Hofmann *et al.*, 1994). The altitudes at which the Mt. Pinatubo cloud
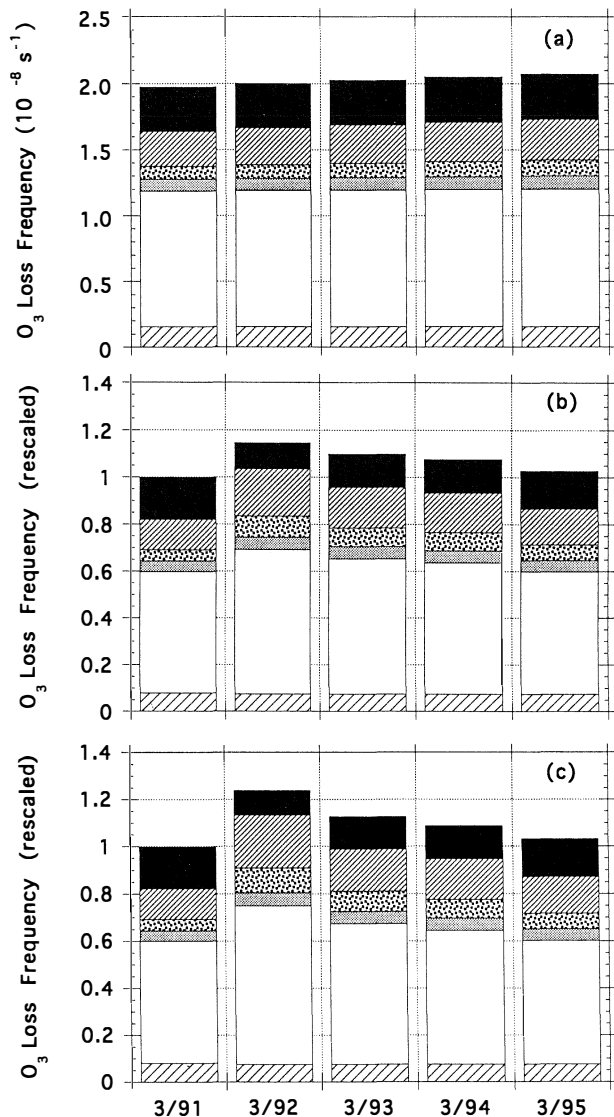
Figure 4-10. Calculated total average loss frequencies and relative contributions of different catalytic loss cycles from March 1991 to March 1995 showing the estimated effect of the Mt. Pinatubo eruption. Average loss frequencies are defined as the total loss rate of ozone between 13 and 23 km, and 32° and 63°N, divided by the total ozone content in this region. The relative contribution of each catalytic cycle is indicated by the different shadings: solid (NO_x cycles); dense diagonal (Cl_x cycles); large dot (Cl_x-Br_x); shaded (Br_x); white (HO_x); and diagonal ($O + O_3$). Panel a) shows loss frequencies for a background aerosol case; panels b) and c) are for volcanically enhanced aerosol and show, respectively, the effect of N_2O_5 hydrolysis alone, and the effects of both N_2O_5 and $ClONO_2$ hydrolysis. (From Rodriguez *et al.*, 1994.)

penetrated the two hemispheres differed markedly, with peak concentrations near or above 22 km in the South, but at lower altitudes in the North (Trepte *et al.*, 1993). In the Southern Hemisphere, ozone losses below 22 km would have been compensated for by slowed destruction above, leading to little net change in the ozone column. However, in the North, the absence of aerosol at higher altitudes meant that little or no compensating slowing of the ozone destruction occurred at the higher altitude, leading to significant overall declines in the column.

Finally, the suggestion has been made that iodine compounds (primarily CH_3I) can reach the low stratosphere in sufficient quantities to perturb significantly the ozone photochemical balance (Solomon *et al.*, 1994b). The relevant reactive iodine compounds have yet to be detected in the stratosphere. However, if confirmed, this process would have a significant impact on our understanding of photochemical ozone loss in the low stratosphere at midlatitudes.

4.5 THE SOLAR CYCLE AND QUASI-BIENNIAL OSCILLATION (QBO) EFFECTS ON TOTAL OZONE

The largest depletions of ozone noted in Chapter 1 of this document have occurred in the lowest part of the stratosphere and are systematic from year to year. While such changes are qualitatively consistent with either local chemical removal by HO_x and halogen cycles (Section 4.4) or the transport of ozone-depleted air from polar regions (Section 4.7), they are not, according to our best understanding, compatible with either changes in solar output or QBO effects. Nevertheless, solar cycle and QBO influences on total ozone must be removed if ozone trends are to be quantified reliably.

4.5.1 Solar Ultraviolet Variability and Total Ozone

Although solar radiation at wavelengths less than 300 nm accounts for only about 1% of the total radiative output of the sun, it is the principal energy source at altitudes between the tropopause and the lower thermosphere. It both drives the photochemistry of the upper atmosphere and is a source of heating, thus affecting the circulation of the upper atmosphere. Variations of the solar ultraviolet (UV) flux can affect column ozone
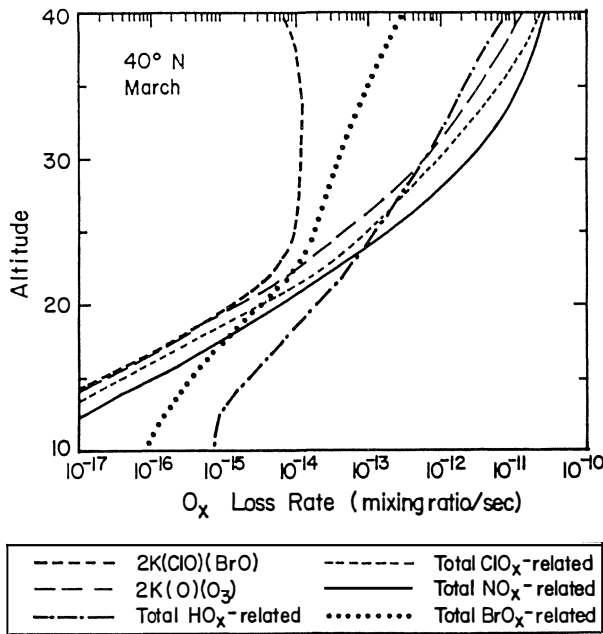
Figure 4-11. Calculated 24-hour averaged O_x loss rates (mixing ratio/sec) from various chemical cycles for 40°N in March for low (*i.e.,* non-volcanic) sulfate aerosol loading. In these circumstances the dominant ozone loss below 22 km is due to reactions involving OH and HO_2, with NO_x dominating between 23 and 40 km. Under higher aerosol loading conditions, coupled HO_x - halogen cycles become more significant. (From Garcia and Solomon, 1994.)

amounts and profiles, with the largest changes occurring in the upper stratosphere (Hood *et al.*, 1993; Brasseur, 1993; Fleming *et al.*, 1994).

Most solar UV variation occurs with time scales of about 11 years (*e.g.,* Cebula *et al.*, 1992) and 27 days. Over the 11-year cycle, Lyman alpha (121.6 nm) radiation varies by about a factor of two (Lean, 1991). The mid-UV (200 - 300 nm) strength varied by about 9% between the 1986 solar minimum and the 1990 solar maximum. Figure 4-12 displays the F10.7 index (a measure of the solar UV flux [*e.g.,* Donnelly, 1988]) superposed on the SBUV/SBUV2 (Solar Backscatter Ultraviolet spectrometer) total ozone that has had the QBO signal, the seasonal signal, and the trend removed by statistical methods (see Stolarski *et al.*, 1991, and Section 4.5.2 below). The figure shows that global average total ozone (40°S to 40°N) changes are correlated

with UV flux variations, changing by about 1.5% (4.5 Dobson units, DU) from solar maximum to solar minimum. These changes are in reasonable agreement with calculations using 2-D models (Fleming *et al.*, 1994; Garcia *et al.*, 1984; Brasseur, 1993; Huang and Brasseur, 1993; Wuebbles *et al.*, 1991).

4.5.2 The Quasi-Biennial Oscillation and Total Ozone

Variability in the equatorial lower stratosphere is dominated by the presence of an oscillation in equatorial winds, with a period of approximately 27 months, known as the quasi-biennial oscillation (QBO). The oscillation affects not only the winds but also the thermal structure and the distribution of ozone and other minor constituents at all latitudes (*e.g.,* Chipperfield *et al.*, 1994a, and references therein). Despite the magnitude of the ozone QBO being relatively small (approx. 5-10 DU at the equator; up to about 20 DU at high latitudes) it is nevertheless significant in ozone trend studies and must be characterized and removed. Ozone trend analy-
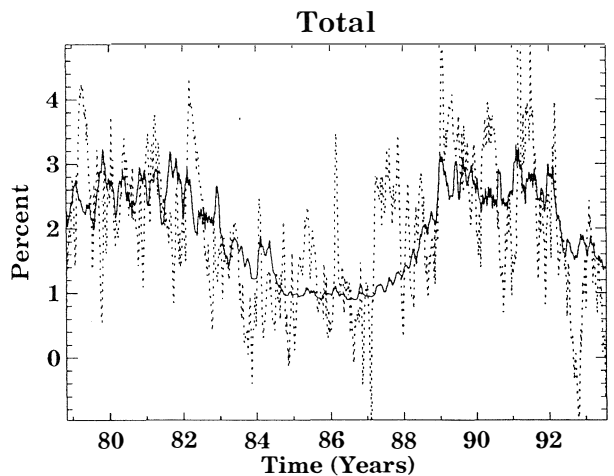
Figure 4-12. Response of SBUV/SBUV2 40°N-40°S average column ozone to the solar cycle as determined by a linear regression model after subtraction of the seasonal cycle, trend, and QBO (dashed curve). Also shown is the 10.7 cm radio flux (solid curve), which is a proxy for the solar output. The figure shows that changes in global column ozone of the order of 1.5% (4.5 DU) are to be expected during the 11-year cycle in solar output, mostly at higher altitudes. (From P. Newman, personal communication, 1994.)

ses (*e.g.,* Stolarski *et al.*, 1991) use linear regression techniques to isolate and remove the QBO signal. Observed equatorial wind data (*e.g.,* at 30 hPa) are employed as the reference time series, with the possibility of a time lag to take into account the observed variations of the QBO signal with latitude. However, observations of the ozone QBO show a strong seasonal and hemispheric asymmetry and the period of the observed ozone QBO at mid- and high latitudes is also not identical to that at the equator, often being closer to two years (Gray and Dunkerton, 1990). The use of equatorial wind data in ozone trend analyses to characterize the QBO signal at all latitudes is therefore not ideal.

II. TRANSPORT PROCESSES LINKING THE TROPICS, MIDDLE, AND HIGH LATITUDES

4.6 INTRODUCTION

The structure of the lower stratosphere in winter, the period when observed declines in ozone at middle latitudes are largest, is shown schematically in Figure 4-1. The diagram is intended to show the winter hemisphere when the polar vortex is well established. While the processes described below are known to occur to some extent at least, their magnitudes and relative contributions to the observed ozone declines have in many cases not been quantified reliably. While different in detail, both hemispheres correspond broadly to this picture.

In an altitude or log(pressure) framework, isentropes rise both in the tropics and in polar regions, indicative of the lower temperatures in both regions. Mixing along these isentropes can be rapid, on a time scale of days to weeks, except where potential vorticity (PV) gradients exist. In these regions, mixing is inhibited by a combination of horizontal wind shearing and dynamical "Rossby wave elasticity." The midlatitude region is bounded by a flexible PV barrier on its poleward side (**a**), and a similar but less distinct tropical barrier to transport (**b**) at ~20 degrees. Mixing along isentropes is relatively rapid in middle latitudes in the so called "surf zone" (**c**). Both barriers undergo episodic erosion events (**d**) when at times substantial volumes of air are transported irreversibly to middle latitudes. Evidence is accumulating that larger volumes of air come

from the sub-tropical than the sub-polar barrier. However, the transport of polar air, containing high active chlorine and low ozone amounts, to midlatitudes has potentially a major influence on middle latitude composition. A mean inflow of air into the polar vortex is thought to occur (**e**) which, when coupled to descent and outflow into the more disturbed region below a potential temperature (θ) of 400 K (~16 km), allows possibly chlorine-activated ozone-depleted polar air to reach middle latitudes (**f**). As a result of tropospheric weather features, air flow in the region below θ ~400 K is less zonal than at higher altitudes, and synoptic-scale eddy advection exchanges air between midlatitudes and polar regions.

At these low altitudes, chlorine activation may occur either on sulfate aerosols or, in the colder polar regions, on polar stratospheric clouds, again possibly influencing midlatitude ozone amounts in the very low stratosphere (**g**). Finally, transport of air from the tropics is highly dependent on the phase of the quasi-biennial oscillation and the degree of distortion of the polar vortex (**h**).

The extent of our understanding of these different processes is discussed below.

4.6.1 Transport of Air from the Tropics to Middle Latitudes

The tropics remain the most poorly documented and understood region of the stratosphere. Limitations in knowledge of its meteorology stem from sparse *in situ* data coverage and the breakdown of the balance approximations by which winds can be calculated from satellite-based temperature retrievals. There have also been fewer tracer measurements in the tropics than in middle latitudes. It is known that, overall, there is mean upwelling through the tropics and that this is where tropospheric source gases enter the stratosphere.

Evidence has been accumulating to support the notion that the tropical stratosphere is to some degree isolated from the active mixing present at midlatitudes in winter. Following injection into the tropical stratosphere of material from nuclear bomb tests (Feely and Spar, 1960) and the eruption of tropical volcanoes (*e.g.,* Mt. Agung; Dyer and Hicks, 1968), a decaying equatorial maximum seemed to persist as a tropical "reservoir" for up to two years. This effect has also been seen more

recently following the El Chichón and Mt. Pinatubo eruptions (Trepte *et al.*, 1993; Hofmann *et al.*, 1994). The existence of at least a partial subtropical transport barrier, at the equatorward edge of the winter midlatitude "surf zone," has also been deduced from theoretical arguments and numerical models (McIntyre 1990; Norton 1994; Polvani *et al.*, 1994). Recent observations of the tracers N_2O and CO_2 in the low stratosphere (Boering *et al.*, 1994) provide direct observational support for the relatively short mixing times in the "surf zone" region.

Analyses of data from the Limb Infrared Monitor of the Stratosphere (LIMS) instrument on Nimbus 7, from *in situ* aircraft data, and from instruments on the Upper Atmosphere Research Satellite (UARS) have all shown strong gradients of tracers and of potential vorticity in the sub-tropics, with occasional filaments of tropical material being entrained poleward (Leovy *et al.*, 1985; Murphy *et al.*, 1993; Randel *et al.*, 1993); this behavior is also reproduced in dynamical models (Boville *et al.*, 1991; Norton, 1994; Pierce *et al.*, 1993; Rood *et al.*, 1992; Waugh, 1993a; Chen and Holton, 1994; Polvani *et al.*, 1994; Bithell *et al.*, 1994).

The tropical lower stratosphere is also strongly influenced by the quasi-biennial oscillation (QBO), which has a significant impact on the meridional circulation (Plumb and Bell, 1982). The QBO affects meridional transport of ozone and other trace species by a modulation of planetary (Rossby) wave transport. When the Rossby wave amplitude increases sufficiently, the waves "break," resulting in irreversible transport in midlatitudes. The latitudinal region in which the waves break (the "surf zone") is affected by the background winds in equatorial regions, particularly in the case of strongly nonlinear waves (O'Sullivan and Young, 1992). Easterly equatorial winds confine the Rossby waves further polewards than westerly winds, resulting in enhanced meridional exchange of air between the subtropical and higher latitudes (see, *e.g.,* Baldwin and Dunkerton, 1990; Garcia, 1991; Dunkerton and Baldwin, 1992).

Extensive observations — ground-based, *in situ*, and satellite-based — of the formation, dispersion, and decay of stratospheric aerosol produced by the eruption of Mt. Pinatubo (15°N) in June 1991 have provided much insight into the processes of transport out of the tropics. These observations and their implications are described in the following.

4.6.2 The Mt. Pinatubo Eruption: Implications for Understanding of Transport Processes

Prior to the June 1991 eruption, the total stratospheric aerosol mass (as inferred using SAGE observations) was approximately 1 Mt, but by the end of 1991 the estimated mass had increased to ~30 Mt. The total mass has since decreased to approximately 10 Mt by mid-1993 and to around 3 Mt by mid-1994 (see Figure 4-13). The formation of the Mt. Pinatubo aerosol cloud in the stratosphere and its subsequent dispersal around the globe, monitored from the ground and satellites, have provided useful tests of our understanding of transport processes.

4.6.2.1 TROPICAL LATITUDES

In many respects, the temporal development of the Mt. Pinatubo aerosol distribution was similar to that observed following other high altitude tropical injections. A distinguishing characteristic of this eruption was the rapid movement of volcanic material across the equator within two weeks of the eruption (Bluth *et al.*, 1992; McCormick and Veiga, 1992). Young *et al.* (1993) re-
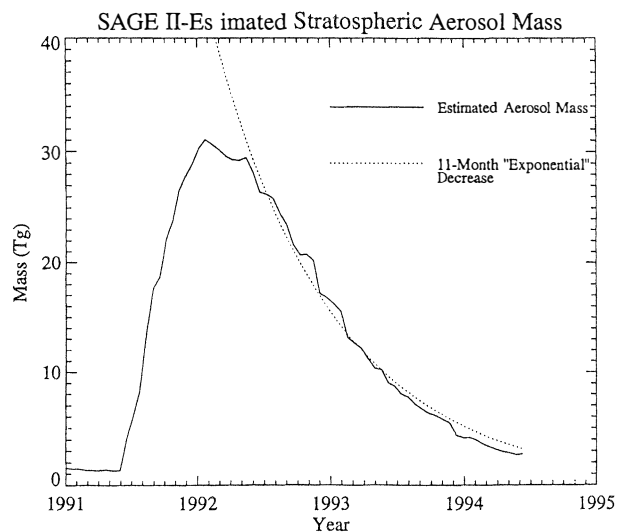
Figure 4-13. SAGE II estimated stratospheric aerosol mass, showing the near exponential decay on a time scale of ~11 months following the eruption in mid-1991. (Thomason and Poole, private communication.)

ported that this drift was induced by local aerosol heating. The heating was also sufficient to cause large increases in tropical stratospheric temperatures (Labitzke and McCormick, 1992) and may have contributed to the upward transport of aerosols to above 35 km by October 1991 (Trepte *et al.*, 1993). The tropical aerosol reservoir has gradually diminished in magnitude since the eruption as aerosols became dispersed poleward and were removed by sedimentation.

It is now appreciated that the detrainment of tropical air to midlatitudes occurs in episodic events when the polar vortex becomes displaced from the pole and interacts with the subtropical flow (*e.g.,* Randel *et al.*, 1993; Trepte *et al.*, 1993; Waugh, 1993a).

Transport from the tropics takes place in two regimes, at different altitudes. In the lower transport regime (about a scale height above the tropopause) air moves rapidly poleward and downward (Fujiwara *et al.*, 1982; Kent and McCormick, 1984). This transport is most effective during winter, especially in the Northern Hemisphere. Poleward spreading of aerosols is also observed during summer associated with tropospheric monsoon circulations. Early appearances of aerosol above Japan and Germany, amongst other places, were associated with this circulation (Hayashida, 1991; Jaeger, 1992). The dispersion rate of the main aerosol cloud was estimated from shipboard lidar measurements to be around 5 degrees latitude per month in the region 8°N to 22°N, during the period July 11 to September 21 (Nardi *et al.*, 1993).

In the upper regime (above 22 km), aerosols are redistributed by motions associated with the QBO (Trepte and Hitchmann, 1992). During the descending QBO westerly wind shear, anomalous subsidence (relative to the climatological upwelling) takes place over the equator, transporting aerosols downward and poleward below the shear layer. However, during the descending QBO easterly shear, enhanced lofting of aerosol occurs over the equator, with poleward flow above the shear layer.

Consistent with this picture, within the upper regime at altitudes where zonal mean westerlies existed, strong meridional gradients of volcanic aerosol, indicative of rapid poleward mixing, were present near 20°N and S (Browell *et al.*, 1993; Trepte *et al.*, 1993), while at heights where easterlies lay over the equator, the sub-

tropical gradients were diminished or absent, with greater mixing taking place at higher altitudes.

4.6.2.2 MIDDLE AND HIGH LATITUDES

Some aerosol spread rapidly to middle and high Northern latitudes in the low stratosphere, being first observed two weeks after the eruption in midlatitudes (Jaeger, 1992), in early August at Andoya (69°N) and on August 11 at Ny-Alesund (79°N) (Neuber *et al.*, 1994). However, the main part of the cloud did not reach Haute-Provence and Garmisch-Partenkirchen (48°N) until mid-October, with the highest backscatter ratios being observed in December 1992. In the Arctic, values of integrated backscatter at Spitzbergen were generally lower than at midlatitudes (Jaeger, 1993). In addition to satellite observations, extensive aerosol measurements from ground-based lidars in middle and high latitudes, and from airborne lidar and *in situ* instruments were performed during the European Arctic Stratospheric Ozone Experiment (EASOE) and NASA Airborne Arctic Stratospheric Expedition (AASE II) campaigns of winter 1991-92. Together, these data indicate efficient latitudinal transport below about 400-450K (15-19 km) but a largely isolated vortex, with little aerosol penetration, at higher altitudes (Tuck, 1989; Brock *et al.*, 1993; Browell *et al.*, 1993; Neuber *et al.*, 1994; Pitts and Thomason, 1993), although the differences in aerosol characteristics between inside and outside the vortex are less apparent when referenced to N_2O (Borrmann *et al.*, 1993; Proffitt *et al.*, 1993). Also, occasional intrusions of aerosol-rich midlatitude air into polar regions have been documented (Rosen *et al.*, 1992; Plumb *et al.*, 1994). Lidar measurements performed during the same period of time at Dumont d'Urville (68°S) showed that the aerosol did not penetrate the Antarctic vortex in 1991 (Godin *et al.*, 1992). In contrast, the smaller volcanic cloud of Cerro Hudson (46°S), which was injected into the lower stratosphere (around 12 km) in August 1991, spread rapidly into polar regions, again revealing efficient transport beneath the vortex (Godin *et al.*, 1992; Pitts and Thomason, 1993; Schoeberl *et al.*, 1993b). (Refer to Figure 4-14.)
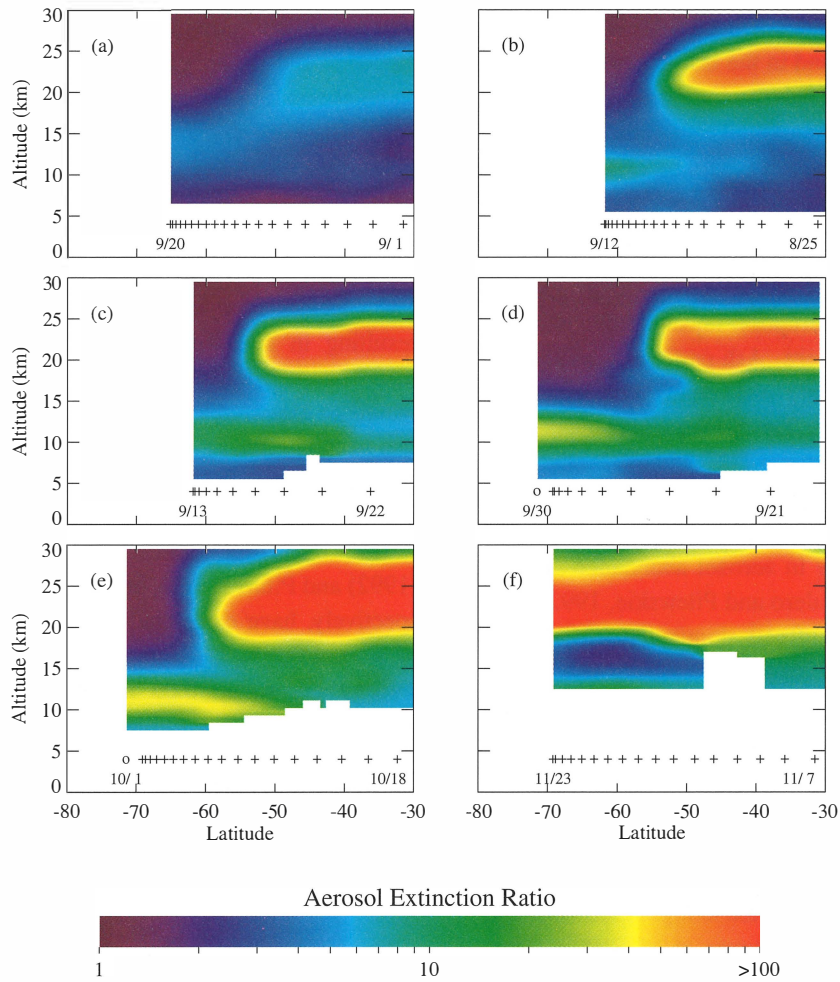
Figure 4-14. Latitude-altitude median cross sections of SAGE II and Stratospheric Aerosol Measurement (SAM II) 1-μm aerosol extinction ratio for six periods shown in each panel. The crosses and circles indicate the daily mean latitudes of the SAGE II and SAM II observations, respectively. The main region of high extinction ratio at 20 - 25 km is due to the Mt. Pinatubo aerosol cloud, while the band at 10 km originates from the Mt. Cerro Hudson eruption. The higher altitude cloud does not penetrate the established polar vortex, while that at lower altitudes progresses poleward more readily. (From Pitts and Thomason, 1993.)

4.6.3 Circulation-Induced Ozone Changes Resulting from the Mt. Pinatubo Eruption

4.6.3.1 RADIATIVE EFFECTS OF STRATOSPHERIC AEROSOL

Changes in stratospheric aerosol loading alter the radiative properties of the atmosphere, and so have the potential to not only modify local temperatures but also to alter the stratospheric circulation. In general, changes both to the absorption and emission of infrared radiation and to the solar heating rate must be considered.

In the infrared, the effects of small aerosol particles (radius less than ~0.1 μm) can generally be neglected, as their extinction is insignificant. Infrared absorption and emission become increasingly important at larger aerosol sizes. The strength of infrared heating also depends on the difference between the aerosol temperature and the radiative temperature of the troposphere below. Thus, the largest differential infrared heating by

aerosol particles of a given size would occur over warm surfaces, such as are found in the tropical troposphere.

The absorption of solar radiation by sulfuric acid particles (of any size) is small. This contrasts with, for example, ash particles, which would be expected to absorb solar radiation strongly.

4.6.3.2 HEATING BY MT. PINATUBO AEROSOLS

The Mt. Pinatubo eruption injected huge amounts of SO_2 into the stratosphere. Ash particles also injected may have caused transitory local heating before falling back into the troposphere. The subsequent conversion of SO_2 into H_2SO_4/H_2O particles (~75% sulfuric acid solution droplets at normal stratospheric temperatures, e.g., Sheridan et al., 1992) generated, within several weeks, sharp increases not only in aerosol abundance and but also aerosol size (e.g., Valero and Pilewskie, 1992).

Infrared radiative effects dominated in the presence of the sulfuric acid aerosols particles, which were transparent to solar radiation. Heating in the stratospheric aerosol layer was strongest over tropical latitudes, not only because most of the aerosol was initially confined to that region, but also because there, the tropospheric radiative temperatures were highest.

Reductions in aerosol optical depth occurred in the tropics as aerosol was transported to higher latitudes and sedimentation took place (Stowe et al., 1992; Mergenthaler et al., 1993). The resulting reduction in differential infrared heating was partially compensated by growth of aerosols to larger sizes (Dutton et al., 1994). Thus, calculated infrared heating anomalies in the tropical lower stratosphere, which reached a maximum of about 0.4 K/day immediately following the eruption (e.g., Brasseur and Granier, 1992), remained at above 0.2 K/day for at least another year.

4.6.3.3 AEROSOL HEATING AND INDUCED RESPONSE

The relationship between aerosol heating and the induced circulation is complex. Locally, temperatures are determined both by local heating and by the remotely-forced meridional circulation. The stratospheric meridional circulation is, in turn, controlled not only by radiation but also by midlatitude wave driving (Haynes et al., 1991), although the control by the latter may be less complete in the tropics than in midlatitudes. Modeling studies (Pitari, 1993) established that changes in the Brewer-Dobson circulation and in planetary wave behavior would occur in response to tropical temperature changes resulting from the increased aerosol loading.

There are also a number of feedback effects, many of which are negative, implying that the actual response would be weaker than radiative calculations alone would suggest. For example, there is a negative ozone feedback effect: enhanced upward motion in the tropical lower stratosphere would reduce ozone concentrations, resulting in smaller (mainly solar but also infrared) ozone heating in the aerosol layer. Also, local warming would be expected to reduce directly the infrared radiative heating rate.

Following the eruption, temperature anomalies of 2-3 K were observed in the tropical lower stratosphere (Labitzke and McCormick, 1992). Brasseur and Granier (1992) and Pitari (1993), using 2-D and 3-D models, respectively, have calculated radiative heating anomalies of around 0.2 K/day in that region and anomalous upwelling of around 0.05 mm/s through much of the tropical stratosphere during the Northern winter. Kinne et al. (1992) deduced a stronger circulation response in a calculation that did not include dynamical feedbacks. Tracer observations confirmed this picture, indicating enhanced upward motion over the central tropics (e.g., G. Toon et al., 1993).

Ozone concentrations in the tropical lower stratosphere were reduced well into the second year after the Mt. Pinatubo eruption (Grant et al., 1992). The ozone reductions immediately following the eruption may be explained almost entirely by aerosol-induced upwelling (Kinne et al., 1992). For longer-term changes, chemical as well as dynamical effects must be considered. Calculations of ozone reduction arising from circulation changes have been made in 2-D (Brasseur and Granier, 1992; Tie et al., 1994) and 3-D (Pitari, 1993; Pitari and Rizi, 1993) models.

In the tropics, models calculate column ozone reductions of the order of 5%. In the model of Pitari and Rizi (1993), this reduction was attributed largely to changes in photolysis rates, with the direct effect of circulation changes being small (0-2%). However, Brasseur and Granier (1992) and Tie et al. (1994) suggest that circulation changes led to somewhat larger reductions (up to ~5%) in column ozone in the months immediately following the eruption. Loss of tropical

ozone in the tropics by heterogeneous chemical processes was, in all instances, found to be small.

At midlatitudes, circulation changes were found to lead to generally small reductions in ozone in the Southern (summer) Hemisphere, but to significant increases (2-8%) at middle and high latitudes in the Northern (winter) Hemisphere in the year following the eruption. However, in the winter hemisphere, the column ozone increases due to transport were more than offset by large (>10%) losses due to heterogeneous chemistry that was more effective largely because of reduced winter photolysis rates, leaving widespread net ozone reductions of 5-10%.

Overall, the calculations suggest that as a result of the Mt. Pinatubo eruption, chemical effects, through heterogeneous reactions and changes in photolysis rates, appear to be the major factors leading to ozone changes globally; changes in atmospheric transport are likely to have produced significant regional effects.

4.7 TRANSPORT OF AIR FROM POLAR REGIONS TO MIDDLE LATITUDES

4.7.1 Transport of Air from High Latitudes: Possible Influence on Midlatitude Ozone Loss

There are differences of view regarding the importance of the transport of air through polar regions to middle latitudes and its impact on midlatitude ozone loss. One view is that containment of air within the polar vortex is, to a good approximation, complete during winter, and that virtually all transport occurs as the polar vortex breaks down during spring. During this process, air from within the polar vortex, in which ozone may have been depleted, mixes with low-latitude air and reduces the midlatitude ozone column purely by dilution. There is then a clear upper limit on ozone loss: no more ozone can be destroyed than the amount contained within the polar vortex when it first forms in early winter.

An alternative view is that expressed as the "flowing processor hypothesis," namely, that the air in polar regions is not well contained and that a substantial volume of air passes through those regions to middle latitudes throughout the winter months. If vortex temperatures are low enough, then polar stratospheric clouds (PSCs) will form within the vortex and heterogeneous chemistry will cause reactive chlorine concentrations to rise. Denitrification, which allows active chlorine compounds to persist for longer, may also occur (as may dehydration). Large amounts of air passing through the vortex to middle latitudes could thus be chemically primed for ozone loss. In such a situation, although temperatures in middle latitudes may never have reached the threshold for PSC formation, the effects of heterogeneous PSC chemistry (and dehydration) would still be apparent. Midlatitude ozone loss could then proceed, initiated by the polar air. Because the volume of lower-stratospheric air exposed to PSC chemistry could be substantially greater than the instantaneous volume of the polar vortex, the potential for ozone loss would be significantly enhanced over simple dilution. Two main transport pathways have been proposed: that air from the polar vortex spreads outwards throughout the hemisphere during the winter at altitudes up to ~35 km (10 hpa); or that air descends rapidly through the lower boundary of the vortex at about θ = 400 K to the sub-vortex region, where it can be transported to lower latitudes.

It is also possible that chlorine activation is not confined to the polar vortex, but could occur on PSCs or on sulfate aerosol outside the vortex, either in the region surrounding the vortex edge or in the very low stratosphere below about θ = 400 K where the polar vortex is less well defined. PSC formation in both regions is certainly possible, and indeed is likely at the temperatures observed in winter.

These different scenarios have very different implications for understanding and predicting midlatitude ozone loss.

4.7.2 Fluid-Dynamical Considerations

The present perception of polar-vortex dynamics is that the vortex, above a "transition isentrope" at about 400K, is very likely to behave in a manner similar to that of idealized polar vortices in single-layer, high-resolution models (*e.g.,* Legras and Dritschel, 1993; Norton, 1994 and references therein), in laboratory experiments (*e.g.,* Sommeria *et al.*, 1989), and in the multi-layer, low-resolution models now being run by several groups. From these studies, it appears that the edge of the vortex acts as a flexible barrier, strongly inhibiting the large-scale, quasi-horizontal eddy transport. However, none of the models suggests that this inhibition is complete.

Fluid-dynamical evidence points not to mean outflow but to weak mean inflow. It is just such inflow that creates the vortex on the seasonal time scale. Total poleward parcel displacements of a few degrees in latitude are enough to create the vortex; these displacements are of the same order as would be given by a simplistic angular momentum budget for a frictionless, exactly circular vortex.

Some additional inflow, of a similar order of magnitude, is required to maintain the vortex against Rossby and gravity wave drag. Conversely, if a strong mean outflow were to exist in the real wintertime polar lower stratosphere, then a strong eastward force of unknown origin would have to be acting to maintain the vortex. An outflow strong enough to conform to the flowing processor hypothesis in its extreme form, *i.e.*, an outflow strong enough to export, say, three vortex masses per winter, would, in the absence of an eastward force, obliterate the vortex on a short time scale of the order of 5 days (McIntyre, 1994).

Eddy-induced erosion of the vortex can act against the mean inflow. Outward eddy transport is limited by the rate at which the vortex edge can be eroded by episodic disturbances and associated midlatitude stirring. There is remarkable consistency with which strong eddy-transport inhibition is predicted over a big range of artificial model diffusivities, and of numerical resolutions from effective grid sizes from about 10 degrees of latitude (Pierce and Fairlie, 1993) through 1 degree of latitude (Juckes and McIntyre, 1987) to effectively infinite resolution obtained via adaptive Lagrangian numerics (*e.g.*, Legras and Dritschel, 1993; Dritschel and Saravanan, 1994). Model studies that use either Eulerian techniques or high-resolution Lagrangian advection techniques (contour advection or many-particle) on model-generated wind fields or on meteorologically analyzed wind fields have also been performed (*e.g.*, Pierce and Fairlie, 1993; Manney *et al.*, 1994; Norton, 1994; Rood *et al.*, 1992; Fisher *et al.*, 1993; Waugh, 1994b; Waugh *et al.*, 1994; Chen *et al.*, 1994). All give weak erosion rates, in the sense that the mass transported is, conservatively, no more than about a third of a vortex mass per month on average, regardless of the ambiguity in defining the vortex edge (due to its filamentary fine structure) and regardless of the very wide range of model resolutions and artificial model eddy diffusivities.

However, the possible roles of unresolvable motions such as breaking inertia-gravity waves in the lower stratospheric vortex edge have yet to be quantified.

Several other transport mechanisms should be considered. For example, if there is significant descent of vortex air into the sub-vortex region, this could be rapidly dispersed throughout the hemisphere. However, in order to sustain a large enough transport through the vortex, diabatic descent rates within the lower-stratospheric vortex would need to be much greater than seems compatible with observed temperatures and with very extensive studies in atmospheric radiation, whose physics is fundamentally well understood (*e.g.*, Schoeberl *et al.*, 1992).

Another possibility is that the sub-vortex region below the transition isentrope around 400-425 K could itself act as a "flowing processor." The transition isentrope exists because of stirring by anticyclones and other synoptic-scale meteorological disturbances underneath the vortex and the upward-evanescent character of the relevant waves. There is less inhibition of quasi-horizontal eddy transport at these lower levels: large eddy exchanges of midlatitude air with the sub-vortex region are thus expected (Tuck, 1989; McIntyre, 1994). The sub-vortex region is also cold enough, in the late Antarctic winter at least, to produce chlorine activation, dehydration, and denitrification (Jones and Kilbane-Dawe, 1994).

It is also possible that chlorine activation can take place in air parcels that are above the transition isentrope but are outside the vortex (see for example, Jones *et al.*, 1990; MacKenzie *et al.*, 1994; and Pyle *et al.*, 1994).

There is evidence that all three mechanisms (shown schematically in Figure 4-1) are realized to some degree, and presumably in different proportions in the South and North. Large transport rates of air from within the vortex seem likely to occur only when the vortex breaks down. However, the above arguments suggest that while transport due to vortex erosion may play a noticeable role in midlatitude ozone loss, it would not appear to be the dominant one.

4.7.3 Observational Studies Relating to Transport through the Vortex

4.7.3.1 EXCHANGE OF AIR ACROSS THE VORTEX BOUNDARY

The appearance near the vortex edge of filamentary structure in many species (see, *e.g.,* Murphy *et al.,* 1989; Tuck *et al.,* 1992; and below), and features such as laminae in ozone profiles (Reid *et al.,* 1993), is highly suggestive that some irreversible exchange of air is occurring across the boundary of the vortex. A number of studies have attempted to quantify outflow rates.

Using data from the Halogen Occultation Experiment (HALOE), Russell *et al.* (1993a) deduced a time constant for the replacement of air between 15 and 20 km by horizontal transfer of less than a month in October 1991. Tuck *et al.* (1993), using HALOE data, have also suggested that dehydration originating from within the Antarctic polar vortex spread over the entire Southern Hemisphere up to the 10-20 hPa region. The extent of the dehydration implied, they argued, that vortex air was being flushed out "several times" during the winter months. However, subsequent revisions of these satellite data based on an improved retrieval (Chapter 3; Figure 3-18) have markedly reduced the vertical and latitudinal extents of the dehydration apparent in the data, implying significantly lower outflow rates than these early studies suggested.

Several other studies have suggested relatively rapid exchange. Tao and Tuck (1994) examined the distribution of temperatures with respect to the vortex edge in the Southern winter of 1987 and the Northern winter of 1988-1989. They find that there is evidence of air chemically unprocessed by PSCs being dynamically resupplied to the vortex, they argue by mixing and descent. Tuck *et al.* (1994) used ER-2 observations of NO_y from the airborne missions in 1987, 1988-1989, and 1991-1992 to attempt to quantify vortex outflow rates. From the appearance of hemispheric and interannual differences in midlatitude NO_y, they concluded that the vortex must have been flushed more than once during the period of denitrification and dehydration.

The latter study is hard to reconcile with a number of other studies. Proffitt *et al.* (1989) argue that NO_y and N_2O observations obtained during the 1987 airborne mission point rather to significant inflow and descent (see Section 4.7.3.2). However, the extent of inflow proposed by Proffitt *et al.* is probably inconsistent with the angular momentum budget (*e.g.,* Plumb, 1990). Jones and MacKenzie (1994) also used the observed relationship between NO_y and N_2O concentrations to attempt to quantify the transport of air from the polar regions to midlatitudes. In that study some instances when recently denitrified air was found outside the vortex were observed, arguing against complete containment, but these features were small in scale. However, they found no evidence of large-scale outflow of air from the polar vortices above $\theta = 400$ K.

4.7.3.2 DESCENT OF AIR THROUGH THE LOWER BOUNDARY OF THE VORTEX

Proffitt *et al.* (1989, 1990, 1993) and Tuck (1989) have argued that the descent of ozone-depleted air through the lower boundary of the polar vortex, where it can be dispersed to lower latitudes, can significantly reduce midlatitude ozone amounts. Using statistical relationships between O_3 and N_2O, Proffitt *et al.* (1993) deduced altitude-dependent changes in ozone during the Northern winter of 1991-1992, with decreases at the bottom of the vortex and increases at the highest altitudes accessible to the ER-2 aircraft. The increase aloft was attributed to ozone-rich air entering the vortex from above, while the reduction lower down was taken to be the result of chlorine-catalyzed loss during descent through the region of PSC formation. Basing the rate of downward motion of air on a cooling rate of 1 K/day (in θ), ozone-depleted air released from the bottom of the vortex in 1991-1992 was, they argued, sufficient to reduce significantly the ozone column in middle latitudes. Using the same methodology, Collins *et al.* (1993) made measurements of the N_2O-O_3 correlation from the DC-8, which they interpret as showing descent of vortex air over the Arctic to levels just above the tropopause during the winter of 1991-1992; they also show 20% ozone reductions in March relative to January and February.

However, there is considerable debate about the importance of the descent of air through the vortex lower boundary for midlatitude ozone. The efficacy of such a process will depend on the rate of descent of air, and thus on diabatic cooling rates. For example, the cooling rate used in Proffitt *et al.,* 1993, (1 K/day) is a factor of 2-10 larger than other published estimates of diabatic cooling rates (*e.g.,* Schoeberl *et al.,* 1992).

4.7.3.3 TRANSPORT IN THE SUB-VORTEX REGION

There is less inhibition of quasi-horizontal eddy transport at the levels below the vortex (θ = 400-425 K) and large eddy exchanges of midlatitude air with the sub-vortex region are thus expected (Tuck, 1989; McIntyre, 1994). Jones and Kilbane-Dawe (1994) have investigated the extent to which ozone can be reduced in this region by *in situ* chemical processes rather than by transport of ozone-depleted air from the vortex above. They pointed out that temperatures in this region fall significantly below the threshold for polar stratospheric cloud formation, and thus for chlorine activation, for much of the Southern winter and, although more variable, the same is frequently seen in the North. Using ozonesonde measurements made during the 1987 Southern winter, Jones and Kilbane-Dawe (1994) identified significant reductions of ozone in the sub-vortex region (~350K) extending to ~55°S. As these reductions occurred at a time when temperatures were cold enough for chlorine activation, and when the ozone vertical gradient was such that diabatic descent would have increased ozone mixing ratios, they attributed these reductions to *in situ* photochemical loss. The total *in situ* ozone loss in the sub-vortex region was, in 1987, a significant fraction of the overall hemispheric reduction. They also argue that in the Northern Hemisphere in some winters (*e.g.*, the winter of 1993-4) the sub-vortex region may allow a significant fraction of lower latitude air to become chlorine-activated, and may, in some years, be more important than at higher altitudes.

4.7.4 Model Studies Relating to Transport through the Vortex

Since the last WMO/UNEP assessment, a number of new modeling studies have been carried out to investigate the extent to which air is mixed between the polar vortex and middle latitudes. Many of these have concentrated on the Arctic vortex, studied extensively in the two polar campaigns, EASOE and AASE II, in the winters of 1991/92. Studies using UARS data have also appeared.

The studies all show mixing, to a greater or lesser extent, but most support the idea of only limited flow through the polar vortex. However, it should be pointed out that chemical tracer measurements suggest that structure exists on scales so far unresolved by even the highest resolution analyses but, as indicated above,

whether this represents a fatal flaw in model studies is not clear.

In separate studies of the AASE and Airborne Antarctic Ozone Experiment (AAOE) data, involving the reconstruction of the chemical constituent fields in PV-θ space followed by an estimation of the meridional circulation and eddy diffusivities, Schoeberl *et al.* (1992) reached similar conclusions to the earlier study of Hartmann *et al.* (1989): that the center of the vortex is highly isolated but that exchange of trace gases does occur, principally at the vortex edge, by erosional wave activity. Consistent with earlier studies, Rood *et al.* (1992) conclude that intense cyclonic activity close to the vortex edge and large planetary-scale events are the major mechanisms of extra-vortex transport. Nevertheless, in their study of a disturbed period in January and February 1989, only a small amount of vortex air was found at lower latitudes.

Erosion at the vortex edge has been demonstrated in greater detail in a number of new studies using the technique of contour advection with surgery (Norton, 1994; Waugh, 1994b; Plumb *et al.*, 1994; Waugh *et al.*, 1994). Results from these studies show thin filaments being dragged around the vortex edge and being carried into middle latitudes. An example during a disturbed period in January 1992 is shown in Figure 4-15. The fine structure evident in the figure is consistent with potential vorticity, but reveals structure on scales not resolvable in the PV maps. Estimates of the outflow of vortex air to midlatitudes by Waugh *et al.*, 1994 (see Table 4-1) suggest, however, that while major erosion events do occur (*e.g.*, Jan. 16-28), the net outflow of air from the vortex appears small, at least above 400 K. Similar conclusions are drawn by Pierce and Fairlie (1993) in a study of the evolution of material lines; by Strahan and Mahlman (1994), who compared high resolution general circulation model results with N_2O observations near the vortex edge; and by Dahlberg and Bowman (1994), who carried out isentropic trajectory studies for nine Northern Hemisphere winters.

A number of studies have attempted to model the chemical effects relating to ozone loss. Chipperfield *et al.* (1994b) and Chipperfield (1994) studied the Arctic winters of 1991/92 and 1922/93. Figure 4-16 shows the distribution of a tracer indicating that air has experienced the conditions (low temperatures and sunlight) necessary for rapid ozone loss. Most of the tracer is well
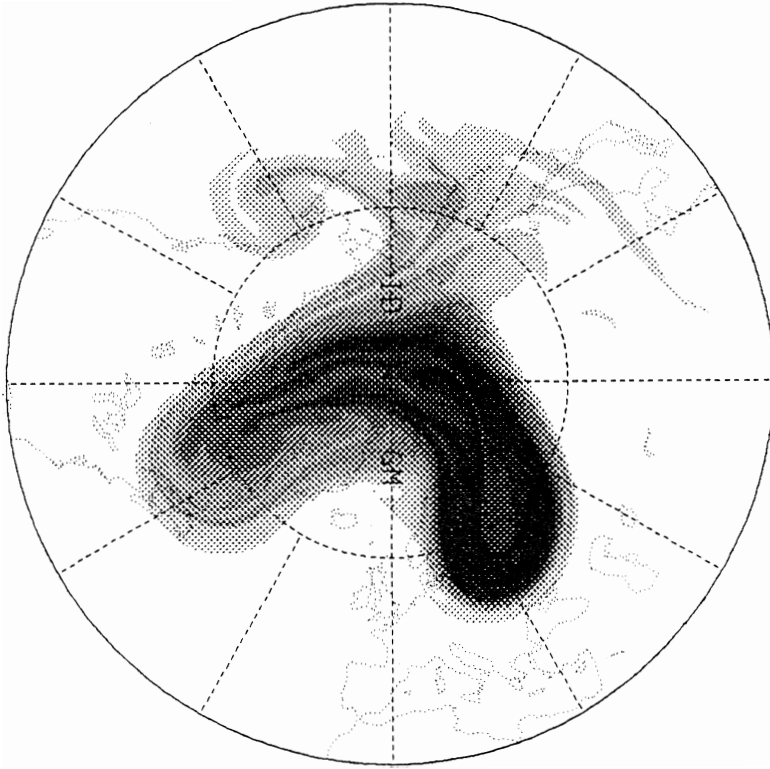
Figure 4-15. High resolution evolution of the vortex on the 450 K isentropic surface, 16-28 January 1992, as determined using contour advection with surgery. Model contours were initialized on 16 January on potential vorticity contours from the NMC analysis. Subsequently the contours were advected with the daily analyzed 450 K balanced winds. Note the transport of a significant volume of air to midlatitudes near 165°E. (From Plumb *et al.*, 1994.)

Table 4-1. Area of air transported out of the vortex expressed as a percentage of the vortex area (P_1) or as a percentage of the area between the vortex and 30°N (P_2) during selected periods during the Northern winter of 1991/2. (From Waugh *et al.*, 1994.)

Period	P_1	P_2
Dec. 6 - 18, 1991	1	0
Dec. 16 - 26, 1991	1	0
Dec. 23, 1991 to Jan. 2, 1992	5	1
Jan. 1 - 11, 1992	7	2
Jan. 7 - 17, 1992	3	1
Jan. 16 - 28, 1992	31	7
Feb. 2 - 11, 1992	2	0
Feb. 9 - 19, 1992	0	0
Feb. 19 - 28, 1992	5	3

Figure 4-16. Modeled distribution of a tracer showing chlorine activation and exposure to sunlight on the 475 K potential temperature surface for January 20, 1992. In this case, the tracer is the number of hours of ozone destruction. As in Figure 4-15, significant transport outside the vortex is seen near 165°E. High ClO_x concentrations are calculated to be present in the same region. (From Chipperfield *et al.*, 1994b.)
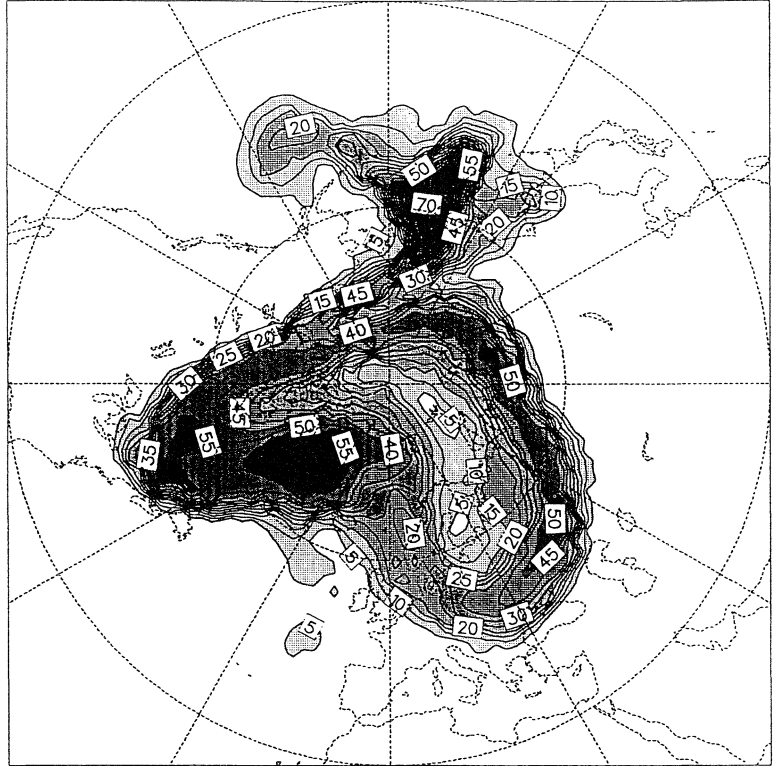
Figure 4-17. Trajectory endpoints for 28 January 1992. The trajectories were initialized on the 475 K potential temperature surface 10 days earlier close to the edge of the polar vortex in a region favorable for PSC formation and in which chlorine activation was expected to have occurred. While the majority of the trajectories remained on the vortex edge, a significant number became detached from the vortex. In the latter group (shown near the Black Sea) O_3 losses of ~1% per day were calculated. (From Pyle *et al.*, 1994.)

4.28
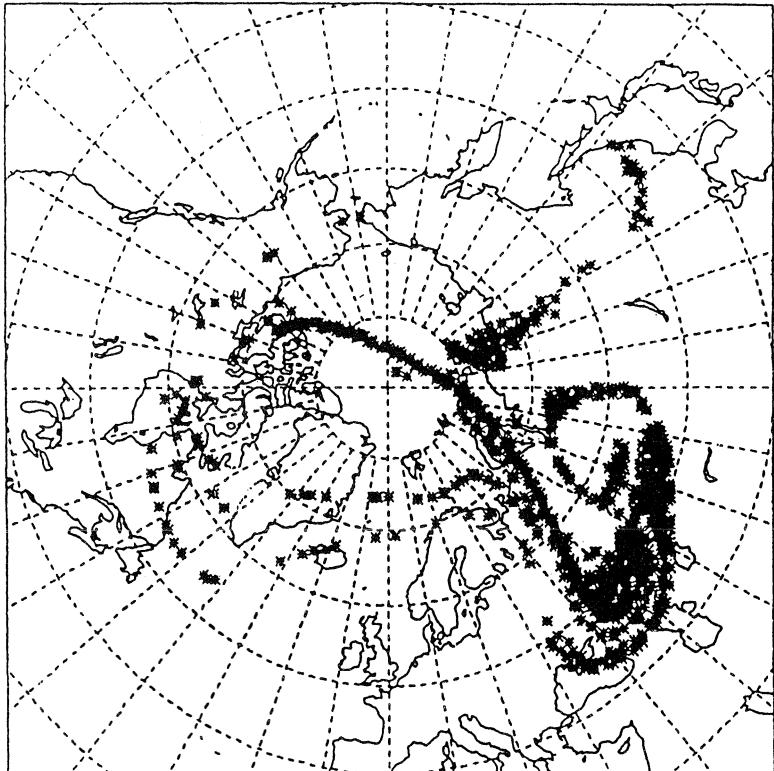
within the polar vortex, but there is an activated region moving away from the vortex edge at 165°E. The level of consistency between these results and the contour advection results of Plumb *et al.* (1994) for the same period (Figure 4-15) is striking, particularly given their differences of approach.

A number of recent studies using trajectories confirm the notion that chlorine activation can occur at the vortex edge (see, *e.g.,* Jones *et al.*, 1990). MacKenzie *et al.* (1994), using ensembles of isentropic trajectories, found examples of air that had been chlorine-activated by PSCs outside the vortex. However, in these cases the relevant low temperatures had been encountered at PV values characteristic of the vortex edge. Such a conclusion is consistent with the work of Tao and Tuck (1994). However, MacKenzie *et al.* (1994) found no evidence of air having been ejected from the center of the vortex. Broadly similar results were obtained by Pierce *et al.* (1994), who performed trajectory studies to analyze the HALOE data in the Southern Hemisphere. In an explicit calculation of photochemical ozone loss, Pyle *et al.* (1994) used trajectories to show that a region of high PV chlorine-activated air had been eroded from the vortex to 45°N in January 1992 (see Figure 4-17). Ozone depletions of around 0.1% per day were calculated for those trajectories staying close to the vortex edge. However, for the trajectories that moved to lower latitudes, a depletion of the order of 1% per day was calculated.

Thus, while it appears that the processes discussed in Section 4.7.1 are indeed affecting midlatitude ozone amounts, these modeling studies suggest that their impact is modest.

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TROPICAL/MIDLATITUDE PROCESSES

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