CHAPTER 3

Heterogeneous Processes: Laboratory, Field, and Modeling Studies

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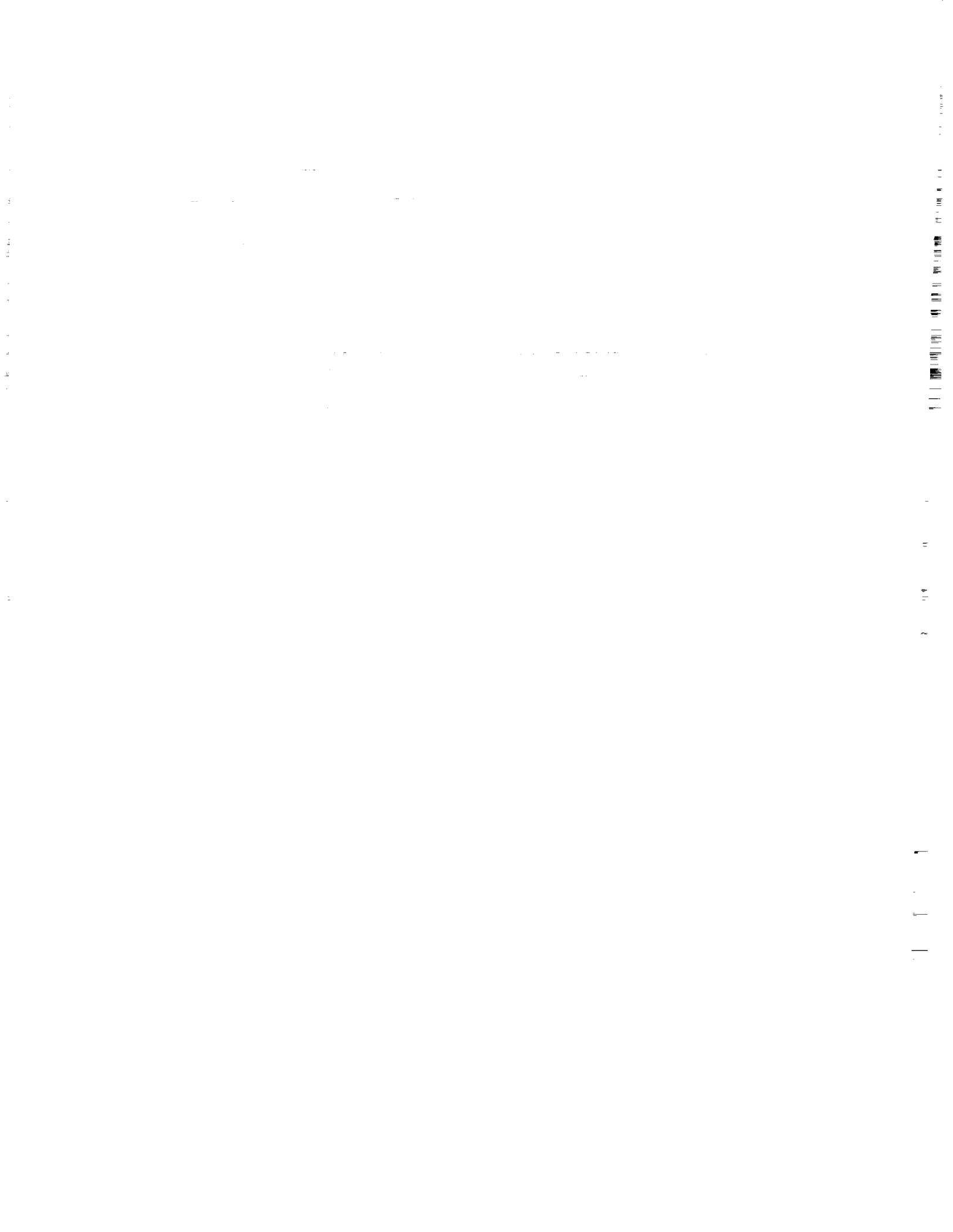
Chapter 3

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Contents

SCIENTIFIC SUMMARY

Since the previous assessment, there have been major advances in understanding the role of heterogeneous reactions on Polar Stratrospheric Clouds (PSCs) and stratospheric sulfate (H_2SO_4/H_2O) aerosols in increasing the abundance of active chlorine compounds in the lower stratosphere.

Reaction Efficiencies: Direct chlorine activation, *e.g.*, via $ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s)$ is very efficient on surfaces which mimic PSCs. Denoxification, *e.g.*, $N_2O_5(g) + H_2O(s) \rightarrow 2\ HNO_3(s)$, is very efficient on H_2SO_4/H_2O surfaces typical of mid-latitude stratospheric aerosols and indirectly enhances active chlorine by inhibiting formation of the reservoir $ClONO_2$. Direct chlorine activation on sulfate aerosols may also occur under volcanic conditions or at very cold temperatures, the latter becoming more important with expected future increases in stratospheric H_2O vapor. Furthermore, there may be other important heterogeneous processes that have not yet been identified.

PSC Physical Characteristics: Additional laboratory studies have confirmed that HNO_3/H_2O clouds can form above the frost point. Significant HNO_3 supersaturation may be required for Type 1 PSC formation, implying that heterogeneous processing by sulfate aerosols may be more important at lower temperatures than previously thought. Type 1 PSCs may exist in two subclasses, which, in turn, may have different surface area characteristics and different heterogeneous processing efficiencies. HNO_3 has been shown to stick readily on pure ice and retard its sublimation, supporting the idea that falling ice crystals are responsible for stratospheric denitrification.

SAM II PSC Climatology:
Antarctic: Average PSC sighting frequency peaks at about 60 percent near 18 km in August. Sighting frequency remains at 10 to 20 percent at lower altitudes—under dehydrated and denitrified conditions—well past the spring equinox. Individually or collectively, the high PSC frequency and persistence of the clouds into sunlit conditions provide firm evidence of a direct link between heterogeneous chlorine activation and South Polar ozone losses.

Arctic: Appreciable PSC sightings occur only from December through February, and the peak average sighting frequency is only about 10 percent. However, the limited spatial coverage of Stratospheric Aerosol Measurements (SAM) II likely yields an underestimate of cloud frequency in the polar region as a whole. More robust PSC statistics will be required before the relationship between lower stratospheric ozone losses in the Northern Hemisphere and heterogeneous chlorine activation on Arctic PSCs can be quantified.

Stratospheric Sulfate Aerosols: Long-term observational records all show a 40 to 50 percent increase in loading over the decade from 1979 to 1989. The effective aerosol surface area available for heterogeneous chemical processing most likely increased by a comparable amount on a global scale during the same period. Additional loading from the June 1991 Mt. Pinatubo eruption will most likely be the greatest of the century to date (exceeding that of El Chichón) and is expected to persist for several years.

Heterogeneous processes must be included in stratospheric chemistry models. Measurements of ClO and HNO_3 are better explained by model calculations that include heterogeneous processing on PSCs and sulfate aerosols. Since there have been more extensive measurements of chemical changes in the polar regions, the picture of heterogeneous processing on PSCs is clearer. Direct heterogeneous chlorine activation in these clouds appears to be rapid and may not be dependent on detailed particle characteristics. Experimental opportunities provided by the Mt. Pinatubo injection should yield the data required to examine this issue more fully with regard to sulfate aerosols.

3.1 INTRODUCTION

The efficiencies of chemical families such as ClO_x and NO_x for altering the total abundance and distribution of stratospheric ozone are controlled by a partitioning between reactive (active) and nonreactive (reservoir) compounds within each family. Gas phase thermodynamics, photochemistry, and kinetics would dictate, for example, that only about 1 percent of the chlorine resident in the lower stratosphere would be in the form of active Cl or ClO, the remainder existing in the reservoir compounds HCl and $ClONO_2$. The consistency of this picture has recently been challenged by the recognition that important chemical transformations take place on polar stratospheric cloud (PSC) particles in both polar regions (The Airborne Antarctic Ozone Experiment (AAOE), Parts 1 and 2, 1989; The Airborne Arctic Stratospheric Expedition (AASE), 1990). Following the discovery of the Antarctic ozone hole, Solomon *et al.* (1986) suggested that the heterogeneous chemical reaction:

$$ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s) \quad (3-1)$$
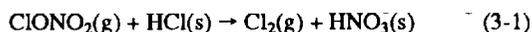
could play a key role in converting chlorine from inactive forms into a species (Cl_2) that would rapidly dissociate in sunlight to liberate atomic chlorine and initiate ozone depletion. The symbols (s) and (g) denote solid phase, or adsorbed onto a solid surface, and gas phase, respectively, and represent the approach by which such a reaction is modeled rather than the microscopic details of the reaction. Reaction (3-1) was expected to be most important at altitudes where PSCs were most prevalent (10 to 25 km), thereby extending the altitude range over which chlorine compounds can efficiently destroy ozone from the 35 to 45 km region (where concentrations of active chlorine are usually highest) to lower altitudes where the ozone concentration is at its peak.

Direct measurements of ozone depletion and enhancements of ClO have strongly supported the Solomon *et al.* (1986) hypothesis and have prompted laboratory studies of Reaction (3-1) and several others on surfaces that mimic the suspected composition of the two main types of PSCs (nitric acid trihydrate, or NAT, Type 1; and water ice, Type 2):

$$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(s) \quad (3-2)$$
$$N_2O_5(g) + HCl(s) \rightarrow ClNO_2(g) + HNO_3(s) \quad (3-3)$$
$$N_2O_5(g) + H_2O(s) \rightarrow 2\ HNO_3(s) \quad (3-4)$$

Since both PSC types are likely to be doped with HCl in the stratosphere, studies have also examined the direct role of HCl on the surface reactions. In addition to the effect that Reactions (3-1) to (3-3) have on chlorine partitioning, all four reactions play an equally important role in sequestering odd nitrogen species as HNO_3, a process that has been popularly termed "denoxification." Although the condensed HNO_3 may be released as vapor if the PSCs evaporate, HNO_3 vapor is quite inert photochemically in the winter polar stratosphere. The sequestration of odd nitrogen helps to maintain high levels of active chlorine by retarding the reformation of the reservoir $ClONO_2$ via the gas phase reaction between ClO and NO_2. Furthermore, if the PSC particles involved grow large enough to undergo appreciable sedimentation, the odd nitrogen is irreversibly transferred (denitrification) from a higher altitude region to a lower one (Hübler *et al.*, 1990).

The efficiencies of such heterogeneous reactions on PSCs coupled with observations of significant ozone loss and ClO enhancement outside of the polar regions have prompted speculation about the role of the H_2SO_4/H_2O (sulfate) stratospheric aerosol layer in promoting similar chemical repartitioning. Studies have focused on Reactions (3-1) to (3-4) occurring on H_2SO_4/H_2O surfaces as well as the physical uptake of HCl and HNO_3 (where l = liquid):

$$HCl(g) + H_2SO_4/H_2O(l,s) \rightarrow HCl(l,s) + H_2SO_4/H_2O(l,s) \quad (3-5)$$
$$HNO_3(g) + H_2SO_4/H_2O(l,s) \rightarrow HNO_3(l,s) + H_2SO_4/H_2O(l,s) \quad (3-6)$$

This chapter will briefly review the current state of knowledge of heterogeneous processes in the stratosphere, emphasizing those results obtained since WMO (1990). Sections are included on laboratory investigations of heterogeneous reactions, the characteristics and climatology of PSCs, stratospheric sulfate aerosols, and evidence of heterogeneous chemical processing.

3.2 LABORATORY MEASUREMENTS

Laboratory studies of heterogeneous reactions generally result in a determination of the mass accommodation coefficient (α), or the fractional loss of a species from the gas phase upon collision with a surface. If such surface contact results in an irreversible transformation of the species, then the mass accommodation coefficient can be equated to a reac-

tion probability (γ). While the interpretation of the results from these studies can be quite complex, the field has matured rapidly since the initial reports by Molina *et al.* (1987) and Tolbert *et al.* (1987). Based on some of the most recent measurements, a reasonable consensus of reaction probabilities on PSC-like surfaces for Reactions (3-1) to (3-4) can be presented (Table 3-1). As will be pointed out, inconsistencies among some previous results can possibly be attributed to concentration effects whereby either the nature of the surface is altered or the experimental conditions are not completely representative of the stratosphere. This underscores the importance of determining reactant loss rates and the effects of the incorporation of HCl and HNO_3 into the solid surface at stratospheric concentration levels. Nevertheless, it should be emphasized that no measurements of reaction probabilities have yet been made on realistic PSC particles. Hence, there may be subtle differences in γ values among various laboratory studies and between laboratory results and the real atmosphere that can be attributed to actual surface characteristics. The reader should note that a far more extensive review and evaluation of laboratory data for heterogeneous processes is being conducted by the NASA Panel for Data Evaluation as part of its assessment of kinetic and photochemical data for use in stratospheric modeling. This review will be published as a 1992 Jet Propulsion Laboratory report and should be consulted by those seeking more detailed information, including estimates of uncertainties.

An explanation for the wide range of γ values for Reaction (3-2) on water ice and NAT surfaces that have appeared in the literature has been proposed by Hanson and Ravishankara (1991a), who suggest that passivation of the water-ice surface by the product HNO_3 at high reactant concentrations would account for the earlier low values of γ (Leu, 1988a; Molina *et al.*, 1987; Tolbert *et al.*, 1987). Similar saturation effects have been noted by M. A. Tolbert (private communication, 1991). While this issue can be fully reconciled only by further study, the plausibility of this explanation provides the basis for the recommended values of γ given here.

Hanson and Ravishankara (1991a) observed no measurable difference in γ for Reactions (3-1) and (3-2) on water ice and interpreted the HCl enhancement of previous studies (Leu, 1988a; Molina *et al.*, 1987) to be associated with a passivated HNO_3/H_2O

Table 3-1: Reaction Probabilities (γ) on PSC-like Surfaces

Reaction	γ_{ice}	γ_{NAT}
(3-1) $ClONO_2 + HCl$	0.3	0.3
(3-2) $ClONO_2 + H_2O$	0.3	0.006
(3-3) $N_2O_5 + HCl$	see text	0.003
(3-4) $N_2O_5 + H_2O$	0.03	0.0006

surface rather than one of pure ice. Hanson and Ravishankara (1991b) and Abbatt *et al.* (1992) report that HOCl produced in Reaction (3-2) rapidly reacts with HCl on ice to yield $Cl_2(g)$ and $H_2O(s)$. Thus, the mechanism for Reaction (3-1) on ice probably involves two steps (*i.e.*, the formation of HOCl, followed by its immediate heterogeneous conversion into Cl_2), and the differentiation between reactions (3-1) and (3-2) is perhaps moot. However, the HOCl + HCl heterogeneous reaction itself provides a mechanism for the conversion of HCl into active chlorine under low NO_x conditions when $ClONO_2$ is suppressed (Prather, 1992). Such a mechanism has not been quantitatively investigated in atmospheric models to date with respect to polar ozone depletion.

The γ for Reaction (3-2) was determined to be significantly lower on NAT surfaces than on water ice (Hanson and Ravishankara, 1991a; Moore *et al.*, 1990; Leu *et al.*, 1991). These groups also report a subsequent enhancement of γ with HCl present on the NAT surface (Reaction 3-1), approaching that obtained on pure water ice. Thus, unlike the case for the reaction $ClONO_2 + H_2O$, the direct heterogeneous reaction between $ClONO_2$ and HCl does apparently occur on Type 1 PSCs.

On water ice, values for γ recently measured for Reaction (3-4) are in good agreement (Hanson and Ravishankara, 1991a; Leu, 1988b; and Quinlan *et al.*, 1990). Because of the lower reaction probability, saturation effects are less pronounced than in the case of Reaction (3-2). However, there is some evidence that Reaction (3-4) may be somewhat faster in a liquid water droplet than on water ice (Van Doren *et al.*, 1990). Hanson and Ravishankara (1991a) observed no enhancement of γ when HCl was present in the ice (Reaction 3-3) at concentrations representative of the stratosphere and suggested that the enhancements observed by Leu (1988b) might be attributable to the very high concentrations of HCl used. Thus, there is no unequivocal evidence for chlorine activation via

Reaction (3-3) on water ice surfaces under stratospheric conditions. On NAT surfaces, Hanson and Ravishankara (1991a) obtained a value of γ for Reaction (3-4) a factor of 50 lower than that on water ice. The much larger value determined by Quinlan et al. (1990) at higher reactant concentrations may be associated with formation of a condensed phase of supercooled HNO_3 liquid on which the reaction probability may be much greater than on NAT. Finally, Hanson and Ravishankara (1991a) observed a factor of 5 increase in γ for the reaction of N_2O_5 on NAT when HCl is present (Reaction 3-3), suggesting that N_2O_5 preferentially reacts with HCl rather than with H_2O on Type 1 PSCs.

Reactions (3-1), (3-2), and (3-4) have also been studied extensively on H_2SO_4/H_2O surfaces, as has the physical uptake of HCl and HNO_3 (Reactions 3-5 and 3-6). (See Tables 3-2 and 3-3). For Reaction (3-2), the measurements by Reihs et al. (1991) and by Hanson and Ravishankara (1991c) as a function of H_2SO_4 weight percentage (W) yield values for γ that are in excellent agreement and imply that this reaction is an unlikely source of perturbed stratospheric chemistry on a global scale. Relative to Reaction (3-2), a 10-fold reduction in γ was observed by Hanson and Ravishankara (1991c) and Tolbert et al. (1988) for the reaction with HCl to produce chlorine (Reaction 3-1). Since these measurements were made for surface compositions typical of mid-latitude stratospheric aerosols (~60 to 75 percent H_2SO_4 by weight), the results are not necessarily valid for surfaces rarer in H_2SO_4. With regard to this point, Hanson and Ravishankara (1991c) and M.-T. Leu, S.B. Moore, and L.F. Keyser (private communication, 1991) confirm the observations of Watson et al. (1990) that the uptake of HCl on sulfuric acid aerosols (Reaction 3-5) is strongly dependent on the H_2SO_4 fraction and that there is a rapid equilibration with gas phase HCl in the stratosphere (see Table

Table 3-2: Reaction Probabilities (γ) on Sulfuric Acid/Water Surfaces

Reaction	Probability
(3-1) $ClONO_2 + HCl + H_2SO_4/H_2O$	$0.1 \times \gamma$ for Reaction (3-2)
(3-2) $ClONO_2 + H_2SO_4/H_2O$	$\log_{10}(\gamma) = 1.87 - 0.074W*$
(3-4) $N_2O_5 + H_2SO_4/H_2O$	0.1

* W = wt. % H_2SO_4

3-3). Thus, $ClONO_2$ is more likely to react with H_2O in a H_2SO_4/H_2O particle than with the dissolved HCl. While these combined observations suggest that Reaction (3-1) on stratospheric aerosols will not be a significant source of active chlorine, Hofmann and Solomon (1989) point out that large increases in aerosol surface area following volcanic eruptions could lead to important enhancements in the production of HOCl via Reaction (3-2). In the polar regions, direct chlorine activation on H_2SO_4/H_2O aerosols can possibly take on added significance. For example, Wolff and Mulvaney (1991) have suggested that water-rich aerosols (<60 percent H_2SO_4 by weight), which can absorb significant levels of HCl, may be present under polar stratospheric conditions. Should stratospheric H_2O vapor content increase with time, such as from the oxidation of CH_4, aerosols in these cold regions would become even more water rich (Steele and Hamill, 1981), which could lead to enhanced direct chlorine activation.

Unlike Reactions (3-1) and (3-2), Reaction (3-4) appears to occur quite rapidly on sulfuric acid/water surfaces with a γ that is relatively independent of temperature and of H_2SO_4 fraction (Hanson and Ravishankara, 1991b; Mozurkewich and Calvert, 1988; Reihs et al., 1991; Van Doren et al., 1991; and A. Fried, M. Mozurkewich, B. Henry, and J.G. Calvert, private communication, 1991). Thus, this reaction represents an important loss process for NO_x and a source of HNO_3 the condensed phase concentration of which is limited by its solubility (Van Doren et al., 1991; Reihs et al., 1990). Such NO_y repartitioning affects stratospheric ozone through both the NO_x and ClO_x cycles (reducing the efficiency of the former and increasing that of the latter).

With respect to data on mass accommodation coefficients alone (see Table 3-3), values of α for HCl (Hanson and Ravishankara, 1991a; Leu, 1988a) and HNO_3 (Leu, 1988a) on pure ice are large, as is that for HNO_3 on concentrated sulfuric acid surfaces (Van Doren et al., 1991). Direct uptake of HNO_3 on H_2SO_4/H_2O is, however, subject to the same solubility limitations as the HNO_3 produced in Reaction (3-4) (Van Doren et al., 1991; Reihs et al., 1990). It is also of note that direct HNO_3 uptake on water ice leads to NAT formation, which reduces further HNO_3 uptake. Such direct uptake may be important in denitrification of the stratosphere (Wofsy et al., 1990) and in contrails of high-speed civil transports (HSCTs).

3.5

The uptake of HCl on NAT surfaces is unresolved at present, with reported α values ranging from ≥ 0.3 (Hanson and Ravishankara, 1991b) to between 8×10^{-3} and 9×10^{-7} (Leu et al., 1991). While the latter measurements may have been subject to solubility limitations, further work is required to reconcile this issue.

The role of these heterogeneous reactions has greatly revised current thinking about stratospheric chemistry and continues to be investigated through direct laboratory studies and intensive atmospheric measurement campaigns. The latter are aimed at assessing the cause(s) of enhanced ozone loss in the Northern Hemisphere, the potential for ozone changes associated with CFC substitute usage or commercial HSCTs, and the role that severe polar ozone loss plays in altering total ozone at neighboring mid-latitudes.

Table 3–3: Mass Accommodation Coefficients (α) on Ice and Sulfuric Acid/Water Surfaces

Reaction	On Ice	On 60–75 wt. % H_2SO_4
(3–5) HCl + H_2SO_4/H_2O	> 0.2	4×10^{-4}*-10^{-5}*
(3–6) HNO_3 + H_2SO_4/H_2O	> 0.2	> 0.1

*Effective uptake coefficient; mass accommodation coefficient has not been measured at low HCl solubilities; for Reaction (3–5), increases by 10^2–10^3 below 50 percent H_2SO_4.

3.3 POLAR STRATOSPHERIC CLOUD CHARACTERISTICS AND CLIMATOLOGY

Data collected during recent Arctic field campaigns have provided additional insight into PSC formation mechanisms and physical characteristics. Particle measurements during AASE (Dye et al., 1991) showed some Type 1 PSC particles formed at temperatures around 195 K, or near HNO_3 saturation with respect to NAT, the suspected composition of Type 1 particles. However, extensive cloud particle formation was not observed until saturation ratios were near 10, a finding supported by balloon-borne observations of Schlager et al. (1990) and Hofmann et al. (1990). These results suggest that relatively few H_2SO_4/H_2O aerosols are frozen at HNO_3 saturation and that further cooling (to about 192 K) is required for the remainder to freeze and serve as PSC nuclei. It should be noted that there is no direct observational evidence to date of frozen H_2SO_4/H_2O particles in the stratosphere. Analyses of AASE lidar data (Browell et al., 1990; Toon et al., 1990a) revealed two subclasses of Type 1 PSCs, both appearing at temperatures at or below the equilibrium threshold for NAT. Type 1a PSCs are composed of nonspherical particles having a volume equivalent radius ≥ 1.0 μm, while Type 1b clouds have spherical or nearly spherical particles with typical radii near 0.5 μm. Toon et al. (1990a) suggested that air parcel cooling rate and the extent to which parcels cool below the initial condensation point were important factors in determining particle characteristics. Other lidar data (McCormick et al., 1990; Poole et al., 1990) showed broad spatial coverage of Type 1b PSCs and systematic evolution of cloud optical properties with decreasing temperature.

A great deal has been learned (and many questions have been raised) about PSC physical chemistry from recent laboratory studies. New vapor pressure measurements (D. R. Worsnop, private communication, 1991) have confirmed that NAT forms at temperatures some 4 to 6 K above the ice point, in support of a previous finding of Hanson and Mauersberger (1988). The new measurements have also observed saturation ratios up to 10 for HNO_3 vapor over ice surfaces, suggestive of the ratio required for Type 1 PSC nucleation on H_2SO_4/H_2O aerosols as discussed above. Ritzhaupt and Devlin (1991), Tolbert and Middlebrook (1990), and Smith et al. (1991) have measured the infrared spectra of thin films of condensed H_2O/HNO_3 mixtures. Each group has reported a set of three similar spectra, although with different chemical assignments. Ritzhaupt and Devlin (1991) and Tolbert and Middlebrook (1990) identified nitric acid monohydrate, trihydrate, and dihydrate spectra, while Smith et al. (1991) ascribed the same spectra to monohydrate, trihydrate, and mixed ice/trihydrate phases. In addition, Koehler et al. (1991) suggest that two forms of NAT are possible: an α-NAT formed at colder temperatures, and a β-NAT formed at warmer temperatures and higher H_2O vapor pressures or, alternatively, by heating α-NAT. There are no direct atmospheric observations of these forms, nor is there laboratory evidence to suggest that they would exhibit differences in heterogeneous reactivity. Tolbert and

Middlebrook (1990) and Worsnop have also observed solid-diffusion-limited evaporation of water through thin (0.02–μm) films of NAT over ice, a finding that supports the notion of Wofsy *et al.* (1990) that falling ice crystals are responsible for denitrification of the winter polar stratosphere (as discussed in Section 3.5.3).

An updated yearly average PSC climatology has recently been derived (Pitts *et al.*, 1991) using 1–μm aerosol extinction data for 1979–1989 from the SAM II sensor aboard Nimbus 7. The Nimbus 7 orbit has degraded to a point such that no SAM II measurements have been possible during Arctic winter since early 1990. Thus, data beyond 1989 were excluded from the analysis, as were some data from 1982 to 83 which were masked by El Chichón volcanic aerosols. The latitude of SAM II measurements varies slowly from about 64° at the winter solstices to about 80° at the spring equinoxes. Hence, early to midwinter observations are typical of conditions near the edge of the polar vortex and likely yield an underestimate of PSC frequencies in the polar regions as a whole. Observations in late winter are more representative of the vortex interior. In light of this systematic variation, it is impractical to use SAM II data to derive seasonal statistics on the fraction of PSCs that form outside the polar vortices.

The results (Figure 3–1) show hemispheric differences in PSC sighting frequency that are consistent with seasonal temperature patterns as well as with the behavior reported in WMO (1990). Antarctic sightings normally begin in May, and average sighting frequency generally increases at all altitudes as winter progresses, reaching a seasonal peak of about 60 percent near 18 km in August. The frequency falls sharply at higher altitudes (as local temperatures rise) after August, but continues at the 10 to 20 percent level well into October at the lower altitudes. Thus, it is clear that Antarctic PSCs continue to form even under dehydrated and denitrified conditions and, on average, persist well past the spring equinox. Individually or collectively, the high PSC frequency and the persistence of the clouds into sunlit conditions provide firm evidence of a direct link between heterogeneous chlorine activation and South Polar ozone losses.

The season for appreciable Arctic PSC sightings extends only from December through February, and the peak average sighting frequency is only about 10

percent. The sighting frequency for Arctic PSCs in March is well below 1 percent on average and exceeded 1 percent in only 2 of the 10 years of measurements analyzed. There have been no Arctic PSC sightings by SAM I during the month of April. While these lower frequencies are consistent with warmer average temperatures (relative to the Antarctic), absolute values are more uncertain due to possible systematic underestimation caused by the limited spatial coverage of SAM II. More robust PSC statistics will be required before the relationship between lower stratospheric ozone losses in the Northern Hemisphere and heterogeneous chlorine activation on Arctic PSCs can be quantified.

3.4 STRATOSPHERIC SULFATE AEROSOLS

Routine balloon-borne and lidar measurements of H_2SO_4/H_2O (sulfate) stratospheric aerosols have been conducted at several Northern Hemisphere sites since the early 1970s. These have been supplemented in a more global sense since the late 1970s with space-borne observations by the SAM II (1978 to present), SAGE I (1979 to 1981), and SAGE II (1984 to present) sensors. Long-term trends in sulfate aerosols will be examined and discussed in this section, along with perturbations induced by major volcanic eruptions (including the June 1991 eruption of Mt. Pinatubo). There will also be a brief discussion of the use of multi-wavelength SAGE II aerosol extinction data to estimate total aerosol surface area, a critical parameter in model calculations of the efficiency of aerosols for catalyzing heterogeneous chemical reactions.

3.4.1 Long-Term Trends and Volcanic Perturbations

The record of integrated aerosol column from 15 to 20 km at Laramie, Wyoming (41° N), is shown in Figure 3–2 for particles with radii $(r) \geq 0.15$ μm and ≥ 0.25 μm respectively (D.J. Hofmann, private communication, 1991). The figure also includes integrated backscatter (from the tropopause + 2 km to $\approx$ 30 km) obtained by the NASA Langley Research Center 48-inch ruby ($\lambda = 0.6943$ μm) lidar system (at 37°N) and is annotated to mark the occurrence of volcanic eruptions during the past two decades. The 1978 to 1979 period is commonly referred to as the "quies-
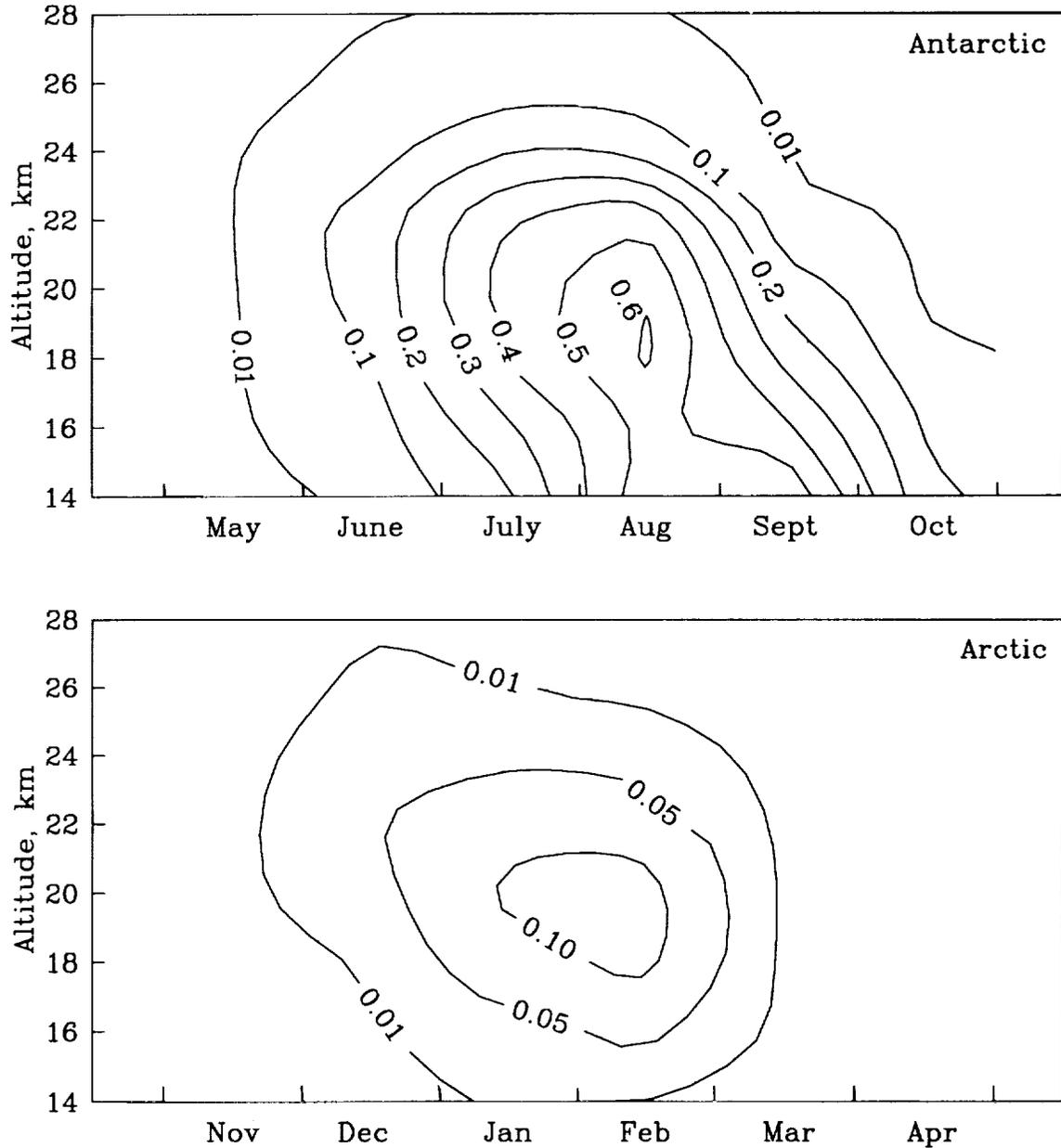
Figure 3–1 Yearly average polar stratospheric cloud sighting frequency by SAM II for the period 1979 to 1989. Sighting frequency is defined, at a particular altitude and time, as the number of observations classified as PSCs divided by the total number of observations.

cent" or "background" aerosol state since it followed by some 5 years the 1974 eruption of Fuego and preceded the series of eruptions in the early 1980s. Hofmann (1990) suggested that such a background state had again been reached by 1989 and calculated that non-volcanic aerosol mass at the stratospheric maximum had increased by 5 ± 2 percent per year over the previous decade, ostensibly due to an increase solely in the number of larger particles. The aerosol columns shown here support this earlier finding in that only the larger particles have increased (by some 40 to 50 percent) over the decade. The Langley backscatter record shows a similar decadal increase, thus demonstrating consistency between the different aerosol monitoring techniques at separate sites.

Figure 3-3 shows 1-μm optical depth (aerosol extinction integrated upward from the tropopause + 2 km) records from SAM II and SAGE I and SAGE II. The SAM II data are weekly Antarctic and Arctic (from $\approx 64°$ to $80°$) averages, while the SAGE data are monthly Northern and Southern Hemisphere averages. The SAM II record shows distinct extrema that are not representative of subpolar sulfate aerosols and do not appear in the SAGE records. The maxima seen during winter in both hemispheres reflect PSC activity, and the sharp minima appearing during Antarctic spring signify downward transport of aerosols (likely a combination of subsidence and sedimentation) inside the Antarctic polar vortex. Away from these extrema, there has been a 40 to 50 percent increase in average optical depth in the polar regions over the decade. This is virtually matched on a global scale by the difference in the average optical depth between SAGE II in 1989 to 1990 and SAGE I in 1979.

The cause of such a consistent increase among the various data records is open to question. Hofmann (1991) suggested that the aerosol mass increase was too large to be caused by increased OCS transport from the troposphere and speculated that the remainder might be due to increases in sulfur emissions from commercial aircraft flying in the upper troposphere and lower stratosphere. Hofmann (personal communication, 1991) found that there had been no appreciable increase over the decade in the 20 to 25 km aerosol column for particles with $r \geq 0.15$ μm or $r \geq 0.25$ μm, suggesting that a lower stratospheric source may indeed be responsible for the observed mass increase. However, since the

impact of major volcanic eruptions (*e.g.*, El Chichón) is very large initially and persists for several years, it is not certain that the stratosphere had totally recovered by 1989 from the combined effects of volcanoes El Chichón and Ruiz.

The stratospheric aerosol loading from the eruptions of Mt. Pinatubo will most likely be the greatest of the century to date, well in excess of that induced by the El Chichón eruption (McCormick and Veiga, 1992). Figure 3-4 shows the zonal mean (from 60°S to 60°N) 1-μm stratospheric aerosol extinction coefficient measured by SAGE II from mid-September to mid-October in 1990 (part a) and 1991 (part b). The 1991 values in the tropics and mid-latitudes are generally 1 to 2 orders of magnitude larger than corresponding 1990 values, with the increases attributable solely to the Mt. Pinatubo eruption. Since this perturbation is expected to last for several years, it is unlikely that the causes of the apparent long-term trend in aerosol loading will be clarified for some years to come.

It is reasonable to estimate that the effective aerosol surface area available for heterogeneous chemical processing likely increased globally during the 1980s by an amount comparable to the increase observed in aerosol column and optical depth. By the same token, a relatively short-term increase in total sulfate surface area of a factor of 10 to 100 can be expected from the Mt. Pinatubo eruption. One might also expect, purely from cloud microphysical principles, that such increases in sulfate aerosols would lead to similar secular increases in total PSC surface area, since the aerosols serve as PSC nuclei. This notion has not been examined (and is likely unresolvable) using current PSC observational data.

3.4.2 Estimation of Surface Area

In addition to the basic 1-μm channel, near-global aerosol extinction measurements are made by SAGE II at wavelengths of 0.385, 0.453, and 0.525 μm. These data can be coupled with Mie scattering theory to estimate total (geometric) aerosol surface area if a form for the underlying particle size distribution is assumed. Since the SAGE II measurements are not very sensitive to particles with $r < 0.1$ μm, the choice of aerosol models is somewhat arbitrary. The lognormal distribution has been more or less the standard model for past analyses of SAGE observations
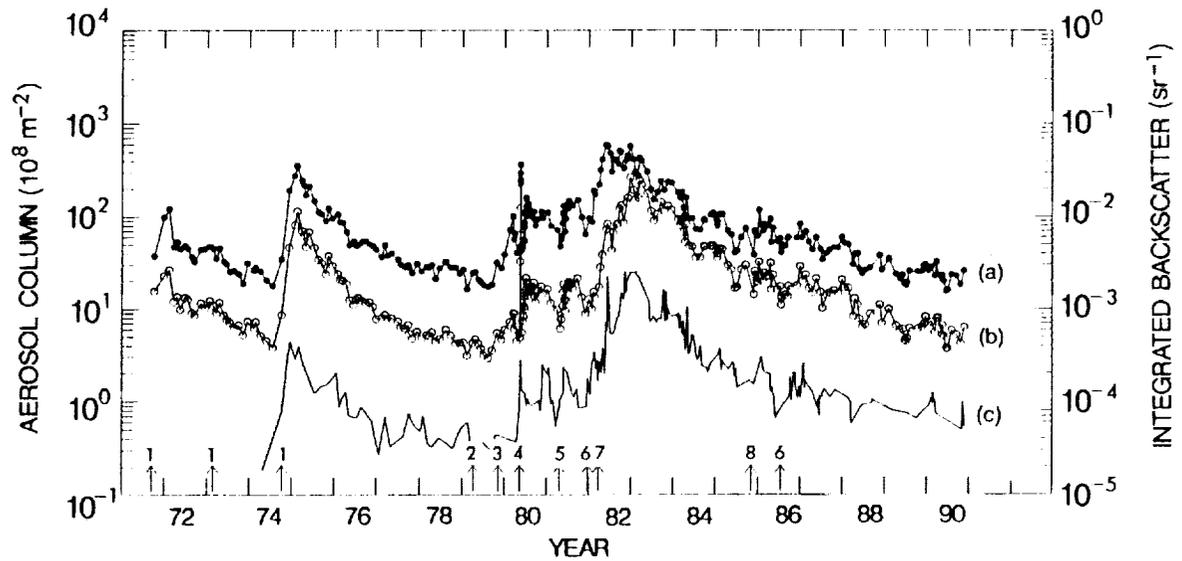
Figure 3–2 Long-term records of: (a) the aerosol column from 15 to 20 km at Laramie, Wyoming, for particles with $r \geq 0.15$ μm; (b) as in (a), but for particles with $r \geq 0.25$ μm; (c) integrated backscatter ($\lambda = 0.6943$μm) measured at NASA Langley Research Center. Volcano key: 1–Fuego, 2–La Soufriere, 3–Sierra Negra, 4–Mt. St. Helens, 5–Alaid, 6–Nyamuragira, 7–El Chichón, 8–Ruiz.
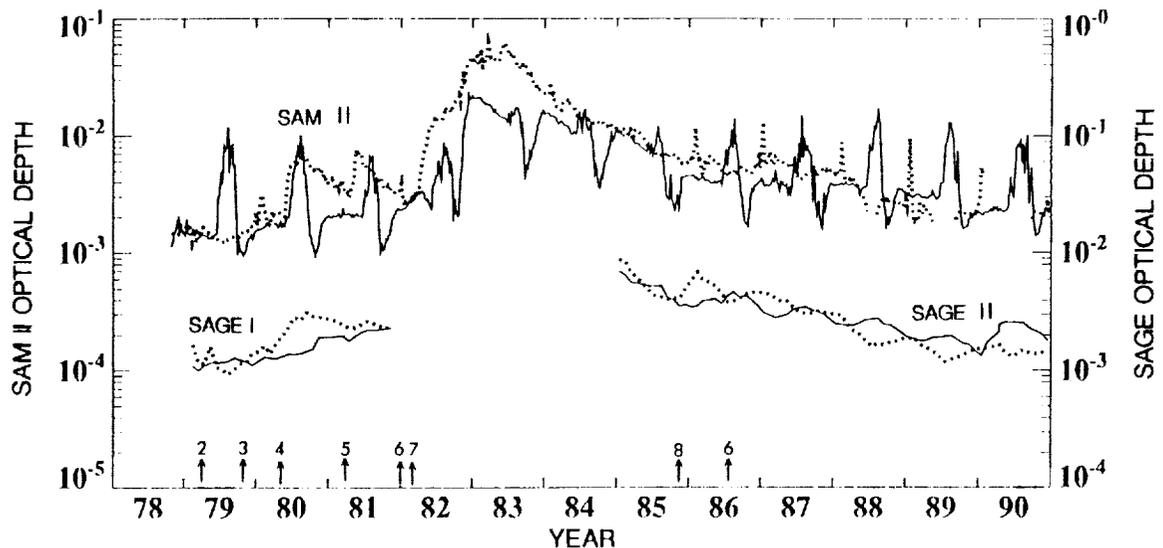
Figure 3–3 Records of 1.0–μm optical depth measured by SAM II in the Antarctic (solid curve) and Arctic (dotted curve) and by SAGE I and SAGE II in the Southern (solid curves) and Northern (dotted curves) Hemispheres. Arrows along x-axis denote volcanic eruptions, key as in Figure 3–2.
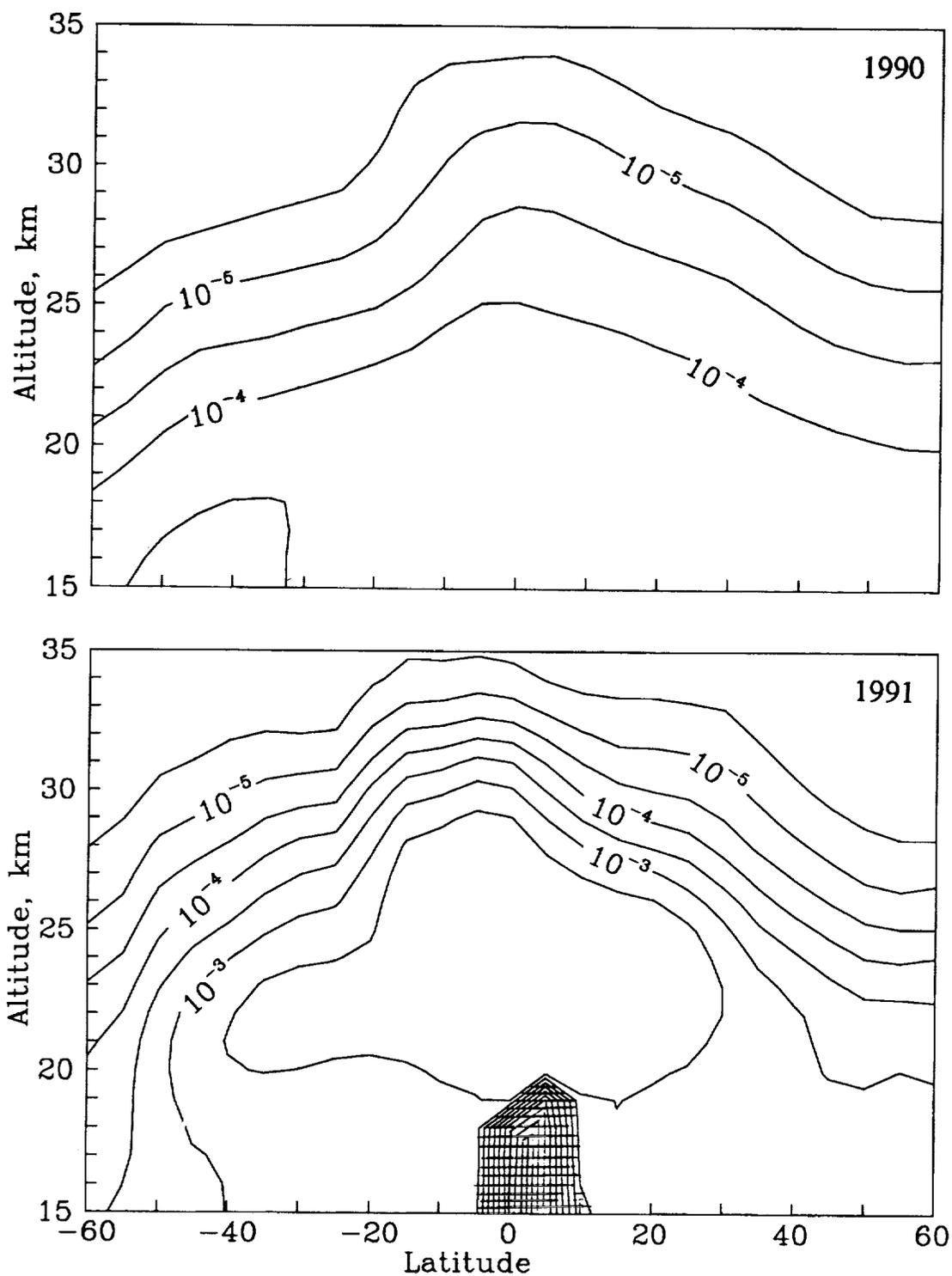
Figure 3–4 Zonal mean (60°S to 60°N) stratospheric aerosol extinction coefficient (km⁻¹) at 1 μm measured by SAGE II from mid-September to mid-October in 1990 and 1991. Values in cross-hatched region exceed the sensitivity of the instrument.

(*e.g.*, Yue and Deepak, 1983) and of *in situ* measurements as well. However, a recent study (Thomason, 1991) showed that a segmented power law model more accurately reproduces the spectral variation in SAGE II data. Total surface areas estimated using the two models exhibit similar spatial and seasonal features, and agree quantitatively to within the uncertainty of the extinction measurements. Figure 3–5 shows sample areas derived by applying the segmented power law to SAGE II data from January to March 1989. Similar estimates (smoothed for simplicity) are used in theoretical calculations described in Chapter 8 to study the efficiency of sulfate aerosols in catalyzing heterogeneous chemical reactions and, hence, in promoting ozone loss. A note of caution is in order, namely that there is no assurance that the surface area available for heterogeneous reactions on aerosols (or PSCs, for that matter) equals the geometric surface area. Discrepancies here would greatly impact the accuracy of calculated heterogeneous reaction rates.

3.5 EVIDENCE FOR HETEROGENEOUS PROCESSES IN THE STRATOSPHERE

The extensive measurements of chemical changes obtained in the polar regions during recent years have firmly established a link between heterogeneous processing by PSCs and ozone loss, especially in the Antarctic. The picture is not clear with regard to the relationship between heterogeneous processing by sulfate aerosols and observed global ozone decreases (as discussed more thoroughly in Chapter 4). Experimental opportunities provided by the Mt. Pinatubo eruption should yield a wealth of data on this issue over the next few years. In either case, many details of (and relationships between) individual mechanisms are not clear at this time. For example, the observation of elevated ClO concentrations provides in itself neither direct evidence nor quantitative information on the efficiency of individual reactions. A complete assessment of a given reaction would require that rates of change in both reactant and product concentrations be measured simultaneously. Since this has not been possible in the lower stratosphere to date, those quantitative tests that have been performed have been necessarily incomplete and indirect. The extent of such indirect tests of heterogeneous processes is described in this section.

3.5.1 Heterogeneous Reactions on PSCs

An increase in ClO concentration observed in Type 1 PSCs during the AASE ER–2 flight of January 24, 1989, was interpreted by Jones *et al.* (1990a) as *in situ* heterogeneous chlorine activation, principally via Reaction (3–1). The rate of ClO increase was quantitatively consistent with the probability for that reaction given in Table 3–1, implying a time constant for release of reactive chlorine of several hours. This verification is indirect as any concurrent decay in HCl or $ClONO_2$, or increase in Cl_2 and HNO_3, could not be monitored. No comparable test has been performed for Type 2 PSCs. The rapid rate of release compared with the time constant for reactive chlorine to return to more benign forms (days to weeks) implies that uncertainties in the precise rates of individual heterogeneous reactions may not be the major source of uncertainty in calculating ClO concentrations. Recent model calculations (*e.g.* Drdla *et al.*, 1991) generally confirm this view, indicating that heterogeneous release of reactive chlorine on PSCs is both rapid and not critically dependent on detailed particle characteristics. This may not be the case, however, if the PSCs are very sporadic or very limited in spatial extent. Finally, observations inside both the Antarctic and Arctic polar vortices of anomalously low ratios of the HCl column content to that of HF have been interpreted as a clear signature of heterogeneous removal of gaseous HCl (Coffey *et al.*, 1989; Toon *et al.*, 1989; Mankin *et al.*, 1990).

3.5.2 Heterogeneous Reactions on Sulfate Aerosols

Since stratospheric sulfate aerosols are ubiquitous rather than episodic in nature (except for periods immediately following major volcanic eruptions), direct estimation of reaction rates on these particles in the lower stratosphere is normally impossible. Although several comparisons between observed and modeled chlorine and odd nitrogen species have been performed recently, it must be noted that these represent a test of both the perturbing (heterogeneous) reactions and the coupled gas phase reactions (primarily the release of NO_2 from HNO_3). Considering chlorine partitioning first, Mather and Brune (1990) analyzed observations of ClO outside the northern polar vortex and deduced that direct heterogeneous
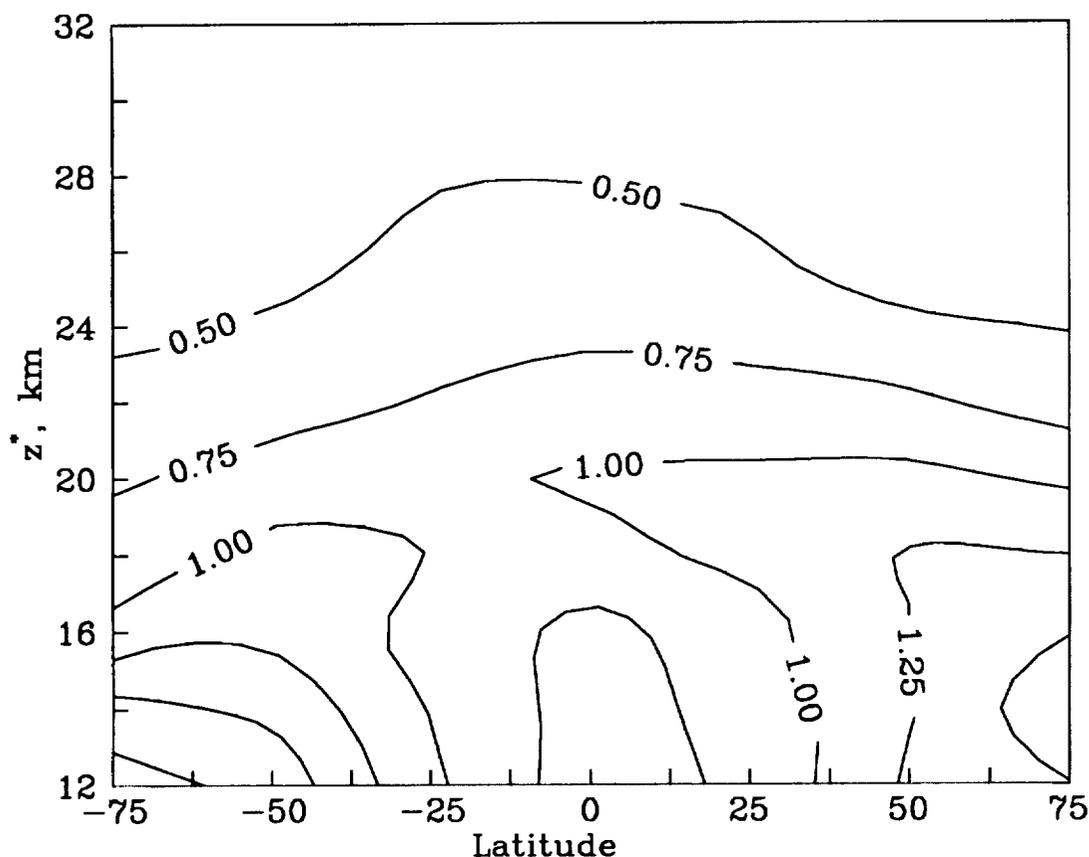
Figure 3–5 Sulfate aerosol surface area ($\mu m^2 cm^{-3}$) derived from SAGE II data for January to March 1989 using segmented power law size distribution model. $z^* = 16 \log_{10}(1000/\text{pressure [mbar]})$.

activation of chlorine is inefficient on background aerosols. This is consistent with the low measured reaction probabilities for direct release of reactive chlorine via Reactions (3–1) and (3–2) of Table 3–2. Chlorine partitioning can also be perturbed (ClO concentrations elevated) indirectly by the heterogeneous conversion of N_2O_5 to HNO_3 (Reaction 3–4, Table 3–2). The study by Rodriguez *et al.* (1991) showed that ClO mixing ratios of up to 150 ppbv that had been observed at 57°N could be reproduced solely via this path using a γ of ≈0.1, consistent with the recommended value in Table 3–2.

In terms of odd nitrogen species, model calculations assuming only gas phase chemistry have for some time been unable to simulate the HNO_3 distribution in the stratosphere, particularly the appearance of higher mid-latitude abundances in the winter hemisphere than in the summer hemisphere (Austin *et al.*, 1986; Jackman *et al.*, 1987). More recently, similar

three-dimensional simulations have been unable to reproduce the spatial and temporal variability of HNO_3 in northern mid-latitudes, and comparison with LIMS data shows that HNO_3 does not behave as a tracer in the lower stratosphere as would be expected on the basis of gas phase chemistry (Rood *et al.*, 1990). Measurements of the NO_2 column at high latitudes (66°S, 78°S) under non-PSC conditions (Pommereau and Goutail, 1988; Solomon and Keys, 1991) strongly suggest that N_2O_5 is converted heterogeneously on background aerosols to a longer-lived reservoir, probably HNO_3 (as by Reaction (3–4), Table 3–2). A preliminary assessment of *in situ* NO measurements at mid-latitudes in the Northern Hemisphere (Kawa *et al.*, 1991) also suggests that some heterogenous conversion of N_2O_5 is required. A further complication has been introduced by recent measurements of the temperature dependence of the HNO_3 photolysis cross section (Rattigan *et al.*, 1991),

which suggest that HNO_3 is photolyzed some 2 to 3 times slower in the lower stratosphere than previously thought. As this process is the dominant loss mechanism for HNO_3 in the lower stratosphere, a change in photolysis rate will influence significantly the odd nitrogen partitioning and, hence, the level of consistency between observations and model results discussed above.

3.5.3 Denitrification Mechanisms

Several viable mechanisms have now been suggested for denitrification and dehydration of the lower stratosphere. Wofsy et al. (1990) suggest that denitrification is initiated by sedimentation of ice particles formed at higher altitudes, a notion supported by recent laboratory results (Section 3.2) that show that HNO_3 vapor readily sticks to ice surfaces, forming a layer of NAT, which retards sublimation of the underlying ice. Calculations by Toon et al. (1990b) do not assume scavenging of vapor by falling particles, yet suggest that HNO_3 and H_2O vapor removal can occur either separately or simultaneously, depending on the period and extent of cooling. Neither mechanism has been tested comprehensively using analyzed wind and temperature fields and observed H_2O and NO_y measurements, and features have been observed that, at first sight, may not be consistent with either approach. For example, the appearance everywhere of dehydration in denitrified air masses over the Antarctic during AAOE might not be expected if the processes were coupled in a manner as suggested by Wofsy et al. (1990b). It must be noted, however, that the earliest AAOE observations were made in mid-August of 1987, or several months after the observed denitrification and dehydration features likely began to evolve. On the other hand, the sudden appearance of denitrification in the Northern Hemisphere during AASE well after Type 1 PSCs were first observed might argue against the Toon et al. (1990b) approach. In this case, it must be noted that ER-2 measurements during the early phase of AASE were generally at latitudes south of the region in which denitrification may have occurred via Type 1 PSC formation alone.

A reliable prediction of the spatial extent of denitrification may not be as critical in explaining Antarctic ozone losses to zeroth order as it is in understanding the interannual variation in the severity of these losses or in assessing the potential for ozone depletion in the Northern Hemisphere. This raises the important question of whether denitrification is essential for significant Northern Hemisphere ozone losses. It is now recognized that synoptically- and orographically-forced PSCs can process quite large volumes of lower stratospheric air (Cariolle et al., 1989; McKenna et al., 1989; Jones et al., 1990b; Lefèvre et al., 1991). In the Arctic, an air parcel typically executes a circuit of the periphery of the vortex in about 5 days, a time scale that is likely much shorter than that required to return reactive chlorine to more benign forms, particularly in light of the newly measured reduced photolysis rates of HNO_3. Thus, if PSCs are present at high northern latitudes, the periodic exposure of parcels to the clouds is likely to affect chlorine partitioning over large volumes of the lower stratosphere. Even in the absence of denitrification, such processing could maintain a highly perturbed, high-ClO_x state, leading to ozone destruction. It may be expected that in such a case, denitrification would lead to only minor increases in ClO_x and ozone loss.

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