VOLUME 90, Nos. 2–4   NOVEMBER–DECEMBER 2008   ISSN 0169-8095

CLOUDS · PRECIPITATION · AEROSOLS · RADIATION · WEATHER MODIFICATION

ATMOSPHERIC RESEARCH

Special Issue
17TH INTERNATIONAL CONFERENCE ON NUCLEATION AND ATMOSPHERIC AEROSOLS
Guest Editors: **Colin D. O'Dowd, Paul E. Wagner**

http://www.elsevier.com/locate/atmosres

A review of global stratospheric aerosol: Measurements, importance, life cycle, and local stratospheric aerosol

Terry Deshler

Department of Atmospheric Science, University of Wyoming, Laramie , Wyoming, USA

ARTICLE INFO

ABSTRACT

Stratospheric aerosol, noted after large volcanic eruptions since at least the late 1800s, were first measured in the late 1950s, with the modern continuous record beginning in the 1970s. Stratospheric aerosol, both volcanic and non-volcanic are sulfuric acid droplets with radii (concentrations) on the order of 0.1–0.5 µm (0.5–0.005 cm^{-3}), increasing by factors of 2–4 (10–10^3) after large volcanic eruptions. The source of the sulfur for the aerosol is either through direct injection from sulfur-rich volcanic eruptions, or from tropical injection of tropospheric air containing OCS, SO$_2$, and sulfate particles. The life cycle of non-volcanic stratospheric aerosol, consisting of photo-dissociation and oxidation of sulfur source gases, nucleation/condensation in the tropics, transport pole-ward and downward in the global planetary wave driven tropical pump, leads to a quasi steady state relative maximum in particle number concentration at around 20 km in the mid latitudes. Stratospheric aerosol have significant impacts on the Earth's radiation balance for several years following volcanic eruptions. Away from large eruptions, the direct radiation impact is small and well characterized; however, these particles also may play a role in the nucleation of near tropopause cirrus, and thus indirectly affect radiation. Stratospheric aerosol play a larger role in the chemical, particularly ozone, balance of the stratosphere. In the mid latitudes they interact with both nitrous oxides and chlorine reservoirs, thus indirectly affecting ozone. In the polar regions they provide condensation sites for polar stratospheric clouds which then provide the surfaces necessary to convert inactive to active chlorine leading to polar ozone loss. Until the mid 1990s the modern record has been dominated by three large sulfur-rich eruptions: Fuego (1974), El Chichón (1982) and Pinatubo (1991), thus definitive conclusions concerning the trend of non-volcanic stratospheric aerosol could only recently be made. Although anthropogenic emissions of SO$_2$ have changed somewhat over the past 30 years, the measurements during volcanically quiescent periods indicate no long term trend in non-volcanic stratospheric aerosol.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The reddish diffraction ring around the sun following large volcanic eruptions was described from Hawaii by Sereno Bishop nine days after the eruption of Krakatoa, in August 1883, and led to the name Bishop's ring. The first published report suggesting a persistent non-volcanic aerosol layer in the stratosphere used purple twilight observations (Gruner and Kleinert, 1927). Quantitative observations of stratospheric aerosol (SA) characterizing the altitudes, sizes, masses, and compositions were first provided by balloon-borne impactor measurements in the late 1950s (Junge et al., 1961). Subsequent measurements by both aircraft- and balloon-borne impactors suggested the global distribution of SA. While condensation nuclei (CN) concentrations decreased or remained constant through the stratosphere, particles > 0.1 µm had a maximum in concentration near 20 km, suggesting an aerosol source in this region. These initial stratospheric measurements were followed by a suite of instruments to measure SA including passive extinction measurements (Volz and Goody, 1962), active scattering measurements (Fiocco and Grams, 1964), and counting and sizing single particles (Rosen, 1964). These initial measurements laid the ground work for the

E-mail address: deshler@uwyo.edu.

beginning of regular measurements of stratospheric aerosol which began in the 1970s. These measurements and their subsequent analysis, coupled with models of aerosol growth and decay within the large scale equator to pole Brewer Dobson circulation have led to our current understanding of stratospheric aerosol. This paper seeks to briefly review this state of knowledge, with some emphasis on long term surface based measurements both remote and in situ. In addition some new unexplained tropical measurements will be presented.

## 2. Stratospheric aerosol measurement record

Surface based measurements, balloon borne, and lidar, include several fairly continuous records of measurements of SA which began in the early 1970s, about a decade after Junge's initial measurements. The balloon-borne measurements have been limited primarily to Laramie, Wyoming, with sporadic measurements from Lauder, NZ (Hofmann et al., 1975; Deshler et al., 2003a). These measurements provide profiles of size resolved aerosol number concentration. Following the initial lidar measurements of Fiocco and Grams (1964), long term lidar measurements began in the 1970s. Lidars provide remote, vertically resolved measurements of atmospheric backscatter from both molecules and aerosols at one or more wavelengths, and lidar sites investigating SA now range in latitude from 90°S to 80°N. The balloon-borne measurements from Laramie along with lidar measurements from two mid latitude sites (Jäger, 2005; Osborn et al., 1995) and two tropical sites (Barnes and Hofmann, 1997; Simonich and Clemesha, 1997) provide the longest SA records available, Fig. 1. Three eruptions have dominated the modern SA record; however, this high level of volcanic activity is a bit anomalous. Solar and stellar extinction data show that since 1880 the stratosphere has been dominated by eight major eruptions (Sato et al., 1993; Stothers, 1996). Four of these occurred between 1880 and 1910 and four since 1960. The long term SA measurements, which began in the 1970s, have captured the complete cycle for three major eruptions with a global stratospheric impact: Fuego (14°N, October 1974, 3–6 Tg of aerosol), El Chichón (17°N, April 1982, 12 Tg) and Pinatubo (15°N, June 1991, 30 Tg) (McCormick et al., 1995). Within this record there have been four periods when volcanic influences were at a minimum, 1974, 1978–1980, 1988–1991, and 1997–present.

For each of the integrated measurements shown in Fig. 1 there exists an SA profile. Example in situ profiles are shown in Fig. 2. The profile in 1992, one year after Pinatubo, was measured after the Pinatubo volcanic SA had become
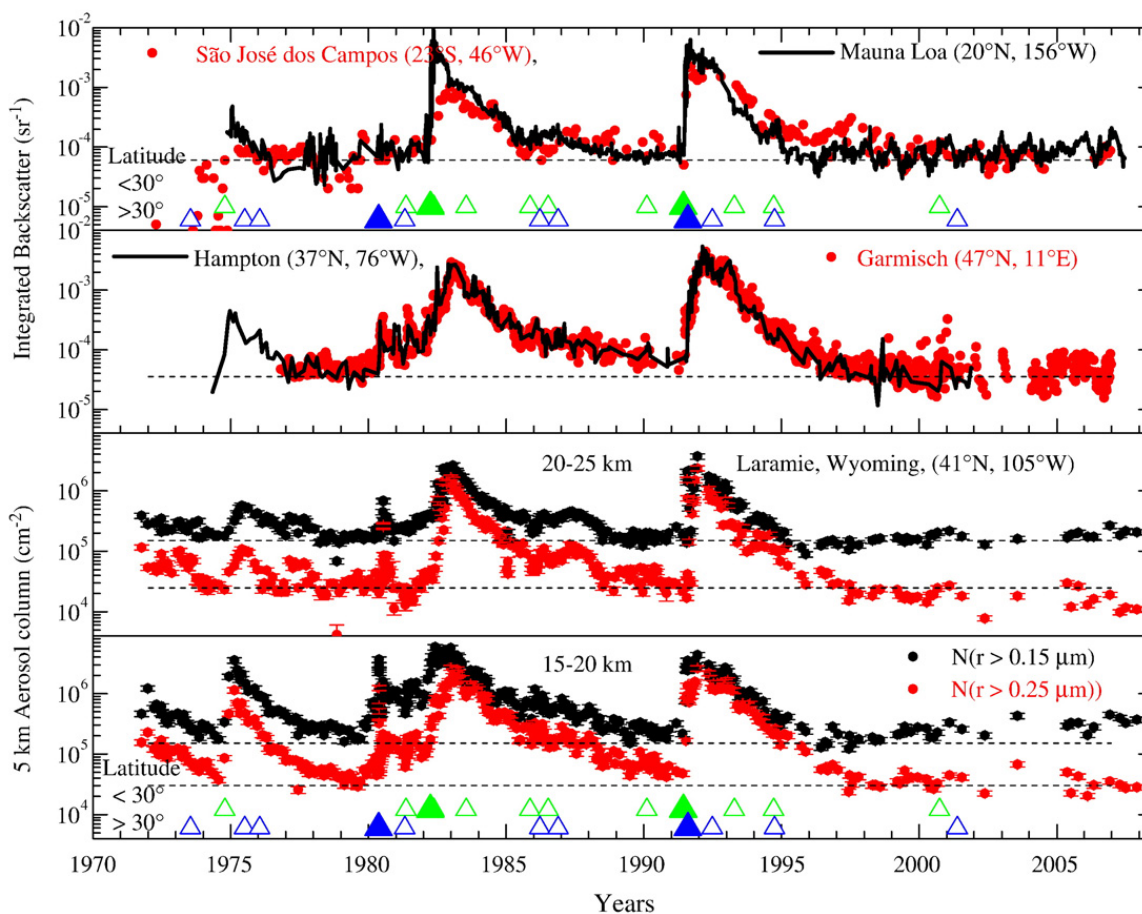
Fig. 1. History (1970–2007) of SA from two tropical lidar sites (São José dos Campos, Brazil and Mauna Loa, Hawaii, USA), two mid latitude lidar sites (Hampton, Virginia, USA, and Garmisch, Germany) and one set of mid latitude in situ measurements. The lidar measurements are presented as integrated SA backscatter above the tropopause at each site. The in situ data are presented as integral columns of number between 15–20 and 20–25 km at two sizes. The time of volcanic eruptions for VEI=4 (open triangle) and VEI=5 (closed triangle) and for latitudes <30° and >30° are shown in the bottom of the top and bottom panels. A complete description of each of these instruments is provided by Deshler et al. (2006). Recent data from São José dos Campos were provided by Dale Simonich and Barclay Clemesha, from Mauna Loa by John Barnes, and from Garmisch by Thomas Trickl. The Hampton measurements have been discontinued.
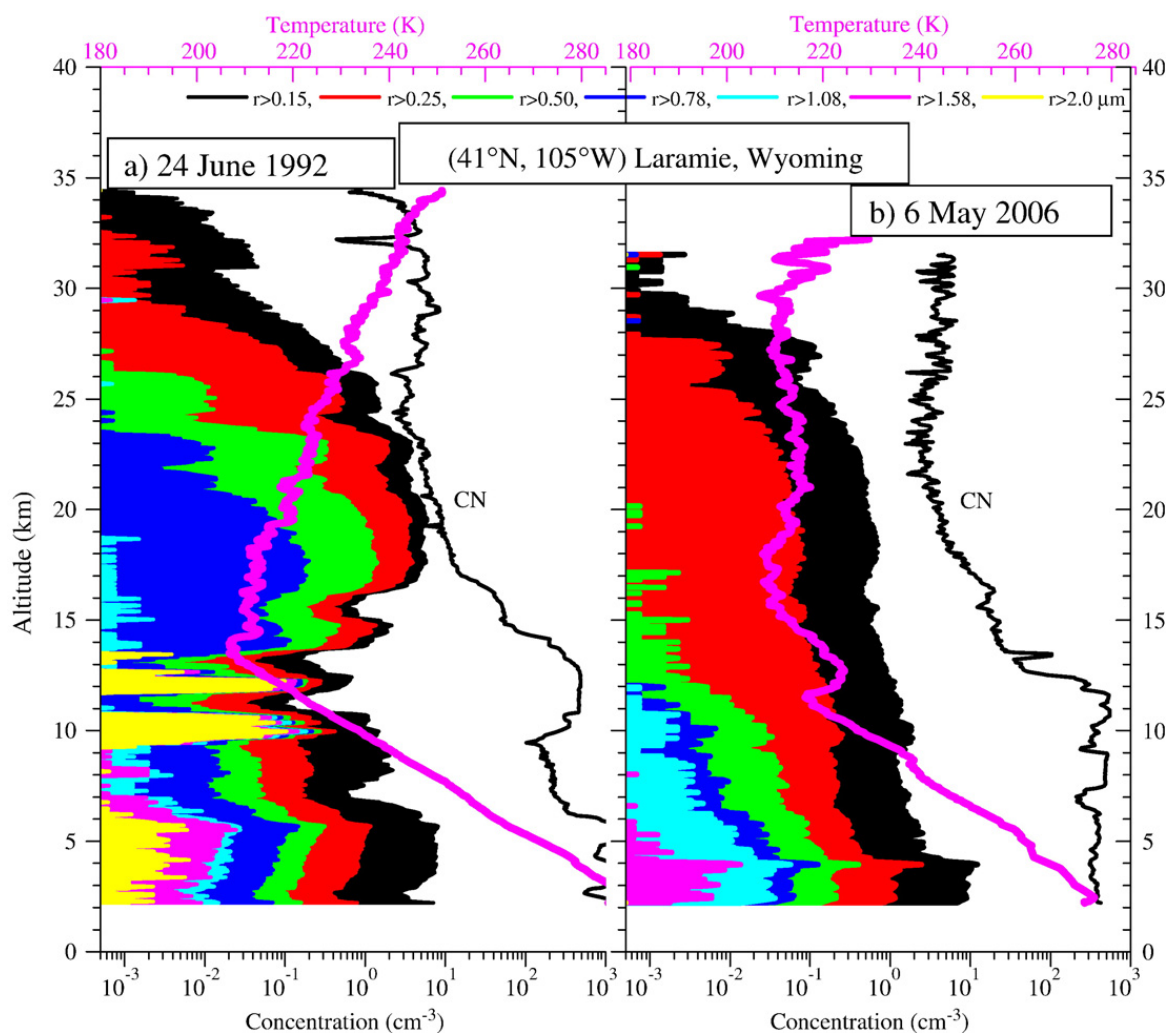
Fig. 2. Stratospheric aerosol profiles above Laramie Wyoming (41°N, 106°W) indicating the concentration of condensation nuclei (CN) and aerosol with radii greater than 0.15, 0.25, 0.50, 0.78, 1.08, 1.58 and 2.0 μm. Temperature with scale at the top is also shown. These profiles were measured in a) June 1992, one year after the Pinatubo eruption and b) May 2006, fifteen years after Pinatubo.

reasonably well mixed both vertically and horizontally, but before significant decay processes had begun. Significant concentrations of particles>0.78 μm radius were observed above 20 km. In 2006, 15 years after Pinatubo, only low concentrations of particles>0.5 μm radius are observed in the stratosphere, and while the concentration of CN is not significantly different than shortly after Pinatubo, there is a significant difference in the concentration of particles>0.15 μm, with the difference increasing as particle size increases. This difference in size distributions is further elaborated in Figs. 3 and 4 which present monomodal and bimodal lognormal size distributions from particle counter data. Fig. 3 indicates the narrow nature of both modes of the SA size distribution one year after Pinatubo and the relatively large size of the first mode median radius. Three years after the eruption both distributions have broadened and separated. The final distribution, 15 years after the eruption, but representative of distributions since about 6 years after Pinatubo shows a narrow first mode and weak second mode. More temporal and altitude dependence of these size distributions is shown in Fig. 4. The primary differences between the volcanically perturbed and quiescent periods are in about a factor 2

decrease in r_1, particularly below about 25 km, and a factor of 10 decrease in N_2, while r_2 decreases only slightly, and N_1 remains nearly static.

Beginning in the late 1970s satellite instruments: SAM II (McCormick et al., 1981) (1979–1994), SAGE (1979–1981) and SAGE II (Thomason et al., 1997b) (1984–2005), added considerably to the SA record. These initial instruments which extended the local measurements to a global picture, have been supplemented with a number of additional instruments, e.g. HALOE (80°S–80°N, 1991–2005), POAM II, III (63–88°S, 54–71°N, 1993–1996, 1998–2005), SAGE III (2003–2006). For a review of these instruments see Thomason and Peter (2006). The current satellite instruments, ACE-FTS, MAESTRO, CALYPSO are all challenged by the low level of SA during background conditions, and there are no replacements in operation for the SAGE II aerosol record.

3. Importance of stratospheric aerosol

SA play a role in the global radiation and chemical balance of the atmosphere. SA scatter solar radiation and must be considered in global climate models. Their impact is small
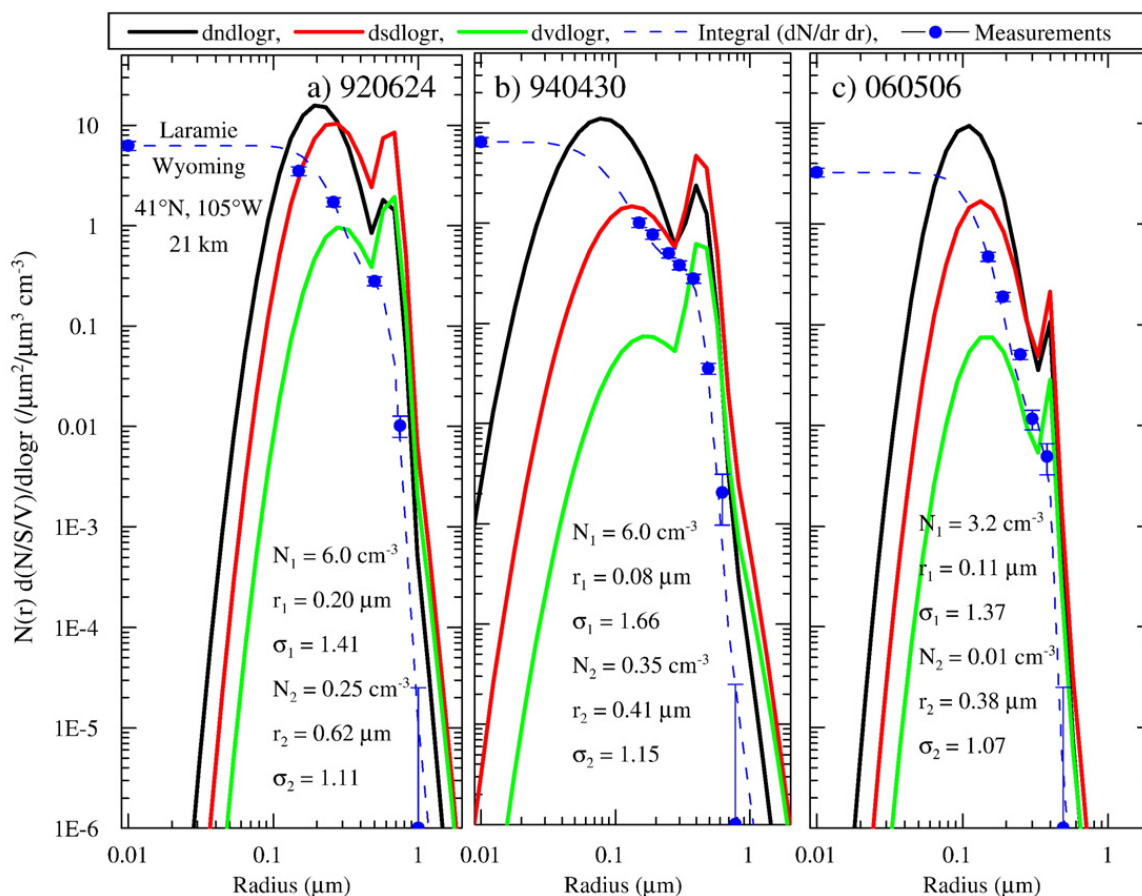
Fig. 3. Differential number (cm^{-3}), surface area ($\mu m^2\ cm^{-3}$), and volume ($\mu m^3\ cm^{-3}$) distributions, as a function of $d\log_{10}(r)$ derived from fitting bimodal lognormal size distributions to in situ optical particle counter measurements at 21 km above Laramie, Wyoming (Deshler et al., 2003). The cumulative number distribution measured is shown as the blue data points with Poisson error bars, and the fitted distribution as the blue dashed line. Parameters of the two modes of the lognormal size distributions fit to the measurements are shown in each size distribution plot along with the date of the measurement at the top. The size distributions are representative of measurements a) one year, b) 3 years, and c) 15 years after the Pinatubo eruption, corresponding to heavy, moderate, and no volcanic aerosol loading.

during non-volcanic, or background, periods, with optical depths of less than 0.01, but is significant following large volcanic eruptions. Optical depths reached 0.1 following El Chichón and Pinatubo. This is high enough to cause measurable impacts on global climate. Both stratospheric warming (Labitzke and McCormick, 1992), and tropospheric cooling (Dutton and Christy, 1992) have been documented. These effects are observable for 2–3 years following the eruption, after which the optical depths have fallen by a factor of 10.

SA play a relatively larger role in the chemical balance of the atmosphere. During volcanically quiescent periods SA affect the budget of several trace gases, in particular NO_x, while after volcanic activity SA can directly increase the abundance of activated chlorine (Hanson and Lovejoy, 1995). Decreases in mid latitude ozone have been observed following both El Chichón (Hofmann and Solomon, 1989) and Pinatubo (Gleason et al., 1993). NO_2 columns were reduced after both El Chichón and Pinatubo (Johnston et al., 1992) from the hydrolysis of N_2O_5 on water bearing volcanic SA (Rowland et al., 1986). At low aerosol loading NO_x increases and induces ozone loss from the nitrogen catalytic cycle (Crutzen, 1970). There are direct measurements of the anticorrelation of aerosol surface area and the NO_x/NO_y ratio (Fahey et al., 1993). The hydrolysis of N_2O_5 saturates as

aerosol surface area increases above ~10 $\mu m^2\ cm^{-3}$, thus SA control NO_x only during periods of low aerosol loading.

In the polar regions SA provide the nucleation/condensation sites for the growth of polar stratospheric clouds (PSCs), providing the surfaces necessary to convert reservoir chlorine molecules to a photo-labile species easily photolyzed with the return of the sun in spring. This leads to the annual ozone hole above Antarctica and to occasional Arctic ozone loss. The stability of the Antarctic polar vortex leads regularly to temperatures conducive for PSCs, and thus ozone loss. In contrast the northern hemisphere topography forces large amplitude planetary waves leading to a warmer and less stable polar vortex. Thus PSCs, and polar ozone loss, are much less frequent.

4. Life cycle of stratospheric aerosol

The initial impactor measurements by Junge et al. (1961) allowed for estimates of the chemical composition of the particles using an electron microprobe analyzer. The only element to appear in appreciable quantities was sulfur, leading to a suggestion that the aerosol were primarily composed of sulfate. Further balloon-borne measurements established the boiling point of SA (Rosen, 1971), which was consistent with a
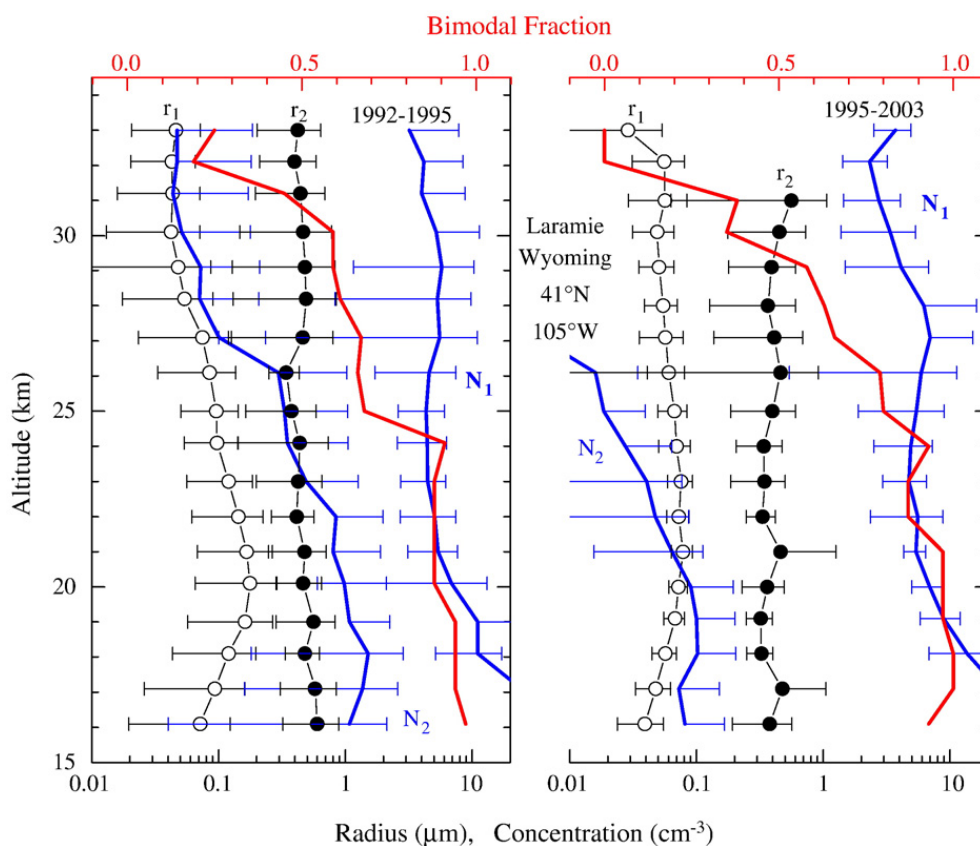
Fig. 4. Vertical profiles of integral number concentration (cm^{-3}) and median radii (μm) from unimodal/bimodal lognormal parameters fit to balloon borne in situ optical particle measurements (Deshler et al., 2003). Averages and standard deviations for modal number concentration, N_1, N_2 (blue lines with error bars), and median radii, r_1, r_2 (dark lines with data points and error bars), and fraction of measurements which were bimodal (red lines, with scale at the top) are shown. The fitting parameters from two time periods are shown, 1992–1995, encompassing the Pinatubo aerosol and its decay, and 1995–2003, representing the current stratospheric background. Both time periods include about 30 individual profiles.

composition of 75% sulfuric acid and 25% water. SA are always under saturated with respect to sulfuric acid, because of the very low vapor pressure of sulfuric acid. Thus any free sulfuric acid molecules are quickly captured by a particle which then condenses water, with an abundance about 10^7 times that of sulfuric acid, to maintain equilibrium with the environment. Slight decreases (increases) in temperature lead to uptake (release) of water. Thus the size and composition of SA are controlled by temperature and the abundance of gas phase sulfuric acid. Heated inlet in situ measurements were completed following both El Chichón and Pinatubo and impactor measurements followed Pinatubo (Hofmann and Rosen, 1984; Deshler et al., 1992; Sheridan et al., 1992). These were all consistent with a sulfuric acid and water composition. Lingering questions concerning contamination from such impactor measurements were laid to rest by direct aerosol composition measurements in 1995, while the Pinatubo aerosol was still decaying (Arnold et al., 1998a) and in 1998 when the Pinatubo influence was minimal (Murphy et al., 1998). Based on these and other measurements it is clear that SA is composed primarily of sulfuric acid and water during both volcanically active and quiescent periods.

4.1. Origin of stratospheric aerosol

For a volcanic eruption to significantly perturb the stratosphere it must have enough energy to penetrate the tropopause and it must be rich in sulfur. Generally eruptions with a volcanic explosivity index (VEI)≥4, will penetrate into the stratosphere (Newhall and Self, 1982). In the period of modern measurements (1960–2006) there have been about 33 eruptions with such a stratospheric impact (Deshler and Anderson-Sprecher, 2006). Of these five, 3 tropical and 2 high latitude, had a VEI≥5. One of these, Mt. Saint Helens (46°N), released less than 1 Tg of SO$_2$ and the silicates and other large particles quickly fell out. The impact of Mt. St. Helens was gone in about a year, Fig. 1. Cerro Hudson, the other high (but southern) latitude eruption (46°S), released ~3 Tg of SO$_2$, but occurred in 1991 just after Pinatubo (~30 Tg of SO$_2$), so the signal from Cerro Hudson, while probably never entering the northern hemisphere, was quickly lost in the Pinatubo aerosol. The other three eruptions, Agung (1963), El Chichón (1982), and Pinatubo (1991) were all at low latitudes and the latter two clearly produced a stratospheric impact lasting 5 or more years, Fig. 1. The impact of Agung is unknown, due to a lack of measurements; however, this eruption, along with a number of eruptions in the late 1960s with a VEI=4 was responsible for the rather large amount of SA observed in the early 1970s when measurements began. The one eruption with a significant stratospheric impact but a VEI<5 is Fuego (1974) at 14°N. The lower VEI produces an impact primarily below 20 km, as indicated in Fig. 1.

Tropical eruptions rich in sulfur directly inject particles and gases to altitudes of >20 km (VEI=4) and to >25 km (VEI=5) in the tropical stratospheric reservoir (Trepte and Hitchman, 1992). The sulfur is oxidized and transformed into

sulfuric acid within about a month. The high concentrations of gas phase sulfuric acid lead to nucleation of new binary particles. The nucleation continues until the sulfuric acid is condensed into either new particles or onto pre-existing particles. The aerosol population then further evolves through coagulation and meridional mixing. The meridional transport of material out of the tropical reservoir depends on season and the phase of the quasi biennial oscillation (QBO). After Pinatubo, filaments showing both condensation on pre-existing particles and new particles were observed about 1 month after the eruption (Deshler et al., 1992). The injection of the precursor gases for SA directly into the tropical reservoir, and the confinement of this reservoir to the tropics prolongs the stratospheric impact of tropical eruptions. Material from the tropical reservoir is generally transported out of the tropical reservoir primarily during winter for a westerly shear QBO, while easterly phase QBOs are more confining (Trepte and Hitchman, 1992). Thus after Pinatubo, aerosol was primarily transported into the northern hemisphere in winter 1992/1993 (Grant et al., 1996). Although it is assumed that the impact of a high latitude eruption would be much shorter lived, since the aerosol would be fairly quickly dispersed pole-ward and downward, there has been no opportunity to test this suggestion.

The fact that non-volcanic SA is also primarily sulfuric acid and water implies that sulfur source gases must be transported across the tropopause, and transformed into sulfuric acid which can then either nucleate new particles or condense on pre-existing particles. In addition sulfate aerosol can also be deposited in the stratosphere as remnants of overshooting convection. Scavenging of particles larger than ~0.1 μm leads to a particle deficit near the tropopause. Carbonyl sulfide (OCS), an inert sulfur bearing molecule was first suggested as the source of stratospheric SO_2 (Crutzen, 1976); however, it has been shown to be insufficient. The most recent comparison of SA models with observations of background aerosol indicates that sulfur source gases for SA must be about equally divided between OCS and SO_2, with direct injection of sulfate particles providing a source equivalent to the sum of the gas phase precursors (Weisenstein and Bekki, 2006).This conclusion is arrived at through sensitivity analysis for the SO_2 and sulfate inputs, while using available measurements of free tropospheric OCS (Notholt and Bingemer, 2006). The input of sulfate aerosol is based on tropical tropopause aerosol measurements from aircraft measurements (Jonsson et al., 1995). SO_2 has a short, highly variable lifetime (10–20 days) with sources that are intense yet regionally limited. SO_2 mixing ratios in the troposphere vary by several orders of magnitude from over 1000 pptv downwind of urban centers and in continental outflow (Reiner et al., 2001; Tu et al., 2004) to the order of 10 pptv in the upper troposphere above remote regions (Meixner, 1984; Andreae et al., 2000). From a broad set of measurements over the Pacific Ocean Thornton et al. (1999) established a marked inter-hemispheric gradient in SO_2 throughout the troposphere, from near 10 pptv at high southern latitudes to over 100 pptv at high northern latitudes. A summary of these and other SO_2 measurements (Notholt and Bingemer, 2006) suggests that the model requirements of an input of 80 pptv SO_2 into the stratosphere, to achieve agreement with satellite extinction measurements below 25 km, are reasonable. Above 25 km OCS is the dominant source of sulfur.

Other minor constituents of SA include meteoritic material, and aircraft and rocket exhaust. These sources are generally not directly observable with the instruments used to measure global SA. Detailed chemical measurements of SA indicate that meteoritic iron inclusions comprise approximately 1% of about half of the stratospheric particles sampled (Cziczo et al., 2001). These observations support the view that meteoritic material arrives predominantly in micro-meteors which vaporize near 100 km and then recondense as nanometer size particles (Hunten et al., 1980) which are then incorporated into SA. Recently a large meteoritic impact was captured by lidar indicating the processes occurring for large meteors can be significantly different (Klekociuk et al., 2005). In this case particles in the disintegration trail of the meteor were estimated to be in the micrometer size range. Such large events are rare.

Estimates of the impact of rocket exhaust (Danilin et al., 2001; Jackman et al., 1996) on global stratospheric aerosol indicate a source over 1000 times smaller than the background stratospheric aerosol, although single rocket plume exhausts have been observed over relatively large time and spatial scales (Newman et al., 2001). The impact of aircraft exhaust on stratospheric aerosol has been studied much more extensively through focused in situ measurements (e.g. Arnold et al., 1998b; Fahey et al., 1995), chance encounters (Hofmann and Rosen, 1978), and models (Kärcher et al., 2000; Kjellstrom et al., 1999). This work has been extensively reviewed by Kärcher (1999). Although there is some indication of an increase in condensation nuclei in the northern hemisphere (Hofmann et al., 1998), the impact on stratospheric aerosol is estimated to be about 1% of the sulfate mass in the air traffic corridor north of 40°N (Kjellstrom et al., 1999). Thus the global impact of aircraft and rocket exhaust on the global burden of stratospheric aerosol is minimal, and long term stratospheric aerosol records show no evidence of an increase in the background stratospheric aerosol (Deshler and Anderson-Sprecher, 2006) in spite of the increases in air traffic over the past 40 years.

4.2. Loss of stratospheric aerosol

The removal of aerosol from the stratosphere follows similar paths for either volcanic or background aerosol. Both types of particles originate from the condensation of sulfuric acid and water onto new or pre-existing aerosol, coagulation, and growth in the presence of additional sulfuric acid vapor. The nucleation of new particles and coagulation occur over short time scales. Even in the presence of high concentrations of particles and sulfuric acid vapor, following large volcanic eruptions, the evolution of the aerosol size distribution through nucleation and coagulation will continue for less than a few months (Hamill et al., 1997). After this time, diffusional growth, mixing, and gravitational settling lead to further changes in size distribution. Gravitational settling is an important factor in controlling the rather constant nature of the background aerosol population, but is a small contributor to the removal of SA. Gravity has the effect of moving the larger particles closer to the tropopause where

they are removed through stratosphere troposphere exchange processes, which are rapid compared with gravitational settling.

The exchange of air between the stratosphere and troposphere occurs, in order of importance, through the extratropical wave driven equator to pole circulation, through tropopause folds, and through subsidence in the polar vortex (Holton et al., 1995). The extratropical tropospheric planetary wave driven circulation creates equatorial upwelling and extratropical downwelling. The peak activity thus occurs in the winter hemisphere, which, depending on the phase of the QBO (Trepte and Hitchman, 1992), has the effect of moving air meridionally and downward from the tropical reservoir. Estimates of the flux of air created by this circulation, which are in agreement with tracer measurements (Holton et al., 1995), suggest stratospheric residence times of approximately two years. This is significantly faster than either tropopause folds or polar vortex subsidence, ~8 years, (Hamill et al., 1997).

The initial SA observations of Junge et al. (1961) concluded that there was a source of SA near 20 km, because of the local maximum in aerosol concentration that did, and does, appear

there in mid latitude measurements, Fig. 2. It is now known that the source of these aerosol is a complex interaction between equatorial upwelling, transportation of sulfur source gases and nascent particles into the stratosphere, nucleation, condensation, and coagulation to develop a relatively static size distribution, and then gravitational settling, and extratropical wave driven downwelling causing removal. The interplay of these various sources, sinks, and forces creates a relatively static aerosol profile during volcanically quiescent conditions, thus the only real opportunity to observe stratospheric decay processes is after large volcanic eruptions, Fig. 1.

Generally after eruptions e-folding times vary between 0.8 and 1.5 yr depending on the observation/geophysical parameter considered, and the influence of minor eruptions. Aerosol volume/extinction will have somewhat faster e-folding times than aerosol number; however, these differences are not large since gravity plays a relatively small roll in SA removal. After El Chichón the loss of stratospheric aerosol was perturbed by a number of minor eruptions, thus there are questions whether background was reached after El
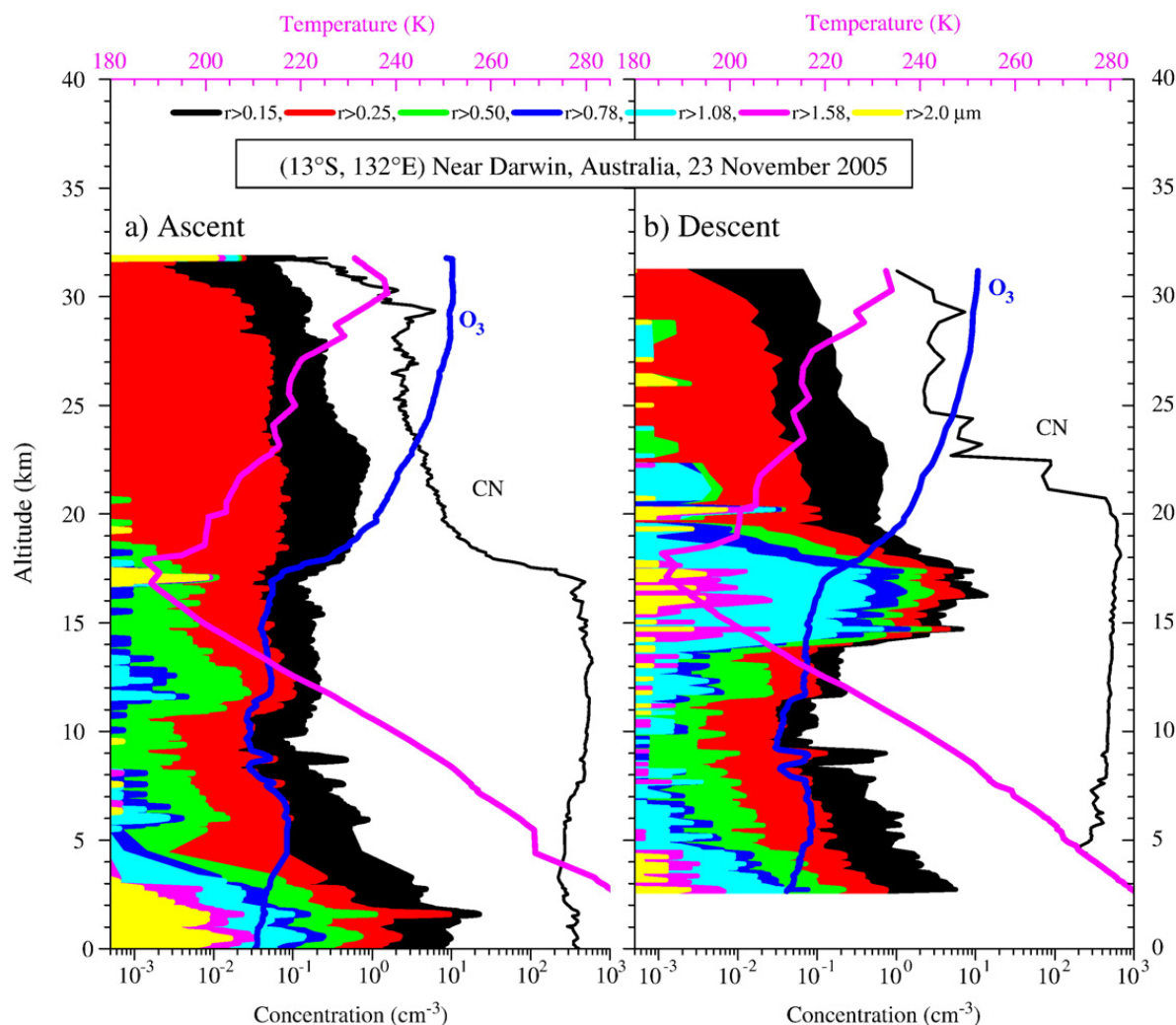
Fig. 5. Stratospheric aerosol profiles above Darwin, Australia (13°S, 132°E) on 23 November 2005 for a) ascent and b) descent. The concentration of condensation nuclei (CN) and aerosol with radii greater than 0.15, 0.25, 0.50, 0.78, 1.08, 1.58 and 2.0 μm is shown. Temperature with scale at the top and ozone mixing ratio (ppmv), scale at the bottom are also shown. The CN counter saturates at approximately 600 cm^{-3}, thus measurements below 17 km on ascent and below 21 km on descent are saturated.

Chichón and before Pinatubo erupted (Thomason et al., 1997a).

From the time that the stratospheric aerosol measurement record began until 1995 the stratosphere has been primarily dominated by volcanic eruptions, while volcanic interludes have been brief, Fig. 1. Thus it has been difficult to assign a lifetime to the non-volcanic component of SA. Early work concluding that non-volcanic SA was increasing may have been premature due to uncertainty as to whether the volcanic influence was really minimal (Hofmann, 1990; Thomason et al., 1997a). Only the long post-Pinatubo quiescent period has allowed the question of trends in background SA to be confidently addressed. Deshler and Anderson-Sprecher (2006) utilized four lidar records and one balloon-borne measurement record, spanning 30 years, and one satellite (SAGE II) record, spanning 20 years, to address this question. The records were investigated by both comparing the volcanically quiescent periods and by fitting a parametric model to each record to account for, and remove, volcanic aerosol. The estimates of the exponential growth/decay coefficient for each record indicate a value not significantly different than zero in 35 of 39 data sets investigated. The conclusion is that background SA has not displayed a long term trend over the period 1970–2005.

5. Local stratospheric aerosol

Stratospheric clouds have been documented in the polar regions since the late 1800s. These clouds became the subject of intense interest after the discovery of their role in stratospheric ozone loss through converting inactive to active chlorine and denitrifying the stratosphere. Observational, laboratory, and theoretical work has since shown that PSC particles above the ice point are either: solid nitric acid trihydrate (NAT) particles; or liquid ternary aerosol (LTA), droplets composed of nitric acid, sulfuric acid, and water. Composition and phase of the particles determines threshold temperatures at which they occur and persist. NAT will exist at temperatures 3–5 K above LTA temperatures, and LTA begin appearing about 3 K above the ice point for polar stratospheric levels of gaseous nitric acid and water (Hanson and Mauersberger, 1988; Carslaw et al., 1994). Particle phase also controls the development of particle size which plays a large role in the extent and rate of dehydration/ denitrification, thus determining the time frame during which chlorine will remain active.

The major remaining question concerning the formation of PSCs in the atmosphere is the process by which NAT forms. LTA growth is strictly a function of gas phase mixing ratios and temperature, as the vapor pressures of sulfuric acid, nitric acid, and water adjust to environmental temperature and molecular collisions. LTA begins to grow on the SA as soon as temperatures reach about 3 K above the ice point. At these temperatures the concentration of NAT particles is often at best only 0.001 of the aerosol population (Fahey et al., 2001; Deshler et al., 2003b; Larsen et al., 2004) indicating clearly a nucleation barrier which is not well understood. Laboratory investigations suggest that LTA must be significantly supercooled for NAT nucleation. Arctic PSC observations in the early 2000s suggest the importance of a small population of NAT particles and that such a population forms at temperatures just a few degrees below the NAT point in both lee waves (Deshler et al., 2003b) and synoptic situations

(Larsen et al., 2004). These latter observations are the clearest evidence yet indicating that NAT forms readily on a small fraction (10^{-4}–10^{-5}) of SA through heterogeneous nucleation.

The mid latitude stratosphere has been the focus of many long term measurement series, and aside from an occasional PSC straying over Europe (Hervig, 1999), there have been no reported observations of unusual local aerosol, until recent work on wildfire generated convection, pyro-cumulonimbus. These phenomena were first discovered in solar occultation measurements, POAM III and SAGE II, collected in 1998 (Fromm et al., 2000). Since this initial discovery the satellite data have been used to establish the occurrence of four additional events in 1992, 2001, 2002, and 2003 (Jost et al., 2004; Livesey et al., 2004; Fromm et al., 2008, respectively). Such events are capable of injecting smoke from massive forest fires to altitudes of up to 7 km above the tropopause (Fromm et al., 2005), have doubled the zonal average aerosol optical depth in the lowermost stratosphere, and in the extreme have become a hemispheric phenomenon with a lifetime of several months (Fromm et al., 2008).

In contrast to the mid latitudes, observations in the tropics have been limited to two lidar sites, and occasional aircraft and balloon measurements. After the polar stratosphere, the tropical tropopause is the next coldest region of the lower atmosphere. Suspicions of the existence of tropical nitric acid and water clouds have been documented by satellite (Hervig and McHugh, 2002) and aircraft measurements (Popp et al., 2006). Evidence from the satellite (HALOE) measurements indicates observations of NAT, LTA, and ice, all very near the equator and between 3 km below to 1 km above the tropopause. The aircraft observations, also near the equator, are of very low concentration ($<10^{-4}$ cm^{-3}) particles (>0.8 μm radius) which contain nitric acid at 1 km above the tropopause. There is evidence from both sets of observations to suggest that the air at and just above the tropopause could be supersaturated with respect to NAT. The two observations, however, are not consistent with each other. The estimates of extinction from the aircraft measurements are a factor of 1000 below the satellite observations. The aircraft observations are consistent with Arctic PSC observations indicating heterogeneous nucleation of NAT on a small fraction of SA.

In addition to these observations there are balloon-borne measurements of particle layers at higher concentrations and warmer temperatures above the tropopause (Rosen et al., 2004) and spanning the tropopause. An example of the latter is shown in Fig. 5. The two profiles are an ascent/descent pair in close proximity to each other, indicating the spatially highly heterogeneous nature of such aerosol layers. Considering the size of the particles (>1.0 μm), the high number concentrations ($>10^{-2}$ cm^{-3}), and the thickness of the layer (6 km), these particles are perhaps the non non-volatile remnants of overshooting thunderstorms; however, a definitive explanation of these observations has yet to be offered. Back trajectories indicated air parcels at the altitudes of the aerosol layers had origins over Australia or the islands to the north of Australia, but did not indicate large vertical motion over the 10 days of the trajectories.

Acknowledgments

Brazil. These include the U.S. National Science Foundation and National Aeronautics and Space Administration, the Deutsche Forschungsgemeinschaft and Bundesministerium für Bildung und Forschung, and the European Union. John Barnes, Dale Simonich, and Thomas Trickl are acknowledged for supplying recent lidar measurements.

References

Andreae, M.O., Elbert, W., Gabriel, R., Johnson, D.W., Osborne, S., Wood, R., 2000. Soluble ion chemistry of the atmospheric aerosol and SO_2 concentrations over the eastern North Atlantic during ACE-2. Tellus 52B, 1066–1087.

Arnold, F., Curtius, J., Spreng, S., Deshler, T., 1998a. Stratospheric aerosol sulfuric acid: first direct in situ measurements using a novel balloon-based mass spectrometer apparatus. J. Atmos. Chem. 30, 3–10.

Arnold, F., Stilp, Th., Busen, R., Schumann, U., 1998b. Jet engine exhaust chemi-ion measurements: implications for gaseous SO_3 and H_2SO_4. Atmos. Environ. 32, 3073–3077.

Barnes, J.E., Hofmann, D.J., 1997. Lidar measurements of stratospheric aerosol over Mauna Loa. Geophys. Res. Lett. 24, 1923–1926.

Carslaw, K.S., Luo, B.P., Clegg, S.L., Peter, Th., Brimblecombe, P., Crutzen, P.J., 1994. Stratospheric aerosol growth and HNO_3 and water uptake by liquid particles. Geophys. Res. Lett. 21, 2479–2482.

Crutzen, P.J., 1970. The influence of nitrogen oxide on the atmospheric ozone content. Q. J. R. Meteorol. Soc. 96, 320–327.

Crutzen, P.J., 1976. The possible importance of CSO for the sulfate layer of the stratosphere. Geophys. Res. Lett. 3, 73–76.

Cziczo, D.J., Thomson, D.S., Murphy, D.M., 2001. Ablation, flux, and atmospheric implications of meteors inferred from stratospheric aerosol. Science 291, 1772–1775.

Danilin, M.Y., Shia, R.-L., Ko, M.K.W., Weisenstein, D.K., Sze, N.D., Lamb, J.J., Smith, T.W., Lohn, P.D., Prather, M.J., 2001. Global stratospheric effects of the alumina emissions by solid-fueled rocket motors. J. Geophys. Res. 106 (D12), 12,727–12,738.

Deshler, T., Anderson-Sprecher, R., 2006. Non-volcanic stratospheric aerosol trends: 1971–2004, Chapter 5 of the SPARC Assessment of Stratospheric Aerosol Properties. In: Thomason, L.W., Peter, Th. (Eds.), WCRP-124, WMO/TD-No. 1295, SPARC Report No. 4.

Deshler, T., Hofmann, D.J., Johnson, B.J., Rozier, W.R., 1992. Balloonborne measurements of the Pinatubo aerosol size distribution and volatility at Laramie, Wyoming during the summer of 1991. Geophys. Res. Lett. 19, 199–202.

Deshler, T., Hervig, M.E., Hofmann, D.J., Rosen, J.M., Liley, J.B., 2003a. Thirty years of in situ stratospheric aerosol size distribution measurements from Laramie, Wyoming (41°N), using balloon-borne instruments. J. Geophys. Res. 108 (D5.), 4167. doi:10.1029/2002JD002514.

Deshler, T., Larsen, N., Weisser, C., Schreiner, J., Mauersberger, K., Cairo, F., Adriani, A., Di Donfrancesco, G., Ovarlez, J., Ovarlez, H., Blum, U., Fricke, K.H., Dörnbrack, A., 2003b. Large nitric acid particles at the top of an Arctic stratospheric cloud. J. Geophys. Res. 108 (D16), 4517. doi:10.1029/2003JD003479.

Deshler, T., Anderson-Sprecher, R., Jäger, H., Barnes, J., Hofmann, D.J., Clemesha, B., Simonich, D., Osborn, M., Grainger, R.G., Godin-Beekmann, S., 2006. Trends in the nonvolcanic component of stratospheric aerosol over the period 1971–2004. J. Geophys. Res. 111, D01201. doi:10.1029/2005JD006089.

Dutton, E.G., Christy, J.R., 1992. Solar radiative forcing at selected locations and evidence for global lower tropospheric cooling following the eruptions of El Chichón and Pinatubo. Geophys. Res. Lett. 19, 2313–2316.

Fahey, D.W., et al., 1993. In situ measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion. Nature 363, 509–514.

Fahey, D.W., et al., 1995. Emission measurements of the Concorde supersonic aircraft in the lower stratosphere. Science 270, 70–74.

Fahey, D.W., et al., 2001. The detection of large HNO_3-containing particles in the winter Arctic stratosphere. Science 291, 1026–1031.

Fiocco, G., Grams, G., 1964. Observation of aerosol layer of 20 km by optical radar. J. Atmos. Sci. 21, 323–324.

Fromm, M., Alfred, J., Hoppel, K., Hornstein, J., Bevilacqua, R., Shettle, E., Servranckx, R., Li, Z., Stocks, B., 2000. Observations of boreal forest fire smoke in the stratosphere by POAM III, SAGE II, and lidar in 1998. Geophys. Res. Lett. 27, 1407–1410.

Fromm, M., Bevilacqua, R., Servranckx, R., Rosen, J., Thayer, J.P., Herman, J., Larko, D., 2005. Pyro-cumulonimbus injection of smoke to the stratosphere: observations and impact of a super blowup in northwestern Canada on 3–4 August 1998. J. Geophys. Res. 110, D08205. doi:10.1029/2004JD005350.

Fromm, M., Tupper, A., Rosenfeld, D., Servranckx, R., McRae, R., 2006. Violent pyro-convective storm devastates Australia's capital and pollutes the stratosphere. Geophys. Res. Lett. 33 (5), L05815. doi:10.1029/2005GL025161.

Fromm, M., Shettle, E.P., Fricke, K.H., Ritter, C., Trickl, T., Giehl, H., Gerding, M., Barnes, J., O'Neill, M., Massie, S.T., Blum, U., McDermid, I.S., Leblanc, T., Deshler, T., 2008. The stratospheric impact of the Chisholm PyroCumulonimbus eruption: Part II, Vertical profile perspective. J. Geophys. Res. 113, D08203. doi:10.1029/2007JD009147.

Gleason, J.F., et al., 1993. Record low global ozone in 1992. Science 260, 523–526.

Grant, W.B., Browell, E.V., Long, C.S., Stowe, L.L., Grainger, R.G., Lambert, A., 1996. Use of volcanic aerosols to study the tropical stratospheric reservoir. J. Geophys. Res. 101 (D2), 3973–3988.

Gruner, P., Kleinert, H., 1927. Die dammerungerscheinen. Probl. Kosm. Phys. 10, 1–113.

Hamill, P., Jensen, E.J., Russell, P.B., Bauman, J.J., 1997. The life cycle of stratospheric aerosol particles. Bull. Am. Meteorol. Soc. 7, 1395–1410.

Hanson, D.R., Lovejoy, E.R., 1995. The reaction of $ClONO_2$ with submicrometer sulfuric acid aerosol. Science 267, 1326–1328.

Hanson, D.R., Mauersberger, K., 1988. Laboratory studies of the nitric acid trihydrate: implication for the south polar stratosphere. Geophys. Res. Lett. 15, 855–858.

Hervig, M., 1999. Stratospheric clouds over England. Geophys. Res. Lett. 26 (8), 1137–1140.

Hervig, M., McHugh, M., 2002. Tropical nitric acid clouds. Geophys. Res. Lett. 29 (7), 1125. doi:10.1029/2001GL014271.

Hofmann, D.J., Rosen, J.M., 1978. Balloon observations of a particle layer injected by stratospheric aircraft at 23 km. Geophys. Res. Lett. 5, 511–514.

Hofmann, D.J., Rosen, J.M., 1984. Measurement of the sulfuric acid weight percent in the stratospheric aerosol from the El Chichón eruption. Geofis. Int. 23, 309–320.

Hofmann, D.J., Solomon, S., 1989. Ozone destruction through heterogeneous chemistry following the eruption of El Chichón. J. Geophys. Res. 94, 5029–5041.

Hofmann, D.J., 1990. Increase in the stratospheric background sulfuric acid aerosol mass in the past 10 years. Science 248, 996–1000.

Hofmann, D.J., Rosen, J.M., Pepin, T.J., Pinnick, R.G., 1975. Stratospheric aerosol measurements, I, Time variations at northern midlatitudes. J. Atmos. Sci. 32, 1446–1456.

Hofmann, D.J., Stone, R., Wood, M., Deshler, T., Harris, J., 1998. An analysis of 25 years of balloon-borne aerosol data in search of a signature of the subsonic commercial aircraft fleet. Geophys. Res. Lett. 25, 2433–2436.

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

Hunten, D.M., Turco, R.P., Toon, O.B., 1980. Smoke and dust particles of meteoric origin in the mesosphere and stratosphere. J. Atmos. Sci. 37, 1342–1357.

Jackman, C.H., Considine, D.B., Fleming, E.L., 1996. Space shuttle's impact on the stratosphere: an update. J. Geophys. Res. 101 (D7), 12,523–12,529.

Jäger, H., 2005. Long-term record of lidar observations of the stratospheric aerosol layer at Garmisch-Partenkirchen. J. Geophys. Res. 110, D08106. doi:10.1029/2004JD005506.

Johnston, P.V., McKenzie, R.L., Keys, J.G., Matthews, W.A., 1992. Observations of depleted stratospheric NO_2 following the Pinatubo volcanic eruption. Geophys. Res. Lett. 19, 211–213.

Jonsson, H.H., Wilson, J.C., Brock, C.A., Knollenberg, R.G., Newton, R., Dye, J.E., Baumgardner, D., Borrmann, S., Ferry, G.V., Pueschel, R., Woods, D.C., Pitts, M.C., 1995. Performance of a focused cavity aerosol spectrometer for measurements in the stratosphere of particle size in the 0.06–2.0 μm diameter range. J. Atmos. Ocean. Technol. 12, 115–129.

Jost, H.-J., Drdla, K., Stohl, A., Pfister, L., Loewenstein, M., Lopez, J., Hudson, P., Murphy, D., Cziczo, D., Fromm, M., Bui, T., Dean-Day, J., Mahoney, M., Richard, E., Spichtinger, N., Pittman, J., Weinstock, E., Wilson, J., Wofsy, S., 2004. In-situ observations of mid-latitude forest fire plumes deep in the stratosphere. Geophys. Res. Lett. L11101. doi:10.1029/2003GL019253.

Junge, C.E., Changnon, C.W., Manson, J.E., 1961. Stratospheric aerosols. J. Meteorol. 18, 81–108.

Kärcher, B., 1999. Aviation-produced aerosols and contrails. Surv. Geophys. 20, 113–167.

Kärcher, B., Turco, R.P., Yu, F., Danilin, M.Y., Weisenstein, D.K., Miake-Lye, R.C., Busen, R., 2000. A unified model for ultrafine aircraft particle emissions. J. Geophys. Res. 105, 29379–29386.

Kjellstrom, E., Feichter, J., Sausen, R., Hein, R., 1999. The contribution of aircraft emissions to the atmospheric sulfur budget. Atmos. Environ. 33, 3455–3465.

Klekociuk, A.R., Brown, P.G., Pack, D.W., ReVelle, D.O., Edwards, W.N., Spalding, R.E., Tagliaferri, E., Yoo, B.B., Zagari, J., 2005. Meteoritic dust from the atmospheric disintegration of a large meteoroid. Nature 436, 1132.

Labitzke, K., McCormick, M.P., 1992. Stratospheric temperature increases due to Pinatubo aerosols. Geophys. Res. Lett. 19, 207–210.

Larsen, N., Knudsen, B.M., Svendsen, S.H., Deshler, T., Rosen, J.M., Kivi, R., Weisser, C., Schreiner, J., Mauersberger, K., Cairo, F., Ovarlez, J., Oelhaf, H., Schmidt, A., 2004. Formation of solid particles in synoptic-scale Arctic PSCs in early winter 2002/2003. Atmos. Chem. Phys. 4, 2001–2013.

Livesey, N., Fromm, M., Waters, J., Manney, G., Santee, M., Read, W., 2004. Enhancements in lower stratospheric CH_3CN observed by UARS MLS following boreal forest fires. J. Geophys. Res. 109, D06308. doi:10.1029/2003JD004055.

McCormick, M.P., et al., 1981. High-latitude stratospheric aerosols measured by the SAM II satellite system in 1978 and 1979. Science 214, 328–331.

McCormick, M.P., Thomason, L.W., Trepte, C.R., 1995. Atmospheric effects of the Mt. Pinatubo eruption. Nature 373, 399.

Meixner, F.X., 1984. The vertical sulfur dioxide distribution at the tropopause level. J. Atmos. Chem. 2, 175–189.

Murphy, D.M., Thomson, D.S., Mahoney, M.J., 1998. In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers. Science 282, 1664–1669.

Newhall, C.G., Self, S., 1982. The Volcanic Explosivity Index (VEI): an estimate of explosive magnitude for historical volcanism. J. Geophys. Res. 87, 1231–1238.

Newman, P.A., Wilson, J.C., Ross, M.N., Brock, C.A., Sheridan, P.J., Schoeberl, M.R., Lait, L.R., Bui, T.P., Loewenstein, M., Podolske, J.R., 2001. Chance encounter with a stratospheric kerosene rocket plume from Russia over California. Geophys. Res. Lett. 28 (6), 959–962.

Notholt, J., Bingemer, H., 2006. Precursor gas measurements, Chapter 2 of the SPARC assessment of stratospheric aerosol properties. In: Thomason, L.W., Peter, Th. (Eds.), WCRP-124, WMO/TD-No. 1295, SPARC Report No. 4.

Osborn, M.T., DeCoursey, R.J., Trepte, C.R., Winder, D.M., Woods, D.C., 1995. Evolution of the Pinatubo volcanic cloud over Hampton, Virginia. Geophys. Res. Lett. 22, 1101–1104.

Popp, P.J., et al., 2006. The observation of nitric acid-containing particles in the tropical lower stratosphere. Atmos. Chem. Phys. 6, 601–611.

Reiner, T., Sprung, D., Jost, C., Gabriel, R., Mayol-Bracero, O.L., Andreae, M.O., 2001. Chemical characterization of pollution layers over the tropical Indian Ocean: signatures of emissions from biomass and fossil fuel burning. J. Geophys. Res. 106 (D22), 28497–28510.

Rosen, J.M., 1964. The vertical distribution of dust to 30 km. J. Geophys. Res. 69, 4673–4676.

Rosen, J.M., 1971. The boiling point of stratospheric aerosols. J. Appl. Meteorol. 10, 1044–1046.

Rosen, J.M., Morales, R.M., Kjome, N.T., Kirchhoff, V.W.J.H., da Silva, F.R., 2004. Equatorial aerosol-ozone structure and variations as observed by balloon-borne backscattersondes since 1995 at Natal, Brazil (6°S). J. Geophys. Res. 109, D03201. doi:10.1029/2003JD003715.

Rowland, F.S., Sato, H., Khwaja, H., Elliott, S.M., 1986. The hydrolysis of chlorine nitrate and its possible atmospheric significance. J. Phys. Chem. 90, 1985–1988.

Sato, M., Hansen, J.E., McCormick, M.P., Pollack, J.B., 1993. Stratospheric aerosol optical depths, 1850–1990. J. Geophys. Res. 98, 22987–22994.

Sheridan, P.J., Schnell, R.C., Hofmann, D.J., Deshler, T., 1992. Electron microscope studies of Mt. Pinatubo aerosol layers over Laramie, Wyoming, during summer 1991. Geophys. Res. Lett. 19, 203–206.

Simonich, D.M., Clemesha, B.R., 1997. A history of aerosol measurements at São José dos Campos, Brazil (23 S, 46 W) from 1972 to 1995. Advances in Atmospheric Remote Sensing with Lidar — Selected papers of the 18. International Laser Radar Conference. Springer-Verlag, Berlin, Germany, pp. 481–484.

Stothers, R.B., 1996. Major optical depth perturbations to the stratosphere from volcanic eruptions: Pyrheliometric period, 1881–1960. J. Geophys. Res. 101, 3901–3920.

Thomason, L.W., and Peter, Th. SPARC Assessment of Stratospheric Aerosol Properties (editors), WCRP-124, WMO/TD-No. 1295, SPARC Report No. 4, 2006.

Thomason, L.W., Kent, G.S., Trepte, C.R., Poole, L.R., 1997a. A comparison of the stratospheric aerosol background periods of 1979 and 1989–1991. J. Geophys. Res. 102, 3611–3616.

Thomason, L.W., Poole, L.R., Deshler, T., 1997b. A global climatology of stratospheric aerosol surface area density deduced from stratospheric aerosol and gas experiment II measurements: 1984–1994. J. Geophys. Res. 102, 8967–8976.

Thornton, D.C., Bandy, A.R., Blomquist, W.W., Driedger, A.R., Wade, T.P., 1999. Sulfur dioxide distribution over the Pacific ocean 1991–1996. J. Geophys. Res. 104, 5845–5854.

Trepte, C.R., Hitchman, M.H., 1992. Tropical stratospheric circulation deduced from satellite aerosol data. Nature 355, 626–628.

Tu, F.H., Thornton, D.C., Bandy, A.R., Carmichael, G.R., Tang, Y., Thornhill, K.L., Sachse, G.W., Blake, D.R., 2004. Long-range transport of sulfur dioxide in the central Pacific. J. Geophys. Res. 109, D15S08. doi:10.1029/2003JD004309.

Volz, F.E., Goody, R.M., 1962. The intensity of twilight and upper atmospheric dust. J. Atmos. Sci. 19, 385–406.

Weisenstein, D., Bekki, S., 2006. Modeling of stratospheric aerosols, Chapter 6 of the SPARC assessment of stratospheric aerosol properties. In: Thomason, L.W., Peter, Th. (Eds.), WCRP-124, WMO/TD-No. 1295, SPARC Report No. 4.