A Sectional Microphysical Model to Study Stratospheric Aerosol: Ions, Geoengineering and Large Volcanic Eruptions

by

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This thesis entitled:
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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Stratospheric aerosols can influence radiative forcing and atmospheric chemistry, yet much remains to be learned about their sources and evolution. To improve understanding of these processes, a sulfate aerosol microphysical sectional model coupled to a climate model (WACCM/CARMA) has been developed. This model includes sulfur emissions, a 63-species chemistry module, and aerosol microphysics (nucleation, coagulation, growth, and deposition). This model was utilized to study stratospheric aerosol under ambient conditions as well as from large volcanic eruptions and hypothetical climate engineering scenarios.

Simulations of ambient aerosol using three nucleation schemes reveal that one theory for ion-induced nucleation from galactic cosmic rays predicts 25% higher nucleation rates in the upper troposphere and lower stratosphere (UTLS) than its related binary homogeneous nucleation scheme, but that the rates predicted by two binary schemes vary by two orders of magnitude. None of the nucleation schemes are superior at matching the limited observations available at the smallest sizes. It is found that coagulation, not nucleation, controls number concentration at sizes greater than approximately 10 nm, suggesting that processes relevant to atmospheric chemistry and radiative forcing in the UTLS are not sensitive to the choice of nucleation schemes. Simulations using all three nucleation schemes compare reasonably well to observations of aerosol size distributions, number concentrations, and mass in the UTLS. The inclusion of van der Waals forces in the coagulation scheme improves comparison to observations in the UTLS.

Simulations of the Mount Pinatubo eruption find stratospheric aerosol mass and aerosol optical depth (AOD) to increase by two orders of magnitude, in agreement with observations,
highlighting the eruption’s significant impact on stratospheric aerosol. The model predicts effective radius to triple six months after the eruption and 525 nm AOD to increase to 0.45 three months after the eruption in the tropics, in agreement with observations. In the mid- and high-latitude Southern Hemisphere, the simulated 525 nm AOD is about one-third that of observations 3 months after the eruption, which may be due to the August eruption of Cerro Hudson in Chile, which is not included in the model. Simulated 525 nm AOD spans a narrower range than observations, tapers more quickly, and peaks at 5°N while the data peaks at 5°S. Possible explanations for these differences include the lack of ash, aerosol heating or the Cerro Hudson eruption in the model, unmatched winds for the year 1991, or biases in the data.

Simulations of stratospheric sulfur injection scenarios reveal numerous insights into the efficacy and consequences of hypothetical geoengineering scenarios. Continuous SO$_2$ injection in a narrow region at the equator is found to have limited efficacy at higher injection rates, while broadening the injection region or injecting SO$_4$ particles instead of SO$_2$ gas can increase sulfate burden, in agreement with previous work. Injection of H$_2$SO$_4$ gas does not increase burdens compared to SO$_2$, in disagreement with previous work using a plume model. It is suggested that the results found in the plume model were not due to injecting H$_2$SO$_4$, but rather to converting gases to particles. Considerably more research is needed on plumes to test assumptions made during modeling studies. Additionally, stratospheric geoengineering significantly perturbs tropospheric aerosol mass burden, number, and size distributions at much greater levels than simulated for the eruption of Mount Pinatubo. Tropospheric burdens increase by a factor of two or three, with the majority of the increases occurring at all latitudes in the 100 hPa thick layer just below the tropopause, as well as most of the troposphere at high latitudes. These perturbations could impact upper tropospheric radiative forcing or chemistry, highlighting the need to further study the efficacy and consequences of geoengineering before its employment is seriously considered.
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I have long been grateful for living in a country that values educational opportunity for all. During much of my adolescence, I lived with my mother and two brothers with just enough money to provide a roof over our head and food on the table. Financing my education was simply not an option. Even so, I was able to attend publically financed schools, enroll in undergraduate university with Pell Grants and Stafford Loans, and enroll in graduate school with NSF and NASA grants. This was only possible because I live in a country that invests in all people with a desire to learn and contribute to society.

I was in industry as an engineer for seven years before I enrolled in graduate school. The decision to change careers was not an easy one, and I am thankful for the people in my life who have helped me in their own ways. I thank my mother, who has provided me with lifelong unwavering love and support, and who has instilled in me an active imagination and appreciation for nature. I thank my father, who has always been somebody who I could laugh with, and who has instilled in me rational and objective thought. And I would like to thank my brothers, with whom I have been close to my entire life. We have shared life experiences from earliest childhood when we played together in my uncle’s fields, and on through life’s transitions of college and relationships and careers. Their choices took them down a straight path of career and family, while mine were a little more meandering. While my brothers express their support for my choices in the form of jokes and sarcasm, we have always had an unspoken bond of support and affection for each other. As much as I love Colorado, I always look forward to visits to Michigan to laugh, play, and talk with them, as well as watch my niece and nephews grow up.

The first few years of graduate school were particularly challenging for me. The scope of research demanded expertise in the fields of atmospheric science and computer science, of which I had no prior competency in either, and I had forgotten much of the basics of physics and
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Black then white are all I see in my infancy.

Red and yellow then came to be,

Reaching out to me, let's me see.

There is so much more and it beckons me
To look though to these infinite possibilities.

As below so above and beyond I imagine,

Drawn outside the lines of reason.

Push the envelope. Watch it bend.

Following our will and wind,

We may just go where no one's been.

We'll ride the spiral to the end
And may just go where no one's been.

Spiral out. Keep going.

- Maynard James Keenan
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Atmospheric aerosols, tiny liquid or solid particles suspended in earth's atmosphere, have long been known to be present in the lower troposphere, where they have immediate impacts on human health and visibility. In 1961, Junge et al. published the first in situ measurements confirming the presence of aerosols in the stratosphere. Vaporization measurements determined the particles to be acidic solutions of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and water (H\textsubscript{2}O) [Rosen, 1971]. Since these measurements were taken during a period of low volcanic activity, they have spurred investigation into the sources of this "ambient" stratospheric aerosol.

1.1 Sources of Stratospheric Aerosol

The stratosphere, located above the troposphere and below the mesosphere and thermosphere, contains the ozone layer, which protects life from damaging ultraviolet radiation. A schematic showing transport between the troposphere and stratosphere is provided in Figure 1.1. The majority of aerosols and their precursor gases are emitted in the planetary boundary layer (PBL), the well-mixed layer closest to the earth’s surface that is approximately 1-km thick. Most of these aerosols remain in the PBL and are returned to the surface through wet and dry deposition. Hence, in the PBL aerosol concentration is highest and lifetime is lowest (on the order of days). However, aerosol and precursor gases can enter the free troposphere during meteorological events such as convection or the passage of frontal boundaries [Martinnson et al., 2001]. The lifetime in the free troposphere is on the order of a few weeks. Once in the free troposphere, aerosols can undergo long-range horizontal transport, resulting in health and
climatic effects thousands of miles away from their source [Singh, 2006]. Some aerosol and gases can be transported to the upper troposphere in convective cells where the lifetime is on the order of a couple months. In deep convective cells in the tropics, aerosol and gases can cross the tropopause and enter the stratosphere [Brock et al., 1995], where the lifetime is about a year or two. Stratospheric aerosol is almost exclusively pure sulfates [Rosen, 1971; Murphy et al., 2007] except near the tropical tropopause where organics are important [Murphy et al., 2007] and in the upper stratosphere where meteoritic smoke contributes [Hervig et al., 2009]. Aerosols can return to the troposphere by air motions across mid-latitude tropopause folds or descent in the polar night. The largest particles can also fall out of the stratosphere. Due to their longer lifetime, aerosol in the free troposphere and stratosphere comprise a significant fraction of total burden. Modeling simulations suggest that 55 ± 23% of sulfate mass is located above 2.5 km [Forster et al., 2007].

**Figure 1.1** Transport between the troposphere and stratosphere.
Aerosol present in the upper troposphere and lower stratosphere (UTLS) can either be transported there from the lower troposphere or be formed in-situ from precursor gases. Aircraft instruments have measured high numbers of sulfates in the tropical upper troposphere [Martinsson et al., 2001; Kojima et al., 2004; Brock et al., 1995] suggesting new particle formation in this region, although other aerosol types such as organics are observed [Murphy et al., 2007]. Classical nucleation theory suggests that the cold tropical upper troposphere is favorable for binary homogeneous nucleation of sulfuric acid and water, although there is some debate whether ions have a significant influence on new particle formation in this region. The topic of new particle formation in the UTLS is explored in Chapter III.

Occasionally, volcanic eruptions inject large quantities of SO$_2$ to the stratosphere that are converted to sulfate aerosols and overwhelm ambient aerosol concentrations and processes. The last large eruption occurred in 1991 with the eruption of Mount Pinatubo, which increased stratospheric aerosol burden by nearly two orders of magnitude, and cooled the earth’s surface by about 0.5 K the following year [Dutton and Christy, 1992]. The eruption of Mount Pinatubo is further explored in Chapter IV. Besides their impact on radiative forcing, stratospheric sulfate aerosols are also implicated in the destruction of ozone via heterogeneous chemistry, particularly after volcanic eruptions [Hoffman and Solomon, 1989]. Due to the radiative cooling observed after volcanic eruptions, the intentional injection of sulfate aerosols into the stratosphere has been suggested as a possible means to counteract warming from greenhouse gases. However, the efficacy and consequences of such “geoengineering” scenarios are not well understood. Geoengineering is further explored in Chapter V.

1.2 The Sulfur Cycle

To better understand the processes that determine the evolution of sulfate aerosols in the UTLS, it is helpful to review the “sulfur cycle” (Figure 1.2).
The sulfur cycle refers to sulfur sources (emissions) and sinks (deposition), chemistry, and microphysics (nucleation, condensational growth, and coagulation).

1.2.1 Emissions

Approximately 100 Tg of sulfur gases are emitted annually in the troposphere, mostly near the earth’s surface. Anthropogenic sources include SO₂ from fossil fuel combustion (72%) and biomass burning (2%). Natural sources include dimethylsulfide (DMS) from marine phytoplankton (19%) and volcanoes (7%) [Haywood and Boucher, 2000]. The global anthropogenic component, which is about three-fourths of total sulfur emissions, peaked in the early 1980’s and has remained roughly constant or decreased slightly since then. The geographic distribution has substantially shifted, with SO₂ emissions decreasing in the USA and Europe, and increasing in Asia and developing countries [Smith et al., 2004]. Future projections suggest that the anthropogenic component will slowly decline over the next century as laws controlling pollution become more common.
The primary sources of stratospheric aerosol are $\text{SO}_2$, DMS, and carbonyl sulfide (OCS) emitted from the earth’s surface. Although surface emissions of OCS are relatively minor (1.3 Tg), its long lifetime of 4.3 years enables long distance transport to the UTLS region [Watts et al., 1999]. Sources of OCS include marshes, soils, volcanoes, and deep-sea vents, as well as oxidation of DMS and carbon disulfide ($\text{CS}_2$). Occasionally, large volcanic eruptions emit large quantities of $\text{SO}_2$ into the stratosphere. The last major stratospheric injection was in 1991, when Mount Pinatubo injected approximately 20 Tg $\text{SO}_2$ into the stratosphere. Although volcanic eruptions are continuously emitting $\text{SO}_2$ into the troposphere, rarely do they contribute much sulfur to the stratosphere, although there is some indication that small volcanic eruptions have been contributing to stratospheric aerosol over the past decade [Vernier et al., 2011].

1.2.2 Chemistry

Sulfur-containing compounds are converted to $\text{H}_2\text{SO}_4$ in the gas phase, and directly to $\text{SO}_4^{2-}$ in the aqueous phase. The predominant gas-phase reactions are the oxidation of sulfur compounds ($\text{SO}_2$, DMS, and OCS) with the hydroxyl radical (OH). The predominant aqueous phase reaction is $\text{SO}_2$ with hydrogen peroxide ($\text{H}_2\text{O}_2$). In the gas phase, nucleation occurs to form the aerosol, while in the aqueous phase, the aerosols (cloud drops) are already present and the reactions involving $\text{SO}_2$ increase the concentration of sulfate within the drops.

1.2.3 Nucleation

Nucleation is the formation of new aerosol particles. This begins on the sub-nanometer-size level as gas molecules collide and cluster, causing a phase change from vapor to liquid or solid. The probability of this phase change is driven by two opposing forces: The chemical potential of the pure material, which favors the molecules being in the condensed phase when the vapor is supersaturated, and the Kelvin effect, which is the increase of free energy as a molecular cluster grows due to the thermodynamic energy (surface tension) required to change
the curvature of the drop as the radius increases. There is a probability, which increases rapidly with supersaturation, that clusters may grow to the “critical radius”. Once such a cluster adds enough molecules to become thermodynamically stable, it is considered an aerosol. Homomolecular nucleation (the nucleation of a single species) is rare in the atmosphere because the vapor pressure needed for nucleation is too high to allow aerosol formation unless the vapor phase is highly supersaturated (roughly 400%). Heteromolecular nucleation (the nucleation of two or more species) can be more common if the vapor pressure of the species over solution is lower than that of the species separately, which is the case for the solution of sulfuric acid and water. Sulfuric acid and water are often supersaturated in the cold tropical upper troposphere, where binary homogeneous nucleation can be a common source of sulfate aerosols [Brock et al., 1995]. Additionally, ions, which are created from galactic cosmic rays, may induce nucleation [Yu and Turco, 2001]. Other types of sulfate nucleation include ternary nucleation involving ammonia or other stabilizing chemicals, or heterogeneous nucleation on dust and carbon, and $\text{SO}_4^{2-}$ addition to sea salt, but these processes are generally limited to the boundary layer.

### 1.2.4 Condensational Growth

Once new particles are formed (e.g. thermodynamically stable), they begin to grow by condensation of water and sulfuric acid. The growth rate is rate limited by the sulfuric acid partial pressure over the aerosol; the higher the acid pressure in the atmosphere, the more the growth. Once a sulfuric acid molecule is added to the aerosol, water is quickly adjusted in the aerosol so that the particle composition remains consistent with the water vapor pressure. Water is many orders of magnitude more abundant than sulfuric acid vapor in the atmosphere, which is why it can be considered to be in equilibrium. In dry regions such as the upper stratosphere, the opposite process can happen; evaporation causes the aerosol to shrink.
Other compounds may grow on the aerosol as well, but sulfuric acid and water are the primary volatile compounds in the stratosphere.

1.2.5 Coagulation

Coagulation is the process by which two existing droplets combine into a larger droplet. This can occur at any size, but is an important removal mechanism (by number) for newly nucleated particles, whose small size allows Brownian motion to quickly diffuse them to larger particles. Inter-particle charges such as van der Waals forces can affect coagulation rates.

1.2.6 Sedimentation and Deposition

Sedimentation is the downward motion of aerosols due to gravitational acceleration. Dry deposition is sedimentation to the ground, and occurs everywhere on earth. For sulfates in the accumulation mode this is not a fast process because the fall velocity, which is a function of the gravitational acceleration and the mass and aerodynamics of the particle, is small, and Brownian diffusion is also small. Wet deposition includes rainout, which is the removal of sulfate aerosols present in cloud drops during precipitation, and washout, which is the removal of aerosol particles by falling raindrops grabbing sulfate aerosols. Rainout is more efficient than washout. In the stratosphere, the fall velocity is relatively small except for very large particles. Dry and wet deposition occurs with both the aerosol and the gas phase precursors.

1.3 Aerosol Size Distribution

The combination of the sulfur cycle processes described in Chapter 1.2 determines the resulting mass, number, and size of the aerosol. The range of sulfate aerosol particle sizes present in earth’s atmosphere is illustrated in Figure 1.3. Aerosol growth begins with nucleation on the sub-nanometer size level and continues into the micron-sized accumulation mode. Aerosol growth rate in the boundary layer ranges from 1-20 nm per hour [Kulmala et al., 2004]. Growth rates in the free troposphere and stratosphere are slower due to lower humidity. The
aerosol growth cycle can be further complicated by the existence of internal and external mixtures of different types of aerosols, each with their own solubilities and optical properties.

![Figure 1.3 Sulfate aerosol particle size diagram.](image)

### Aerosol Modes

Aerosols are generally comprised of up to four size modes:

1. **Nucleation mode (<1 to 20 nm):** The nucleation mode results from fresh particle nucleation and is responsible for the majority of the aerosol number concentration. These particles are typically too small to significantly impact radiative forcing.

2. **Aitken mode (20 to 80 nm):** The Aitken mode consists of slightly larger particles, often recently nucleated, that are undergoing condensational growth and coagulation and will soon increase in size and decrease in number to become a part of the accumulation mode. The Aitken mode is often called a “transient mode” for this reason.

3. **Accumulation mode (80 nm to 2 µm):** The accumulation mode consists of particles that are too small to sediment and too large to coagulate rapidly with larger particles. Hence, the accumulation mode tends to be the most stable and long-lasting mode in the atmosphere. The final particle size within this mode range is a function of water vapor pressure and temperature.
In the stratosphere, this size mode tends to be about 0.1 µm, except after volcanic eruptions when the size mode can be 0.4 µm or larger.

4. Large particle mode (2 to 100 µm): This mode is dominated by directly injected particles such as sea salt and mineral dust. Sulfates often deposit on these particles. The particles in this mode fall out of the atmosphere in relatively short periods, and are not usually present in the stratosphere except as volcanic ash or meteorites.

1.4 Aerosol Radiative Effects

Accurately determining aerosol number and size distribution is important for determining the aerosol impacts on chemistry and climate. To better understand their climate impacts, it is useful to review the concept of Radiative Forcing (RF). RF is defined as the change in net (down minus up) irradiance (solar plus longwave; in W m⁻²) at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values. ΔTs, the global mean equilibrium temperature change at the surface, may be crudely calculated through a linear relationship: ΔTs = λ RF, where λ is the climate sensitivity parameter [Ramaswamy et al., 2001].

Aerosols can induce both a “direct” and an “indirect” RF on climate (Figure 1.4). Aerosols directly affect climate by scattering and absorbing shortwave and longwave radiation. The direct RF is determined by three primary aerosol optical properties: single scattering albedo (ωo), specific extinction coefficient (ko), and the scattering phase function. These optical properties vary as a function of radiation wavelength, relative humidity, and particle composition, size and spatial distribution, which vary as a function of time [Ramaswamy et al., 2001]. Due to the relatively high mass and optical depth, sulfates are believed to be the single most influential type of anthropogenic aerosol on climate [IPCC, 2007]. Sulfate is an almost entirely scattering
aerosol ($\omega_o = 1$) but with a small degree of absorption in the near-infrared spectrum [Penner et al., 2001]. From the near infrared to ultraviolet, the sulfate real refractive index is about 1.3 to 1.5 and the imaginary refractive index is less than $10^{-3}$ [Palmer and Williams, 1975]. Hence, sulfate has a significant cooling effect. Sulfate extinction (km$^{-1}$) is a measure of its radiative scattering and is calculated by summing up the product of particle number, cross-sectional area, and extinction coefficient ($Q_{\text{ext}}$). $Q_{\text{ext}}$ is a fractional correction for the effective aerosol cross-sectional area that interacts with radiation. $Q_{\text{ext}}$ can be very small for particles much smaller than the radiation wavelength, and approaches 2 at the large particle limit. Aerosol optical depth (AOD) is a unit-less quantity calculated by integrating extinction vertically across all atmospheric layers.

![Figure 1.4](image)

**Figure 1.4** Schematic of aerosol direct and indirect radiative effects. (courtesy of Christa Hasenkopf)

The relationship between particle size and mass extinction efficiency is illustrated in Figure 1.5. Mass extinction efficiency can vary by an order of magnitude or more across the size range known to exist in the upper troposphere and stratosphere. At 525 nm wavelength, particles of radius 0.3 µm have the highest extinction efficiency, scattering about five times as much radiation per unit mass as particles of radius 1.0 µm (see Chapter V for the consequences
of this property on hypothetical geoengineering scenarios). At 1024 nm wavelength, particles of radius 0.6 µm have the highest extinction efficiency.

![Figure 1.5 Mass extinction efficiency of sulfate aerosols as a function of particle radius. Extinction coefficients are calculated as a function of weight percent at the two wavelengths shown using the refractive indices of Palmer and Williams [1975]. The aerosol is assumed to be 50 weight percent H₂SO₄ and 1.5 g cm⁻³ density.](image)

Aerosols indirectly affect climate by modifying the microphysical properties of clouds, which can alter cloud radiative properties, amount, and lifetime. The indirect RF depends on the effectiveness of an aerosol to act as a cloud condensation nucleus, which is a function of its size, chemical composition, mixing state, and ambient environment [Penner et al., 2001]. The ‘first indirect effect’, also called the ‘cloud albedo effect’ or the ‘Twomey effect’, is the microphysical effect of increasing cloud droplet number concentration (and decreasing droplet size) when liquid water content is held constant. This increases the mass scattering efficiency. The ‘second indirect effect’, also called the ‘cloud lifetime effect’ or the ‘Albrecht effect’, is the
effect on liquid water content, cloud height, and lifetime of clouds [Ramaswamy et al., 2001]. The aerosol indirect effect is an area of active study, but is not a focus of this thesis.

1.5 Thesis Outline

The primary goals of my thesis were to develop a sulfate aerosol microphysical computer model and implement it for several applications related to better understanding stratospheric sulfate aerosol and its sulfur gas precursors. Chapter II describes this computer model in detail. Chapter III describes the use of this model to study the impacts of different nucleation schemes, including the contribution of ions from cosmic rays, on the properties of aerosols in the UTLS. Chapter IV describes the use of this model to study the 1991 eruption of Mount Pinatubo. Chapter V describes the use of this model to study hypothetical stratospheric sulfur “geoengineering” schemes. Chapter VI provides a summary and future work.
Chapter II

The WACCM/CARMA Model

This thesis required substantial development of a comprehensive microphysical computer model. The WACCM/CARMA coupled microphysical sectional sulfate aerosol model with sulfur chemistry is one of the most comprehensive models available for studying sulfate aerosols in earth’s atmosphere (Figure 2.1) [English et al., 2011a].

**Figure 2.1** Diagram of WACCM/CARMA model.

WACCM is the Whole Atmosphere Community Climate Model [Garcia et al., 2007]. CARMA is the Community Aerosol and Radiation Model for Atmospheres [Toon et al., 1988]. The coupled
model treats all of the processes in the sulfur cycle. Model coupling is done by implementing a single column version of CARMA as a WACCM physics package. This basic framework has been used to study sulfate nucleation [English et al., 2011a], dust [Su and Toon, 2011], sea salt [Fan and Toon, 2011], noctilucent clouds [Bardeen et al., 2010], meteoric smoke [Bardeen et al., 2008], and black carbon [Mills et al., 2008; Ross et al., 2010]. The WACCM state is passed to CARMA one column at a time. CARMA calculates changes to the constituents, and the tendencies are sent back to WACCM where they are used to adjust the model’s state. Each CARMA aerosol size bin is added as a unique WACCM constituent [Bardeen et al., 2008]. Although CARMA is capable of interacting radiatively and chemically with WACCM, for this thesis the interactions were mainly disabled. This version of WACCM utilizes the Stratospheric Aerosol and Gas Experiment (SAGE) II sulfate surface area densities for radiative transfer and ozone heterogeneous chemistry calculations.

WACCM3 version 3.1.9 tag 9 is used with 30-minute time steps at 4° latitude by 5° longitude horizontal resolution with 66 vertical levels based on hybrid-sigma coordinates. The WACCM mass-conserving finite volume dynamical core based on a flux-form semi-Langrangian transport scheme [Lin and Rood 1996, 1997] is used. The vertical diffusion algorithm in WACCM handles eddy and molecular diffusion for gases.

CARMA 2.3 is used, configured for one-dimensional columns using the same vertical grid as WACCM. The model was designed with 38 sulfuric acid mass bins ranging from 0.2 nm to 1 µm radius, with mass doubling between bins. This was expanded to 42 bins for volcanic and geoengineering simulations. The particles are assumed to have spherical shape. Split-time stepping is enabled for nucleation and growth routines when sulfuric acid is supersaturated. Nucleation and growth are treated simultaneously in the model. If sulfuric acid gas concentrations become unstable (negative), the CARMA time step is retried with double the number of substeps. On rare occurrences the model reached over 1000 substeps, but typically the model ran with only 1 or 2 substeps. Increasing the number of timesteps past the point at
which negative gas amounts were found did not significantly change results. Additionally, nucleation was limited to 40% of the sulfuric acid available. The model contains only sulfate aerosol. Although other aerosols, such as organics, are known to compose a significant fraction of the aerosol mass in the stratosphere [Froyd et al., 2009, Murphy et al., 2007], sulfates are believed to be the primary source of new particles in this region, and the primary aerosol in the lower and middle stratosphere [Murphy et al., 2007].

Following is a description of the model design for each of the components of the sulfur cycle that were introduced in Chapter 1.2. Model output is compared to available observations in Chapter III.

2.1 Emissions

The model includes emissions of carbonyl sulfide (OCS) and sulfur dioxide (SO₂), two primary sulfur emissions of importance to the UTLS and stratosphere. OCS is specified with a constant surface concentration of 510 pptv. SO₂ is specified from a two-dimensional monthly mean surface emissions dataset [Lamarque et al., 2010, Smith et al., 2011]. The model does not include emissions of DMS or volcanic SO₂, which are minor contributions to total stratospheric aerosol except after large volcanic eruptions.

2.2 Chemistry

A 63-species chemistry module has been implemented. It utilizes WACCM’s standard 56-species chemical package which includes Oₓ, NOₓ, HOₓ, ClOₓ, and BrOₓ chemical families along with CH₄ and its products and 7 ions [Kinnison et al., 2007]. Michael Mills originally added seven sulfur-bearing gases: S, SO, SO₂, SO₃, HOSO₂, H₂SO₄, and OCS. Their reaction rates and photo-dissociation rates are summarized in Table 2.1.
Table 2.1  Sulfur reaction and photolysis rates in WACCM/CARMA model

<table>
<thead>
<tr>
<th>Binary Reactions</th>
<th>Rate (cm$^3$/s)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 OCS + O → SO + CO</td>
<td>$2.1 \times 10^{11} \exp(-2200/T)$</td>
<td>Sander et al. [2006]</td>
</tr>
<tr>
<td>R2 OCS + OH → SO$_2$ + {C} + H</td>
<td>$1.1 \times 10^{13} \exp(-1200/T)$</td>
<td>Cheng and Lee [1986]</td>
</tr>
<tr>
<td>R3 S + OH → SO + H</td>
<td>$6.6 \times 10^{11}$</td>
<td>Jourdain et al. [1978]</td>
</tr>
<tr>
<td>R4 S + O$_2$ → SO + O</td>
<td>$2.3 \times 10^{12}$</td>
<td>Davis et al. [1972]</td>
</tr>
<tr>
<td>R5 S + O$_3$ → SO + O$_2$</td>
<td>$1.2 \times 10^{11}$</td>
<td>Clyne and Townsend [1975]</td>
</tr>
<tr>
<td>R6 SO + OH → SO$_2$ + H</td>
<td>$2.70 \times 10^{11} \exp(335/T)$</td>
<td>Blitz et al. [2000]</td>
</tr>
<tr>
<td>R7 SO + O$_2$ → SO$_2$ + O</td>
<td>$1.25 \times 10^{15} \exp(-2190/T)$</td>
<td>Sander et al. [2006]</td>
</tr>
<tr>
<td>R8 SO + O$_3$ → SO$_2$ + O$_2$</td>
<td>$3.4 \times 10^{12} \exp(-1100/T)$</td>
<td>Sander et al. [2006]</td>
</tr>
<tr>
<td>R9 SO + NO$_2$ → SO$_2$ + NO</td>
<td>$1.4 \times 10^{11}$</td>
<td>Brunning and Stief [1986a]</td>
</tr>
<tr>
<td>R10 SO + CLO → SO$_2$ + CL</td>
<td>$2.8 \times 10^{11}$</td>
<td>Brunning and Stief [1986a]</td>
</tr>
<tr>
<td>R11 SO + BRO → SO$_2$ + BR</td>
<td>$5.7 \times 10^{11}$</td>
<td>Brunning and Stief [1986b]</td>
</tr>
<tr>
<td>R12 SO + OCLO → SO$_2$ + CLO</td>
<td>$1.9 \times 10^{12} \exp(-330/T)$</td>
<td>Clyne and MacRobert [1981]</td>
</tr>
<tr>
<td>R13 HSO$_3$ + O$_2$ → SO$_3$ + HO$_2$</td>
<td>$1.3 \times 10^{12} \exp(-330/T)$</td>
<td>Sander et al. [2006]</td>
</tr>
<tr>
<td>R14 SO$_3$ + H$_2$O → H$_2$SO$_4$</td>
<td>$2.26 \times 10^{23} \times T \exp(6544/T)$</td>
<td>Lovejoy [1996]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ternary Reactions</th>
<th>Rate</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 SO$_2$ + OH + M → HSO$_3$ + M</td>
<td>$k_o= 3.0 \times 10^{31} (T/300)^{1.3}$</td>
<td>Blitz et al. [2003]</td>
</tr>
<tr>
<td></td>
<td>$k_{infty}= 1.6 \times 10^{12}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Photolytic Reactions</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1 H$_2$SO$_4$ + hv → SO$_3$ + H$_2$O</td>
<td>Vaida et al. [2003]</td>
</tr>
<tr>
<td>J2 SO$_2$ + hv → SO + O</td>
<td>Okabe [1978], Yung and DeMore [1982]</td>
</tr>
<tr>
<td>J3 SO$_3$ + hv → SO$_2$ + O</td>
<td>Burkholder and McKeen [1997]</td>
</tr>
<tr>
<td>J4 OCS + hv → S + CO</td>
<td>Molina et al [1981]</td>
</tr>
<tr>
<td>J5 SO + hv → S + O</td>
<td>Yung and Demore [1982]</td>
</tr>
</tbody>
</table>
A recent literature search revealed that all of the reaction rates are up to date, except for R14 which now has an equation that is about 15% slower.

2.3 Nucleation

Three nucleation schemes are implemented in CARMA: two binary homogeneous nucleation (BHN) schemes and one ion-mediated nucleation (IMN) scheme.

2.3.1 Zhao BHN scheme

The “Zhao BHN” scheme predicts the binary homogeneous nucleation rate of sulfuric acid and water using classical nucleation theory [e.g. Flood 1934, Reiss 1950, Hamill et al., 1977] with modifications for calculating the saddle point in Gibbs free energy by Zhao and Turco [1995]. Instead of searching for the Gibbs free energy saddle point in two-dimensional space, the coordinate system is transformed to a function of cluster volume and sulfuric acid weight fraction of a solution droplet. This provides for a unique solution in a 1-dimensional parameter space. Water equilibrium vapor pressure over a binary solution is calculated using the technique of Lin and Tabazadeh [2001] and water vapor pressure by Murphy and Koop [2005]. (see Appendix A for an analysis of the behavior of these equations). Sulfuric acid equilibrium vapor pressure over binary solution is calculated in the same manner as aerosol growth/evaporation: using the method of Ayers et al., [1980] with a temperature correction by Kulmala [1990] and thermodynamic constants from Giauque [1959]. Many similar schemes for BHN have been published [Kulmala, 1990] with varying choices for thermodynamic parameters. Since these schemes are analytic they generally are well behaved over the entire range of parameter space covered in WACCM, although their predicted nucleation rates are known to vary by an order of magnitude or more.
2.3.2 Yu BHN scheme

The “Yu BHN” scheme predicts the binary homogeneous nucleation rate of sulfuric acid and water by assuming the “quasi-unary” nucleation of sulfuric acid in equilibrium with water vapor [Yu, 2008], also known as kinetic nucleation theory. Since the growth of clusters is largely determined by the availability of sulfuric acid, the binary nucleation can be reduced to unary nucleation of sulfuric acid except that the clusters containing different numbers of sulfuric acid molecules also contain a semi-fixed number of water molecules at a given temperature and relative humidity. The kinetically self-consistent “Yu BHN” model is constrained by the measured bonding energetics of H$_2$SO$_4$ monomers with hydrated sulfuric acid dimers and trimers [Hanson and Lovejoy, 2006; Kazil et al., 2007] and gives BHN nucleation rates in good agreement with available experimental data. While the laboratory data used to constrain the “Yu BHN” model substantially reduces the model uncertainty, they were measured under tropospheric conditions and cannot be extrapolated to dry stratospheric conditions. As a result, the application of the present “Yu BHN” scheme should be limited to the troposphere. The “Yu BHN” scheme is available as a set of two lookup tables, a low temperature table for temperatures between 180 and 250 K, and a high temperature table for temperatures between 250 and 300 K. The low temperature table is five-dimensional, with inputs for sulfuric acid concentration, relative humidity, temperature, pre-existing aerosol surface area, and ion-pairs. (Ion pairs are set to zero for BHN simulations). The high temperature table is three-dimensional, with inputs for sulfuric acid concentration, relative humidity, and temperature. If input values are outside of the limits of the table, the values are adjusted to the minimum values. As mentioned earlier, this scheme was developed for the troposphere and the tables do not cover the full range of relative humidity, surface area and temperature found above the middle stratosphere. It was discovered that the tables predict unrealistic nucleation rates in the middle and upper stratosphere, due to relative humidity being adjusted from calculated values as low as $10^{-8}$ to the table minimum.
values (0.1% for the low temperature table and 1% for the high temperature table). The problem of extending the range of the tables was largely resolved by setting the nucleation rate to zero if RH was less than the table minima. However, there may remain some unrealistic nucleation rates in the middle stratosphere and above due to the boundary conditions of the lookup tables. The tables should be used with caution in these regions. Further details of the input parameters, out-of-bounds investigation, and predicted nucleation rates from the Yu BHN scheme are provided in Appendix B.

2.3.3 Yu IMN scheme

The “Yu IMN” scheme predicts ion-mediated nucleation rates of sulfuric acid and water. Ions of positive and negative charge stabilize the molecular cluster due to molecular attractions of opposite polarity. This scheme uses the same low temperature lookup table as the Yu BMN scheme, while a different high temperature table is used, as described in Yu [2010]. For the Yu IMN scheme, a globally constant input value of 10 ion-pairs per cm$^3$ is prescribed. Although the ionization rate varies spatially and temporally, it is relatively constant in the UTLS and is estimated to be between 5 and 20 ion-pairs per cm$^3$ [Usoskin et al., 2009]. This table was developed for tropospheric conditions as well and thus has the same limitations as the Yu BHN scheme. Thus, nucleation was set to zero if relative humidity was below the table minimum values (0.1% for the low temperature table or 0.3% for the high temperature table). Further details of the input parameters, out-of-bounds investigation, and predicted nucleation rates from the Yu IMN scheme are provided in Appendix B.

2.4 Condensational Growth

Numerical calculations for condensational growth (and evaporation) are solved by CARMA using the piecewise parabolic method of Colella and Woodward [1984]. Growth depends on supersaturation of sulfuric acid and water, which in turn is a function of numerous
thermodynamic parameters. Sulfate surface tension is calculated using the constants from Sabinina and Terpugow [1935]. Sulfuric acid equilibrium vapor pressure over binary solution is calculated using the method of Ayers et al. [1980] with a temperature correction by Kulmala [1990] and thermodynamic constants from Giauque [1959]. Since the bins only carry sulfate, the equivalent sulfate aerosol size (including sulfuric acid and water) is determined by the technique of Tabazadeh et al. [1997], which calculates weight percent sulfuric acid as a function of temperature and water activity. Weight percent sulfuric acid is assumed to be independent of particle size. A literature search was conducted to identify these equations as being most current. An analysis of their behavior across a range of temperatures and relative humidities is provided in Appendix A.

2.5 Coagulation

CARMA calculates the effect of coagulation of particles of equivalent aerosol size using the numerical approach described in Toon et al. [1988]. Coagulation coefficients are calculated to include Brownian, convective and gravitational effects. A sticking coefficient of 1 is used, which assumes that all particles stick together upon colliding. A correction for the impact of inter-particle van der Waals forces on coagulation has been added to the model [Chan and Mozurkewich, 2001]. This correction has been found to significantly improve aerosol number concentration compared to observations in the ambient stratosphere (see Chapter III).

2.6 Sedimentation and Deposition

Fall velocities are calculated by assuming a Stokes-Cunningham equation with Knudsen number corrections from Fuchs [1964], using the equivalent aerosol size (sulfuric acid plus water). Since WACCM handles advection by winds as well as eddy diffusion, no additional eddy diffusion of aerosol particles is added by CARMA. However, CARMA treats Brownian diffusion of aerosols, which becomes important above 100 km as the heterosphere is approached. As
with growth, numerical calculations for fall velocity are solved by CARMA using the piecewise parabolic method of Colella and Woodward [1984].

Wet deposition for all constituents (including the aerosol bins from CARMA) is calculated using WACCM’s existing techniques [Barth et al., 2000]. All of the aerosol bins are assumed to have a constant 0.3 solubility parameter. WACCM treats dry deposition of gases [Barth et al., 2000], while dry deposition of aerosols is not treated in this model.

Chapter Acknowledgements

Thanks to Mike Mills for help building the sulfate model and thanks to Charles Bardeen for help coupling CARMA and CAM. This work was supported by NSF Awards ATM-0856007 and AGS-0942106, NASA Award NNX09AK71G, and NASA GSRP Fellowship NNX-09AM38H. NCAR is sponsored by the National Science Foundation.
Chapter III

Simulations of Ion-induced Nucleation

3.1 Introduction

The tropical upper troposphere is known to be a net source region of new particles [e.g. Brock et al., 1995; Clarke and Kapustin, 2002]. These particles may cross the tropopause and accelerate stratospheric ozone destruction via heterogeneous chemistry [Hofmann and Solomon, 1989], impact climate by modifying cirrus cloud properties in the upper troposphere [Jensen et al., 1996], and possibly descend to the marine boundary layer and act as cloud condensation nuclei (CCN) there [Clark, 1993]. The upper troposphere and lower stratosphere (UTLS) does not have a standard spatial definition, but for this work it is roughly the region between 50 and 500 hPa. Climate geoengineering schemes are receiving increased attention in recent years especially those related to UTLS aerosols such as stratospheric sulfur injection [e.g. Crutzen, 2006, Robock et al., 2008, Heckendorn et al., 2009] and cirrus cloud modification [e.g. Rasch et al., 2008b]. However, mechanisms of UTLS new particle formation (NPF) continue to be poorly understood.

Classical nucleation theory suggests binary homogeneous nucleation (BHN) of sulfuric acid and water is favored in the UTLS due to cold temperatures and availability of supersaturated sulfuric acid and water [Brock et al., 1995]. Other nucleation processes are also possible but are generally associated with nucleation at warmer temperatures or closer to surface sources, including ternary nucleation mediated by ammonia [Coffman and Hegg, 1995] or by organic molecules [Zhang et al., 2004]. Ion-mediated nucleation (IMN) of sulfuric acid and water has received increased attention in recent years as a possible link between solar activity
and climate [Yu and Turco, 2001, Lovejoy et al., 2004]. Ions produced by cosmic rays entering earth’s atmosphere may stabilize molecular clusters, increasing the formation rate and number of new particles. As these ions are produced in much of the earth’s atmosphere [Usoskin et al., 2009], they can potentially influence nucleation rates in any region. While numerous modeling and observational studies have investigated IMN in the lower troposphere [e.g. Yu and Turco 2001, 2011, Lovejoy et al., 2004, Eisele et al., 2006], study of the UTLS region is more limited. Kanawade and Tripatha [2006] modeled IMN with a sectional aerosol model and found agreement with UTLS observations, but did not compare with BHN simulations. Pierce and Adams [2009] and Snow-Kropila et al. [2011] simulated changes in IMN from solar cycle changes using a sectional model and found the IMN contribution to cloud condensation nuclei to be two orders of magnitude too small to account for observed changes in cloud properties. Yu and Luo [2009] simulated IMN with a sectional microphysical aerosol model and found reasonable agreement in the troposphere, but did not compare to BHN, and did not compare to observations in the UTLS. Yu et al. [2010] compared nucleation rates and number concentration from IMN and two different BHN schemes in the troposphere to aircraft observations, but did not study the aerosol evolution (size, mass, effective radius) and did not study stratospheric properties. Kazil et al. [2010] found that simulations agree best with observations in the lower and mid-troposphere when IMN and BHN are included across the entire model domain and organic cluster formation is included but limited to the continental boundary layer, but did not compare to observations in the stratosphere. Here, the first simulations have been completed using a sectional aerosol microphysical model that includes two different BHN schemes and an IMN scheme [English et al., 2011a]. Model output is compared to UTLS observations of size distribution [Lee et al., 2003, Deshler et al. 2003], number concentration [Borrmann et al. 2010, Brock et al., 1995, Heintzenberg et al., 2003], and Stratospheric Aerosol and Gas Experiment (SAGE) II aerosol extinctions and effective radii [Chu et al., 1989]. A detailed description of the model is provided in Chapter II.
3.2 Comparisons with a Reference Simulation (Zhao BHN)

This research has found that for most particle properties all three nucleation schemes produce nearly identical results. Therefore, first one nucleation scheme (Zhao BHN) is compared with observations. Then, differences between the schemes are highlighted. Initial values for atmospheric state, gas properties and aerosol properties are read in from a baseline run with a five-year spinup time. A three-year simulation was conducted, with the third year analyzed. Analysis of sulfate mass and number concentration indicate that the model achieved steady state in less than one year when using the common spin-up file.

3.2.1 Sulfur gas precursors

A comparison of modeled OCS to observations is provided in Figure 3.1.

![Figure 3.1](image)

**Figure 3.1** Modeled OCS mixing ratios compared to observations. (a) Modeled OCS mixing ratio; annual and zonal average as a function of atmospheric pressure and latitude. (b) Modeled OCS versus $N_2O$, compared to balloon observations by Geoff Toon [private communication]. Observations are from ascent and descent profiles at dates and locations noted. Simulation lines are an average of JJA at the latitude ranges noted. Each simulation line represents model output at a specific latitude at 4° increments between 30° and 70° at all longitudes.
Modeled OCS is uniformly mixed in the troposphere, due to its long photochemical lifetime there. In the stratosphere, its mixing ratio decreases with altitude due to photolytic conversion of OCS to SO$_2$. A comparison of OCS correlated with N$_2$O, a long-lived tracer with well-understood chemistry, is provided for model calculations and from balloon-borne observations [Geoff Toon, private communication]. The close agreement in the slope of this correlation indicates that the model correctly treats photochemical losses of OCS.

Spatial distributions of modeled SO$_2$ concentrations are provided in Figure 3.2.

**Figure 3.2** Spatial distributions of modeled SO$_2$. (a) Simulated surface SO$_2$ mixing ratio; annual average as a function of latitude and longitude. (b) Simulated SO$_2$ mixing ratio; annual and zonal average as a function of atmospheric pressure and latitude.
Surface SO₂ concentrations vary by five orders of magnitude across the earth’s surface, with highest concentrations in the industrial mid-latitudes, particularly in eastern Asia, eastern United States, and Europe. SO₂ mixing ratio decreases with altitude in the troposphere, with the highest concentrations near 30°N, correlating with the peak latitude of surface emissions. SO₂ mixing ratios decrease rapidly just above the tropopause due to slow vertical transport relative to chemical loss mainly by reaction with OH. A peak occurs in the tropics above 25 km where OCS is converted into SO₂, and SO₂ increases again in the upper stratospheric due to photolytic conversion of H₂SO₄ back to SO₂ [Mills et al., 2005].

Comparisons of modeled SO₂ to observations are provided in Figure 3.3. Figure 3.3a shows latitudinal variation in SO₂ mixing ratios in the Pacific upper troposphere between 8 and 12 km from model calculations and Pacific Exploratory Mission (PEM)-West A, PEM-West B, and Atmospheric Chemistry Experiment (ACE)-2 aircraft observations [Thornton et al., 1999]. The model calculations are slightly lower than the observations, but generally within or close to the observed variability. Figure 3.3b shows vertical profiles of SO₂ mixing ratios compared to six ACE-2 aircraft observations [Curtius et al., 2001]. The model calculations are generally within the measurement variability expressed by the error bars although the model overpredicts the SO₂ observations in the upper troposphere above 300 hPa. The observations are limited to a narrow latitude range of 28-32°N. As shown by the calculations from various latitudes, SO₂ concentrations are a strong function of latitude (and longitude) in this range. Compared to PEM-TB aircraft observations in the tropics [Wang et al., 2001] (Figure 3.3c), the model overpredicts near the surface and underpredicts above 700 hPa. It is possible that the lack of dimethylsulfide emissions in the model contributes to lower SO₂ concentrations in the mid-troposphere at non-industrial latitudes. Overall, considering the limited number of observations and the high variability of available observations, it is concluded that the model SO₂ emissions and chemistry are generally well-behaved. It would be extremely valuable for UTLS studies to obtain SO₂ observations above 200 hPa.
Figure 3.3 Comparison of modeled SO$_2$ to observations. (a) Simulated SO$_2$ concentration between 8-12 km at varying latitudes compared to an average of PEM-West A, PEM-West B, and ACE-2 aircraft observations over the Pacific Ocean between 110°E and 80°W, binned into 10-degree segments with error bars representing plus/minus one standard deviation [Thornton et al., 1999]. Model calculations are an annual average in the same longitude and altitude region. (b) Vertical profiles of simulated SO$_2$ mixing ratio at different latitudes compared to ACE-2 aircraft observations [Curtius et al., 2001]. Observations are an average and standard deviation of 6 flights in July 1997 from 28°N to 32°N. Simulation lines are an average of the month of July at each of the latitudes noted. (c) Vertical profile of simulated SO$_2$ mixing ratio between 30°N and 30°S compared to PEM-TB aircraft observations [Wang et al., 2001]. Observations are an average and standard deviation of DC-8 flights between 38°N and 36°S in March and April 1999. Simulation is an average of March and April from 38°N to 36°S.
Sources of $H_2SO_4$ vapor in the model are $SO_2$ and OCS oxidation and aerosol evaporation, while sinks include nucleation, condensation, and photolysis at high altitudes. Modeled $H_2SO_4$ spatial distribution and comparison to observations is provided in Figure 3.4.

(a) Simulated $H_2SO_4$ mixing ratio; annual and zonal average as a function of atmospheric pressure and latitude. (b) Vertical profile of simulated $H_2SO_4$ mixing ratio compared to PEM-TA [Bates et al., 1998, Hoell et al., 1999] aircraft observations binned into averages plus/minus standard deviation at different altitudes [Lucas and Prinn, 2003] from flights in August and September 1996 between 24°N and 24°S. Simulation lines are an average of July and August between 24°N and 24°S. (c) Vertical profile of simulated $H_2SO_4$ number concentration at 43°N compared to various balloon-borne observations at the same latitude [Arnold et al., 1981, Reiner and Arnold, 1997, Schlager and Arnold, 1987, Viggiano and Arnold, 1981]. Simulation is an average of the months of September and October while the observations were taken at the dates listed.

Figure 3.4 Modeled $H_2SO_4$ and comparison to observations.
As shown in Figure 3.4a, simulated H$_2$SO$_4$ vapor mixing ratios increase from 25 to 35 km due to sulfate aerosol evaporation. It is so warm and dry above 35 km that the sulfuric acid vapor pressure exceeds the total (gas + particle) mixing ratio of sulfuric acid; hence the particles completely evaporate. H$_2$SO$_4$ also has a local maximum in the Northern Hemisphere subtropical upper troposphere due to availability of SO$_2$ and OH for chemical conversion. As Figure 3.4b shows, simulated H$_2$SO$_4$ mixing ratios are generally within the standard deviation of PEM-TA aircraft observations [Lucas and Prinn, 2003]. H$_2$SO$_4$ averages about 0.1 pptv throughout most of the tropical troposphere and lower stratosphere. As Figure 3.4c shows, simulated H$_2$SO$_4$ concentrations in the stratosphere at 43°N closely match balloon-borne observations [Arnold et al., 1981, Reiner and Arnold, 1997, Schlager and Arnold, 1987, Viggiano and Arnold, 1981], with a peak near 35 km.

### 3.2.2 Sulfate aerosol properties

Simulated sulfate mass mixing ratios versus N$_2$O are compared to a compilation of NASA aircraft observations [Wilson et al., 2008] in Figure 3.5. Simulated sulfate mass mixing ratio generally is within the variability in the mid-latitude UTLS (220 to 300 ppbv N$_2$O). Simulated sulfate mass mixing ratio is about 50% too high at low N$_2$O values (polar mid-stratosphere). It is possible that simulated sedimentation rates are to slow in the midlatitude stratosphere. Recent calculations with the WACCM/CARMA model including both sulfates and meteoric smoke improves this correlation. However, as is discussed later, the model underpredicts aerosol volume (also measured by Wilson et al. [2008]) versus CO. It is possible that these conflicting differences in aerosol volume and sulfate mass versus tracer abundance are related to transport or tracer chemistry issues within WACCM. It is also possible there are errors in the observations, or errors with comparing aircraft flights on particular days with averaged model data.
Model calculations are compared to SAGE II extinction measurements at two wavelengths in Figure 3.6. SAGE data is averaged from low volcanic years 2000-2005 to reduce the impact of volcanoes on the comparison. Here, the calculation is within about 50% of
Figure 3.6 Modeled sulfate extinction compared to SAGE II. Simulated sulfate extinction compared to Stratospheric Aerosol and Gas Experiment (SAGE) II satellite retrievals [Chu et al., 1989] at two wavelengths (525 nm and 1024 nm) and the latitude regions specified. SAGE data are averaged from years 2000-2005. Simulations are 1-year average. Simulated extinction coefficients are simulated as a function of weight percent and wavelength using the refractive indices of Palmer and Williams [1975].
the observations at both wavelengths for all three latitude regions from the tropopause through
the mid-stratosphere. Below the tropopause, SAGE II has higher extinction than the
calculations, with high variability. It is likely clouds are interfering with measurements below the
tropopause, as has been noted in prior analyses of SAGE II extinction measurements [Wang et
al., 1995, 1996]. It is also possible that other aerosol types not treated in the model are
contributing to extinction, and recent work by graduate student Pengfei Yu has found that
organic aerosols are responsible for this discrepancy in the upper troposphere. In the upper
stratosphere, WACCM extinctions decline sharply with higher altitude, while SAGE II extinctions
level off at about $10^{-6}$ km$^{-1}$ at 1024 nm near 35 km. Hervig et al. [2009] have observed from AIM
solar occultation measurements that micrometeorites, sedimenting down from the mesopause,
have an extinction near $10^{-6}$ at 1037 nm near 35 km. Recent calculations with the
WACCM/CARMA model including both sulfates and meteoric smoke improves this correlation
between the model and SAGE II data above 35 km [Neely et al., 2011], reinforcing the
suggestion that micrometeorites contribute extinction to the upper stratosphere. Hunten et al.
[1980] originally suggested the presence of these particles, and they have long been sought in
rocket measurements with little quantitative success. It is interesting that SAGE II has seen
them throughout its observational record, but their presence was not recognized.

While WACCM extinction is within 50% of SAGE II in the mid-latitudes, WACCM is
higher than SAGE II at 1024 nm in the tropics, suggesting that the WACCM particles are slightly
too large in the tropics. Indeed, simulated effective particle radius is about 25% higher than
SAGE II in the UTLS (Figure 3.7). Model calculations of size distributions in the UTLS at 41°N
are compared to balloon-borne observations [Deshler et al., 2003] in Figure 3.8. Vertical
profiles of simulated particle concentration are within 50% of observations at the smallest size
(>0.01 µm), while at larger sizes the model underpredicts number concentration below the
tropopause and overpredicts number concentration in the mid-stratosphere.
Figure 3.7  Modeled sulfate effective radius compared to SAGE II. Simulated sulfate effective radius compared to SAGE II satellite retrievals at the latitude regions specified. SAGE data are averaged from years 2000-2005. Simulations are 1-year average, using wet particle radii for calculations. Solid lines represent standard calculation for effective radius using wet particle radii.

Vertical profiles of simulated sulfate number concentration in the nm size range are compared to aircraft observations [Borrmann et al., 2010, Brock et al., 1995] in Figure 3.9.
Figure 3.8  Simulated size distributions for the Zhao BHN simulation (dotted lines) compared to balloon-borne observations above Wyoming [Deshler et al. 2003] (solid lines) at specified wet particle radii in µm. Observations are an average of years 2000-2010. Simulations are an annual average at 41°N and 104°W.

In Figure 3.9, two Zhao BHN calculations are compared: a run with Brownian coagulation and no inter-particle forces (noVW), and the base case in which the Brownian coagulation kernels are adjusted to include the effect of van der Waals forces between the particles. Van der Waals forces have been observed to be important for sulfuric acid aerosols in several laboratory studies [Schmid-Ott and Burtscher, 1982, Alam, 1987, Huang et al., 1990] and this simulation
Modeled sulfate mixing ratio vertical profile compared to data. (a) Vertical profile of simulated sulfate particle mixing ratios in the tropics (30°S to 30°N) compared to aircraft observations [Borrmann et al. 2010]. (b) Vertical profile of simulated sulfate particle mixing ratios in the extratropics (average of 30°S to 90°S and 30°N to 90°N) compared to aircraft observations [Brock et al. 1995]. Observations are medians plus/minus 25th/75th percentiles. Brock et al. mixing ratios include particles greater than 8 nm diameter and are based on 5 worldwide aircraft campaigns between 1987 and 1994, with data points attributed to the eruption of Mt. Pinatubo removed. Scout (SCOUT-O3; Stratospheric-Climate Links with Emphasis on the Upper Troposphere and Lower Stratosphere) and Trocc (TROCCINOX; Tropical Convection, Cirrus, and Nitrogen Oxides Experiment) mixing ratios include particles greater than 6 nm diameter and are from 2005 aircraft campaigns. It is assumed that no water is present on the particles. Simulated mixing ratios in both regions include 8.0 nm dry diameter and larger. The “Zhao no VW” simulation uses Brownian coagulation kernels based on collision theory, while the other three simulations include the effect of van der Waals forces on coagulation results in calculations using the calculations of Chan and Mozurkewich [2001].

includes a size-dependent expression for the Hamaker constant based on laboratory measurements [Chan and Mozurkewich, 2001]. In both the tropics (Figure 3.9a) and extratropics (Figure 3.9b), simulated and observed particle mixing ratios increase in the troposphere, peak near the tropopause where the highest nucleation rates are observed, and decrease in the stratosphere, as expected. Including the effect of van der Waals forces on coagulation results in calculations that are within the error bars of the observations. Prior to
including the effect of van der Waals forces on coagulation, the model had always overpredicted particle mixing ratio in the mid-stratosphere despite modifications to nucleation schemes, sulfur emissions, fall velocity schemes, and growth equations. The impact of including van der Waals forces highlights how important coagulation rates are to stratospheric aerosol properties.

Simulated aerosol number, area, and volume versus carbon monoxide (CO) are compared to an average of 13 flights in the tropical UTLS between 2004 and 2006 in Figure 3.10. Again, the Zhao BHN calculations with and without the van der Waals coagulation correction are compared. Simulated number concentrations (Figure 3.10b) for both simulations are within the error bars at lower CO, but increase to up to an order of magnitude too high above 55 ppbv CO. In the model, this CO region is present near 200 hPa and 20°N, where the model predicts peak nucleation. It is possible that the model and observations do not have corresponding geographical areas with the same CO values. Model output were too limited in the range of longitudes covered by aircraft observations, so all longitudes were included. The Zhao no VW scheme predicts higher aerosol number where peak nucleation is observed, but lower number outside this region. Simulated aerosol area (Figure 3.10c) and volume (Figure 3.10d) are about half the observations. It is odd that the model underestimates aerosol area and volume in the Northern Hemisphere between 3°S and 23°N, yet overestimates aerosol mass in the Northern Hemisphere between 60 and 90°N (Figure 3.5c). The comparisons are made with coordinates of CO and N₂O, respectively, rather than geographic location, so this discrepancy may be due to differences between modeled and observed geographic locations or errors in the observations. Additionally, the Zhao no VW predicts higher nucleation at higher CO but lower nucleation at lower CO, as shown in Figure 3.10b. The Zhao no VW area plot (Figure 3.10b) is higher than with the VW correction due to slower growth rates.
Figure 3.10 (a) Simulated CO mixing ratio; annual and zonal average as a function of atmospheric pressure and latitude. (b) Simulated number, (c) Simulated area, and (d) Simulated volume versus CO compared to a compilation of aircraft observations provided by J. C. Wilson and J. M. Reeves. Average (solid) and median (dotted) observations are drawn from Earth Science Project Office Archives database of 2577 data points from 13 flights between January 2004 and August 2007 spanning 3°S to 21°N, 78°W to 95°W, and 8 to 19 km altitude. The particle collector has a lower cutoff of 4 nm diameter. It is assumed that no water is present on the particles when area and volume are computed. Simulations are annual averages spanning 3°S to 21°N, 60 to 250 hPa, and all longitudes, binned into increments of 6 ppbv CO. Simulations include particles with 4.0 nm dry diameter and higher. The Zhao no VW simulation does not have the van der Waals correction, while the three nucleation scheme comparisons (Zhao BHN, Yu BHN, and Yu IMN) include the correction.
3.3 Simulations of Three Nucleation Schemes

Three simulations were completed, one for each nucleation scheme: Zhao BHN, Yu BHN, and Yu IMN. Simulations are each three years in length (with initialized values from a shared 5-year spin-up simulation). All three schemes were computationally similar in efficiency, requiring approximately 11 hours to complete 3-years of simulation time on 96 dual-core processors on the NASA Pleiades supercomputer. The microphysical model reduced computing speed by about a factor of 2. Unless otherwise indicated, comparisons are done using the average of the 3rd year of the simulations.

3.3.1 Differences in Nucleation Rates

Contour plots of simulated nucleation rates are provided in Figure 3.11. All three schemes predict similar patterns of nucleation – the highest rates are predicted in the tropical upper troposphere, with lower nucleation rates predicted in other parts of the troposphere and polar stratosphere, but their magnitudes differ significantly. Near the surface, the Yu IMN scheme predicts several orders of magnitude higher nucleation rates than the Yu BHN, suggesting that ion nucleation from cosmic rays can have a large influence on new particle formation in this region, in agreement with many other studies [Yu and Turco, 2001, Lovejoy et al., 2004, Eisele et al., 2006, Kazil et al., 2010, Snow-Kropla et al., 2011]. In the UTLS, where conditions are favorable for BHN, the Yu IMN scheme predicts only 25% higher nucleation rates than the Yu BHN scheme, consistent with some studies [e.g. Kazil et al., 2010] but different from others [e.g., Yu et al., 2010]. Since BHN is favored under highly supersaturated H$_2$SO$_4$ and H$_2$O environments, it is likely that the differences between studies are due to differences in UTLS temperatures and availability of H$_2$SO$_4$ and H$_2$O. Regardless, the present results do suggest that ions produced from cosmic rays may impact nucleation rates in the UTLS to a small degree.
Figure 3.11 Modeled sulfate nucleation rates for each scheme; annual and zonal average as a function of atmospheric pressure and latitude. (a) Zhao BHN. (b) Yu BHN. (c) Yu IMN.

Peak and average nucleation rates and critical radii sizes in the UTLS are provided in Table 3.1. The Zhao BHN scheme (classical nucleation theory) predicts two orders of magnitude higher rates than the Yu BHN scheme (kinetic nucleation theory), suggesting that the uncertainty associated with BHN computations is much larger than the effects of ions on nucleation in the UTLS. The large differences between BHN schemes have been documented
Table 3.1 Modeled critical radii and nucleation rates in the UTLS (between 50 and 500 hPa and 50°S and 50°N). All calculations are for the annual average of the third simulation year, except for 30-min peak rate, which is the maximum rate found across all 30-minute timesteps for the third simulation year. Annual average is the average across all grid boxes in the specified UTLS range. Annual peak rate is for the grid box with the highest annual rate in the specified UTLS range.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Critical radius (nm)</th>
<th>Annual average rate (cm$^3$ s)</th>
<th>Annual peak rate (cm$^3$ s)</th>
<th>30-min peak rate (cm$^3$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhao BHN</td>
<td>0.45</td>
<td>53.08</td>
<td>5099</td>
<td>432279</td>
</tr>
<tr>
<td>Yu BHN</td>
<td>0.72</td>
<td>0.50</td>
<td>71</td>
<td>2587</td>
</tr>
<tr>
<td>Yu IMN</td>
<td>0.72</td>
<td>0.75</td>
<td>70</td>
<td>2761</td>
</tr>
</tbody>
</table>

previously [Korhonen et al., 2003, Yu et al., 2010], and can be partially explained by differences in predicted critical radii - the Yu schemes predict critical radii that are 60% larger than the Zhao BHN scheme. The larger sizes of new particles predicted by the Yu schemes partially offset lower nucleation rates, resulting in a less substantial difference in sulfate mass and number concentration at larger sizes (e.g. Zhao BHN predicts a 100 times higher particle number creation rate from nucleation but only 17 times higher particle mass creation rate). Finally, note that the Yu BHN and Yu IMN lookup tables, designed for tropospheric conditions, were originally found to predict unrealistic nucleation rates in the middle and upper stratosphere due to exceptionally low relative humidities (<0.1%) being outside the table bounds. While setting nucleation to zero if relative humidity was less than the table minimum resolved much of this issue, it is possible that this approach may predict too little nucleation in certain regions. However, an analysis of the input parameters has found that the tables behave well in the UTLS region and below (see Appendix B).

3.3.2 Effects of nucleation rates on aerosol size distributions

Simulated size distributions are compared with observations from 56 aircraft flights from a range of NASA field programs summarized by Lee et al. [2003]. Size distributions are
calculated for three regions: Tropical troposphere (7-17 km), mid-high latitude UTLS (7-13 km), and high-latitude stratosphere (17-21 km), and the data are separated into series with or without recent new particle formation (NPF). Recent NPF was defined as meeting two conditions: i) number concentrations of particles with diameter 4-6 nm exceed those of particles with diameter 6-9 nm, and ii) number concentrations of particles with diameter 4-9 nm exceed 1 cm$^{-3}$. Simulation size bin ranges are selected based on the closest bins available to the size specified in Lee et al. [2003]. Simulated 1-day averages of the third year are checked for NPF conditions and segregated into two sets of data (with and without recent NPF). Simulation “data” points include values for 360 days in the third simulation year. The model outputs daily averages, so these criteria will not provide instantaneous indicators of recent NPF. Additionally, since the model output is across the entire year, while the aircraft data are obtained on specific days, differences may be due to temporal variability. A summary of the number of simulation data points considered NPF days and no NPF days is provided in Table 3.2.

**Table 3.2** Count and percent of model simulation days that meet conditions for NPF as defined by Lee et al. [2003].

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Zhao BHN</th>
<th>Yu BHN</th>
<th>Yu IMN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Count</td>
<td>%</td>
<td>Count</td>
</tr>
<tr>
<td>Tropical Troposphere</td>
<td>360/360</td>
<td>100%</td>
<td>360/360</td>
</tr>
<tr>
<td>Mid-High Latitude UTLS</td>
<td>360/360</td>
<td>100%</td>
<td>348/360</td>
</tr>
<tr>
<td>High Latitude Stratosphere</td>
<td>14/360</td>
<td>3.9%</td>
<td>2/360</td>
</tr>
</tbody>
</table>

All three schemes reported all days were NPF days in the tropical troposphere, most days were NPF days in the high-latitude UTLS, and very few NPF days occurred in the high-latitude stratosphere. Lee et al. reported 16% of size distributions to be considered NPF events.

Size distributions for each of the three regions are provided in Figure 3.12.
Figure 3.12 Size distributions (corrected for Standard Temperature and Pressure [STP]) for the 3 simulated nucleation schemes compared to observed size distributions from 56 NASA flights between 1998-2000 as reported by Lee et al. [2003]. Size distributions when recent NPF was observed at three different regions: (a) tropical troposphere, (b) mid-high latitude UTLS, and (c) high-latitude stratosphere. Observations define recent NPF when two conditions are met (see text). Simulations were subjected to the same criteria by analyzing daily averages across the third simulation year for all grid boxes within the region. Simulation size bin ranges are selected based on the closest bins available to the size specified in Lee et al. (d) Size distributions in the mid-high latitude UTLS when recent NPF was not observed. Here, only the Yu BHN simulation is plotted because the Zhao BHN and Yu IMN schemes did not predict any days with no NPF.
In the tropical troposphere (Figure 3.12a), high numbers of particles are observed and predicted, as expected due to this region being conducive to NPF. Relative differences in number concentrations between the three schemes at the smallest sizes are explained by differences in nucleation rates. All three schemes predict approximately two times too many of the smallest particles, and are missing the observed size mode at 30 nm. It is possible that this discrepancy is due to the lack of other aerosol types in the model. Advection of aged aerosol from other regions could contribute to growth rather than nucleation, reducing the number concentration at the smallest sizes and possibly creating a mode near 30 nm. A similar trend is observed in the mid-high latitude UTLS region where NPF was observed (Figure 3.12b); all three of the simulations predict two times too many particles at the smallest sizes. In the mid-high latitude UTLS where NPF was not observed (Figure 3.12d), only the Yu BHN predicted days with no NPF. This simulation replicates both the 10 nm and 100 nm modes that are observed, albeit with a larger 10 nm mode and a smaller 100 nm mode. In the high-latitude stratosphere (Figure 3.12c), all three schemes reproduce the observed 100 nm mode, with particle number within a factor of two of that observed. All three schemes predict a broader mode than observed, with the Yu BHN scheme better reproducing the mode at the small end. However, only 14, 2, and four days, respectively for the Zhao BHN, Yu BHN, and Yu IMN schemes met the criteria for stratospheric NPF. When plotting all simulation output regardless of whether the grid cells met the criteria for recent NPF (Figure 3.13), all three simulations predict a similar size mode in the stratosphere. In most cases, the three nucleation schemes produce simulations that differ at the smallest sizes due to differing nucleation rates, but become nearly indistinguishable from one another at sizes larger than 10 nm. On the other hand, the Zhao no VW curve has higher number concentrations than any of the nucleation schemes. This reinforces the conclusion that coagulation, not nucleation is the dominant process determining aerosol number at atmospherically relevant sizes.
Figure 3.13 Same as Figure 3.12 except all simulation grid boxes are averaged, regardless of whether they met the criteria for recent NPF.

3.3.3 Effects of nucleation rate on aerosol number concentrations

Vertical profiles of simulated sulfate number concentration (>8 nm) for the three nucleation schemes are compared to aircraft observations [Borrmann et al., 2010, Brock et al., 1995] in Figure 3.9. All three simulations with varying nucleation rate correlate very well with observations in both the tropics (Figure 3.9a) and extratropics (Figure 3.9b). Although
nucleation rates differ by up to two orders of magnitude, there is very little difference in number concentration of particles >8 nm. Likewise, comparisons of aerosol number (>4 nm) versus CO suggest differences due to nucleation schemes (Figure 3.10b), but aerosol area (Figure 3.10c) and volume (Figure 3.10d) are virtually unaffected by nucleation scheme. Again, this suggests that the choice of nucleation scheme is nearly irrelevant compared to the impacts of coagulation at atmospherically relevant sizes.

Similar trends are seen when comparing simulated zonal-averaged number concentrations in the upper troposphere to aircraft observations from the CARIBIC campaign [Heintzenberg et al., 2003] (Figure 3.14). In the 4-12 nm size range (Figure 3.14b), predicted number concentrations vary by a factor of 5 between nucleation simulations, with the highest nucleation rates (Zhao BHN) being associated with the highest number concentration. But at sizes above 12 nm (Figs. 15c and 15d), the differences in number concentration between the nucleation schemes become muted as coagulation become dominant. When comparing the model to the observations, however, in this comparison there are numerous discrepancies. Observed number concentrations peak near the equator while the simulations peak near industrial latitudes. In the 4-12 nm size range (Figure 3.14b), both observations and simulations peak at about 20,000 cm^{-3} at Standard Temperature and Pressure (STP) (273 K, 1013.25 hPa), while at the larger sizes the simulations underpredict number concentration by up to an order of magnitude. The discrepancy at larger sizes may be due to the model treating only sulfates and not other types of aerosols, such as organics or biomass burning products. The underprediction could also be due to uncertainties in the emission of gaseous precursors, particularly dimethylsulfide or volcanic emissions, which are not included in the WACCM/CARMA model. It could also be due to the model not including other types of nucleation near the surface, which is known to be important in this region [Kazil et al. 2010]. Any of these discrepancies may be due to a mismatch between the spatial scale of the observations and simulations. The observations are taken across a flight path at a specific altitude, latitude, and longitude, while the model just
Figure 3.14 Upper troposphere number concentration compared to observations

(a) Calculated number concentration greater than 4 nm dry diameter as a function of latitude and longitude, using an annual average of the Zhao BHN simulation between 216-316 hPa (approximately 8.5-11.3 km). Comparison of zonal-average number concentrations to aircraft observations as a function of latitude over the altitude region 8.5-11.3 km for three particle diameter ranges: (b) 4-12 nm, (c) >12 nm, and (d) >18 nm. Observations are averages of 6 commercial flights between Germany, Namibia, and South Africa in May, July, and December 2000 [Heintzenberg et al., 2003]. Simulations are annual and zonal averages at the bin ranges closest to the dry diameters specified (4.0 nm, 12.8 nm, and 16.2 nm diameters, respectively).
averages a region over the entire altitude and latitude range. A contour plot of simulated number concentration for the Zhao BHN case as a function of latitude and longitude between 216-316 hPa (Figure 3.14a) shows that number concentration can vary by up to two orders of magnitude at the same altitude across the globe.

### 3.3.4 Effect of nucleation rate on Effective Radius and Extinction

Vertical profiles of effective radii and extinctions for each of the three simulated nucleation schemes are compared to SAGE II satellite observations in Figures 3.7 and 3.15.

Figure 3.15 Simulated sulfate extinctions for the three simulations compared to SAGE II at two wavelengths (525 nm; solid lines, and 1024 nm; dotted lines) in the latitude regions specified.

All three nucleation schemes yield essentially identical results. Effective radius is important for radiative forcing, while extinction is proportional to surface area, which is important to heterogeneous chemistry. Hence the choice of nucleation rate should not be important to radiative forcing or atmospheric chemistry.
3.4 Conclusions

A three-dimensional general circulation model with sulfur chemistry and sectional aerosol microphysics (WACCM/CARMA) has been implemented with three nucleation schemes: two BHN schemes - one based on classical nucleation theory (Zhao BHN) and one based on kinetic nucleation theory lookup tables (Yu BHN) – as well as an IMN scheme look-up table (Yu IMN). The two Yu schemes often are found to be out of the table limits in the middle stratosphere and above due to limits on boundary conditions of table inputs; this problem was mostly resolved by setting nucleation to zero if relatively humidity is less than the table minimum value, but the tables should be used with caution in these regions. Further thermodynamic data are needed to extend the Yu schemes into dry stratospheric conditions (RH<0.1%).

Calculations suggest that ion-mediated nucleation rates in the UTLS are 25% higher than binary only, consistent with some studies [e.g. Kazil et al., 2010] but different from others [e.g., Yu et al., 2010]. However, the two binary schemes vary by two orders of magnitude, consistent with other studies [Korhonen et al., 2003, Yu et al., 2010]. More importantly, it is found that coagulation, not nucleation, controls number concentration at sizes greater than approximately 10 nm in the UTLS and the middle and upper stratosphere. The dominance of coagulation over other microphysical processes is consistent with other recent work using microphysical models; Pierce and Adams [2009] found coagulation to be more important than nucleation in tropospheric studies, and Timmreck et al. [2010] found coagulation to drive stratospheric particle sizes from the eruption of Mount Toba to much larger values than previously assumed. Lee et al. [2003] suggested that ion nucleation was important in the UTLS, on the basis of their ability to match observed size distributions with a model based on ion clusters. In contrast, this work has found each type of nucleation scheme to produce identical size distributions at sizes greater than 10 nm due to the dominance of coagulation. Hence fitting the size distribution is not diagnostic of the type of nucleation occurring (binary or ion). Unfortunately, the rate of
nucleation is not easily determined from data either, because all of the particle properties for particles larger than 10 nm are not altered even for two-order-of-magnitude changes in the nucleation rate.

The model has been compared to observations from the tropopause to the mid-stratosphere. Above about 30 km, the model underpredicts SAGE extinctions. It is suggested that this is due to the importance of micrometeorites, as modeled by Neely et al. [2011] and observed by Hervig et al [2009]. It is also found that including van der Waals forces improves the model calculations for the numbers of particles in the UTLS. In summary, it is concluded that this model contains the sulfate microphysical processes needed for simulations in the UTLS, and that the properties of particles with sizes relevant to climate, cloud physics and heterogeneous chemistry are not sensitive to the details of the nucleation scheme or to the presence or absence of ion nucleation.

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Chapter IV

Simulations of Mount Pinatubo

4.1 Introduction

Large volcanic eruptions are useful to study because of their dramatic influences on radiative forcing and the ozone layer. They also provide insight into the efficacy and consequences of hypothetical geoengineering injections. The most recent large SO$_2$ injection to the stratosphere took place in 1991 with the eruption of Mount Pinatubo in the Philippines (15.14˚N, 120.35˚E). The eruption injected 14-26 Tg SO$_2$ (7-13 Tg S) into the stratosphere [Read et al., 1993; Krueger et al., 1995], mostly on June 15 and 16, 1991. The SO$_2$ was converted to H$_2$SO$_4$ with an e-folding time of 35 days [Bluth et al., 1992; Read et al., 1993]. The eruption occurred during the easterly phase of the quasi-biennial oscillation (QBO), which caused the volcanic cloud to move westward and encircle the earth in about a month. In the first months after the eruption, most of the aerosol burden was within the region between 20˚S and 30˚N [McCormick and Veiga, 1992; Stowe et al., 1992]. A reduction in net radiative flux of 3 to 10 W m$^{-2}$ was measured in summer and fall 1991 [Minnis et al., 1993]. The lower stratosphere warmed by 2-3 K [Labitzke and McCormick, 1992; Labitzke, 1994] and the lower troposphere cooled by about 0.5 K [Dutton and Christy, 1992]. Additionally, strong ozone loss was observed [Grant et al., 1994; Herman and Larko, 1994; Randel et al., 1995] mainly from heterogeneous chemistry on sulfate aerosols [Hofmann and Solomon, 1989]. By spring 1992 the stratospheric aerosol burden had reached its peak and began to subside [Ansmann et al., 1996]. Four to five years after the eruption the background aerosol level was again present.
Very few microphysical aerosol simulations of Mount Pinatubo have been completed. Zhao et al. [1995] used a 1-d version of CARMA to fully simulate aerosol microphysics, found effective radii to grow to 0.3-0.5 µm about 6-months after the eruption, and size distribution, concentration, mass ratio and surface area to reasonably compare to observations. At least five Pinatubo studies have been conducted using the ECHAM2 model with interactive aerosols using prescribed microphysics and chemistry. Thomas et al. [2009] found that simulating Pinatubo with the observed easterly QBO predicted cooling along the equator and warming over the subtropics, and the opposite effect if Pinatubo erupted during a westerly QBO. Lohmann et al. [2003] conducted sensitivity studies on the impact of Mount Pinatubo on cirrus and found an impact if a monomodal aerosol distribution was prescribed, but not if a bimodal distribution was prescribed. Timmreck et al. [1999b] calculated radiative forcing and found good agreement with observations but were unable to reproduce the persistence of optical depth after the end of 1991. Timmreck et al. [1999a] found improved transport in the model compared to observations when advection was artificially decreased with a damping term. Graf et al. [1993] calculated the dynamical response to Pinatubo aerosol heating and found an increased polar night jet in the Northern Hemisphere, stronger zonal winds in the stratosphere, stronger tropospheric 60˚N westerlies and 30˚N easterlies, and a northward shift of the Azores High, in agreement with observations. Here, the first simulations of Pinatubo are conducted using a microphysical aerosol sectional model coupled to a 3-D general circulation model (GCM) and stratospheric aerosol properties are compared to observations.

4.2 Methods

Two simulations of the eruption of Mount Pinatubo were completed using the WACCM/CARMA sulfate microphysical model (see Chapter II), a 10-year simulation using the van der Waals correction for coagulation by Chan and Mozurkevich [2001] and an 18-month simulation without the correction. The model was allowed to run freely and the simulated
eruption occurred during an easterly phase of the QBO, although the magnitude and duration was not constrained to actual observations that year. Due to the minimal differences between the two simulations, only the simulation with the van der Waals correction is compared to the majority of observations. For this application, the Zhao BHN nucleation scheme was used, and the model was expanded from 38 to 42 bins to treat the particle sizes encountered with large sulfur injections (the largest size bin is shifted from 1.0 to 2.6 µm dry diameter). 10 Tg of sulfur in the form of SO₂ gas was injected continuously over 48-hours on June 14 and 15 of the first simulation year in a region encompassing 2˚S to 14˚N and 95˚E to 115˚E. The vertical profile of the injection was specified as a semi-normal distribution between 15.1 and 28.5 km with a peak at 20 km.

4.3 Results

The eruption of Mount Pinatubo was the first large stratospheric injection in which numerous atmospheric instruments monitored the evolution of stratospheric aerosol, providing a unique opportunity to understand the impacts of a volcanic eruption on stratospheric aerosol. Here, the temporal and spatial magnitudes of simulated effective radius, AOD, and mass burdens are analyzed and compared to available observations. It should be noted, however, that the observations have numerous limitations and uncertainties. The Stratospheric Aerosol and Gas Experiment (SAGE) II does not measure effective radius directly, but infers it from the wavelength dependence of AOD, and had difficulty measuring high AOD associated with this event due to limb magnification of measurements in the horizontal direction. The Advanced Very High Resolution Radiometer (AVHRR) does not directly measure AOD, but makes assumptions about particle properties such as scattering phase function and single scattering albedo to retrieve optical depth. When quantified, associated error bars are usually large. In other cases error bars are unavailable or do not fully encompass the full range of observational uncertainty.
A comparison of the time evolution of effective radius is provided in Figure 4.1.

![Figure 4.1](image)

**Figure 4.1** Time evolution of zonal-average effective radius compared in two regions: 15 to 20°N at 17 to 27 km (solid lines) and 35 to 45°N at 15 to 27 km (dotted lines). A second-order polynomial is fit to a compilation of observations mainly over California and Wyoming [Russell et al. 1996] (dotted black line). SAGE II (solid black line) is a time series of retrieved column integrated effective radius in the 15 to 20°N latitude band [Bauman et al., 2003]. Model results are monthly averages of wet sulfate effective radius for the simulation with the van der Waals coagulation correction (red lines) and without (green lines).

Simulations with and without the van der Waals coagulation correction predict zonal-average ambient effective radius in the UTLS of about 0.2 µm and a peak effective radius about 6 months after the simulated eruption of about 0.75 µm at 15 to 20°N and 0.70 µm at 35 to 45°N. Therefore, the van der Waals coagulation correction is not important when simulating large perturbations to stratospheric aerosol from a volcanic eruption. (The van der Waals correction significantly impacts ambient stratospheric aerosol number concentration, however; see Chapter III). Simulated peak effective radius is about 20% higher than the average of
observations, but well within the error bars of observations which extend from 0.4 to >1.0 \(\mu m\). After the peak, the simulated effective radius tapers more quickly than observations and is about 20% lower after about two to four years.

A comparison of the time evolution of stratospheric AOD in the visible (500 and 525 nm) is provided in Figure 4.2. The model predicts zonal-average 525 nm AOD between 50 and 55°N to peak at 0.25 about nine months after the eruption. This is about two orders of magnitude higher than ambient AOD in the stratosphere (~0.002) and on the order of the AOD persistently

![Figure 4.2](image)

**Figure 4.2** Time evolution of zonal-average stratospheric AOD in the visible at 50 to 55°N for the model (red line) compared to observations (black lines and circles). Observations are summarized by Ansmann et al. [1996]. AVHRR (solid line) is measured at 500 nm wavelength while SAGE II (dotted line) and LIDAR (circles) are at 525 nm. SAGE+LIDAR (dashed line) is SAGE data constrained to lidar observations. The lidar error bars are the standard deviation derived from the combined effect of signal noise, uncertainties in the atmospheric input parameters used in the determination, and the atmospheric variability. Modeled stratospheric AOD at 525 nm is for the simulation with the van der Waals coagulation correction and is calculated by subtracting average total column ambient AOD, which was 0.2. Simulated extinction coefficients are calculated as a function of weight percent and wavelength using the refractive indices of Palmer and Williams [1975].
observed in the troposphere. Simulated AOD is generally within the range of error bars of the observations. As with a comparison of effective radius, it is possible that the simulated AOD decreases too quickly and is lower than observations after about two years.

A spatial comparison of stratospheric AOD at two wavelengths is provided in Figure 4.3.

Figure 4.3  Spatial and temporal evolution of AOD for the model and observations. (a) AVHRR at 500 nm (b) SAGE II at 525 nm (c) Model at 525 nm (d) SAGE II at 1024 nm (e) Model at 1024 nm. Observations summarized by Russell et al. [1996]. Modeled stratospheric AOD is calculated for the simulation with the van der Waals coagulation correction. Simulated extinction coefficients are calculated as a function of weight percent and wavelength using the refractive indices of Palmer and Williams [1975].
In all cases, the model and observations find the highest AOD near the latitude of the eruption, and later a second peak in the Northern Hemisphere mid-latitudes as the cloud evolved and traveled towards the poles. The timing and magnitude of simulated AOD at 525 nm compares well with AVHRR at 500 nm near the equator. For both, AOD peaks about three months after the eruption at about 0.4 near the equator. The model also predicts a peak in the Northern Hemisphere between 40 and 60°N about a year after the eruption, in agreement with AVHRR, although the magnitude is higher. Simulated AOD is significantly higher than SAGE II observations at both wavelengths. There are also considerable differences between the AVHRR and SAGE II measurements, which are measured at wavelengths of 500 nm and 525 nm respectively. Russell et al. [1996] have concluded that most of the discrepancy is due to the evolution of particle size distribution combined with the wavelength differences of the instruments. It is also possible that the differences between SAGE II and AVHRR are due to errors in the retrievals. Assuming SAGE II AOD can be trusted, there are several explanations for the differences between the model and the observations. It is possible that AOD is enhanced in the model because it does not treat ash. Ash particles, which were also present in the stratosphere after Pinatubo, are relatively large and would remove some H$_2$SO$_4$ from the stratosphere in the first weeks after the eruption. This reduction in H$_2$SO$_4$ would reduce nucleation of new sulfate aerosols and lower AOD. This would also explain why the model predicts a sharper dissipation gradient of AOD in the two years following the eruption (Figure 4.2). Without ash, more H$_2$SO$_4$ would be available to grow the aerosol to larger sizes, which then fall out of the stratosphere rapidly.

A comparison of monthly AOD as a function of latitude is provided in Figure 4.4. As with other comparisons of AOD between the model and AVHRR (Figures 4.2 and 4.3), the magnitude of peak AOD compares well, and is within 10% for all months except June. The observed AOD in June was enhanced by Saharan dust [Minnis et al., 1993], which is not included in the model. Spatially, there are a few discrepancies, however. The observed peak
AOD at 525 nm is around 5°S while the simulated peak AOD is around 5°N, which is closer to the latitude of the eruption (15°N). Additionally, simulated AOD spans a narrower latitude range than the observations. These latitudinal discrepancies may be caused by differences in meteorology (QBO and Brewer-Dobson circulation) between the model and observations. The model was allowed to run freely; meaning the meteorology was not constrained to the actual wind patterns present during the 1991 eruption. Another possible explanation is that the model does not treat aerosol heating, which could invigorate atmospheric circulation. The more compact aerosol cloud in the model means a higher concentration of H₂SO₄ and aerosol in the tropics, which would enhance coagulation rate and growth rate, which could also explain why simulated AOD tapers more quickly than observations (Figure 4.2). In September and October in the Southern Hemisphere mid- and high-latitudes, observed AOD is about three times higher.
than the simulation (0.15 versus 0.05, respectively). This may be due to the eruption of Cerro Hudson in Chile, which is not included in the model. Cerro Hudson’s main eruption from August 12-15 in 1991 released slightly less than 1 Tg S up to 18 km altitude [Pitts and Thomasan, 1993] and would have contributed to AOD in the Southern Hemisphere.

Time evolution of sulfate burdens is provided in Figure 4.5.

Simulated sulfate burden in the stratosphere peaks at about 8 Tg S, which is roughly two orders of magnitude higher than the stratospheric burden at ambient conditions, and within the range of 5.7-8.6 Tg estimated by observations [McCormick and Veiga, 1992]. Peak burden occurs about five months after the eruption in November 1991. Backscatter and extinction measurements suggest that peak burden occurred sometime in the winter or spring of 1992 [Ansmann et al., 1996]. Simulated peak burden occurs near the beginning of this estimated time period. The simulated peak would occur too soon if the simulated aerosol cloud is inadequately spread out.

**Figure 4.5** Time evolution of simulated sulfate burden (Tg Sulfur) for various regions. “First 100 hPa” represents the region spanning from the tropopause to 100 hPa below the tropopause. “600-1000 hPa” spans from 600 hPa to the surface. See Chapter V for method of identifying tropopause.
in the model, which would boost coagulation and growth, making particles larger and falling out sooner. Note also the differences in timing to reach the peak for different aerosol properties. At 15°N, 525 nm AOD peaks about 3 months after the eruption (Figure 4.4), while burden peaks about 5 months after the eruption (Figure 4.5) and effective radius peaks about 6 months after the eruption (Figure 4.1). This illustrates the radius dependence of AOD. Even though burden peaks in November, AOD peaks before then because the particles are continuing to grow to sizes that are less efficient at scattering radiation.

The simulated eruption of Mount Pinatubo significantly perturbs the tropospheric burden (Figure 4.5, green lines). The peak in tropospheric burden occurs about 11 months after the simulated eruption, which is about 6 months later than the stratospheric burden due to the time it takes for the aerosol to move toward high latitudes and fall to the troposphere. At its peak, tropospheric burden nearly doubles, and the vast majority of this increase is added to the layer between the tropopause and 100 hPa below the tropopause. This could impact cirrus or tropospheric chemistry, although observational analyses of Pinatubo impacting cirrus cloud are debated (see Chapter V for more discussion).

4.4 Conclusions

Simulations of the Mount Pinatubo eruption have been conducted, providing an opportunity to compare microphysical calculations to observations. Simulations and observations suggest that stratospheric aerosol mass and AOD increased by roughly two orders of magnitude after the eruption, highlighting the eruption's significant impact on stratospheric aerosol. The magnitude and timing of peak effective radius and 525 nm AOD compare well between the model and observations. The model predicts zonal-average stratospheric effective radius at 15°N to increase from 0.2 µm at ambient conditions to 0.7 µm six months after the eruption, which is within the error bars of observations. Both the model and observations find 525 nm AOD increases to 0.45 near the equator about 3 months after the eruption, and find a
second maximum in the Northern Hemisphere mid-latitudes about 9-12 months after the eruption.

There are a few discrepancies between the model and observations. In the mid- and high-latitude Southern Hemisphere, the simulated 525 nm AOD is about one-third that of observations 3 months after the eruption, which may be due to the August eruption of Cerro Hudson in Chile, which is not included in the model. Simulated peak 525 nm AOD is around 5°N while the observed peak is around 5°S. Additionally, simulated AOD spans a narrower latitude range than the observations, and tapers more quickly. These latitudinal discrepancies may be caused by differences in meteorology (QBO and Brewer-Dobson circulation) between the model and observations, as the model was run freely and not constrained to the actual wind patterns present during the 1991 eruption. Another possible explanation is that the model does not treat aerosol heating, which could invigorate atmospheric circulation. The more compact aerosol cloud in the model could enhance growth and sedimentation rates, causing AOD to decline more quickly than observations. Since both simulations with and without the van der Waals correction predict nearly identical time evolution of effective radius, the details of the coagulation scheme likely does not explain differences between the model and observations. Likewise, details of the nucleation scheme also should only impact aerosol number at the smallest sizes and not effective radius or AOD (see Chapter III). It should also be noted that observations are restricted to a few regions and exhibit high variability, making it difficult to conclude with certainty the extent of model error.

A broader comparison to observations could clarify the extent of agreement (or disagreement) with the model. It would be useful to run a climatology simulation forced with the QBO in the easterly phase to eliminate the impacts of dynamics on the results. It would also be useful to include ash in the simulations. Further study of the simulated eruption of Mount Pinatubo is planned, with the goal of submitting a paper to a peer-reviewed journal in early 2012.
5.1 Introduction

Although continued emission of greenhouse gases is very likely to cause future climate change, international agreements to limit emissions have so far failed and greenhouse gas concentrations continue to rise [IPCC, 2007]. Even if carbon emissions are eliminated completely in the next 10 years, significant climate change is still possible due to the thousand-year lifetime of carbon dioxide in the atmosphere-ocean system and the long lag-time of the response of the climate system to the greenhouse gases that have already been added to the atmosphere [Solomon et al., 2010]. Concern about future climate changes has inspired increased attention to various schemes to engineer the climate on a global scale, dubbed “geoengineering”. Geoengineering could potentially be used to counteract expected greenhouse gas warming as well as severe and unforeseen perturbations to the earth’s climate system as it responds to global warming. One type of geoengineering involves removal of carbon dioxide from the atmosphere. Another class, which is considered here, involves reducing the input of solar radiation in order to cool the planet. Unfortunately, solar radiation management would not remedy other consequences of CO₂ emissions, such as ocean acidification.

One solar radiation management method that is receiving increased attention, originally proposed by Budyko [1974, 1977], involves injecting gases into the stratosphere that condense to form reflective sulfate aerosols [Dickinson, 1996; Crutzen, 2006]. Stratospheric injection is more effective than tropospheric injection because the stratospheric aerosol has a longer lifetime and therefore a smaller injection rate can be used. Volcanoes act as natural tests to this
idea. The June 1991 eruption of Mt. Pinatubo injected roughly 10 Tg S in the form of SO$_2$ into the stratosphere [Read et al., 1993, Krueger et al., 1995]. A reduction in net radiative flux of 3 to 10 W m$^{-2}$ was measured in summer and fall 1991 [Minnis et al., 1993], and global average surface temperature dropped by 0.5°C the following year [Dutton and Christy, 1992]. Using volcanoes as an analog to geoengineering can be misleading, however, because volcanic cloud lifetimes are shorter than typical climate response times [Pollack et al., 1982], and because of possible nonlinear impacts of injection rate and location on aerosol microphysics.

Initial stratospheric geoengineering simulations using GCMs found a linear association between SO$_2$ injection magnitude, sulfate burden, and temperature reduction [Rasch et al., 2008a; Robock et al., 2008]. However, these simulations used prescribed size distributions based on observations following the Pinatubo eruption, despite indications from a 1-d microphysical sectional model that the climate effects of stratospheric injections may be self-limiting due to particle growth [Pinto et al., 1989]. More recently, climate simulations have been completed that include the microphysics of particle growth. Heckendorn et al. [2009] fed calculations from a 2-d microphysical model simulating nucleation, growth, and coagulation to a global climate model, GCM. Their model simulations using an SO$_2$ injection at the equator and a pressure altitude of 50 hPa resulted in aerosols that grew to more than twice the size of those from Mt Pinatubo, resulting in a significantly lower particle lifetime and lower radiative forcing. Niemeier et al. [2010] used a middle atmosphere GCM coupled with a microphysical modal model with nucleation, condensation, and coagulation, and predicted that injecting SO$_2$ at 30 hPa instead of 50 hPa increases aerosol burden by about 50%. They assumed a size distribution represented in lognormal modes. Hommel and Graff [2011] used an uncoupled microphysical sectional model with nucleation, growth, and coagulation in zero-dimensional space and found a similar sulfate burden as Heckendorn et al. and Niemeier et al. Pierce et al. [2010] suggested injection of H$_2$SO$_4$ vapor instead of SO$_2$ as a method to increase sulfate burden. SO$_2$ converts to H$_2$SO$_4$ over time scales on the order of weeks, and the H$_2$SO$_4$ vapor, or
the particles newly nucleated from the vapor, tend to get scavenged by already existing large particles, making them grow even larger. While the SO$_2$ is broadly distributed in the stratosphere due to its relatively long lifetime, H$_2$SO$_4$ condenses to sulfate aerosol on the order of hours, possibly restricting the portion of the stratosphere affected by the injection directly, minimizing the peak particle size and increasing sulfate burden. Pierce et al. [2010] used an aerosol plume model to simulate the H$_2$SO$_4$ conversion to particles, in conjunction with a 3D GCM for their simulations. When handing off the plume model output to the GCM after 24-hrs, they injected particles prescribed using a lognormal size distribution with a specified peak size. When injecting H$_2$SO$_4$ as particles using the plume model, sulfate burden nearly doubled relative to an SO$_2$ injection by Heckendorn et al. [2009]. About half of this improvement was due to modifying the size distribution by using the plume model, and the other half due to broadening the injection zone relative to that used by Heckendorn et al. [2009].

Study of the impacts of stratospheric geoengineering on tropospheric aerosol is much more limited than studies of stratospheric aerosol. Kravitz et al. [2009] found that stratospheric SO$_2$ injection produced increased acid deposition especially in high latitudes, but the geoengineering contribution was much smaller than from ambient tropospheric SO$_2$ injections, and two orders of magnitude too small to cause ecological harm. Niemeier et al. [2010] predicted increased burden in the upper troposphere or lower stratosphere region, but did not quantify the tropospheric perturbations.

Here, the first simulations are completed using a 3-d sectional aerosol model coupled to a GCM comparing injections of SO$_2$ gas, H$_2$SO$_4$ gas, and SO$_4$ particles in two different regions: a narrow latitude band around the equator similar to that of Heckendorn et al. [2009], and a broader injection region similar to that assumed by Pierce et al [2010]. The type of species injected and the size of the injection zone are investigated for their impact on stratospheric aerosol burden and tropospheric aerosol burden.
### 5.2 Methods

Simulations were conducted using the WACCM/CARMA microphysical sectional aerosol model (details in Chapter II). Similar to the Mount Pinatubo simulations (see Chapter IV), the Zhao BHN nucleation scheme was used, and the model was expanded from 38 to 42 bins. A series of SO$_2$ injection rates was investigated, as well as a comparison between narrow and broad injection zones, and a comparison of injection species (Table 5.1).

#### Table 5.1 Description of geoengineering simulations completed.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Species</th>
<th>Injection(s)</th>
<th>Injection Region</th>
<th>Similar to</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$ narrow</td>
<td>SO$_2$ gas</td>
<td>1, 2, 5, 10 Tg S/yr, continuous</td>
<td>4ºN – 4ºS, all lon, 18.8–19.9 km</td>
<td>Heckendorn et al.</td>
</tr>
<tr>
<td>SO$_4$ narrow</td>
<td>Sulfate aerosol</td>
<td>10 Tg S/yr, continuous, lognormal width 1.5, 100 nm peak radius</td>
<td>4ºN – 4ºS, all lon, 18.8–19.9 km</td>
<td>------</td>
</tr>
<tr>
<td>SO$_2$ broad</td>
<td>SO$_2$ gas</td>
<td>10 Tg S/yr, continuous</td>
<td>32ºN – 32ºS, all lon, 19.9–24.6 km</td>
<td>Pierce et al.</td>
</tr>
<tr>
<td>SO$_4$ broad</td>
<td>Sulfate aerosol</td>
<td>10 Tg S/yr, continuous, lognormal width 1.5, 100 nm peak radius</td>
<td>32ºN – 32ºS, all lon, 19.9–24.6 km</td>
<td>Pierce et al.</td>
</tr>
<tr>
<td>H$_2$SO$_4$ broad</td>
<td>H$_2$SO$_4$ gas</td>
<td>10 Tg S/yr, continuous</td>
<td>32ºN – 32ºS, all lon, 19.9–24.6 km</td>
<td>Pierce et al.</td>
</tr>
<tr>
<td>SO$_4$ plume</td>
<td>Sulfate aerosol</td>
<td>10 Tg S/yr, continuous, lognormal width 1.5, 100 nm peak radius</td>
<td>4ºN – 4ºS, 135ºE – 145ºE, 18.8–19.9 km</td>
<td>------</td>
</tr>
<tr>
<td>Pinatubo</td>
<td>SO$_2$ gas</td>
<td>10 Tg S/yr, 48-hr burst on June 14-15 of year 2</td>
<td>16ºN – 4ºS, 92.5ºE – 117.5ºE, 15.1–28.5 km lognormal (20-km peak)</td>
<td>Heckendorn et al.</td>
</tr>
<tr>
<td>Unperturbed</td>
<td>------</td>
<td>------</td>
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<td>------</td>
</tr>
</tbody>
</table>
All simulations were run from the same initialization file. All simulations except Pinatubo were run for 5 years, with the 5th year analyzed. The Pinatubo simulation was run for 6 months before its eruption was simulated on June 21, and the following year (June 21 of year 1 through June 20 of year 2) is compared to the other simulations (see Chapter IV for more details). Simulations were conducted in two latitudinal regions centered at the equator: an 8 degree wide zone similar to that specified by Heckendorn et al. [2009] and a 64 degree wide zone similar to that specified by Pierce et al. [2010], and two longitudinal regions: all longitudes similar to that specified by Heckendorn et al. [2009] and Pierce et al. [2010] as well as an 8 degree wide zone to compare to the plume studies of Pierce et al. [2010]. Three different injection species were studied: SO$_2$ gas similar to Heckendorn et al. [2009], SO$_4$ aerosol similar to Pierce et al. [2010], and H$_2$SO$_4$ gas. Comparisons are also made to simulations of a Pinatubo eruption and an unperturbed stratosphere.

5.3 Geoengineering Efficacy

Three topics are presented and discussed: The effect of injection rate on mass loading and optical depth; the effect of geographic distribution of the injection on mass loading and optical depth; and the effect of the material injected on mass loading and optical depth.

5.3.1 SO$_2$ injection rates

Figure 5.1 (solid black line) compares steady-state atmospheric sulfate burdens for a limited spatial injection region (4°N–4°S and 18.8–19.9 km) and a range of SO$_2$ injection rates (0, 1, 2, 5, and 10 Tg/yr S).
Figure 5.1  Sulfate aerosol burden (Tg S) as a function of SO$_2$ injection. This work injects SO$_2$ between 4°S and 4°N in the 18.8-19.9 km grid box at all longitudes. “Whole Atmosphere” represents a direct comparison to Heckendorn et al. and Rasch et al. “First 100 hPa” represents the region spanning from the tropopause to 100 hPa below the tropopause. “Second 100 hPa” spans 100 hPa below the tropopause to 200 hPa below the tropopause. “600-1000 hPa” spans from 600 hPa to the surface. See text for method of identifying tropopause.

The relationship between sulfate mass burden and SO$_2$ injection rate is non-linear with reduced efficacy at higher injection rates. To achieve a 6 Tg S burden, an injection rate of 10 Tg S yr$^{-1}$ is required, which is within 10% of the injection rate predicted by other studies that calculated aerosol size distributions [Heckendorn et al., 2009; Hommel and Graf, 2011; Niemeyer et al., 2010 (not shown)]. This injection rate to obtain 6 Tg S burden is five times higher than the injection rate predicted by simulations that assumed prescribed size distributions [Rasch et al., 2008a]. As pointed out by others, for a given injection rate the aerosol mass burden is reduced when microphysics is treated because the larger particles that occur in the simulations fall out more quickly than the smaller ones assumed in simulations that don’t treat microphysics.

WACCM/CARMA simulations with varying SO$_2$ injections have their peak AOD (Figure 5.2) and sulfate column mass (Figure 5.3) near the equator, corresponding to the injection zone.
Figure 5.2  Annual zonal average of AOD at 525 and 1024 nm wavelength for each of the SO$_2$ injection scenarios. Pinatubo is a 1-year average starting immediately after the eruption. Extinction coefficients are calculated as a function of weight percent and wavelength using the refractive indices of Palmer and Williams [1975].

Figure 5.3  Column mass and effective radius for each of the SO$_2$ injection scenarios. Annual zonal average of aerosol column mass (Tg) and wet sulfate effective radius (µm) for each of the SO$_2$ injection scenarios. Pinatubo is a 1-year average starting immediately after the eruption. Column Mass is reported per grid box (4° latitude by 5° longitude). Effective radius is weighted by the surface area in each grid box vertically to apply a fair weighting to grid boxes with more surface area.
The ten-fold increase in SO$_2$ mass injected between the 1 Tg S yr$^{-1}$ and the 10 Tg S yr$^{-1}$ cases yields peak AOD that differs by factors of only 2.8 at 525 nm and 3.1 at 1024 nm (Figure 5.2). Similarly, peak zonal average sulfate column mass (at the equator) increases by only a factor of five for a factor of ten increase in injection rate (Figure 5.3). AOD increases less than column mass because in addition to being proportional to column mass, AOD is also inversely proportional to the particle radius for particles of the sizes considered here. Surface area-weighted effective radius (Figure 5.3) increases as injection rate increases at all latitudes, and is highest near the equator where the falling velocities of only the largest particles exceed the wind velocity of the rising Brewer-Dobson circulation, and near the poles where the particles have aged and are returning to the troposphere. These trends are illustrated more clearly when plotting averages in the tropics (30°S to 30°N) as a function of injection rate (Figure 5.4).

Figure 5.4  Effective radius, column mass, and AOD as a function of SO$_2$ injection. Hydrated sulfate effective radius (µm), sulfate column mass ($10^{-2}$ Tg/grid box), and sulfate AOD at 525 nm and 1024 nm in the tropics (30°S to 30°N) for each of the SO$_2$ injection scenarios. The scenarios inject SO$_2$ between 4S and 4N in the 18.8-19.9 km grid box at all longitudes. Column Mass is reported per grid box (4° latitude by 5° longitude). Effective radius is weighted by the surface area in each grid box vertically to apply a fair weighting to grid boxes with more surface area. Extinction coefficients are calculated as a function of weight percent and wavelength using the refractive indices of Palmer and Williams [1975]. An area-weighted average across latitude is conducted for all fields.
Between the 1 Tg simulation and the 10 Tg simulation, effective radius nearly triples, column mass increases by a factor of 4, and 525 and 1024 nm AOD increase by a factor of 3. Hence, relative to models that do not treat microphysics, the optical depth is reduced not only because the mass burden is reduced, but also because the particle size increases when microphysics is treated. Therefore SO$_2$ injections may have limited efficacy for optical depth at higher injection rates.

Finally, note that AOD (Figure 5.2) and sulfate column mass (Figure 5.3) are about three times higher in the Northern Hemisphere than the Southern Hemisphere. Some of this increase is attributed to more surface sulfur sources in the Northern Hemisphere industrial latitudes as shown for the unperturbed case in Figure 5.2; however there appears to be an additional contribution that could be due to an asymmetry in the location of the Brewer-Dobson circulation about the equator in the WACCM model. This distribution should be investigated in more detail to better understand if equatorial injections for geoengineering may induce a hemispherically asymmetric forcing on the climate. The WACCM/CARMA model does not include a quasi-biennial oscillation (QBO) in tropical winds, or radiative heating from sulfate aerosols, both of which could influence the dynamics that partition sulfate between the hemispheres [Bauman et al., 2003].

The geoengineering simulations just discussed had a constant SO$_2$ injection rate. The Mount Pinatubo eruption was also simulated, assuming an injection of 8.5 Tg S. Since the Pinatubo injection is a pulse, it results in a cloud whose properties evolve in time, so it is difficult to compare with the steady state geoengineering cases. The Pinatubo zonal-average 525 nm AOD peaks about 3 months after the eruption at about 0.46 at 5°N, which is about double that of the 10 Tg geoengineering case. Sulfate mass burden peaks about 5 months after the eruption, which is about 40% higher than in the 10 Tg geoengineering case. More details regarding the time evolution of Mount Pinatubo are provided in Chapter IV. For purposes of a fair comparison to geoengineering simulations, Pinatubo is averaged across one year immediately following the
eruption, similar to the approach of Heckendorn et al. [2009]. Comparing the simulated Pinatubo eruption to the 10 Tg geoengineering case, peak AOD is about 17% higher at 525 nm and 14% higher at 1024 nm despite similar SO$_2$ injections (Figure 5.2). While these differences might suggest that continuous injection of SO$_2$ is slightly less effective than a single burst into a clean atmosphere, it should be noted that the Pinatubo injection was placed over a wider altitude and latitude range, but a narrower longitude range than the geoengineering case (see Table 5.1). As discussed next, the spatial differences in injection can be very important to the resulting mass in the stratosphere.

Analysis of size distributions in three different regions of the stratosphere (Figure 5.5) illustrates how particle size evolves with changing injection rates. At higher injection rates, the peak particle size gets larger. The particle size also increases at lower levels of the stratosphere (90 hPa compared to 39 hPa), probably because of sedimentation of the largest particles. At 90 hPa, there is a size mode for geoengineering scenarios not present in the unperturbed atmosphere that increases in size from about 1 µm radius for the 1 Tg injection to about 1.5 µm for the 10 Tg injection. This trend was also found by Heckendorn et al. [2009], where the peak size at 90 hPa was found to grow from about 0.6 to 1.0 µm. Unfortunately, Heckendorn et al [2009] did not provide effective radius, so it is difficult to compare the two sets of simulations. This work includes the coagulation correction for Van der Waal's forces [Chan and Mozurkevich, 2005], which has been found to increase the effective radius by less than 10% for Pinatubo (see Chapter IV for more details). Generally the geoengineering cases have a broader size distribution than the Pinatubo case, rather than a different mode. This increase in the number of large particles with increasing injection rate occurs because the largest particles continue to see additional vapor for condensational growth. The differences in particle size by number correspond to even larger differences in particle size by surface area (Figure 5.5). Clearly with greater mass there is also greater particle surface area, suggesting that ozone loss should increase, as has been calculated previously for geoengineering [Heckendorn et al.,
2009; Tilmes et al., 2009] as well as observed after the eruption of Mount Pinatubo [Prather, 1992]. The differences in the typical particle size are further amplified when comparing volume

![Graphs showing aerosol size distribution](image)

**Figure 5.5** Annual and zonal average of aerosol number, area, and volume size distribution for each SO$_2$ injection scenario at the equator and 39, 55, and 90 hPa.
distributions, suggesting that the higher injection scenarios have a higher proportion of sulfate mass in the largest sizes, which fall out of the atmosphere more rapidly. Larger particles are also less effective at scattering incoming solar radiation as the radius further deviates from the optimum mass scattering radius near 150 nm. These results reinforce the original conclusion postulated by Pinto et al. [1989] as well as recent microphysical simulations [Heckendorn et al. 2009; Niemeier et al., 2010; Hommel and Graf, 2011] that there may be an upper limit to the radiative forcing that can be obtained with sulfate aerosols.

5.3.2 Injection Region

Next, the impacts of varying injection region for 10 Tg S injection scenarios are compared. Injecting SO$_2$ into a broader latitude region (32°N–32°S and 19.9-24.6 km) produces about a 60% higher mass burden than the equivalent SO$_2$ injection in a narrow region (10.1 Tg versus 6.3 Tg) (Figure 5.6). Injecting a lognormal distribution of SO$_4$ particles in a broad region produces about 40% higher mass burden than the equivalent injection of SO$_4$ particles in a narrow region (13.8 Tg versus 9.6 Tg). Likewise, stratospheric aerosol lifetime increases for broad injections by about 80% for SO$_2$ injection and 50% for SO$_4$ particle injection relative to injections in narrow latitudinal bands (Figure 5.6). Injecting into a broader region improves burden for two reasons. First, particle growth by H$_2$SO$_4$ condensation is reduced because H$_2$SO$_4$ vapor is more dilute, and second, coagulation is reduced because aerosol concentration is also more dilute. The benefit of a larger injection region is less for SO$_4$ particle injection because this scenario is generally influenced by concentration of aerosol only, and not H$_2$SO$_4$. The impacts of these processes that result from changes in injection region are illustrated when looking at equatorial size distributions at three different levels of the stratosphere (Figure 5.7). Injecting SO$_2$ or SO$_4$ particles into a narrow region (green and blue dotted lines) generally results in a broader size distribution than injections into a broad region (green and blue solid
Figure 5.6  (left panel) Aerosol burden (Tg S) in the stratosphere and troposphere for various 10 Tg S injection scenarios. The sum is equivalent to whole atmosphere burden, since the burden above the stratopause was calculated to be less than $1 \times 10^{-6}$ Tg. Shown are averages and standard deviations across 360 daily averages for the 5th simulation year for each simulation except Pinatubo. Pinatubo is calculated by averaging across one year immediately following the eruption. See text for method of identifying tropopause. (right panel) Stratospheric aerosol lifetime for various 10 Tg S injection scenarios. All lifetimes are calculated by dividing aerosol burden by mass injection rate, except Pinatubo, which is calculated by the elapsed time between the month of peak burden and the month of $e^{-1}$ burden.

The distributions become especially wide with SO$_2$ gas due to the availability of H$_2$SO$_4$ gas for growth in addition to SO$_4$ particles for coagulation.

The trends for area and volume distributions are comparable to those with number distributions. The differences are most noteworthy near the injection level (55 hPa) and become muted at higher or lower levels. Sulfate effective radius (Figure 5.8) is also generally larger across most latitudes and levels for the narrow injection simulations.

The combination of increased burden and reduced effective radius for broad injections results in higher AOD in most regions except near the equator, where the narrow injections have a higher injection rate (Figure 5.9).
Figure 5.7  Stratospheric aerosol distributions for 10 Tg injection scenarios. Annual zonal average of aerosol number, surface area, and volume size distribution for each 10 Tg S geoengineering scenario at the equator and 39, 55, and 90 hPa.
Figure 5.8  Effective radius vertical contour plots for 10 Tg injection scenarios. Hydrated sulfate effective radius for each of the various 10 Tg S injection scenarios; annual and zonal average as a function of atmospheric pressure and latitude. Pinatubo simulation is an average of the first year after the simulated eruption.
It is particularly interesting to note that the Pinatubo simulation produces lower AOD than all but one of the 10 Tg geoengineering cases. Generally this difference reflects the confined injection region for Pinatubo relative to the other cases. The differences in AOD are driven mainly by differences in sulfate column mass, although a smaller effective radius for the broad injections is a factor (Figure 5.10). Note that the effective radius for SO₂ injections is similar in most places except a narrow band near the equator. However, this is where the majority of the sulfate column mass is located, reducing the efficacy of a narrow injection. All of the injections also have a similar effective radius around 30°N, which could be driven by surface emissions present across all cases. Overall, a broad injection can be considered an improvement over a narrow injection when comparing averages from 30°S to 30°N (Figure 5.11). AOD for broad injections of SO₂ gas and SO₄ particles are about 20-60% higher at both 525 nm and 1024 nm, with SO₂...
Figure 5.10 Column mass and effective radius for 10 Tg injection scenarios. Annual zonal average of aerosol column mass (Tg) and hydrated sulfate effective radius (µm) for each of the 10 Tg S Geoengineering simulations. Pinatubo is a 1-year average starting immediately after the eruption. Column Mass is reported per grid box (4° latitude by 5° longitude). Effective radius is weighted by the surface area in each grid box vertically to apply a fair weighting to grid boxes with more surface area.

Injections showing a larger benefit from a broad injection. Note however that due to the spatial differences in AOD (Figure 5.9), different climatic outcomes may result from a narrow versus a broad injection, and the potential impacts should be studied further.

When comparing a narrow SO₄ particle injection across all longitudes (“SO₄ narrow”) to a narrow SO₄ particle injection across only 10 degrees longitude with the same total injection (“SO₄ plume”), the resulting aerosol burdens (Figure 5.6), lifetime (Figure 5.6), size distributions (Figure 5.7), effective radii (Figures 5.8 and 5.10), AOD (Figure 5.9), column mass (Figure 5.10), and averages in the tropics (Figure 5.11) are all comparable. This suggests that the zonal winds distribute the aerosol particles around the world quickly enough to not impact microphysics.
5.3.3 Injection species

Next, the efficacies of injecting three different sulfur species are compared: SO$_2$ gas, H$_2$SO$_4$ gas, and SO$_4$ particles. Pierce et al. [2010] suggested that injecting H$_2$SO$_4$ gas instead of SO$_2$ would result in a larger sulfate mass abundance for a given injection rate. This work finds, on the other hand, that injecting H$_2$SO$_4$ gas does not produce any discernable benefit over SO$_2$ injection. Aerosol burden (Figure 5.6), stratospheric lifetime (Figure 5.6), size distributions (Figure 5.7) AOD (Figure 5.9), column mass (Figure 5.10), and effective radius (Figure 5.10) are all similar for the two scenarios. It is concluded that the vapor injected is not what matters; rather, what matters is the latitudinal band over which the material is injected, and injecting particles instead of a gas. Differences between this work and Pierce et al. [2010] are likely due to assumptions made with their plume model.
Pierce et al. [2010] did not inject H$_2$SO$_4$ into their global microphysical model. Instead, they injected H$_2$SO$_4$ into a plume model, and let the plume evolve until all of the gas had been converted into particles, and the particle concentration had been reduced to ambient values. They then put the plume particles into the global microphysical model, assuming a range of injected particle sizes. Pierce et al. did not discuss results from the plume model itself. However, there are many issues with this approach. Coagulation is non-linear so it is critical that plumes be allowed to interact with other plumes that have been produced previously. For instance, to inject 10 Tg S yr$^{-1}$ from aircraft emitting H$_2$SO$_4$, and able to carry 1 ton of H$_2$SO$_4$ per aircraft, would require about 80,000 aircraft flights per day. It is most likely these flights would be concentrated in a few areas of the Earth to make the logistics of operating the aircraft more economical. Hence plume interaction would almost certainly occur. The details of the plume model, such as expansion rate, may be important to the particle sizes that exit the plume. Pierce et al. injected the particles over a large fraction of the Earth, rather than in a geographically confined zone, which would further reduce the particle size.

This WACCM/CARMA model is not able to address these many complexities involving sub-grid scale injection, which would require a global model with many subgrid-scale embedded aircraft plumes. However, some illustrative simulations have been performed. Figure 5.6 shows that injecting SO$_4$ particles with a lognormal distribution of width 1.5 and peak radius of 100 nm produces 51% higher mass burdens than SO$_2$ injection in a narrow region and 37% higher burdens than in a broad region. Higher mass burden is achieved because coagulation is inherently slower at delivering mass to a growing particle than growth from the gas phase. Hence the particles remain smaller if particles are injected instead of a gas, and therefore do not fall out of the stratosphere as fast. In the limit when particles are smaller than the mean free path, the ratio of the coagulation growth rate to the condensational growth rate is approximately equal to the ratio of the thermal velocity of the particle to the thermal velocity of the colliding aerosol, or equivalently the square root of the ratio of their masses. This effect is supported by
comparisons of effective radius. For SO$_4$ particle injection, global zonal-average effective radius (Figure 5.8) peaks at roughly 0.9 µm for a narrow region and 0.8 µm for a broad region, which is 37% and 11% smaller, respectively, than that from an SO$_2$ injection. Comparing surface area-weighted average of effective radius as a function of latitude (Figure 5.10), effective radius for a SO$_4$ particle injection is about 10% lower than for SO$_2$ injection at most latitudes. Finally, a comparison of average effective radius between 30°S and 30°N (Figure 5.11) suggests effective radius for an SO$_4$ particle injection is about 15% smaller. Comparison of size distributions (Figure 5.7) also illustrates the narrower distributions attained with an SO$_4$ particle injection instead of SO$_2$ gas. The advantage of higher burden and smaller particles is illustrated when comparing AOD (Figure 5.9, blue lines versus green lines). In both narrow and broad injection regions, AOD from SO$_4$ particle injection is more than twice that of SO$_2$ injection at 525 nm and nearly twice that of SO$_2$ at 1024 nm. Higher AOD for SO$_4$ particle injections comes from both higher sulfate column mass and smaller effective radius (Figure 5.10).

The primary advantage of injecting SO$_4$ particles is to control the particle size distribution, as noted by Pierce et al. [2010]. However, it is unlikely that the size distribution remains as narrow as assumed in their plume model, an uncertainty that they acknowledge. Given that the availability of very small particles for coagulation onto larger particles is a controlling factor for peak size, it is critical to correctly identify the size distribution. Since the results presented here for H$_2$SO$_4$ injection are virtually identical to those for SO$_2$ injection, it is clear that the Pierce et al. plume model is the critical factor in their results, rather than injecting H$_2$SO$_4$ instead of SO$_2$. It would be valuable to validate these assumptions with size distributions observed in an actual plume.

5.4 Tropospheric Burdens

In this section, perturbations to tropospheric aerosol resulting from stratospheric sulfur injections are studied. In order to accurately quantify perturbations to tropospheric aerosol, the
height of the tropopause must be adequately represented. This is a difficult task. The constantly changing temperature profile of the atmosphere argues against using an average tropopause height. If the tropopause is defined based on cold-point temperature, the tropopause can be unrealistically high when there is an extended region of stable temperatures that sometimes occurs in high latitudes. The WACCM/CARMA model sometimes predicts a cold-point tropopause in southern hemisphere high latitudes as high as 80 hPa. If the tropopause is based on ozone concentration, the method becomes inadequate during the Antarctic spring ozone hole. Additionally, the ozone concentration separating tropospheric from stratospheric air can vary from 50 to 380 ppb [Zahn et al., 1999; Pan et al., 2004]. A third technique to identify the tropopause is based on a minimum lapse rate. Use of a modified version of the World Meteorological Organization definition [WMO, 1957] produces a realistic tropopause location that can handle the nuances of uncommon temperature profiles that sometimes occur in the simulated daily average temperatures. For this analysis, the tropopause is identified as the lowest level at which the lapse rate is closer to zero than \(-4 \text{ K km}^{-1}\) at that level and the level above it. If the lapse rate at the level above the current level is \(+2 \text{ K km}^{-1}\) or more, the current level is flagged as the tropopause regardless of whether the current level lapse rate is less than \(-4 \text{ K km}^{-1}\). The search begins above the boundary layer to avoid designation of boundary layer inversions as the tropopause. Tropopause levels were constrained to be between the levels 85 to 433 hPa.

A comparison of identified tropopause locations for the annual zonal average of the unperturbed simulation is provided in Figure 5.12. This modified lapse rate definition identifies an average tropopause of about 100 hPa in the tropics and 250 hPa at high latitudes. This approach yields an average tropopause at about the same location as a method searching for 200 ppb ozone concentration. This method identifies a tropopause that is higher than the 60 ppb ozone method, and lower than the cold-point method. An analysis of 360 daily averages at each of the 72 longitudes finds that the designated tropopause location ranges from 86 to 160
Figure 5.12  Simulated tropopause level (hPa) as a function of latitude for varying identification methods, based on an annual zonal average for the unperturbed simulation. The lapse rate method (described in the text) was employed for this work. The bars show minimum and maximum tropopause levels at each latitude across all longitudes and 360 daily averages for the 5th simulation year.

hPa in the tropics, 120 to 433 hPa at southern hemisphere high latitudes, and 190 to 433 hPa at northern hemispheric high latitudes. This range of daily tropopause locations approximately spans from the 60 ppb ozone average location at the low end to the cold point average tropopause location at the high end.

Based on this designation of tropopause location, stratospheric geoengineering induces significant perturbations to tropospheric aerosol. When comparing the narrow-region SO$_2$ injection scenarios, sulfate burden in the troposphere increases as the injection rate increases (Figure 5.1, green solid line), with the tropospheric burden for the 10 Tg injection nearly triple that of the unperturbed case. This increase is consistent with tropospheric burdens found in other microphysical studies [Debra Weisenstein, private communication]. The majority of this
increase occurs in the first 100 hPa below the tropopause. Note in Figure 5.1 that the slope of the 600-1000 hPa line is near zero, suggesting that perturbations of sulfate near the surface from geoengineering are insignificant compared to traditional sulfur sources (which are represented by the zero injection point in Figure 5.1). A significant portion of the atmospheric burden for all of the 10 Tg geoengineering scenarios is in the troposphere (Figure 5.6, pink columns).

Increases in specific regions of the troposphere are provided in Figure 5.13.

**Figure 5.13** Percent increase in sulfate mass burden in different regions for each 10 Tg S geoengineering simulation compared to the unperturbed case. “First 100 hPa” represents the region spanning from the tropopause to 100 hPa below the tropopause. “Second 100 hPa” spans 100 hPa below the tropopause to 200 hPa below the tropopause. “600-1000 hPa” spans from 600 hPa to the surface. See text for method of identifying tropopause.

Total tropospheric burdens increase by about 200% for all of the 10 Tg scenarios, with the increases slightly less for the broad region injections than the narrow region injections. There is no significant difference in tropospheric burden increases between injections of SO$_2$ gas, H$_2$SO$_4$
gas, or SO\textsubscript{4} particles. The vast majority of the tropospheric increases occur in the first 100 hPa below the tropopause, where the burdens increase by a factor of about 15. Again, the narrow injections cause a larger perturbation. Tropospheric burdens in the next 100 hPa down from the tropopause are doubled, while burdens near the surface increase by about 50%.

Comparison of sulfate volumetric mixing ratio between the unperturbed case and the SO\textsubscript{2} narrow 10 Tg injection (Figure 5.14) suggests increased burdens across much of the upper troposphere and high latitudes.

![Figure 5.14](image)

**Figure 5.14.** Tropospheric sulfate aerosol burden (pptv) for the unperturbed case and the “SO\textsubscript{2} narrow” geoengineering simulation; annual and zonal average as a function of atmospheric pressure and latitude. See text for method of identifying annual zonal average tropopause location (black lines).

Sulfate concentrations near the equator at the 120 hPa level increase 100-fold, from about 50 pptv to about 5 ppbv. Similarly, sulfate concentrations near the South Pole and 400 hPa increase from about 3 pptv to 300 pptv. Increases in sulfate burden relative to ambient concentrations for each of the 10 Tg geoengineering scenarios are illustrated in Figure 5.15.
Figure 5.15 Percent increase in tropospheric sulfate aerosol burden for each 10 Tg S geoengineering simulation compared to the unperturbed case; annual and zonal average as a function of atmospheric pressure and latitude. Pinatubo simulation is an average of the first year after the simulated eruption. See text for method of identifying annual zonal average tropopause location (black lines).
Sulfate increases are largest in the clean high latitude regions for all of the injection scenarios, as well as the upper troposphere at all latitudes, where burdens increase by about a factor of 100. Note that all of these increases are about double that calculated for the year after the Pinatubo eruption (Figures 5.6, 5.13, 5.15) due to the continuous injection, larger particle size, and faster falling velocities for the geoengineering cases, as well as their accumulated burden from previous years. It should be noted that the WACCM/CARMA model does not include DMS emissions. The unperturbed simulation predicts a global atmospheric sulfate burden of 0.49 Tg S, which is lower than the range of IPCC simulations that include DMS (0.55 to 1.1 Tg S) [Forster et al., 2007]. Although DMS contributes only about 20% to surface sulfur emissions globally [Haywood and Boucher, 2000], it likely would significantly increase sulfur burdens for the unperturbed simulation in the high latitude Southern Hemisphere. Therefore the fractional sulfate increases for geoengineering simulations may be artificially high in these regions.

An assessment of aerosol number, surface area, and volume distributions in the upper troposphere (Figure 5.16) reveals significant changes to aerosol properties for all 10 Tg geoengineering simulations. In both the tropical upper troposphere (at the equator and 120 hPa) as well as the high latitude upper troposphere (90°S and 400 hPa), stratospheric geoengineering produces a size mode at approximately 1 μm radius that is not present in the unperturbed simulation. Large increases to aerosol surface area and volume are predicted as well. As expected, the narrow tropical injection scenarios perturb the tropical upper troposphere more significantly while the broader injection scenarios perturb the high latitude upper troposphere more significantly. The Pinatubo simulation also predicts changes to upper tropospheric aerosol, but the perturbations are generally much smaller than those from geoengineering. Finally, note that despite high numbers of particles smaller than 300 nm predicted for all simulations in the tropical upper troposphere due to binary homogeneous nucleation of sulfuric acid and water in this region [English et al., 2011a], geoengineering produces a new size mode.
Figure 5.16 Annual zonal average of aerosol number, surface area, and volume distribution for each 10 Tg S geoengineering simulation in the tropical upper troposphere (the equator and 120 hPa; left column), and the southern high latitude upper troposphere (90°S and 400 hPa; right column).
This enhancement of tropospheric sulfate burdens could have implications for tropospheric cloud properties, radiative forcing, and tropospheric chemistry. After the eruption of Mt. Pinatubo, large aerosols were found in the upper troposphere [Sato et al., 1993; Stenchikov et al., 1998; Niemeier et al., 2009]. Some observational analyses showed an increase in cirrus clouds and a decrease in low clouds [Minnis et al., 1993; Ackerman and Strabala, 1994], which could cause surface warming, offsetting some of the cooling induced by the stratospheric aerosols. However, other observational analyses have failed to show a connection between Pinatubo and cirrus [Luo et al., 1997]. It is possible that El Nino contributed to the change in cirrus properties that year [Song et al., 1996], but other analyses suggest El Nino was insignificant compared to the effects of Mt. Pinatubo [Wang et al., 1995]. Modeling sensitivity studies have found Pinatubo to perturb cirrus if a monomodal aerosol distribution is prescribed but not a bimodal distribution [Lohmann et al., 2003]. Clearly this is an issue that needs more research in the context of geoengineering. Furthermore, these calculations suggest that geoengineering perturbs tropospheric aerosol more than Mount Pinatubo. If geoengineering with larger injection rates increases the thin cloud to thick cloud ratio further, while reaching a reflective cooling plateau in the stratosphere, the effectiveness of sulfate injections could be further limited. Finally, these simulations predict sulfate burdens in the lower atmosphere near the south pole to increase by up to two orders of magnitude (Figure 5.15), increasing the likelihood of acid deposition, which has been previously noted, though it was concluded that this increase is several orders of magnitude too small to cause ecological harm [Kravitz et al., 2009].

In addition to modifying cirrus, enhanced tropospheric particles could modify atmospheric chemistry by providing surfaces for heterogeneous reactions, or radiative heating rates. Sulfuric acid aerosols are known to heat the stratosphere after large volcanic eruptions, and could do the same in the tropopause region if high concentrations were maintained by persistent injections for geoengineering.
5.5 Conclusions

A 3-d coupled microphysical sectional model has been used to study the effect of sulfur injection magnitude, injection zone size, and injection species (SO$_2$, H$_2$SO$_4$, and SO$_4$ particles) on aerosol properties in the stratosphere and troposphere. Continuous SO$_2$ injection in a narrow region centered at the equator is found to have limited efficacy at higher injection rates, in agreement with Heckendorn et al. [2009] and others. Broadening the injection region to 32°N–32°S and 19.9-24.6 km increases the sulfate burden by approximately 50% for a 10 Tg S yr$^{-1}$ injection, and injection of SO$_4$ particles instead of SO$_2$ gas increases sulfate burden by another 50%, in agreement with Pierce et al. [2010]. Injection of H$_2$SO$_4$ gas does not increase burdens compared to SO$_2$ injection. Here, it is suggested that the results found by Pierce et al. were not due to injecting H$_2$SO$_4$, but rather to converting gases to particles in aircraft exhaust plumes. Considerably more research is needed on plumes to consider issues such as interactions between plumes, the particle size as a function of mass injected by single aircraft, and coagulation within plumes before they spread, among other topics. While previous studies have suggested geoengineering injections are less effective than volcanic ones in increasing sulfate mass burdens, the opposite is generally true for most of the cases studied here. The main reason is that volcanic injections are spatially confined, while most of the geoengineering scenarios considered here specified injections over broad regions. Hence, geographical distribution of the injection may be more important than the injection rate in general.

Significant perturbations to tropospheric aerosol burdens are found for all geoengineering simulations. Tropospheric burdens increase by a factor of two or three, with the majority of the increases occurring at all latitudes in the 100 hPa thick layer just below the tropopause, as well as most of the troposphere at high latitudes. Aerosol size, surface area, and volume are all perturbed in the tropical upper troposphere as well as the high latitude upper troposphere, and at much greater levels than simulated for the eruption of Mount Pinatubo.
These perturbations could impact cirrus clouds, and as a result, radiative forcing and geoengineering efficacy, and alter chemical reaction rates and radiative heating in the upper troposphere. More work needs to be done to clarify whether cloud properties are modified from changes in aerosol abundance or upper tropospheric heating.

These results highlight the unforeseen impacts that stratospheric geoengineering may entail. In addition to cirrus cloud modification and limited efficacy at higher injection rates, stratospheric sulfur injections may cause ozone destruction [Tilmes et al., 2009; Heckendorn et al., 2009], changes to the hydrological cycle [Trenberth and Dai, 2007], acid deposition at the poles [Kravitz et al., 2009], as well as consequences yet unknown. Geoengineering by solar radiation management also would not offset other adverse consequences of CO$_2$ emissions such as ocean acidification. Although geoengineering is riddled with risks, costs, and uncertainties, humanity’s current path of releasing greenhouse gases also creates risks, costs, and uncertainties. Therefore, geoengineering should receive further study to better constrain its risks, costs, and uncertainties, but not distract from efforts to quickly reduce CO$_2$ and other greenhouse emissions.

This work has just been submitted to the Journal of Geophysical Research [English et al., 2011b].

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Chapter VI

Summary and Future Work

6.1 Summary

Stratospheric aerosols can influence radiative forcing, atmospheric chemistry, the ozone layer, and upper tropospheric clouds, yet much remains to be learned about their sources and evolution. To improve understanding of these processes, a comprehensive sulfate aerosol microphysical sectional model coupled to a climate model (WACCM/CARMA) has been developed and implemented. This model includes emissions of SO$_2$ and OCS with the option to add volcanic and geoengineering sulfur injections, a 63-species chemistry module including 7 sulfur species, a choice of three nucleation schemes, coagulation with a correction for van der Waals forces, growth and evaporation based on the latest vapor pressure equations, and sedimentation and wet deposition. This model was utilized to study stratospheric aerosol under ambient conditions as well as from large volcanic eruptions and hypothetical climate engineering scenarios.

Simulations were conducted with three different nucleation schemes to study ambient aerosol. Simulations reveal that one theory for ion-induced nucleation from galactic cosmic rays predicts 25% higher nucleation rates in the UTLS than its related binary homogeneous nucleation scheme, but that the rates predicted by two binary schemes vary by two orders of magnitude. None of the nucleation schemes are superior at matching the limited observations available at the smallest sizes. It is found that coagulation, not nucleation, controls number concentration at sizes greater than approximately 10 nm, suggesting that processes relevant to atmospheric chemistry and radiative forcing in the UTLS are not sensitive to the choice of
nucleation schemes. Simulations using all three nucleation schemes compare reasonably well to observations of size distributions, number concentration across latitude, and vertical profiles of particle mixing ratio in the UTLS. The inclusion of van der Waals forces in the coagulation scheme improves comparison to observations in the UTLS. Finally, it is suggested that micrometeorites, which are not included in this model, dominate the aerosol properties in the upper stratosphere above about 30 km.

Simulations of the Mount Pinatubo eruption have been conducted, providing an opportunity to compare microphysical calculations to observations. Simulations and observations suggest that stratospheric aerosol mass and AOD increased by roughly two orders of magnitude after the eruption, highlighting the eruption's significant impact on stratospheric aerosol. The magnitude and timing of peak effective radius and 525 nm AOD compare well between the model and observations. The model predicts zonal-average stratospheric effective radius at 15°N to increase from 0.2 µm at ambient conditions to 0.7 µm six months after the eruption, which is within the error bars of observations. Both the model and observations find 525 nm AOD increases to 0.45 near the equator about 3 months after the eruption, and find a second maximum in the Northern Hemisphere mid-latitudes about 9-12 months after the eruption. There a few discrepancies between the model and observations. In the mid- and high-latitude Southern Hemisphere, the simulated 525 nm AOD is about one-third that of observations 3 months after the eruption, which may be due to the August eruption of Cerro Hudson in Chile, which is not included in the model. Simulated peak 525 nm AOD occurs at 5°N while the observed peak is at 5°S. Additionally, simulated AOD spans a narrower latitude range than the observations, and tapers more quickly. These latitudinal discrepancies may be caused by differences in meteorology (QBO and Brewer-Dobson circulation) between the model and observations, as the model was run freely and not constrained to the actual wind patterns present during the 1991 eruption. Another possible explanation is that the model does not treat aerosol heating, which could invigorate atmospheric circulation. The more compact aerosol
cloud in the model could enhance growth and sedimentation rates, causing AOD to decline more quickly than observations. Since both simulations with and without the van der Waals correction predict nearly identical time evolution of effective radius, the details of the coagulation scheme likely do not explain differences between the model and observations. Likewise, details of the nucleation scheme also should only impact aerosol number at the smallest sizes and not effective radius or AOD. It should also be noted that observations are restricted to a few regions and exhibit high variability, making it difficult to conclude with certainty the extent of model error.

Simulations of stratospheric sulfur injection scenarios reveal numerous insights into the efficacy and consequences of hypothetical geoengineering scenarios. Continuous SO$_2$ injection in a narrow region centered at the equator is found to have limited efficacy at higher injection rates, in agreement with previous microphysical studies. Broadening the injection region to 32°N–32°S and 19.9-24.6 km increases the sulfate burden by approximately 50% for a 10 Tg S yr$^{-1}$ injection; and injection of SO$_4$ particles instead of SO$_2$ gas increases sulfate burden by another 50%, in agreement with Pierce et al. [2010]. Injection of H$_2$SO$_4$ gas does not increase burdens compared to SO$_2$ injection. Here, it is suggested that the results found by Pierce et al. were not due to injecting H$_2$SO$_4$, but rather to converting gases to particles in aircraft exhaust plumes. Considerably more research is needed on plumes to consider issues such as interactions between plumes, the particle size as a function of mass injected by single aircraft, and coagulation within plumes before they spread, among other topics. While previous studies have suggested geoengineering injections are less effective than volcanic injections for increasing sulfate mass burdens, the opposite is generally true for most of the cases studied here. The main reason is that volcanic injections are spatially confined, while most of the geoengineering scenarios considered here specified injections over broad regions. Hence, geographical distribution of the injection may be more important than the injection rate in general. In all cases, significant perturbations to tropospheric aerosol burdens are found.
Tropospheric burdens increase by a factor of two or three, with the majority of the increases occurring at all latitudes in the 100 hPa thick layer just below the tropopause, as well as most of the troposphere at high latitudes. Aerosol size, surface area, and volume are all perturbed in the tropical upper troposphere as well as the high latitude upper troposphere, and at much greater levels than simulated for the eruption of Mount Pinatubo. These perturbations could impact cirrus clouds, and as a result, radiative forcing and geoengineering efficacy, and alter chemical reactions rates and radiative heating in the upper troposphere. More work needs to be done to clarify whether cloud properties are modified from changes in aerosol abundance or upper tropospheric heating. These results highlight the unforeseen impacts that stratospheric geoengineering may entail, in addition to known adverse consequences including ozone destruction, changes to the hydrological cycle, and acid deposition at the poles. Geoengineering by solar radiation management also would not offset other adverse consequences of CO$_2$ emissions such as ocean acidification. Although geoengineering is riddled with risks, costs, and uncertainties, humanity’s current path of releasing greenhouse gases also creates risks, costs, and uncertainties. Therefore, geoengineering should receive further study to better constrain its risks, costs, and uncertainties, but not distract from efforts to quickly reduce CO$_2$ and other greenhouse emissions.

6.2 Future Work

There are many more science questions that could be explored with this WACCM/CARMA model. The preliminary simulations of Mount Pinatubo could be expanded upon with more comparisons to observations and further investigation into the contributions of dynamics versus microphysics to explain discrepancies. The model could be used to simulate the eruption of super-volcanoes such as Toba that may have nearly wiped out humanity 70,000 years ago. Very few microphysical studies have been completed on super-eruptions. Much more work needs to be conducted on geoengineering efficacy and consequences, particularly
the potential limitations of stratospheric geoengineering due to particle growth, and its impacts on upper tropospheric cirrus as well as stratospheric ozone.

Improvements could be made to the model to make it more comprehensive. Aerosol heating should be added to the model, which could particularly impact high perturbation scenarios such as volcanoes and geoengineering. A model is currently being used that contains micrometeorites in addition to pure sulfate to treat the two major types of aerosol present in the stratosphere. Another model is under development that adds a nitric acid aerosol species to treat the ternary system known to be present in Polar Stratospheric Clouds. Another model is under development that adds a sea salt species to study sea salt sulfate aerosol in the troposphere. Other species types and nucleation mechanisms could be added to more fully treat boundary layer nucleation processes. It is also recommended to couple this model to the newest versions of the NCAR models (CAM5 and WACCM5) to capture the latest model improvements.
Bibliography


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Appendix A

Vapor Pressure Equations

Summary of behavior of equations calculating equilibrium vapor pressures of sulfuric acid and water over sulfate solution for the range of conditions encountered in the WACCM/CARMA model. The equations utilized in the model are noted. All of the equations had stable behavior; the chosen equations had a wider temperature range of application [Lin and Tabazadeh, 2001] or were based on more recent laboratory measurements [Murphy and Koop, 2005]. The abbreviation “eq. vp. over sln” means equilibrium vapor pressure over solution (sulfate is a binary solution consisting of sulfuric acid and water).

$\text{H}_2\text{SO}_4$, implemented in model [Kulmala, 1990; Ayers et al., 1980; Giauque, 1959].
H₂O, implemented in model [Lin and Tabazedeh, 2001]

H₂O, no longer in use [Zhang et al., 1993]
H$_2$O, percent difference between Lin and Tabazadeh [2001] and Zhang et al. [1993]
at two temperature ranges
H$_2$SO$_4$ weight percent in sulfate solution, log and linear x-axes
[Tabazadeh et al., 1997; Murphy and Koop, 2005]
Comparison of Tabazadeh *et al.* [1997] weight percent calculations using two different equations for H$_2$O equilibrium vapor pressure: Murphy and Koop [2005] (implemented in model) and Clegg and Brimblecone [1995] (no longer in use)
Difference between Tabazadeh et al. [1997] with Murphy and Koop [2005] and with Clegg and Brimblecone [1995]
Appendix B

Yu Nucleation Look-up Tables

Summary of input parameter resolution and boundaries to calculate nucleation rates for four tables: BHN/IMN low temperature table, BHN mid-temperature table, BHN high temperature table, and IMN high temperature table. The use of all four tables combined allows treatment of BHN and IMN at the temperature range 180-300K. Input parameters listed as: name (resolution) units; followed by each input value.

---BHN/IMN Low Temperature Table (180-250K) (31,31,36,12,11)---

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Resolution</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2SO4</td>
<td>(31)</td>
<td>#/cm³</td>
</tr>
<tr>
<td>RH</td>
<td>(31)</td>
<td>%</td>
</tr>
<tr>
<td>T</td>
<td>(36)</td>
<td>K</td>
</tr>
<tr>
<td>Q (ions)</td>
<td>(12)</td>
<td>#/cm³/s</td>
</tr>
<tr>
<td>SA</td>
<td>(11)</td>
<td>µm³/cm³</td>
</tr>
</tbody>
</table>

| Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 | Value 7 | Value 8 | Value 9 | Value 10 | Value 11 | Value 12 | Value 13 | Value 14 | Value 15 | Value 16 | Value 17 | Value 18 | Value 19 | Value 20 | Value 21 | Value 22 | Value 23 | Value 24 | Value 25 | Value 26 | Value 27 | Value 28 | Value 29 | Value 30 | Value 31 | Value 32 | Value 33 | Value 34 | Value 35 | Value 36 | Value 37 | Value 38 | Value 39 | Value 40 | Value 41 | Value 42 | Value 43 | Value 44 | Value 45 | Value 46 | Value 47 | Value 48 | Value 49 | Value 50 | Value 51 | Value 52 | Value 53 | Value 54 | Value 55 | Value 56 | Value 57 | Value 58 | Value 59 | Value 60 | Value 61 | Value 62 | Value 63 | Value 64 | Value 65 | Value 66 | Value 67 | Value 68 | Value 69 | Value 70 | Value 71 | Value 72 | Value 73 | Value 74 | Value 75 | Value 76 | Value 77 | Value 78 | Value 79 | Value 80 | Value 81 | Value 82 | Value 83 | Value 84 | Value 85 | Value 86 | Value 87 | Value 88 | Value 89 | Value 90 | Value 91 | Value 92 | Value 93 | Value 94 | Value 95 | Value 96 | Value 97 | Value 98 | Value 99 | Value 100 |
*Note: if T<250 K the code bypasses this table and uses the combined BHN/IMN table listed first.

### Mid and High Temperature BHN Tables (227-263K and 264-300K) (61,99,74)

<table>
<thead>
<tr>
<th>H2SO4 (61)</th>
<th>#/cm3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E+05</td>
<td>1.17E+05</td>
</tr>
<tr>
<td>6.31E+05</td>
<td>7.36E+05</td>
</tr>
<tr>
<td>3.42E+06</td>
<td>3.98E+06</td>
</tr>
<tr>
<td>1.85E+07</td>
<td>2.15E+07</td>
</tr>
<tr>
<td>1.00E+08</td>
<td>1.17E+08</td>
</tr>
<tr>
<td>5.41E+08</td>
<td>6.31E+08</td>
</tr>
</tbody>
</table>

### High Temperature IMN Table (250-300K) (31,25,26,11,8)

<table>
<thead>
<tr>
<th>H2SO4 (31)</th>
<th>#/cm3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.000E+05</td>
<td>6.295E+05</td>
</tr>
<tr>
<td>6.295E+07</td>
<td>7.924E+07</td>
</tr>
</tbody>
</table>

### RH (99) %

<table>
<thead>
<tr>
<th>T (74)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>227</td>
<td>228</td>
</tr>
<tr>
<td>231</td>
<td>232</td>
</tr>
<tr>
<td>233</td>
<td>234</td>
</tr>
<tr>
<td>235</td>
<td>236</td>
</tr>
<tr>
<td>237</td>
<td>238</td>
</tr>
<tr>
<td>...etc... 99</td>
<td></td>
</tr>
</tbody>
</table>

### Q (ions) (11) #/cm3/s

<table>
<thead>
<tr>
<th>T (26)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.500E+02</td>
<td>2.520E+02</td>
</tr>
<tr>
<td>2.720E+02</td>
<td>2.740E+02</td>
</tr>
<tr>
<td>2.920E+02</td>
<td>2.940E+02</td>
</tr>
</tbody>
</table>

### SA (8) µm3/cm3

<table>
<thead>
<tr>
<th>T (227-263K and 264-300K)</th>
<th>µm3/cm3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000E+00</td>
<td>2.000E+01</td>
</tr>
</tbody>
</table>
The table below summarizes Yu nucleation table boundaries, most extreme values encountered in the WACCM model, and number of instances WACCM was outside the Yu table boundaries for a 3-month simulation. (90 days x 48 timesteps/day x 1-500 substeps x 66 levels x 46 latitudes x 72 longitudes = >944 million total possible instances). This analysis helped identify spatial regions that were outside table bounds. For instance, relative humidity (RH) was often below the table minimum in the upper stratosphere, leading to false nucleation predictions in this region (see Chapter 2.3.2).

<table>
<thead>
<tr>
<th></th>
<th>T min</th>
<th>T max</th>
<th>RH min</th>
<th>RH max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yu's Table Edges - LT (180-250K)</td>
<td>180</td>
<td>250</td>
<td>0.1</td>
<td>99.5</td>
</tr>
<tr>
<td>Yu's Table Edges - HT (250-300K)</td>
<td>250</td>
<td>300</td>
<td>3</td>
<td>99</td>
</tr>
<tr>
<td>WACCM 1000-0 hPa # times out-of-range 1000-0 hPa</td>
<td>115</td>
<td>671</td>
<td>2E-10</td>
<td>54187</td>
</tr>
<tr>
<td></td>
<td>21 million</td>
<td>5 million</td>
<td>N/A</td>
<td>&gt;6 million</td>
</tr>
<tr>
<td>WACCM 1000-1 hPa # times out-of-range 1000-1 hPa typical location (hPa)</td>
<td>179.9</td>
<td>316</td>
<td>7E-05</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3 million</td>
<td>360 million</td>
<td>6 million</td>
</tr>
<tr>
<td>Trop</td>
<td>WACCM 1000-300 hPa</td>
<td>186</td>
<td>318</td>
<td>1.3</td>
</tr>
<tr>
<td>UTLS</td>
<td>WACCM 300-40 hPa</td>
<td>172</td>
<td>248</td>
<td>4.0E-02</td>
</tr>
<tr>
<td>Strat</td>
<td>WACCM 40-1 hPa</td>
<td>172</td>
<td>339</td>
<td>3.0E-04</td>
</tr>
<tr>
<td>Meso</td>
<td>WACCM 1-0.05 hPa</td>
<td>170</td>
<td>671</td>
<td>1.0E-04</td>
</tr>
<tr>
<td>Thermo</td>
<td>WACCM 0.05-0 hPa</td>
<td>115</td>
<td>303</td>
<td>2.0E-10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SA=Surface Area</th>
<th>SA min µm² cm⁻³</th>
<th>SA max µm² cm⁻³</th>
<th>H₂SO₄ min molec cm⁻³</th>
<th>H₂SO₄ max molec cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yu's Table Edges - LT (180-250K)</td>
<td>1</td>
<td>100</td>
<td>1.0E+05</td>
<td>1.0E+08</td>
</tr>
<tr>
<td>Yu's Table Edges - HT (250-300K)</td>
<td>1</td>
<td>100</td>
<td>5.0E+05</td>
<td>5.0E+08</td>
</tr>
<tr>
<td>WACCM 1000-0 hPa # times out-of-range 1000-0 hPa</td>
<td>1.0E-51</td>
<td>&lt;100</td>
<td>7.0E-06</td>
<td>3.50E+08</td>
</tr>
<tr>
<td></td>
<td>1.5 billion</td>
<td>0</td>
<td>360 million</td>
<td>2.0E+05</td>
</tr>
<tr>
<td>WACCM 1000-1 hPa # times out-of-range 1000-1 hPa typical location (hPa)</td>
<td>2.6E-30</td>
<td>&lt;100</td>
<td>0.5</td>
<td>3.5E+08</td>
</tr>
<tr>
<td></td>
<td>500,000</td>
<td>0</td>
<td>250 million</td>
<td>231,000</td>
</tr>
<tr>
<td>Trop</td>
<td>WACCM 1000-300 hPa</td>
<td>N/A</td>
<td>&lt;100</td>
<td>1.0E-02</td>
</tr>
<tr>
<td>UTLS</td>
<td>WACCM 300-40 hPa</td>
<td>N/A</td>
<td>&lt;100</td>
<td>2.0E-03</td>
</tr>
<tr>
<td>Strat</td>
<td>WACCM 40-1 hPa</td>
<td>N/A</td>
<td>&lt;100</td>
<td>7.0E-06</td>
</tr>
<tr>
<td>Meso</td>
<td>WACCM 1-0.05 hPa</td>
<td>N/A</td>
<td>&lt;100</td>
<td>2.0E+02</td>
</tr>
<tr>
<td>Thermo</td>
<td>WACCM 0.05-0 hPa</td>
<td>N/A</td>
<td>&lt;100</td>
<td>N/A</td>
</tr>
</tbody>
</table>