Formation of ozone and growth of aerosols in young smoke plumes from biomass burning: 1. Lagrangian parcel studies

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Formation of ozone and growth of aerosols in young smoke plumes from biomass burning: 1. Lagrangian parcel studies

Matthew James Alvarado and Ronald G. Prinn

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We have developed a new model of the gas- and aerosol-phase chemistry of biomass burning smoke plumes called Aerosol Simulation Program (ASP). Here we use ASP combined with a Lagrangian parcel model to simulate the chemistry in smoke plumes from three fires: the Otavi savannah fire in Namibia, an Alaska boreal forest fire, and the Timbavati savannah fire. Our model explained the observations of ozone in the Otavi and Alaska plumes fairly well, but our initial model simulation of the Timbavati plume underestimated the concentrations of ozone, OH, and secondary aerosol matter. The Timbavati simulation agrees with observations if we increase OH to equal its observed levels. Heterogeneous reactions of NO2 and SO2 could explain the needed higher concentrations of OH and the rapid formation of ozone, nitrate, and sulfate in the smoke plume if the uptake coefficients on smoke aerosols are large (O(10^-3) and O(10^-4), respectively). Uncharacterized organic species in the smoke plume were likely responsible for the rapid formation of aerosol organic carbon. The changes in the aerosol size distribution were dominated by plume dilution and condensational growth. The single scattering albedo of the modeled fresh smoke increases from 0.866 to 0.902 over 1 h of aging. The change in aerosol scattering with relative humidity for the modeled fresh smoke matches observations up to 66% RH, but the model greatly overestimates the humidification factor at 80% RH (2.88 versus an observed value of 1.70–1.79). For the aged smoke, the modeled humidification factor is 1.22, slightly below the observed value of 1.40.


1. Introduction

The combustion of biomass is a major source of atmospheric trace gases and aerosols which can impact global atmospheric chemistry and climate [Cribb and Andreae, 1990; Intergovernmental Panel on Climate Change (IPCC), 2001]. Emissions of NOx and nonmethane organic compounds (NMOCs) from biomass burning can lead to enhancements of tropospheric ozone [Cribb and Andreae, 1990; Levine, 1994; Marufu et al., 2000; Andreae and Merlet, 2001; Chan et al., 2001; McKeen et al., 2002; Leung et al., 2007], while primary and secondary aerosols from biomass burning can affect the climate directly by the scattering or absorption of sunlight [Hobbs et al., 1997; Reid et al., 2005a] and indirectly through their effects on cloud droplet number concentration, cloud albedo, and cloud precipitation efficiency [Hobbs and Radke, 1969; Eagan et al., 1974; Rosenfeld, 1999]. In general, regional- and global-scale models of atmospheric chemistry and climate take estimates for the primary emissions of trace gases and aerosols from biomass burning and “mix” them into much larger-scale grid boxes (e.g., with 10–200 km horizontal scales) before performing any calculations of gas-phase chemistry, aerosol-phase chemistry, or aerosol dynamics. This procedure ignores the substantial nonlinear chemical and physical transformations (e.g., gas-phase chemistry, coagulation of aerosols, condensation of vapors, etc.) that can take place in the highly concentrated environment of young biomass burning smoke plumes [Andreae and Merlet, 2001; Jost et al., 2003]. These transformations can lead to significant changes in the gas phase composition of the smoke and the number, size, composition, and shape of the emitted particles [Liousse et al., 1995; Hobbs et al., 2003; Jost et al., 2003; Li et al., 2003; Posfai et al., 2003; Reid et al., 2005a, 2005b]. As these changes are not correctly included in large-scale models, these large-scale models may misrepresent the true impacts of biomass burning smoke on atmospheric chemistry and climate [Jost et al., 2003].

In addition, there are several unresolved questions about the chemical and physical changes that take place within young biomass burning smoke plumes (defined here as plumes less than 4 h downwind from the fire source). For example, the observations of the smoke plume from the
Timbavati savannah fire in South Africa show rapid formation of ozone within the smoke plume [Hobbs et al., 2003]. Previous modeling studies of the gas phase chemistry in the Timbavati smoke plume [Trentmann et al., 2005; Mason et al., 2006] have not been able to simulate this chemistry. The observations also show a large increase in the normalized mass concentrations of secondary aerosol matter (nitrate, sulfate, and organic carbon (OC)) as the smoke moves downwind. In addition, Hobbs et al. [2003] suggested that the initial reduction in total aerosol number concentration in the plume was due to particle coagulation, while the increase in number concentration further downwind was due to particle nucleation. However, there have been no previous modeling studies to explore the growth and chemical transformation of aerosols in the Timbavati smoke plume due to the formation of secondary aerosol matter, coagulation, and nucleation.

[4] The goals of this paper (and a companion paper [Alvarado et al., 2009]) are to model the growth of smoke particles within young biomass burning plumes, evaluate the impact of these particles on the gas-phase chemistry and formation of ozone within the plume, and to evaluate the errors caused by the automatic dilution of plume emissions in global atmospheric chemistry models (GACMs). In this paper (part 1), we use a new gas- and aerosol-phase chemistry model (Aerosol Simulation Program (ASP)) to study the chemical evolution of three young smoke plumes from biomass burning. All of these studies are done in a Lagrangian framework, where the concentrations within a single parcel are tracked over time. This approach has been used in previous modeling studies of the gas-phase chemistry of biomass burning smoke plumes by Mauzerall et al. [1998], Mason et al. [2001], Jost et al. [2003], Trentmann et al. [2005], and Mason et al. [2006]. A second paper (part 2) [Alvarado et al., 2009] describes our 3-D Eulerian simulations of the coupled fluid dynamics, radiative transfer, gas-phase chemistry, and aerosol-phase chemistry within a young savannah fire smoke plume, and compares the results of the plume model to the large grid box approach currently used in GACMs.

[5] Section 2 briefly describes the chemical and Lagrangian parcel models used in these studies. The three plumes that are modeled in this paper are from the Otavi East African savannah fire (section 3), Alaskan boreal forest fire B309 (section 4), and the Timbavati South African savannah fire (section 5). Gas-phase composition measurements are available for all three smoke plumes, but aerosol-phase composition measurements are only available for the Timbavati smoke plume. Thus, we model the gas-phase chemistry of the Otavi and Alaskan plumes, and model both the gas- and aerosol-phase compositions of the Timbavati plume. The Timbavati study represents the first attempt, to our knowledge, to simultaneously model the gas- and aerosol-phase chemical evolution of a young biomass burning smoke plume.

2. Model Description

2.1. Aerosol Simulation Program

[6] The gas- and aerosol-phase chemical model developed for this work (ASP) selectively uses the model framework and computer codes developed by Steele [2004] for the Mixed Eulerian-Lagrangian Aerosol Model (MELAM). We have extensively added to, tested, and modified the original MELAM model codes, including new and modified routines for gas-phase and heterogeneous chemistry, a moving center sectional aerosol size distribution, the thermodynamics of solid electrolytes, hydrophobic organic species, and aqueous organics, kinetic, flux-limited condensation of H2SO4 and organic species, a hybrid gas-to-particle mass transfer scheme, a semi-implicit coagulation routine, and a core-in-shell Mie calculation of aerosol optical properties. These routines are described in detail by Alvarado [2008], which also compares the model results to experimental data, other model predictions, and analytical solutions where available. A schematic structure and flow diagram for ASP is provided in Figure 1, and a brief overview of the components of the model is given in Appendix A.

Figure 1. Flow chart for the Aerosol Simulation Program (ASP). Section numbers refer to the text.
2.2. Lagrangian Parcel Model

[7] For these studies, we used ASP in a Lagrangian parcel model. The Lagrangian parcel model approach used in this study has been used in several previous studies of the gas-phase chemistry of smoke plumes from biomass burning [Mason et al., 2001; Jost et al., 2003; Trentmann et al., 2005; Mason et al., 2006]. The model equations are included in Appendix A.

[8] In applying the model to observations of young smoke plumes, the values for νs, the initial plume width, are taken from observations of the initial width of the young smoke plume, while the value of Ks, the cross-wind horizontal diffusion coefficient, is determined by a least squares fit to the concentrations of a conservative tracer, usually CO [e.g., Trentmann et al., 2005]. CO is used as a tracer in these studies because the lifetime of CO (1 to 3 months) is much longer than the time scale of the young smoke plumes, and the high initial concentration of CO means that gas-phase production can be considered negligible. The Lagrangian time for the measurements is derived from the average observed wind speed in the plume and the distance of the sampling location from the fire source. Uncertainty and variation in the wind speed leads to uncertainty in the Lagrangian time of the measurements; this uncertainty is represented in Figures 3, 4, 6, and 7 by horizontal error bars on the measurements.

[9] The photolysis rates for the Lagrangian parcel model are calculated using the Tropospheric Ultraviolet and Visible (TUV) Radiation Model version 4.1 [Madronich and Flocke, 1998] for 15 min increments, which are then linearly interpolated within the model. For the Lagrangian studies, we assume a “clear sky” radiation field that ignores the effect of aerosol absorption and scattering on photolysis rates. The impact of aerosols on the radiative field and photolysis rates for the Timbavati smoke plume is discussed in the companion paper.

3. Otavi Smoke Plume

[10] The Otavi smoke plume was emitted by a savannah fire near the city of Otavi in Northern Namibia on 13 September 2000. The trace gas composition of the Otavi plume was investigated by Jost et al. [2003] as part of the Southern African Regional Science Initiative 2000 (SAFARI 2000) field campaign using the UK Met Office C-130 aircraft.

[11] The observations of the trace gas composition of the Otavi smoke plume made by Jost et al. [2003] included high-frequency (0.25 – 1 Hz) measurements of CO by vacuum-UV fluorescence, O3 by UV photometric analyzer, and of acetone and acetonitrile by chemical ionization mass spectroscopy. Measurements were made during 10 transects of the plume at an altitude of about 2.5 km AMSL (1 km AGL). Two flask samples were analyzed for nonmethane hydrocarbons (NMHCs) using an automated gas chromatograph with a flame ionization detector. Jost et al. [2003] report NOx concentrations near the fire, where the sampling time was long enough to get accurate data. In addition, Jost et al. [2003] used a Lagrangian parcel model to investigate the formation of ozone within the Otavi smoke plume.

[12] In this section we present the results of our Lagrangian modeling study of the Otavi plume. Section 3.1 describes the chemical and physical parameters used by our model to simulate the Otavi plume. Section 3.2 then compares the results of our model to the available observations and to the previous modeling study of Jost et al. [2003].

3.1. Model Initialization

[13] Table 1 shows the temperature, pressure, relative humidity, and other parameters used to simulate the conditions of the Otavi smoke plume. Photolysis rates for the Otavi fire were derived using TUV v4.1 at 3 km above sea level. The initial plume width (νs) was set to 500 m. Least squares fitting of the plume average CO data gives a value of Ks of 400 m2 s−1 [Jost et al., 2003]. This is in line with the data and empirical equation of Gifford [1982] for horizontal atmospheric diffusion, which predicts Ks of O(100 m2 s−1) for a lateral standard deviation of O(100 m).

[14] The initial and background concentrations used to model the Otavi plume are given in the auxiliary material. Background concentrations were estimated using measurements made upwind of the fire sources, where available. When not, background concentrations were estimated using results from global and regional chemical transport models [Jost et al., 2003].

3.2. Results and Comparison to Observations

[15] Figure 2a shows the modeled and observed CO concentrations for the Otavi smoke plume. The data points are the plume average measurements reported by Jost et al. [2003]. The Ks value of 400 m2 s−1 gives a good match to the change in the plume average CO concentrations for the Otavi fire.

[16] Figure 2b shows the modeled and observed O3 concentrations. Our model gives a fairly good match to the observed formation of ozone within the Otavi smoke plume, with only a slight underestimate (approximately 5 ppb) of the downwind concentrations.

[17] Figure 2c shows the observed plume average acetone concentrations. The measurements are compared with the acetone concentrations from the model of Jost et al. [2003] and the (acetone containing) KETL concentrations from our model simulation. Both models underpredict the level of acetone measured in the plume between 30 and 80 min after emission, suggesting that both models are missing a second-

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*Values taken from Jost et al. [2003].

**Values taken from Mason et al. [2006, Table III].

1Auxiliary materials are available in the HTML. doi:10.1029/2008JD011144.
Figure 2. Modeled and measured concentrations in the Otavi smoke plume of (a) CO, (b) O₃, (c) CH₃C(O)CH₃ (KETL), (d) NO₂, (e) NO, and (f) HCHO. The data points are the plume average measurements reported by Jost et al. [2003].
ary source of acetone within the smoke plume. Our model shows slightly lower levels of acetone (KETL) than the model of Jost et al. [2003], possibly due to different reaction rates for acetone and KETL between the two models. Our model values of NO, NO₂, and HCHO concentrations, shown in Figures 2d–2f, agree well with the model of Jost et al. [2003]. In general, we find that our lumped chemical mechanism represents the gas-phase chemistry in the Otavi smoke plume with an accuracy comparable to the species-specific mechanism of Jost et al. [2003].

4. Alaska Smoke Plume

The Alaska smoke plume (emitted by Alaska Fire Service fire B309) was measured by Goode et al. [2000] on 27 June 1997 using airborne Fourier transform infrared spectrometry (AFTIR) on a King Air B-90 aircraft. The fire, ignited by lightning, burned within the black spruce forest-shrub-bog mosaic of the Innoko Wildlife Refuge. Four samples were collected and analyzed by AFTIR during transects of the smoke plume, while an additional three samples were collected and analyzed while flying down the long axis of the smoke plume [Mason et al., 2006]. In general, the sampling time for the AFTIR instrument is 3–5 s, so that these measurements are effectively point values rather than plume average values. The gas-phase chemistry for this plume has been previously studied in the model intercomparison of Mason et al. [2006].

In this section we present the results of our Lagrangian modeling study of the Alaska plume. Section 4.1 describes the chemical and physical parameters used by our model to simulate the Alaska plume. Section 4.2 then compares the results of our model to the available observations.

4.1. Model Initialization

Table 1 shows the temperature, pressure, relative humidity, and other parameters used to simulate the conditions of the Alaska smoke plume. The initial and background concentrations used to model the Alaska plume are included in the auxiliary material. Background concentrations were estimated from upwind measurements, where available, and using global and regional chemical transport models otherwise. Photolysis rates for the Alaska fire were derived using TUV v4.1 at 2 km above sea level. The initial plume width (y₀) was set to 13,735 m. Least squares fitting of the available CO data gives a value of Kᵥ of 34,000 m² s⁻¹ [Mason et al., 2006]. This value is much larger than the value of 400 m² s⁻¹ used in the Otavi case because of the larger plume size in this case. The data and empirical equation of Gifford [1982] for horizontal atmospheric diffusion predicts a Kᵥ of O(10,000 m² s⁻¹) for a lateral standard deviation of O(10 km), in line with the values used here for the Alaska plume.

4.2. Results and Comparison to Observations

Figure 3a shows the modeled and observed CO concentrations for the Alaska smoke plume. The solid black line shows the modeled CO concentration for the best fit value of Kᵥ, (34,000 m² s⁻¹), There is one observational sample with a significantly higher concentration of CO than is predicted using this value of Kᵥ, and two observational samples that show significantly lower concentrations of CO. To account for this apparent variability in plume dispersion, we ran two additional models runs, one with a low (slow) Kᵥ of 6,700 m² s⁻¹ and one with a high (fast) Kᵥ of 134,750 m² s⁻¹.

Figure 3b shows the modeled and observed concentrations of O₃. Our model gives a fairly good match to the observed O₃ formation in the Alaska plume, covering five of the six ozone observations within the uncertainty of the plume dispersion rates, Lagrangian age, and measurement precision. However, our model does not match the highest downwind ozone measurement. The two models used by Mason et al. [2006] predict higher ozone concentrations at 3 h downwind than our model (100 ppb and 87 ppb, respectively, for the best fit dilution rate).

Figures 3c–3h compare our model results to observations of additional plume gases. The model appears to overestimate the concentrations of nitrogen oxides, although the low number of measurements and high uncertainties make it difficult to draw any definitive conclusions. Our model results for nitrogen oxides are higher than those of Mason et al. [2006]; for example, our NO₂ concentration at 3 h downwind is 30 ppb, versus 20 ppb in the work by Mason et al. [2006]. Figure 3f shows the model may be underestimating HCHO, but the low number of measurements and high uncertainties inhibit us from drawing any specific conclusions. The modeled and measured concentrations of ethylene (ETHE) agree, suggesting that the chemistry of ethylene in the Alaska plume is correctly represented in the model. Figure 3h shows the modeled ACID concentration and the sum of the measurements of formic and acetic acid. Our model underestimates the observed concentrations of these acids, but our results are similar to the models of Mason et al. [2006].

5. Timbavati Smoke Plume

The Timbavati smoke plume in South Africa was sampled by Hobbs et al. [2003] on 7 September 2000 as part of SAFARI 2000. This grass fire was intentionally ignited in the lowveld of South Africa. Measurements of both the gas and aerosol phase composition of the smoke plume were made aboard the University of Washington Convair-580 research aircraft. The gas-phase chemistry for the Timbavati smoke plume has been previously modeled by Treutmann et al. [2005] and in the model intercomparison of Mason et al. [2006].

Below we summarize the results of our Lagrangian modeling study of the plume. Section 5.1 describes the available gas and aerosol phase observations for the smoke plume. Section 5.2 describes the chemical and physical parameters used by our model to simulate the Timbavati plume. Section 5.3 compares the results of our model to the available observations and discusses several hypotheses that could improve the match between the model and observations. Model sensitivity tests and scale analyses are presented to evaluate these hypotheses.

5.1. Summary of Observations

5.1.1. Gas Phase Observations

Measurements of the gas-phase composition of the Timbavati plume were made using a Teo 43S pulsed fluorescence analyzer for SO₂, AFTIR, and samples collected in electropolished stainless steel canisters for later laboratory
Figure 3. Modeled and measured concentrations in the Alaska smoke plume of (a) CO, (b) O$_3$, (c) NO$_x$, (d) NO, (e) NO$_2$, (f) HCHO, (g) C$_2$H$_4$ (ETHE), and (h) HC(O)OH plus CH$_3$(O)OH (ACID).
analysis [Hobbs et al., 2003]. A detailed description of the analytical procedure for the steel canisters is given by Colman et al. [2001]. A typical sampling (flask filling) time for the canister measurements was 30 s. The composition of the canisters was analyzed using gas chromatography with flame ionization, electron capture and mass spectrometer detection [Hobbs et al., 2003]. A laboratory study of emissions from African biomass burning by Christian et al. [2003] using similar sampling and detection methods identified only 70% of the gas-phase carbon emitted as non-methane organic compounds (NMOCs), suggesting that the reported NMOCs account for roughly 70% of the carbon released by the Timbavati fire as NMOC [Trentmann et al., 2005]. We examine the potential effects of these uncharacterized organic compounds on the plume chemistry in section 5.3.2.

[27] In addition, Hobbs et al. [2003] estimated the average OH concentration within the Timbavati smoke plume using the observed decay rates of five species (propene, ethylene, 1-butene, ethane and CO) in the plume. The average derived OH concentration for the first 40 min in the Timbavati plume is $(1.7 \pm 0.2) \times 10^7$ radicals cm$^{-3}$, suggesting a highly oxidizing plume environment.

5.1.2. Aerosol Phase Observations

[28] The total aerosol number concentration in the smoke plume was measured with a TSI 3025A ultrafine condensation particle counter. The instrument has a size range of 0.003–3 $\mu$m in diameter, but does not give information on the particle size distribution within that range. Particle size spectra from 0.5 to 3.0 $\mu$m in diameter were continuously measured with a TSI 3320 aerodynamic particle sizer. Unfortunately, most aerosol particles from savannah burning have a number mean diameter of only 0.11 $\pm$ 0.01 $\mu$m [Reid et al., 2005b], so the size distribution measurements available for Timbavati are not very useful for initializing or evaluating the model aerosol size distribution. The light-scattering coefficient of the particles was measured continuously using a MS Electron nephelometer.

[29] Aerosol bulk chemical composition was measured by collecting particles on Teflon and quartz filters [Hobbs et al., 2003]. Since the time that it took for the aircraft to cross the smoke plume (0.1 min) was too short to pass enough smoke through the filters, a “grab bag” technique was used where a 2.5 m$^3$ Velostat plastic bag was filled with smoke in 7–12 s. The sample in the grab bag was then passed through the filters for subsequent analysis. Details of the Teflon filter analyses are given by Gao et al. [2003]. The quartz filters were analyzed by Kirchstetter et al. [2003] for particulate carbon. Black carbon (BC) concentrations were estimated by Kirchstetter et al. [2003] with an optical transmission technique.

5.2. Model Initialization

[30] Table 1 shows the temperature, pressure, relative humidity, and other parameters used to simulate the conditions of the Timbavati smoke plume. Photolysis rates for Timbavati were derived using TUV v4.1 at 1 km above sea level. The initial plume width ($y_o$) was set to 2,000 m on the basis of the observed plume width and $K_y$ was set to 7,000 m$^2$ s$^{-1}$ [Trentmann et al., 2005].

[31] The gas-phase compounds included in our simulation of the Timbavati smoke plume are given in the auxiliary material. Background concentrations were estimated from upwind measurements, where available, and using global and regional chemical transport models otherwise. Furans (at an initial concentration of 18.426 ppb) were included in the modeling study of Trentmann et al. [2005], but are here assumed unreactive as they are not included in the Caltech Atmospheric Chemistry Mechanism (CACM). The potential sensitivity of ozone formation to furan chemistry is considered in section 5.3.3 below.

[32] The initial and background concentrations of aerosols included in the baseline model runs are also in the auxiliary material. Since size distribution data for particles smaller than 0.5 $\mu$m in diameter is not available for the Timbavati fire, we estimated the size distribution for the initial smoke aerosol from literature values. The mean geometric diameter $D_g$ (0.11 $\mu$m) and standard deviation $\sigma$ (1.91) for the initial smoke are from Reid and Hobbs [1998]. The initial number concentration (116,000 cm$^{-3}$) and aerosol composition were chosen to match the mass concentrations reported for Sample 1 by Hobbs et al. [2003]. We assumed that sufficient ammonium ions were present to neutralize the measured anions. Furthermore, we assumed that the initial aerosol OC was 60% water-soluble organic carbon (WSOC) and 40% insoluble OC, on the basis of Decesari et al. [2006]. Cellulobiose (CBIO) was used as a proxy for the initial WSOC, while long-chain alkanes (POA1) were used as a proxy for the insoluble OC.

[33] The background aerosol number concentration of 1000 cm$^{-3}$ matches the value reported by Hobbs et al. [2003]. $D_g$ (0.116 $\mu$m) for this mode is for remote continental aerosols [Seinfeld and Pandis, 1998], where $\sigma$ (2.0) has been increased to match the aerosol mass concentrations reported by Hobbs et al. [2003]. We represent the background aerosol OC with humic acid (CPD3).

5.3. Results and Comparison to Observations

[34] Figure 4a shows the modeled and observed CO concentrations for the Timbavati smoke plume. The solid black line shows the modeled CO concentration for the best fit value of $K_y$ (7,000 m$^2$ s$^{-1}$). There is significant variation in measured CO values about this best fit line. Figure 4b shows similar variability in the sum of the CO and CO$_2$ concentrations in the smoke plume. Following Trentmann et al. [2005], we accounted for this variability in plume dispersion by performing two additional models runs, one with a low (slow) $K_y$ of 2,500 m$^2$ s$^{-1}$ and one with a high (fast) $K_y$ of 15,000 m$^2$ s$^{-1}$.

[35] Figure 4c shows the modeled and measured O$_3$ concentration for the baseline model run using the three values of $K_y$ discussed above. Our model results for ozone are nearly identical to those of Trentmann et al. [2005] and Mason et al. [2006]. However, our baseline model underestimate the formation of O$_3$ within the smoke plume. In addition, the baseline chemistry model runs underestimate the concentration of OH.

[36] Figure 5 compares the observed and modeled aerosol mass concentrations at 47 min downwind from the fire source. The model runs here use the medium $K_y$ of 7000 m$^2$ s$^{-1}$. The baseline model run overestimates the concentration of potassium (K$^+$) downwind, as well as underestimating the ratios of nitrate, sulfate, and OC to potassium.
Given the poor match between the model simulations using the baseline chemistry and the available observations, we explored many hypotheses to attempt to improve this match. Below, we discuss several sensitivity tests performed on the model for the Timbavati smoke plume to address the overestimate of K$^+$, the underestimate of OC, the underestimate of O$_3$ and OH, and the underestimate of sulfate. We explore the sensitivity of the modeled aerosol mass concentrations to heterogeneous reactions of NO$_2$, SO$_2$, and CH$_3$OH. We then use these sensitivity tests to design an “expanded” chemistry case and explore the growth of aerosols, change in aerosol number concentration, and change in aerosol optical properties in this case.

5.3.1. Potassium Concentrations

In the observations reported by Hobbs et al. [2003], the ratio of excess K$^+$ to excess CO decreases with time, from a value of $21 \mu$g m$^{-3}$ K$^+$/ppmv CO at a distance of 1 km from the fire source to values of $6.9 \mu$g m$^{-3}$ K$^+$/ppmv CO at 5 km downwind and $3.6 \mu$g m$^{-3}$ K$^+$/ppmv CO at 26.2 km downwind. However, since the deposition of submicron particles and the chemical loss of CO are both small on the 1 h time scale considered here, both aerosol K$^+$ and gas-phase CO should be acting as conservative tracers, with a constant ratio between them as they move downwind.

It is possible that this discrepancy could be explained by different initial ratios of K$^+$ and CO being produced by the savannah fire. Hobbs et al. [2003] address this concern by pointing out that the fire was predominantly flaming and was consistently moving into fresh fuel, with modified combustion efficiency (MCE) values of 0.91–0.94 (except for one outlier of 0.88 in a nonaerosol sample). In addition, if the ratio of K$^+$ to CO was fluctuating randomly, the odds...
of a monotonically decreasing sequence would be 1 chance
in 6, which is not impossible, but certainly unlikely.

[40] Instead, we propose that the observed decrease in
the ratio is an artifact of the different sampling methods and
averaging times of the aerosol and CO measurements made
during the Timbavati fire. The canister sampling used to
measure CO in this case had an averaging (canister-filling)
time of approximately 30 s, while the “grab bag” techni-
ques used for the aerosol filter sampling had an averaging
(bag-filling) time of 7–12 s. Thus, near the source, the
canister measurements may have sampled a larger proportion
of background versus plume air than the aerosol mea-
surements, leading to an upward bias in the ratio of excess K+
to excess CO. As the plume expanded horizontally, this bias
decreased, explaining the monotonic decrease of the ratio.

[41] On the basis of this argument, we reduced the initial
aerosol mass concentrations in the model to better match the
observed downwind concentration of K+ while keeping the
generic mean diameter and the standard deviation of the
lognormal submicron mode constant. The rescaling reduced
the initial aerosol mass concentration by a factor of
3.4. This resulted in a lower total number concentration
(34,000 cm−3). To keep the initial aerosol number
concentration near the observed value of 100,000 cm−3, we
therefore added a second small-aerosol lognormal mode
with a number concentration of 66,000 cm−3, geometric
mean diameter of 0.02 μm, and geometric standard devia-
tion of 1.175. This mode, which starts in the smallest size
bin of the model, has the same composition as the submi-
cron mode, but its small size means it has a negligible
impact on the mass concentrations and optical properties of
the aerosol. It should be noted that our rescaled initial
aerosol model is only one of several hypothetical size
distributions that could fit the available measurements.
The rescaled distribution is merely our best estimate of the
size distribution in the absence of direct measurements.
The rescaled aerosol is used in all of the model runs discussed
below.

### 5.3.2. Organic Carbon Concentrations

[42] When the initial aerosol is rescaled to reflect the
downwind concentration of potassium, the baseline model
chemistry only predicts 14 μg/m3 of OC downwind, well
below the observed value of 34 μg/m3. This suggests that
the baseline model is missing a source of secondary
condensed organic matter. The laboratory study of Christian
et al. [2003] suggested that 30% of the carbon emitted as
gas-phase nonmethane organic compounds (NMOCs) is
unidentified by current techniques. If these species reacted
to form condensed organic carbon, they could explain the
observed formation of OC.

[43] To test this possibility, we included the uncharac-
terized compounds in our model. We estimated that 600 ppb
of carbon is uncharacterized in the initial emissions from the
Timbavati smoke plume. We used monoterpenes (BIOH in
the CACM scheme) as a proxy compound for these unchar-
acterized organic species, giving an initial concentration of
60 ppb BIOH, as monoterpenes have 10 carbons per
molecule. Note that we are not saying that the uncharac-
terized compounds are monoterpenes; we are merely using
the BIOH compound class in the model as a proxy for a
high molecular weight, reactive organic compound. The use
of the BIOH compound class likely provides an upper limit
to the formation of secondary OC from the uncharacterized
compounds.

[44] Including the uncharacterized compounds in the
chemical model as BIOH increased the secondary formation
of organic aerosol. Using the rescaled initial aerosol and
including the uncharacterized organic compounds, the
modeled concentration of organic carbon at 47 min down-
wind is 30.9 μg/m3, which is close to the observed value of
34 μg/m3.

### 5.3.3. O3 and OH Concentrations

[45] As seen in Figure 4c, our baseline model chemistry
underestimates the observed concentrations of ozone. We
examined two possible explanations: (1) that the oxidation
of oxygenated organic species not included in the baseline
model is responsible for the high observed O3 formation and
(2) that heterogeneous reactions taking place on the aerosol
particles are responsible for the high levels of O3 observed.

#### 5.3.3.1. Unidentified Oxygenates

[46] To test if unidentified oxygenated organics were
responsible for the high observed O3 formation, we ran
sensitivity tests where additional ketones (as KETL and
KETH in the CACM scheme), aldehydes (ALD2), alcohols
(ALCH), and furans were added to the initial concentra-
tions. As furan chemistry is not included in the CACM, we
designed an addition to the mechanism to include the
chemistry of furans. This mechanism is shown in Table 2,
where the additional classes introduced to CACM are
denoted FURAN, RP20, RO25 + RO24, RO26 + RO27,
RO28 + RO29, RO30 + RO31, RO32 + RO33, RO34 + RO35,
RO36 + RO37, and RO38 + RO39. The reaction rates for
FURAN are based on 2-methylfuran [Bierbach et al.,
1995], while those for RP20 are based on butenediol
[Bierbach et al., 1994]. The reaction data for the peroxy
radicals RO25 and RO26 are taken from the University
Table 3. Results of Ozone Sensitivity Tests

<table>
<thead>
<tr>
<th>O3 (ppb) at 60 min</th>
<th>Ks = 7000 m/s</th>
<th>Ks = 2500 m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference (with 60 ppb BIOH)</td>
<td>71.8</td>
<td>86.5</td>
</tr>
<tr>
<td>+30 ppb KETL</td>
<td>72.2 (+0.4)</td>
<td>87.1 (+0.6)</td>
</tr>
<tr>
<td>+30 ppb KETH</td>
<td>–</td>
<td>87.1 (+0.6)</td>
</tr>
<tr>
<td>+30 ppb ALD2</td>
<td>72.3 (+0.5)</td>
<td>87.3 (+0.8)</td>
</tr>
<tr>
<td>+30 ppb ALCH</td>
<td>–</td>
<td>89.1 (+2.6)</td>
</tr>
<tr>
<td>+Furan mechanism</td>
<td>–</td>
<td>90.7 (+4.2)</td>
</tr>
<tr>
<td>+CH3OH-NO2 Hetero. Rxn (Rate × 10)</td>
<td>76.1 (+4.3)</td>
<td>100.4 (+13.9)</td>
</tr>
<tr>
<td>+NO2→HONO+HNO3 = 10^-3</td>
<td>77.3 (+5.5)</td>
<td>99.5 (+13.0)</td>
</tr>
<tr>
<td>+NO2→HONO = 10^-3</td>
<td>82.6 (+10.8)</td>
<td>110.6 (+24.1)</td>
</tr>
<tr>
<td>OH fixed at 1.7 × 10^7 radicals/cm^3</td>
<td>109.4 (+37.6)</td>
<td>144.4 (+57.9)</td>
</tr>
<tr>
<td>Observations</td>
<td>60–135</td>
<td>60–135</td>
</tr>
</tbody>
</table>

of Leeds Master Chemical Mechanism, CACM, and Jenkin et al. [1997].

[47] Table 3 shows the change in the modeled ozone concentration at 60 min downwind when 30 ppb of KETL, KETH, ALD2, and ALCH are added, respectively, and when 18.426 ppb of FURAN is added using the above mechanism. The final ozone concentration at 60 min is fairly insensitive to the concentrations of these oxygenated compounds, and the changes observed are not large enough to explain the high concentrations of ozone observed in the Timbavati fire.

5.3.3.2. Heterogeneous Formation of HONO

[48] Our second hypothesis was that heterogeneous reactions taking place on the aerosol particles are responsible for the high levels of O3 observed. This was suggested by model runs we performed where we fixed the OH concentration in the model at the reported value of 1.7 × 10^7 radicals/cm^3 [Hobbs et al., 2003]. This dramatically increased the modeled concentration of O3 and greatly improved the match between the model and the observations, as shown in Table 3. This suggests that the baseline model chemistry is missing a source of OH.

[49] We explored the possibility that this missing source of OH came from heterogeneous production of HONO within the smoke plume. In this scheme, NO2 reacts on the surface of particles to produce HONO, which then photolyzes to produce OH and NO. Heterogeneous production of HONO has been reported to take place on humic acid aerosols [Stemmler et al., 2006, 2007], aqueous aerosols [Jacob, 2000], and soot aerosols [Nienow and Roberts, 2006]. We investigated two different reaction stoichiometries. The first (NO2 → HONO) was reported by Stemmler et al. [2006, 2007] for sunlight-activated humic acid aerosol surfaces with an uptake coefficient of 10^-5 - 10^-6. The second (NO2 → 0.5 HONO +0.5 HNO3) has been reported by many investigators to take place on aqueous aerosols. The review of Jacob [2000] reports uptake coefficients ranging from 10^-3 - 10^-6, and recommends a value of 10^-3 for this reaction.

[50] A third possibility for heterogeneous chemistry was proposed by Trentmann et al. [2005]. They found that including the reaction of methanol and NO2 (CH3OH + 2 NO2 → HO2 + HCHO + HNO3 + NO) in their model increased the ozone formation in the Timbavati smoke plume when they increased the reaction rate to 10 times the value originally reported by Tabazedeh et al. [2004] for this reaction on cloud droplets.

[51] Figure 6 shows the ozone concentration predicted when the above three heterogeneous reactions are included. In the model run, an uptake coefficient of 10^-3 is used for both NO2 reactions. We found that uptake coefficients lower than this value resulted in negligible changes to O3 and OH concentrations. In addition, the rate of the methanol reaction has been increased by a factor of 10 as in the work by Trentmann et al. [2005]. All runs were performed at the slow horizontal diffusion rate (Ks = 2500 m^2/s) to minimize O3 dilution, and include the uncharacterized organic compounds as monoterpenes. The impact of these reactions is also shown in Table 3. With these high uptake coefficients, these three reactions each do an equally good job of explaining the formation of O3 in the Timbavati smoke plume, but still underestimate the highest values of ozone observed.

[52] Of these three added reactions, including the reaction NO2 → HONO provides the best match to the reported OH concentration (not shown), while including NO2 → 0.5 HONO +0.5 HNO3 provides the best match to the observed aerosol nitrate concentration (see Figure 8). Furthermore, the uptake coefficient of 10^-3 used above is within the range of reported values for the reaction NO2 → 0.5 HONO +0.5 HNO3 on aqueous aerosols, but is outside the range reported for the reaction NO2 → HONO on humic acid aerosols. Thus, of the three heterogeneous reactions considered here, the reaction NO2 → 0.5 HONO +0.5 HNO3 with an uptake coefficient of 10^-3 is the most consistent with the available observations for the Timbavati fire.

Figure 6. Ozone formation predicted when different heterogeneous reactions are included. The uptake coefficients are 10^-3 for both NO2 reactions, and the rate of the methanol reaction has been increased by a factor of 10. All runs include the uncharacterized organic compounds as monoterpenes (BIOH) and were performed using the slow dilution rate (Ks = 2500 m^2/s). Results for the reaction NO2 → 0.5 HONO +0.5 HNO3 using the baseline and fast dilution rates are shown in Figure 7a.
burning aerosols deserves further laboratory and field investigation.

[54] We have also examined how the reaction $\text{NO}_2 \rightarrow 0.5 \text{HONO} + 0.5 \text{HNO}_3$ changes the results for the Otavi and Alaska smoke plumes discussed earlier. For the Otavi fire, we are able to use measurements of the total aerosol number concentration in the plume to estimate the impact of the heterogeneous production of HONO on ozone formation. We find that the impact of the heterogeneous chemistry is negligible in the Otavi smoke plume, as the initial $\text{NO}_2$ concentrations are a factor of 10 lower in Otavi than in Timbavati and the initial total aerosol number concentration is a factor of 3 lower. For Alaska, no measurements of total aerosol number concentration are available, so we cannot perform a model run to evaluate this case. However, the initial $\text{NO}_2$ concentration for the Alaska smoke plume is comparable to Timbavati, suggesting that this heterogeneous chemistry could also boost the modeled ozone formation in the Alaska plume by 10–20 ppb. As can be seen in Figure 3b, the increase in ozone could help match the highest downwind $\text{O}_3$ observation, which is not explained by the baseline chemistry model. The increased loss of gaseous $\text{NO}_2$ due to the heterogeneous reactions would also provide a better match with observations of NO and $\text{NO}_2$ for the Alaska fire (Figures 3d and 3e). Thus, the proposed heterogeneous reaction is consistent with the observations of all three smoke plumes considered here.

[55] On the basis of the above results, we added the heterogeneous reaction $\text{NO}_2 \rightarrow 0.5 \text{HONO} + 0.5 \text{HNO}_3$ to our model runs, using an uptake coefficient of $10^{-3}$ and included the uncharacterized compounds as $\text{BIOH}$, as discussed in section 5.3.2. We next examine how the model including this expanded chemistry compares with the gas-phase composition measurements made in the Timbavati smoke plume.

[56] Figure 7a shows the modeled and measured ozone concentrations for this expanded chemistry case. The addition of heterogeneous formation of HONO has increased the modeled $\text{O}_3$ concentrations above the baseline runs. However, the expanded chemistry case still has difficulty matching the two highest ozone observations for the Timbavati smoke plume. In addition, this model run gives lower ozone concentrations downwind that the sensitivity study of Trentmann et al. [2005] using the heterogeneous reaction of $\text{CH}_3\text{OH}$ and $\text{NO}_2$ (77 ppb versus 85 ppb for the middle dilution case).

[57] Figures 7b and 7c compare the modeled NO and $\text{NO}_2$ concentrations, respectively, for the expanded chemistry case to the available airborne FTIR measurements in the Timbavati plume. The high detection limits of 20 ppb mean that all three horizontal diffusion rates modeled are consistent with the available downwind observations of $\text{NO}_2$, which are generally below the detection limit. Our results for $\text{NO}_2$ are similar to the sensitivity study of Trentmann et al. [2005].

[58] Figure 7d shows that the modeled HONO concentration in the expanded case stays between 0.5 ppb and 6 ppb over the hour simulated here. These HONO concentrations are well below the detection limit for HONO by AFTIR (~20 ppb [R. Yokelson, personal communication, 2006]) and thus the available AFTIR measurements cannot be used to rule in or rule out the possibility of heterogeneous HONO formation. Figure 7e shows that the OH concentrations in the expanded chemistry model cases show a maximum of $8 \times 10^6$ radicals/cm$^3$, which is about half of the reported value of $1.7 \times 10^7$ radicals/cm$^3$.

[59] Figures 7f–7i compare the modeled concentrations of $\text{CH}_3\text{OH}$, ETHE, HCHO, and ACID, respectively, for the expanded chemistry case to the available observations. The observations of ACID in Figure 7i represent the sum of the observations of formic and acetic acid. The model is consistent with the available $\text{CH}_3\text{OH}$ observations, but underestimates some of the observed concentrations of ETHE, HCHO, and ACID downwind.

5.3.4. Sulfate Concentrations

[60] Gas-phase formation of sulfate is included in the baseline model chemistry, but produces a sulfate concentration at 47 min downwind of only 3.1 $\mu$g/m$^3$, which is much lower than the observed value of 8.1 $\mu$g/m$^3$. In addition, the downwind $\text{SO}_2$ concentration (not shown) is overestimated relative to the observations. We examined three possible explanations for these discrepancies: (1) uncertainty in the gas-phase formation rate of sulfate, (2) aqueous oxidation of sulfate taking place within the plume aerosol particles, and (3) heterogeneous oxidation of $\text{SO}_2$ on aerosol surfaces.

5.3.4.1. Uncertainty in the Gas-Phase Formation Rate

[61] The IUPAC kinetic data evaluation for the gas-phase formation of $\text{SO}_2$ (http://www.iupac-kinetic.ch.cam.ac.uk) states this reaction rate is uncertain by a factor of 2. Doubling the reaction rate increases the predicted sulfate concentration at 47 min downwind from 3.1 $\mu$g/m$^3$ to 4.2 $\mu$g/m$^3$, which is still about a factor of 2 lower than the observed value of 8.1 $\mu$g/m$^3$. We also explored whether the low formation rate of sulfate could be explained by the model underpredicting the OH concentration within the plume. Fixing the OH concentration to the average value of $1.7 \times 10^7$ radicals/cm$^3$ reported by Hobbs et al. [2003] increased the predicted sulfate concentration at 47 min downwind from 3.1 $\mu$g/m$^3$ to 5.0 $\mu$g/m$^3$. Thus, an improved model prediction of OH would still not be sufficient to explain the observed secondary sulfate formation.

5.3.4.2. Aqueous Chemistry of $\text{SO}_2$

[62] One possible explanation for the underestimate of secondary sulfate formation is aqueous chemistry taking place on the surface of the particles. However, the low relative humidities observed in the Timbavati plume make this unlikely, as less than 19 $\mu$g/m$^3$ of condensed water was present in the smoke plume in the model simulations. This low level of condensed water results in aqueous sulfate formation rates that are several orders of magnitude smaller than the gas-phase formation rate. Thus, aqueous conversion of $\text{SO}_2$ to sulfate within the plume was likely negligible compared to gas-phase chemistry, and cannot explain the rapid formation of sulfate observed in the Timbavati fire.

5.3.4.3. Heterogeneous Chemistry of $\text{SO}_2$

[63] With gas-phase formation of sulfate too slow and aqueous-phase formation even slower, it is still unclear what caused the rapid secondary formation of sulfate in the Timbavati smoke plume. Buzcu et al. [2006] had similar problems explaining the rapid formation of secondary sulfate they observed in a wood smoke pollution event over Texas. After ruling out gas-phase and aqueous-phase chemistry, they proposed a heterogeneous reaction where
Figure 7. Modeled and measured concentrations in the Timbavati smoke plume (expanded chemistry case) of (a) \(O_3\), (b) NO, (c) \(NO_2\), (d) HONO, (e) OH, (f) \(CH_3OH\), (g) \(C_2H_4\) (ETH), (h) HCHO, and (i) \(HC(O)OH\) plus \(CH_3C(O)OH\) (ACID). Model runs include the heterogeneous reaction \(NO_2 \rightarrow 0.5\ HONO + 0.5\ HNO_3\ \(\gamma_{NO_2} = 10^{-5}\) and include the uncharacterized compounds as monoterpenes (BIOH).
SO₂ is oxidized on the surface rather than the interior of the particles to form sulfate:

\[ \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \]  

They found a good match between their model and observations when they assumed that the uptake coefficient for this reaction was \(10^{-2}\). The possibility of heterogeneous chemistry of SO₂ is also consistent with the results of Lammel and Leip [2005], who found that the observed rate of sulfate formation in the cloud-free (but aerosol containing) Berlin urban plume was much faster than could be explained by gas-phase chemistry alone.

Using the same procedure as Buzcu et al. [2006], we found that including reaction (R1) with an uptake coefficient of \(2 \times 10^{-4}\) increased the predicted sulfate concentration at 47 min downwind from 3.1 \(\mu\)g/m³ to 6.9 \(\mu\)g/m³, which is much closer to the observed value of 8.1 \(\mu\)g/m³. The uptake coefficient of \(10^{-2}\) reported by Buzcu et al. [2006] gave a sulfate mass concentration at 47 min of 68.9 \(\mu\)g/m³, much higher than the observed value. The value of \(2 \times 10^{-4}\) was chosen because it gave the best match with the observed sulfate concentration without reducing the modeled nitrate concentration well below the observed value.

While there is little data for SO₂ uptake on biomass burning aerosols, the heterogeneous chemistry of SO₂ on soot aerosols has been studied by many investigators. Reported values for the uptake coefficient on soot vary over several orders of magnitude from \(3 \times 10^{-5}\) to \(10^{-8}\) [Britton and Clarke, 1980]. On the basis of these prior studies and our model results, we conclude that heterogeneous chemistry of SO₂ is a more likely explanation for the observed high rate of sulfate formation than aqueous chemistry or the uncertainty in gas-phase chemistry. Thus, the uptake coefficient of SO₂ on biomass burning smoke aerosol deserves further laboratory investigation.

### 5.3.5. Aerosol Mass Concentrations

Figure 8 shows the observed and modeled aerosol mass concentrations at 47 min downwind for the Timbavati smoke plume. These model runs all use the rescaled initial aerosol, include the uncharacterized organic compounds as BIOH, and use the medium horizontal diffusion value of 7000 m²/s. The model runs differ in the heterogeneous chemistry that they include. The rescaled initial aerosol improves the match between the modeled and measured potassium (K⁺) concentrations. Including the uncharacterized compounds as BIOH improves the match between the modeled and measured OC concentrations. The model, which treats BC as a conservative tracer, consistently underpredicts the measured concentration of BC. However, it is possible that some of the secondary organic carbon also absorbs in the visible spectrum, and may therefore lead to an overestimate of BC concentration in the measurements [Andreae and Gelencser, 2006].

**Timbavati Normalized Size Distributions**

Figure 9. Normalized aerosol size distributions for the Timbavati case. Number concentrations have been normalized to remove the effect of dilution (\(K_y = 7000\) m²/s). Model runs include the heterogeneous reaction \(\text{NO}_2 \rightarrow 0.5 \text{HONO} + 0.5 \text{HNO}_3 (\gamma_{\text{NO}_2} = 10^{-3})\), the heterogeneous reaction \(\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 (\gamma_{\text{SO}_2} = 10^{-3})\), and the uncharacterized compounds as monoterpenes (BIOH).
with an uptake coefficient of 2 and 10. Figure 8) with an uptake coefficient of 10 gives the best match to the observed aerosol sulfate concentration, while the run that includes \( \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \) (green in Figure 8) with an uptake coefficient of \( 2 \times 10^{-4} \) gives the best match to the observed aerosol sulfate concentration. However, this (green) run underpredicts the concentration of aerosol chloride relative to the observations. This suggests that our aerosol chemical model may not be capturing the correct partitioning between the gas and aerosol phase for these inorganic species. Unfortunately, since the measurements of the Timbavati smoke plume did not include gas-phase measurements of HCl and HNO\(_3\), we cannot use those measurements to evaluate the partitioning calculated by our thermodynamic model. We suggest that future work should try to measure the relevant ammonium, nitrate and chloride species in both the gas and aerosol phase simultaneously.

5.3.6. Aerosol Growth and Dilution

Figure 9 shows the normalized aerosol size distributions at the beginning of the model run and at 47 min downwind for two cases: one where coagulation is included in the model (blue dashed line) and one where it is not (red dotted line). These number concentrations are normalized to the concentration of a hypothetical conservative tracer to remove the effects of plume dilution. We can see that condensational growth, due to the secondary formation of sulfate, nitrate, and condensable organic carbon, dominates the growth of the aerosol size distribution, with coagulation having only a minor impact.

Figure 10 shows the total aerosol number concentration measured in the Timbavati smoke plume as the plane flew along the length of the plume at a different time. Our model simulates the decrease of the aerosol number concentration in the first 10 min after emission fairly well. This decrease is primarily due to plume dilution in our model runs, with coagulation having only a minor effect. This is in contrast to the discussion of Hobbs et al. [2003] which attributed the initial decrease to coagulation of the highly concentrated particles. One possible explanation for the discrepancy is that Hobbs et al. [2003] attempted to account for plume dilution by interpolating canister measurements of CO taken during transects of the plume. These observations are not necessarily comparable with the number concentration data, which were measured continuously as the plane flew along the length of the plume at a different time. Our procedure, which uses both canister and airborne FTIR measurements of CO to calculate a range of horizontal diffusion rates, may better represent the effects of plume dilution on the total aerosol number concentration.

We find that our model does not match the observed increase in total aerosol number concentration seen in Figure 10 beyond 10 min downwind. Hobbs et al. [2003] suggested that this increase could be due to the production of new particles by gas-to-particle conversion (nucleation). To evaluate whether nucleation could account for the increase in total aerosol number concentration observed in the Timbavati smoke plume, we performed a scale analysis of the nucleation of new particles by sulfuric acid and condensable organic vapors. We used the parameterized nucleation scheme of Fan et al. [2006], which accounts for the enhanced nucleation effect of secondary condensable organics. This scheme generally gives a higher nucleation rate than the binary \( \text{H}_2\text{SO}_4\)-H\(_2\)O parametrization of Kulmala et al. [1998]. Over 1 h, this nucleation scheme would increase the modeled number concentration by only 500 particles/cm\(^3\), which is not enough to explain the high number concentration of particles observed downwind of the Timbavati fire.

5.3.7. Aerosol Optical Properties

The optical properties of the smoke aerosol change significantly with time [Reid et al., 2005a]. Table 4 shows the modeled optical properties at a wavelength of 550 nm for both the initial smoke aerosol and for the smoke aerosol aged for 1 h within the smoke plume. The model values are compared with the range of reported values for fresh and
aged savannah fire smoke, respectively. The model values for the single scattering albedo \(\omega_{\text{aero}}\) fall within the ranges for fresh and aged savannah fire smoke reported by Reid et al. [2005a]. The increase of the single scattering albedo with aging in our model is caused by the growth of the smoke aerosol due to the condensation of secondary organic carbon, sulfate, and nitrate onto the particles. Other processes not included in our model could also influence the single scattering albedo of smoke particles, such as the change of black carbon particles from a fractal to a coated sphere shape, or a change in the mixing state of the smoke particles. The model value for the asymmetry parameter \(g_{\text{aero}}\) for fresh smoke is slightly higher than the reported range, but the model value for the aged smoke agrees well with the range reported by Reid et al. [2005a].

[73] Our calculated aerosol mass scattering efficiency \(\alpha_s\) (m\(^2\)/g) at 550 nm was 2.77 m\(^2\)/g for the fresh smoke, which is below the range of 3.6 ± 0.4 m\(^2\)/g recommended by Reid et al. [2005a] for fresh grassland and savannah smoke, but within the range recommended by IPCC [2001] for fresh smoke (3.6 ± 1.0 m\(^2\)/g). Reid et al. [2005a] also note that typical values for fresh smoke can vary between 2.8 to 4.2 m\(^2\)/g, putting our value at the bottom of that range. For the aged smoke, our modeled \(\alpha_s\) of 2.35 m\(^2\)/g is also below the ranges given by Reid et al. [2005a] and IPCC [2001] for aged smoke, although it matches the IPCC [2001] range better. Furthermore, we see a decrease in \(\alpha_s\) with time, while the review of Reid et al. [2005a] suggests that this parameter increases with time.

[74] Our calculated aerosol mass absorption efficiency \(\alpha_a\) (m\(^2\)/g) of 0.429 m\(^2\)/g for fresh smoke is slightly lower than the range of 0.8 ± 0.3 m\(^2\)/g recommended by Reid et al. [2005a] for fresh grassland and savannah smoke, but is within the range recommended by the IPCC [2001] (0.54 ± 0.2 m\(^2\)/g). For the aged smoke, our model value of \(\alpha_a\) is 0.255 m\(^2\)/g, which is near the bottom of the range reported by the IPCC [2001] and just below the range reported by Reid et al. [2005a]. It should be noted that since the production of black carbon is closely related to the combustion efficiency of the fire, fires of different combustion efficiencies can produce aerosols with very different mass absorption efficiencies, which may explain the low values computed here for the Timbavati fire.

[75] To see if our model was correctly representing the scattering of radiation due to the smoke aerosols, we compared the model calculated values for the aerosol scattering coefficient \(k_s\) (m\(^-1\)) with the nephelometer measurements made during transects of the Timbavati smoke plume. The nephelometer-measured \(k_s\) within the Timbavati smoke plume varied across the plume, but the maximum values reported were about 2.2 \(\times\)10\(^{-3}\) m\(^{-1}\) near the fire source and 4.0 \(\times\)10\(^{-3}\) m\(^{-1}\) at 26.2 km downwind from the source. Our model gives a (plume average) initial \(k_s\) value of 7.0 \(\times\)10\(^{-3}\) m\(^{-1}\) and a value of 2.1 \(\times\)10\(^{-3}\) m\(^{-1}\) at 47 min downwind (26.2 km), roughly in agreement with the observations.

**Table 4. Aerosol Optical Properties for the Timbavati Fire**

<table>
<thead>
<tr>
<th>Parameter at (550 nm)</th>
<th>Fresh Smoke</th>
<th>Aged Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model (^a)</td>
<td>Reported Range</td>
</tr>
<tr>
<td>Single scattering albedo (\omega_{\text{aero}})</td>
<td>0.866</td>
<td>0.82 ± 0.05 (^b)</td>
</tr>
<tr>
<td>Asymmetry parameter (g_{\text{aero}})</td>
<td>0.654</td>
<td>0.55 ± 0.06 (^b)</td>
</tr>
<tr>
<td>Mass scattering efficiency (\alpha_s) (m(^2)/g)</td>
<td>2.77</td>
<td>3.6 ± 0.4 (^c)</td>
</tr>
<tr>
<td>Mass absorption efficiency (\alpha_a) (m(^2)/g)</td>
<td>0.429</td>
<td>0.8 ± 0.3 (^c)</td>
</tr>
<tr>
<td>Humidification factor (\text{f}(\text{RH}))</td>
<td>2.88</td>
<td>1.70–1.79 (^d)</td>
</tr>
</tbody>
</table>

\(^a\)These runs use the rescaled initial aerosol concentrations and include the uncharacterized compounds as BIOH, the heterogeneous reaction NO\(_2\) + HNO\(_2\) \(\rightarrow\) HONO + 0.5 HNO\(_3\) \(\gamma_{\text{HONO}} = 10^{-3}\), and the heterogeneous reaction SO\(_2\) → H\(_2\)SO\(_4\) \(\gamma_{\text{SO}_2} = 2 \times 10^{-3}\). Aged smoke is at 1 h after emission.

\(^b\)Range reported for grassland and savannah smoke by Reid et al. [2005a].

\(^c\)Range recommended for biomass burning smoke by IPCC [2001].

\(^d\)Measurements made for Timbavati smoke plume by Magi and Hobbs [2003].

Figure 11. Humidographs for the Timbavati (a) fresh smoke and (b) aged smoke. The dashed red line is the observed change in the relative scattering coefficient versus as measured by Magi and Hobbs [2003]. The black line is the model result.
The humidification factor \( f(RH) \) represents the relative increase in aerosol scattering as the relative humidity is increased from 30% to 80%. The reported values of \( f(RH) \) given in Table 4 are from the measurements made by Magi and Hobbs [2003] in the Timbavati smoke plume. Our value of \( f(RH) \) for fresh Timbavati smoke of 2.88 is much higher than the values of 1.70 and 1.79 reported by Magi and Hobbs [2003]. Figure 11a compares our model results for the relative scattering increase over the RH range of 30–80% with the measurements of Magi and Hobbs [2003] for the fresh smoke. We can see that the model and measurements agree well up to a relative humidity of 66%, at which point the model aerosol takes on much more water than the measurements would suggest. Below 66%, the aerosol water uptake is primarily due to the water soluble OC. The large increase in water content for the model aerosol comes from the deliquescence of aerosol NH\(_4\)Cl. Since all of the model runs considered here take place at a relative humidity of less than 50%, the agreement between model and observation is adequate for our purpose. However, this unrealistic result for the humidification factor of fresh smoke shows that further work is necessary to determine how to more correctly model the water uptake by fresh biomass burning aerosols at higher relative humidities.

Figure 11b compares our model results for the aged smoke for the relative scattering increase over the relative humidity range of 30–80% with the relevant measurements of Magi and Hobbs [2003]. Both the model and the measurements show that \( f(RH) \) decreases as the smoke ages, and neither shows a sharp deliquescence point below 80% RH. The model agrees with the measurements up to a relative humidity of 50%, at which point the aged model aerosol takes up less water than is suggested by the measurements. This suggests that the organic surrogates used to represent aerosol organic carbon are not reflecting the water uptake properties of the true aged organic aerosol mixture.

The modeled optical properties are sensitive to changes in the real refractive index assumed for OC. Increasing the real refractive index of OC to 1.65 from our reference value of 1.45 increases the mass scattering efficiency and scattering coefficient by 32% to 3.66 m\(^2\)/g, increases the aerosol mass absorption efficiency by 11% to 0.477 m\(^6\)/g, reduces the asymmetry parameter by 4.5% to 0.625, and increases the single scattering albedo by 2.2% to 0.885. Increasing the real refractive index for OC would be consistent with the experimental work of Hungershofer et al. [2007], who reported a mean effective complex refractive index for smoke particles emitted from the combustion of savanna grass as 1.60 + 10\(^{-4}\)i. The increase improves the match with the reported values for mass scattering efficiency and asymmetry parameter for fresh and aged savannah and grassland smoke, but increases the single scattering albedo to values slightly above the reported range.

### 6. Conclusions

We have combined our gas and aerosol phase chemical model ASP with a Lagrangian parcel model to simulate the aging of smoke in three young smoke plumes from biomass burning. For the Otavi and Alaska smoke plumes, for which gas measurements only were available, we simulated the gas phase chemistry alone, but discussed the implications of including heterogeneous chemistry. For the Timbavati smoke plume, for which both gas and aerosol measurements were available, we simulated both the gas- and aerosol-phase chemistry simultaneously and interactively.

We found that our baseline model can explain the formation of ozone in the Otavi and Alaska plumes fairly well, but has difficulty explaining the concentration of ozone and growth of aerosols observed in the Timbavati smoke plume. We investigated several hypotheses to explain the overestimate of K\(^+\), and the underestimates of OC, O\(_3\), OH, gas-phase organic acids, sulfate, and nitrate in the baseline model simulation for Timbavati.

We found that the overestimate of potassium downwind in the baseline model simulation was most likely related to an overestimate of the initial aerosol concentration caused by the differing averaging (bag or canister filling) times of the aerosol bag and gas canister measurements. We rescaled our initial aerosol mass concentrations to match the downwind observations of K\(^+\) and added a second small mode to keep the initial aerosol number concentration near the observed value.

We found that the 30% of gas-phase carbon that is currently uncharacterized in canister measurements of smoke plumes may be a source of aerosol organic carbon. Including these compounds in the model (using the proxy compound BIOH in CACM) greatly improves the match between the model and the observations for aerosol OC.

Fixing the model OH concentration at the reported value for the Timbavati smoke plume greatly improved the model’s match with the observed concentration of ozone. This suggests that the model may be missing a source of OH. We found that a heterogeneous reaction of NO\(_2\) to make HONO could be the missing OH source if the uptake coefficient on smoke aerosols is large [O(10\(^{-3}\)] for spherical particles, and significantly lower values for highly fractal particles. This chemistry appears consistent with the observations of all of the three smoke plumes considered in this paper. Adding additional oxygenated compounds to the model simulation did not significantly increase the ozone formation.

We found that heterogeneous reactions of NO\(_2\) and SO\(_2\) could explain the rapid formation of nitrate and sulfate if the uptake coefficient on smoke aerosols is large [O(10\(^{-3}\)] and O(10\(^{-4}\)) respectively). Our scale analysis suggests that the aqueous formation of sulfate was negligible in the dry conditions of the Timbavati smoke plume.

We found that the changes in the aerosol size distribution are dominated by plume dilution and condensational growth. In our model, the reduction of aerosol number concentration observed in the first 10–15 min downwind of the Timbavati fire is caused by plume dilution, not by coagulation as suggested by Hobbs et al. [2003]. Our scale analysis suggests that nucleation was negligible in the Timbavati smoke plume. The growth in aerosol number concentration observed after 15 min downwind may have been caused by small particles (<3 nm in diameter) growing into the detectable size range of the condensation particle counter, or by a sampling artifact caused by the plane moving closer to the high concentration plume centerline.

The model calculations agree with the reported values of aerosol single scattering albedo and asymmetry.
factor, but underestimate the aerosol mass scattering efficiency. The model also has difficulty matching the observed aerosol humification factors. The mass scattering efficiency is sensitive to the value of the real refractive index for organic carbon. Increasing the real refractive index from 1.45 to 1.65 improves the match between modeled and reported values for mass scattering efficiency, but results in an overestimate of the aerosol single scattering albedo.

Our results suggest several directions for future field campaigns. Understanding the sources and sinks of OH in the smoke plumes is critical to understanding the formation of ozone in these smoke plumes, and so direct measurements of OH concentrations in the smoke plumes are needed. Better characterization of the nonmethane organic compounds (NMOCs) emitted by biomass burning are needed as our results suggest the uncharacterized portion of these gases is responsible for the formation of aerosol organic carbon within the young smoke plumes. Measurements of the evolution of the aerosol size distribution in young smoke plumes are needed to constrain models of smoke aerosol growth, nucleation and coagulation. Simultaneous measurements of these parameters in multiple smoke plumes would greatly advance our knowledge of smoke plume chemistry.

Appendix A

A1. Overview of the Aerosol Simulation Program

A1.1. Gas-Phase Chemistry

The gas-phase chemistry in the model is based on the Caltech Atmospheric Chemistry Mechanism (CACM) of Griffin et al. [2002, 2005]. CACM was modified in this work to (1) integrate all radical species rather than assuming steady state, (2) fit the reaction rates calculated by the group contribution method of Kwok and Atkinson [1995] to an Arrhenius temperature dependence, and (3) explicitly calculate heterogeneous reaction rates on the basis of the aerosol surface area concentration using the method of Jacob [2000].

A1.2. Aerosol Size Distribution

Aerosols are represented in the model as a moving center sectional size distribution, based on the work of Jacobson [1997, 2002, 2005]. In this representation, size bin boundaries remain fixed while the particle size within the bin is allowed to change with time. When the particle size reaches the bin boundary, all of the particle mass and number concentration is moved to the adjacent bin. We use a single size distribution, implicitly assuming that the particles in each size bin are internally mixed.

Each particle is assumed to consist of an aqueous embryo and an insoluble sphere, following the method of Gorbunov and Hamilton [1997]. We assume that the aqueous embryo consists of water, inorganic ions, aqueous NH$_3$, and aqueous organic species. The insoluble core is assumed to include any aerosol black carbon (BC), hydrophobic organics, and solid electrolytes present.

A1.3. Aerosol Thermodynamics and Mass Transfer

ASP uses the Mass Flux Iteration (MFI) method of Jacobson [2005] to calculate the equilibrium concentrations of gas and aerosol species. The inorganic thermodynamics routines in ASP are based on those of MELAM [Stegelmeyer, 2004], but have been expanded to include the ions Ca$^{2+}$, Mg$^{2+}$, and their salts, and to predict the formation of solid salts at low relative humidities. The thermodynamics routines for organic species in the aqueous and hydrophobic organic phases are based on the Model to Predict the Multiphase Partitioning of Organics (MPMPO) of Griffin et al. [2003, 2005] and Pun et al. [2002]. We assume that an aqueous phase and a mixed hydrophobic organic phase are always present in the aerosol. Partitioning of organics between the gas and hydrophobic phase is governed by Raoult’s law, while partitioning of organics into the aqueous phase is governed by Henry’s law. Following Pun et al. [2002], we assume that (1) there is no interaction between the aqueous phase inorganic ions and the aqueous phase organics and (2) the activity coefficients of the organic ions (formed by the dissociation of organic acids) are equivalent to those of the corresponding molecular solute. We further assume that the pH of the aqueous phase is dominated by the strong inorganic acids and bases, and that the pH effects of the dissociating organic acids are negligible. We have expanded on the MPMPO model by allowing all organic species, including surrogates of primary organic aerosol (POA), to partition into the gas, aqueous, and hydrophobic organic phases, and by adding 5 surrogate compounds recommended by Dececeri et al. [2006] to represent water soluble organic carbon (WSOC) in regions affected by biomass burning. We have also developed a hybrid mass transfer scheme, where the flux-limited kinetic equations governing the condensation/evaporation of H$_2$SO$_4$ and organic species are integrated, and NH$_3$, HNO$_3$, and HCl are assumed to be in equilibrium between the gas and aerosol phases. Scale analysis suggests that this equilibrium assumption is valid within the concentrated environment of the smoke plume.

A1.4. Aerosol Coagulation

The coagulation of aerosol is calculated using the semi-implicit scheme of Jacobson [2005]. The model includes the convectively enhanced Brownian coagulation kernel and the gravitational collection coagulation kernel; possible enhancement of coagulation by van der Waals’ forces are not included.

A1.5. Aerosol Optical Properties

To calculate the optical properties of the aerosol we assume that the particle consists of a spherical core of BC surrounded by a reflective spherical shell containing the rest of the particle mass. Reid et al. [2005a] report that the assumption of spherical particles for the calculation of optical properties is generally justifiable for biomass burning smoke particles. The refractive index of the solution of water and inorganic ions at 550 nm is calculated using the method of Tang [1997] and Tang et al. [1997]. The refractive index used for organic compounds at 550 nm is 1.45 + 0.001i, for sulfate salts is 1.52 + 0.0005i (the value for (NH$_4$)$_2$SO$_4$), and for chloride salts is 1.45 + 0.0015i (the value for NaCl) [Jacobson, 2005]. The average refractive index of the shell is calculated using the volume average.
dielectric constant mixing rule [Jacobson, 2005]. The core-in-shell Mie calculation is performed using the publicly available program DMI Lay, which is based on the work of Toon and Ackerman [1981].

A2. Lagrangian Parcel Model

[95] We assume a Lagrangian parcel of fixed vertical extent ($H$) and down-trajectory length ($L$), but variable cross-trajectory width ($y(t)$) [Mason et al., 2001]. The temperature and pressure of the parcel are assumed to be constant. The full continuity equations for the Lagrangian parcel model are

$$
\frac{dC_q}{dt} = -\frac{4K_y}{y_v^2 + 8Ky_v} (C_q - C_q^i) + \frac{v_d}{H} C_q
+ \left(\frac{dc_{q,i}}{dt}\right)_{\text{cond}} + \left(\frac{dc_{q,i}}{dt}\right)_{\text{chem}}
$$

(A1)

$$
\frac{dn_i}{dt} = -\frac{4K_y}{y_v^2 + 8Ky_v} (n_i - n_i^i) + \frac{v_d}{H} n_i
+ \left(\frac{dn_i}{dt}\right)_{\text{cond}} + \left(\frac{dn_i}{dt}\right)_{\text{coag}}
$$

(A2)

$$
\frac{dc_{q,i}}{dt} = -\frac{4K_y}{y_v^2 + 8Ky_v} (c_{q,i} - c_{q,i}^i) - \frac{v_d}{H} c_{q,i}
+ \left(\frac{dc_{q,i}}{dt}\right)_{\text{cond}} + \left(\frac{dc_{q,i}}{dt}\right)_{\text{coag}} + \left(\frac{dc_{q,i}}{dt}\right)_{\text{chem}}
$$

(A3)

where $C_q$ is the concentration of gas-phase species (molecules/cm$^3$ air), $n_i$ is the number concentration of particles in size bin $i$ (particles/cm$^3$ air), $c_{q,i}$ is the concentration of aerosol species $q$ in size bin $i$ (mol/cm$^3$ air), $y_v$ is the initial plume width and $K_y$ represents the horizontal diffusivity of the atmosphere. The superscript $i$ indicates the concentration of the given species in the atmosphere outside of the parcel.

[96] The first term on the right-hand side of each continuity equation represents the effect of plume dispersion on the concentrations. The second term is the effect of deposition on the concentrations, where $v_d$ is the deposition velocity (cm/s). We set the deposition velocity equal to 0 for gas-phase species and use the terminal velocity of the aerosol particles as the deposition velocity for aerosol species. The remaining terms represent the change in gas and particle-phase concentrations due to mass transfer between the gas and aerosol phases (cond), coagulation of particles (coag), and irreversible and reversible chemistry (chem), calculated using the ASP model as described above. The integration of the different terms of the continuity equations is operator split for computational efficiency, with the time step for gas-phase chemistry, plume dispersion, and deposition set at 1 s, the time step for mass transfer and aerosol equilibrium set at 20 s, and the time step for coagulation set at 60 s (see Figure 1).

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