Supporting Information

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SI Text

Box Model Simulations. A box model was used to simulate chemistry in the Atlanta atmosphere. The concentration of species i was described using the equation

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot (uc_i) + Q_{\mathrm{chem},i} + Q_{\mathrm{aerosol},i} + Q_{\mathrm{depos},i} + E_i, \quad \textbf{[S1]}$$

where c_i is the concentration of species i, u is the air mass velocity, $Q_{\mathrm{chem},i}$ is the rate change of species i in the gas phase, $Q_{\mathrm{aerosol},i}$ is the rate change of species i in the aerosol phase, $Q_{\mathrm{depos},i}$ is the loss rate of i due to deposition, and E_i is the emission rate of i.

The size of the modeling region was set to 36 × 36 km (1,296 km^2) with a 600-m boundary layer height. It was assumed that the air mass entering Atlanta contained background levels of pollutant concentrations (1). Boundary conditions for biogenic species were obtained from Riemer et al. (2). These concentrations were incorporated in the model as Dirichlet boundary conditions (3). The dry deposition mechanism was adapted from the California Institute of Technology (CIT) model (4) and was incorporated in the modeling region as a bottom boundary condition. Rates of dry deposition were calculated assuming that the entire Atlanta area is a "mixed urban environment" with residential, commercial, and industrial structures. The top of the modeling region incorporated a no-flux boundary condition.

Meteorological conditions for Atlanta for the period from July 27 to July 31, 2010 were obtained from the National Oceanic and Atmospheric Administration's National Weather Service. Information included temperature, relative humidity, wind speed, precipitation, and cloud coverage. The episode was characterized by clear skies and dry conditions, except for 0.1 inches of rain in the second day and variable cloud coverage in the last day. The average temperature during the episode was 28.4 °C, and the average humidity was 68.5%. To account for precipitation, a parameterization of wet deposition was implemented on the basis of Martin et al. (5). Cloud coverage was parameterized as a multiplication factor (HV) to total solar radiation. The parameterization is presented in Table S1.

Emission rates were calculated using the US Environmental Protection Agency National Emissions Inventory for 2002 (http://www.epa.gov/ttn/chief/eiinformation.html) and the Sparse Matrix Operational Kernel Emissions (SMOKE) model, to determine the specific emissions for the metropolitan area of Atlanta at the 36-km resolution. Size distribution of particle emissions was determined on the basis of measurements reported by Woo et al. (6).

The Caltech Atmospheric Chemistry Mechanism (CACM) (7) was used to describe the gas-phase chemistry. CACM is based on the work of Stockwell et al. (8), Jenkin et al. (9), and Carter (10) and includes O_3 chemistry and a state-of-the-art mechanism of the gas-phase precursors of secondary organic material (SOM). The full mechanism consists of 361 chemical reactions and 191 gas-phase species, which describe a comprehensive treatment of the oxidation of volatile organic carbon species.

Inorganic aerosol formation is calculated using the Simulating Composition of Atmospheric Particles at Equilibrium 2 model (SCAPE2) (Meng et al.) (11), whereas organic aerosol formation is calculated using the Model to Predict the Multiphase Partitioning of Organics (MPMPO) [Griffin et al. (12) and Pun et al. (13)]. MPMPO allows the simultaneous formation of SOM in a hydrophobic organic phase and a hydrophilic aqueous phase. In addition, MPMPO modifies SCAPE2 to account for the interaction between organic ions present in the aqueous phase and the inorganic aerosol components. The module consists of 37 size-resolved aerosol-phase species, in eight different-size bins ranging from 0.04 to 10 μm. It is assumed that all particulate material is internally mixed.

The MPMPO module treats explicitly the surrogate secondary organic material on the basis of their hydrophilic/hydrophobic character. The SOM surrogates in the model are described below.

Hydrophilic.

A1: anthropogenic, dissociative, low no. C (2)
A2: anthropogenic, dissociative, high no. C (8)
A3: anthropogenic, nondissociative
A4: biogenic, dissociative
A5: biogenic, nondissociative.

Hydrophobic.

B1: anthropogenic, benzene based, low volatility
B2: anthropogenic, benzene based, higher volatility
B3: anthropogenic, naphthalene based
B4: anthropogenic, aliphatic
B5: biogenic, aliphatic.

The rate for N_2O_5 hydrolysis on particles to produce nitric acid followed the implementation described by Riemer et al. (14). The reaction rate was described by the equation

$$\left.\frac{d[N_2O_5]}{dt}\right|_{\mathrm{het}} = -\frac{1}{4} c_{N_2O_5} S \gamma_{N_2O_5} [N_2O_5], \quad \textbf{[S2]}$$

where $c_{N_2O_5}$ is the molecular speed of N_2O_5, S is the surface area of the aerosol, and $\gamma_{N_2O_5}$ is the uptake coefficient of N_2O_5 on particles.

Two different simulations were carried out. In case a, for N_2O_5 reactivity a homogeneous particle was assumed, and the uptake coefficient of N_2O_5 was described by the equation

$$\gamma_{N_2O_5} = 0.002f + 0.02(1-f), \quad \textbf{[S3]}$$

where f = (nitrate mass/(sulfate mass + nitrate mass)). Eq. **S3** is based on a simplified parameterization of the relative concentration of nitrate loading with respect to the total nitrate and sulfate loading (15).

In case b, for N_2O_5 reactivity, an organic-rich coating and an inorganic-rich core were assumed, and the reactive uptake coefficient was described by Eq. **S4**,

$$\frac{1}{\gamma_{N_2O_5}} = \frac{1}{\gamma_{\mathrm{core}}} + \frac{1}{\gamma_{\mathrm{coat}}}, \quad \textbf{[S4]}$$

where γ_{core} and γ_{coat} were described by the equations

$$\gamma_{\mathrm{core}} = 0.002f + 0.02(1-f) \quad \textbf{[S5]}$$

$$\gamma_{\mathrm{coat}} = \frac{4RTH_{\mathrm{org}}D_{\mathrm{org}}R_{\mathrm{c}}}{c_{N_2O_5} l R_{\mathrm{p}}}, \quad \textbf{[S6]}$$

where R is the ideal gas constant, T is temperature, H_{org} is Henry's law coefficient for N_2O_5 on organic liquid, D_{org} is the diffusion coefficient of N_2O_5, R_{c} is the radius of the inorganic core, l is the thickness of the film, and R_{p} is radius of the particle. Eqs. **S4–S6** assume that the rate of reaction depends on both the ratio of sulfate and nitrate in the core and the solubility and diffusion of N_2O_5 in the organic coating. In case *b* the organic-rich coating was assumed to include all primary organic aerosol components and the hydrophobic portion of the secondary organic material, whereas the inorganic-rich core was assumed to include all other material in the particle phase.

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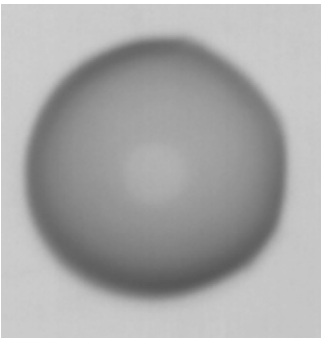
Table S1. Relation between cloud coverage and solar radiation used in the box model simulations

Condition	HV
Clear	0.9
Scattered clouds	0.8
Partly cloudy	0.5
Light rain	0.3
Mostly cloudy	0.3
Overcast	0.2
Rain	0.2
Haze	0.1
Heavy rain	0.1
Thunderstorm	0.1

Cloud coverage was parameterized as a multiplication factor (HV) to total solar radiation.

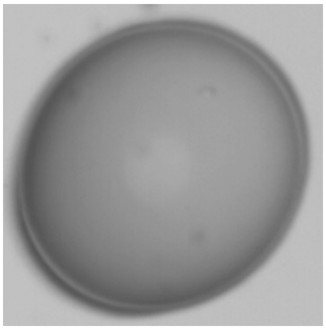


Movie S1. Optical image movie; a particle consisting of ammonium sulfate (diameter = 21.6 μm). Images were recorded as the relative humidity (RH) was decreased from 50% to 35% at a temperature of 270 ± 1 K. The ramp rate was ~0.6% RH min^{-1}. For the particle shown, efflorescence occurred at 37.4 ± 4%. A rough indication of the RH during the movie is included.

Movie S1

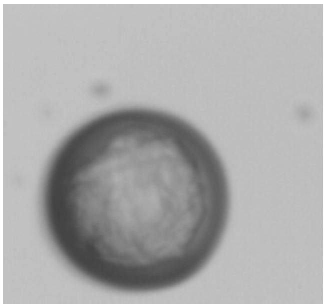
Movie S2. Optical image movie; a particle consisting of ammonium sulfate (diameter = 21.6 μm). Images were recorded as the RH was increased from 62% to 80% RH at a temperature of 270 ± 1 K. The ramp rate was ~0.6% RH min^{-1}. For the particle shown, deliquescence occurred at 78.0 ± 4%. A rough indication of the RH during the movie is included.

Movie S2



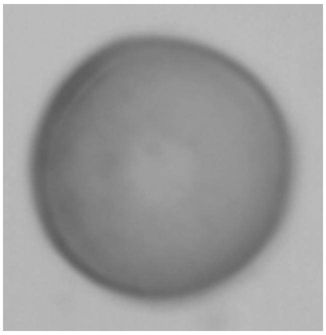
Movie S3. Optical image movie; a particle (org:sulf = 1.4 and diameter = 28.0 μm) consisting of ammonium sulfate mixed with SOM generated by the ozonolysis of α-pinene. Images were recorded as the RH was decreased from 90% to 35% at a temperature of 270 ± 1 K. The ramp rate was ~0.6% RH min^{-1}. For the particle shown, liquid–liquid phase separation occurred at an RH greater than 90 ± 4% and efflorescence occurred at 40.5 ± 4%. A rough indication of the RH during the movie is included.

Movie S3



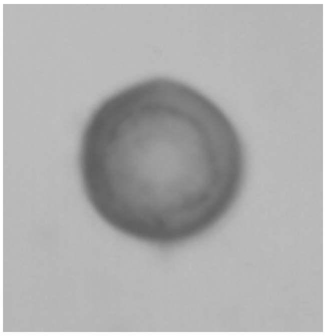
Movie S4. Optical image movie; a particle (org:sulf = 1.4 and diameter = 28.0 μm) consisting of ammonium sulfate mixed with SOM generated by the ozonolysis of α-pinene. Images were recorded as the RH was increased from 60% to 80% RH at a temperature of 270 ± 1 K. The ramp rate was ~0.6% RH min^{-1}. For the particle shown, complete deliquescence occurred at 77.0 ± 4%. A rough indication of the RH during the movie is included.

Movie S4



Movie S5. Optical image movie; a particle (org:sulf = 1.0 and diameter = 18.3 μm) generated from a filter sample collected August 6 and 7, 2010 in Atlanta. Images are shown as the RH was decreased from 68% to 35% at a temperature of 270 ± 1 K. The ramp rate was ~0.6% RH min^{-1}. For the particle shown, liquid–liquid phase separation occurred at an RH greater than 90% ± 4%, whereas efflorescence occurred at an RH of 37.0 ± 4%. A rough indication of the RH during the movie is included.

Movie S5



Movie S6. Optical image movie; a particle (org:sulf = 1.0 and diameter = 18.3 μm) generated from a filter sample collected August 6 and 7, 2010 in Atlanta. Images are shown as the RH was increased from 50% to 80% at a temperature of 270 ± 1 K. The ramp rate was ~0.6% RH min^{-1}. For the particle shown, deliquescence occurred at 71.6 ± 4%. A rough indication of the RH during the movie is included.

Movie S6