Modeling Secondary Organic Aerosols and Aerosol Radiative Forcing using the Volatility Basis Set Approach in WRF-Chem

Manish Shrivastava, Jerome Fast, James Barnard, and Rahul Zaveri

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Motivation

Uncertainties in Organic Matter:

- Comprises ~50% of submicron mass worldwide [Zhang et al. 2007], and analyses of aerosol mass spectrometer data suggests it is comprised of mostly oxygenated material [Jimenez et al. 2010]
- Simulated organic matter mass usually too low because SOA formation is not adequately represented by models

WRF-Chem:

- SOA not treated in MOSAIC – assume organic matter is nonvolatile POA
- SOA treatment coupled with MOSAIC being tested and evaluated - likely available for next release of WRF
- Link new organic species to the aerosol optical property module (direct radiative forcing) & cloud-aerosol interaction modules (indirect radiative forcing)

Average AOD during March 2006

Measured vs Modeled SOA from Volkamer et al. [2006]

What is the impact of uncertainties in SOA on direct and indirect radiative forcing for climate?
Recent Modeling

- Simulated organic aerosol mass has improved recently: \( SOA_{\text{model}} \sim SOA_{\text{estimated}} \)
- But, many assumptions are employed by new treatments that cannot yet be tested

Examples

**Box Modeling Study** - Dzepina et al. [2009]

- Measured:
  - OOA
  - HOA

**3-D Modeling Study** - Hodzic et al. [2010]

- Measured:
  - biomass burning
  - anthropogenic

- used volatility basis set approach in Chimere model for Mexico City
  - Donahue et al. 2006; Robinson et al. 2007; Shrivastava et al. 2008

- Compared old and new approaches using AMS data in Mexico City
Megacities Initiative: Local and Global Research Observations

Measurements of Organic Matter

1. Aerosol Mass Spectrometer (AMS) at 4 ground sites and on 2 aircraft
2. Other ground instrumentation (OC/EC, PILS)
Our Approach

**Organic Aerosol Treatment:**
- Modified *Robinson et al.* [2007] volatility basis set by adding 2 oxygen atoms per generation of oxidation
- # of volatility bins: 9 for **fresh** and 8 for **aged**
- Separate volatility species for **fossil** and **biomass burning** sources
- Predict both **oxygen** and **carbon** mass for each volatility species to obtain O:C ratios
- Traditional anthropogenic and biogenic SOA (4-product VBS set) using yields from *Tsimpidi et al.* [2010] with no further aging
- Prognostic SOA species: currently **380 for 4 size bins**, (684 for 8 size bins)
- Coupled with SAPRC-99 gas-phase mechanism (*Pablo Saide, U. Iowa*) and MOSAIC aerosol model
- Dry deposition for all species treated the same

**Aerosol Optical Properties:**
- For now, assume new organic species all have the same refractive index, density, etc.
Preliminary Results
Temporal Variability in OM at T0 Site

- **Total Organic Matter**
  - Mean: 16.1 (observed)
  - 7.7 (1 * emissions)
  - 12.7 (2 * emissions)

- **HOA (primary)**
  - Mean: 6.0
  - 2.8
  - 6.2

- **OOA (secondary)**
  - Mean: 7.6
  - 4.5
  - 5.9

- **BBOA (biomass burning)**
  - Mean: 2.6
  - 0.5
  - 0.5

Data and PMF analysis from Jose Jimenez and Allison Aiken (Univ. CO)
Diurnal Average OM: T0 Site

Default Emissions

- Observed (AMS) simulated
- Dashed = 2004 emissions and POA

2 * HOA Emissions

- Observed (AMS) simulated
- Missing SOA

Total Organic Matter

Organic Components

- Dots = derived
- Solid = simulated

Data and PMF analysis from Jose Jimenez and Allison Aiken (Univ. CO)
O:C Ratio at T0 Site

Capturing diurnal variation in O/C ratio (higher in afternoon), but still too low

Adding 2 oxygen atoms per generation of oxidation instead of 1

Data and PMF analysis from Jose Jimenez and Allison Aiken (Univ. CO)
Diurnal Average OM: T1 Site

Data from Liz Alexander (PNNL) and PMF analysis from Manjula Canagaratna (Aerodyne)

Default Emissions

2 * HOA Emissions

Total Organic Matter

Organic Components

dots = derived
solid = simulated

concentration (mg m\(^{-3}\))

Mexico City

T1

SOA too high

SOA ok
Diurnal Average OM: Remote Sites

Data from Chris Doran (PNNL) and Darrel Baumgardner (UNAM)
Organic Matter Aloft: March 15

**Carbon Monoxide**
- Use CO to evaluate transport & vertical mixing
- Observed emissions
  - 1* emissions
  - 2* emissions

**Total Organic Matter**
- Observed emissions
- 1* emissions
- 2* emissions

**HOA (primary)**
- 2* HOA emissions closer to AMS data

**G-1 Flight Path**
- AMS data from Liz Alexander (PNNL) and Manjula Canagaratna (Aerodyne)
- G-1 Flight Path diagram
  - Dots = fires detected by MODIS (low biomass burning day)
  - Peak CO

**OOA (secondary)**

**BBOA (biomass burning)**
Organic Matter Aloft: March 19

Carbon Monoxide

Total Organic Matter

HOA (primary)

G-1 Flight Path

OOA (secondary)

BBOA (biomass burning)

dots = fires detected by MODIS (high biomass burning day)

AMS data from Liz Alexander (PNNL) and Manjula Canagaratna (Aerodyne)
Further Downwind

21 UTC March 10, 2006

HOA (primary), ~1800 m AGL
- 30 mg m\(^{-3}\)
- 18 mg m\(^{-3}\)
- 10 mg m\(^{-3}\)
- SW ambient transport
- 0.3 mg m\(^{-3}\)
- 1.5 mg m\(^{-3}\)

OOA (secondary), ~1800 m AGL
- 30 mg m\(^{-3}\) (left)
- 18 mg m\(^{-3}\) (right)
- SW ambient transport

Layer aloft between 2 - 4 km

Export of organics into free atmosphere

Accumulation zone along plateau edge
Organic Matter Aloft: March 10

**Carbon Monoxide**
- CO (ppmv)
- city
- downwind

**C-130 Flight Path**
- transport
- peak CO

**Total Organic Matter**
- CO detected by MODIS (high biomass burning day)
- too much SOA formation or vertical displacement of plume?

**HOA (primary)**

**OOA (secondary)**

**BBOA (biomass burning)**
- observed
- 1 * emissions
- 2 * emissions

AMS data from Pete DeCarlo (PSI) and Jose Jimenez (UC)
Aerosol Effect on Shortwave Radiation

- Aerosols reduce downward shortwave radiation over Mexico City and downwind over the Gulf of Mexico
- SOA contributes to ~50% of reduction in shortwave radiation
- Caveat: simulated OM often too low over the city and too high downwind
Summary and Next Steps

- Simulated OM in better than assuming non-volatile POA
- SOA contributed to a large fraction of total reduction in downward SW radiation
- Nevertheless, uncertainties remain:
  - **Primary**: emissions in 2006 inventory likely too low, also uncertainty in spatial variability in emission rates
  - **Secondary**: too low in city, ~observed at downwind site and over the city, but better aloft over city
  - **Biomass Burning**: likely missing sources

Next Steps:
- Additional debugging and testing of volatility basis set
- Develop simplified volatility basis set (fewer bins) to \( \downarrow \) CPU time (by factor of 3)
- Coupling new organic aerosol species with cloud-aerosol interactions

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