HEMISPHERIC-SCALE CHEMICAL AND MICROPHYSICAL AEROSOL MODEL

Stephen E. Schwartz, Carmen M. Benkovitz, Robert McGraw and Douglas L. Wright, Jr.

DOE Atmospheric Chemistry Program
Annual Science Meeting

Alexandria VA
30 Nov. - 2 Dec. 1999
OUTLINE

Recap on GChM-O (Global Chemical Model driven by Observation-derived meteorological data)

Application of GChM sulfur chemistry in CCM3 (Collaboration with NCAR)

Disproportionate influence of volcanic sulfur on sulfate burden

Recent model advances

Recap on using the Method of Moments to represent aerosol microphysics

Obtaining aerosol integral properties from moments

Application of Method of Moments to hemispheric scale calculations in GChM-O

Representing cloud microphysics by the Method of Moments

Theory: Examination of ternary NH₃ - H₂SO₄ - H₂O nucleation

Ongoing and future work and Collaborations
CHEMICAL AND MICROPHYSICAL AEROSOL MODEL

DRIVEN BY

OBSERVATION-DERIVED METEOROLOGICAL DATA

OBJECTIVES

*Develop, evaluate, and apply* models describing the chemical and microphysical properties of atmospheric aerosols resulting from energy related and other activities on a hemispheric geographical scale.
COMPONENTS OF THE TRANSPORT - TRANSFORMATION - REMOVAL MODEL

**METEOROLOGY**
- Winds
- Clouds
- Precipitation
  - ECMWF

**EMISSIONS**
- NAPAP
- EMEP
- Dignon
- Bates/Lamb

**TRANSPORT**
- Bott/Easter

**CHEMISTRY**

**Gas**
- \( \text{SO}_2 + \text{OH} \) [OH] \( \text{Spivakovsky/Logan} \)
- \( \text{DMS} + \text{OH} \) DMS chem \( \text{Yin/Seinfeld} \)

**Aqueous**
- \( \text{SO}_2 + \text{H}_2\text{O}_2 \) [H\text{H}_2\text{O}_2] Seasonal
- \( \text{SO}_2 + \text{O}_3 \) [O\text{O}_3] Seasonal

**DRY DEPOSITION**
- Wesely

**WET DEPOSITION**
- Berkowitz/Hales

**COMPONENTS**
- DMS
- SO\text{O}_2
- MSA
- SO\text{O}_4^{2-}
Sulfate Column Burden by Production Mechanism

Gas phase

Aqueous Phase

Primary

October 15, 1986 at 6 UT
COMPARISON OF MODEL AND OBSERVATIONS

Typical comparisons for 24-hr Sulfate mixing ratio at surface

<table>
<thead>
<tr>
<th>Location</th>
<th>Model-Obs</th>
<th>Obs-Obs</th>
<th>Median Spread</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manitoba, Canada</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deutelbach, Germany</td>
<td>503</td>
<td>503</td>
<td>1.9</td>
</tr>
<tr>
<td>Jungfrauoch, Switzerland</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jarzewan, Poland</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Obs-Obs</td>
<td>503</td>
<td>503</td>
<td>1.5</td>
</tr>
<tr>
<td>Model-Obs Same locations</td>
<td></td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>All locations</td>
<td>7907</td>
<td></td>
<td>2.3</td>
</tr>
</tbody>
</table>

Benkovitz and Schwartz, *JGR*, 1997
SO$_4$ Global Burden by Source Region
Anthropogenic Sources Only

Rasch, Barth, Kiehl, Schwartz, Benkovitz, *JGR*, in press, 1999
ANTHROPOGENIC SULFATE COLUMN BURDEN
BNL Sulfate Model in NCAR CCM3

Kiehl et al., JGR, in press
ANTHROPOGENIC SULFATE DIRECT SHORTWAVE FORCING, ANNUAL AVERAGE

BNL Sulfate Model in NCAR CCM3

Global Mean, -0.56 W m\(^{-2}\)

*Kiehl et al., JGR, in press*
SHORTWAVE FORCING, ANNUAL AVERAGE

BNL Sulfate Model in NCAR CCM3

GHG's + O₃ + Sulfate (Direct and Indirect)

Two Formulations of Cloud Droplet Concentration

Kiehl et al., JGR, in press
VOLCANIC SULFUR EMISSIONS
Location and Magnitude during ACE-2 Time Frame

Average Emissions Flux, June 1 to July 25, 1997

Expressed as Average over 1° Grid Cell

- < 10 μmoles m⁻² s⁻¹
- ≥ 10 and ≤ 100
- ≥ 100 and ≤ 600
- ≥ 600 and ≤ 5000
- > 5000
Volcanos Contribute Disproportionately to Sulfate Burden

<table>
<thead>
<tr>
<th>Contribution to Emissions</th>
<th>Sulfate Burden</th>
<th>Sulfate Column Burden for June 26, 1997 at 0UT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogenic</td>
<td>12%</td>
<td>6%</td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>84%</td>
<td>66%</td>
</tr>
<tr>
<td>Volcanos</td>
<td>4%</td>
<td>28%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

μmoles m⁻²
Aerosol Chemical Transport Model GChM-O
Global Chemistry Model Driven by Observation-Derived Meteorological Data

**MEASUREMENT**
- Winds
- Clouds
- Precipitation
  - ECMWF
  - $1^\circ \times 1^\circ$, 27 levels

**EMISSIONS**
- Sulfur species
  - SO$_2$
  - Primary Sulfate
  - DMS Daily
- Sealsalt aerosol
  - Smith, O'Dowd

**TRANSPORT**
- Bott/Easter

**CHEMISTRY** (Rate Constants NASA, 1997)
- Gas Phase
  - $\text{SO}_2 + \text{OH} \rightarrow \text{H}_2\text{SO}_4$
  - $\text{DMS} + \text{OH} \rightarrow \text{DMS chem}$
  - $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$
- Aqueous Phase
  - $\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$
  - $\text{SO}_2 + \text{O}_3 \rightarrow \text{H}_2\text{SO}_4$
  - O$_3$, OH, HO$_2$, Daily MOZART (Brasseur et al.)

**AEROSOL MICROPHYSICS**
- Nucleation
- Coagulation
- Growth (clear air, cloud)
  - Method of Moments - McGraw

**WET DEPOSITION**
- Berkowitz/Hales

**DRY DEPOSITION**
- Time, Location dependent
  - Size Resolved
  - Wesely

**DMS**
- SO$_2$
- MSA
- SO$_4^{2-}$

**Version**
- Version 1
- Version 2
- Version 3
AEROSOL DYNAMICS BY THE METHOD OF MOMENTS

The method of moments is an approach to describing aerosol properties and dynamics in terms of the moments $\mu_k$ of the radial number size distribution $f(r)$.

$$\mu_k = \int_0^\infty r^k f(r) dr$$

Aerosol properties (e.g., light scattering coefficient) can be accurately represented as simple functions of low order moments.

Aerosol dynamics can be represented by growth laws (differential equations) in the moments.

The moments advect and mix just like chemical species--they are conserved and additive.

Hence representing aerosol properties and dynamics in 3-D transport models is equivalent to representing a small number of additional chemical species.
METHOD OF MOMENTS
Heuristic Description

Consider accretion of monomer by existing aerosol.

This can be considered a reaction between monomer (m) and aerosol surface area (A)

\[ m + A \rightarrow \text{slightly larger distribution} \]

Rate  =  \( kmA \)

Aerosol surface area density is

\[ A = \int_{0}^{\infty} \pi r^2 f(r) dr = \pi \mu_2 \]

So accretion of monomer by existing aerosol is a reaction between monomer and second moment.
LIMITATION TO THE METHOD OF MOMENTS

GROWTH LAW RESTRICTION

For exact closure of the moment evolution equations the growth law must be of the form:

$$\phi(r) \equiv \frac{dr}{dt} = a + br$$

where $a$ and $b$ are independent of $r$. Then integral is evaluated as:

$$\int r^{k-1} \phi(r) f(r) \, dr = a \int r^{k-1} f(r) \, dr + b \int r^k f(r) \, dr$$

$$= a \mu_{k-1} + b \mu_k$$

• This includes the important case of free-molecular growth, for which $b = 0$.

• For other growth laws the Quadrature Method of Moments replaces exact closure with an approximate but much less restrictive closure condition.
QUADRATURE METHOD OF MOMENTS

INTEGRAL APPROXIMATION VIA n-POINT GAUSSIAN QUADRATURE

• The moments are evaluated as

\[ \mu_k \equiv \int_0^\infty r^k f(r) dr \equiv \sum_{i=1}^{n} r_i^k w_i \]

The abcissas \(r_i\) and weights \(w_i\) are specified in terms of the low-order moments of \(f(r)\).

• Quadrature-based closure is obtained by the approximation

\[ \int r^{k-1} \phi(r) f(r) dr \approx \sum_{i=1}^{n} r_i^{k-1} \phi(r_i) w_i, \quad k \geq 1. \]

MOMENT INVERSION

Low order moments \(\mu_k\) can be efficiently converted to quadrature abcissas \(r_i\) and weights \(w_i\). For 3-point quadrature, 6 moments are required.

• Once the abcissas and weights have been determined, the unknown distribution function integrals are obtained by the summation.

CALCULATIONS FOR DIFFUSION CONTROLLED GROWTH

• For diffusional growth

\[ \frac{dr}{dt} = \frac{k}{r} \]

the moment evolution equations are not in closed form. One approach has been to use assumed distributions parameterized in terms of moments (e.g. Laguerre).

Diffusion controlled growth of water drops for 20 s at \( T = 278 \, K \) and fixed saturation of 101%.

Dotted curve: Initial normalized Khrgian-Mazin distribution with mean particle radius of 5 \( \mu m \).
Solid curve: Exact evolved distribution obtained by numerical calculation.
Dashed-dotted curve: Laguerre distribution parameterized by the moments 0 through 2 obtained by the Laguerre closure method.

**QMOM CALCULATIONS FOR DIFFUSION CONTROLLED GROWTH**

- Quadrature MOM permits calculation of the evolution of the moments directly, without a priori assumptions about the form of the evolving distribution.

DISTRIBUTIONS USED IN TEST OF RETRIEVAL OF OPTICAL PROPERTIES FROM MOMENTS

SYNTHESIS OF OPTICAL PROPERTIES FROM MOMENTS OF SIZE DISTRIBUTION

Multiple Isomomental Distribution Aerosol Synthesis (MIDAS) Method
(Six moments, $\mu_0 - \mu_5$)

Extinction Coefficient
Asymmetry Parameter
Normalized Forcing

- Exact, 632.8 nm
- Synthesized, lognormal, 632.8 nm
- Synthesized, modified gamma, 632.8 nm
- Synthesized, modified gamma, solar spectrum

SIZE OF SULFATE PARTICLES
Dependence on Latitude, Longitude, Altitude
Mediterranean Sea, October 15, 1986, 1200 UTC

Particle mean radius is proportional to radius of disk, 10-250 nm.

D. Wright, unpublished
Method of Moments in Subhemispheric Model

AEROSOL SULFATE, October 22, 1986

Number conc. $\mu_0$ (32 m)

Mean radius $r = \mu_1/\mu_0$

Effective radius $r_e = \mu_3/\mu_2$

TOA Forcing

Wright, McGraw, Benkovitz & Schwartz, GRL, submitted, 1999
CLOUD DROPLET ACTIVATION FROM MOMENTS OF AEROSOL SIZE DISTRIBUTION

Multiple Isomomental Distribution Aerosol Synthesis (MIDAS) Method

MIDAS CLOUD ACTIVATION

![Graph showing cloud droplet activation from moments of aerosol size distribution.](image)

- **exact**
- **MIDAS**
- **quadrature**

**cumulus**

\[ S_{\text{max}} = 0.5 \% \]

**stratiform**

\[ S_{\text{max}} = 0.05 \% \]

D. L. Wright and R. L. McGraw, to be submitted
COLLABORATIONS

Helsinki, Kuopio, London, Caltech
Examine nucleation mechanisms and rates

NCAR
Incorporate BNL chemistry model in CCM3 to examine direct and indirect forcing

Purdue
Evaluate model by comparison of model output and satellite data

NOAA PMEL
Interpret modeling results during ACE-2 campaign

Caltech, Irvine
Incorporate moment methods into regional aerosol models and compare with alternative approaches

Duke
Incorporate moment method into GFDL GCM to examine aerosol forcing for various scenarios
Compare moment and bin methods in low-dimensional calculations
Apply moment methods to evaluation of regional scale PM 2.5

LLNL
Implement aerosol microphysics in LLNL chemical transport model
CURRENT ACTIVITIES/FUTURE PLANS

• GChM-O Version 2 (Sulfate Mass, Enhanced Chem, 360° Long, 0-81° Lat)
• Develop enhancements to representation of aerosol microphysical properties.
• Incorporate additional species: Seasalt, Dust, Carbonaceous
• GChM-O Version 3 (QMOM for Aerosol Properties)
  ACE-2  Sulfate, Seasalt, Dust
  ACE-1  Sulfate and Seasalt
• Collaborate with others in applying these methods.

COMPARISON WITH OBSERVATIONS!