Review of Cloud Processing of Gases and Aerosols in Current AQ Models

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Background


- Reviewed the representations of cloud processing of gases and aerosols in some of the current state-of-the-art regional air quality models.

- Focusing on three key processes, aerosol activation (or nucleation scavenging of aerosols), aqueous-phase chemistry, and below-cloud scavenging of gases and aerosols.

- Sensitivity tests (using the AURAMS model) to assess the impact on (or uncertainties in) air quality model predictions from:
  - *different aerosol activation schemes*
  - *different below-cloud particle scavenging algorithms*, and
  - *Inclusion of cloud processing of water soluble organics as a potential pathway for SOA formation*

- Recommendations
Talk outline

• Main findings
• Highlights of the sensitivity studies
• Recommendations
List of models reviewed -1 (NA)

- **AURAMS**: sectional, 12 bins (0.01–40.96 µm in diameter); 9 components (SO4, NO3, NH4, SS, POA, SOA, EC, CM, aerosol water).
- **CAMx/PMCAMx**: sectional, 10 bins (0.04–40 µm) or 2 bins (2.5 and 10 µm, or “fine” and “coarse”); 8 mandatory PM (fine) species (SO4, NO3, NH4, anthrop. SOA, bio. SOA, polymerized anthrop. SOA, polymerized bio. SOA, aerosol water).
- **CMAQ**: modal, 3 log-normal modes (Aitkin, accumulation, and coarse); 9 components (SO4, NO3, NH4, EC, POC, SOC, SS, and other).
- **GATOR**: sectional, 16 bins (0.014–74 µm); 18 solid species including various organic salts, organic carbon, elemental carbon, and trace elements.
- **STEM**: sectional, 4 bins (0.1–10 µm); inorganic aerosol ions (SO4, NO3, NH4, sodium, chloride, and other anions), sea salt, and dust.
- **WRF-CHEM**: (1) modal (with MADE/SORGAM), 2 sub-micron log-normal modes; or (2) sectional (with MOSAIC), 8 bins (0.04–10 µm); 9 components (SO4, NO3, NH4, chloride, sodium, other inorganics, organic carbon, elemental carbon, water).
List of models reviewed -2 (Europe)

- **CHIMERE**: sectional, 6 bins (0.01–40 μm); 6 components (primary particulate matter, sulphate, nitrate, ammonium, SOA, and water).
- **COSMO-MUSCAT**: modal/bulk: multiple modes (represented by average mode diameter); primary PM (dust, elemental carbon organic carbon), secondary inorganic aerosol component (sulphate, nitrate, ammonium).
- **EMEP Unified Model**: 4 mono-disperse aerosol modes (nucleation, Aitken, accumulation, and coarse); 7 components (sulphate, nitrate, ammonium, organic carbon, elemental carbon, mineral dust, and sea salt).
- **LOTOS-EUROS**: Bulk (or 2 sections/modes): fine (primary and all secondary components) and coarse (primary); secondary inorganic aerosol components (sulphate, nitrate, ammonium), SOA, primary PM2.5 and PM2.5–10, black carbon, sea salt.
Major findings – aerosol activation

• Not all models have explicit representation of this process. Amongst the models that do consider this process, the representation varies from mechanistically based parameterization to simple empirical formula or a fixed activation diameter for sectional models; with a modal approach it is usually assumed that all accumulation mode particles are incorporated in cloud droplets.

• The modification to aerosol size distribution due to aerosol activation and subsequent aqueous-phase production is often crudely represented in current AQ models (limitation from size representation).

• The modelled droplet number concentration and averaged size distribution of ambient PM are shown to be highly sensitive to the algorithms for aerosol activation.

• The impact on modelled ambient PM$_{1.0}$ mass (on average) is more significant than on PM$_{2.5}$ mass from the current sensitivity test.
Major findings – aqueous-phase chemistry

- Almost all of the regional air quality models reviewed have some representation for the aqueous-phase oxidation pathways leading to the production of sulphate in cloud.
- The models differ in chemistry mechanisms, from more complete* atmospheric aqueous-phase chemistry, to sulphur oxidation focused chemistry, to highly parameterized single first-order reaction representation.
- Almost all models use a bulk approach for the aqueous-phase chemistry; a few have an option to use a variable-size-resolution-model approach to allow either a bulk or, when necessary, a two-bin representation in order to separate the droplets formed on larger, more alkaline particles from those formed on smaller, more acidic particles. Models also differ in how cloud water pH is determined.
- Not all models have a comprehensive representation of size distributed mass addition over the aerosol size spectrum from the aqueous-phase production.
Major findings – cloud processing of WSOC

• The process is not well understood but increasingly gaining attention as a potentially important pathway for atmospheric SOA formation. Mechanisms are not well established.

• Review of existing studies suggests a minimum effective $K_H$ of $10^3$ M/atm for a species to partition significantly to the aqueous phase.

• The weight of evidence from recent laboratory studies suggests that during the daytime the radical reactions dominate cloud organic chemistry, largely OH-initiated oxidation converting aldehyde groups to carboxylic acid groups (most likely contributing to SOA formation through cloud processing).

• Few of the current regional AQ models formally include the aqueous-phase pathway for the SOA formation. Limited tests with CMAQ attempted to assess the implication of cloud processing of organic gases on a regional scale showed some success in improving model prediction of SOA.

• The results from the AURAMS sensitivity run in this study, designed as an upper-limit test, also suggest that indeed water soluble organic gas uptake to clouds and subsequent processing can be an important mechanism in addition to the traditional secondary organic gas uptake to the particle organic phase.
Major findings – wet deposition

- The majority of the models reviewed in this study uses a scavenging coefficient ($\Lambda$) approach for below-cloud aerosol scavenging by rain.
- Variation in the formulation of $\Lambda$ (almost all considers mono-disperse rain droplet spectrum but differs in the parameterization of mean droplet size and terminal velocity, etc.)
- The AURAMS sensitivity tests, using two different theoretical $\Lambda$ parameterizations (corresponding to the lower and upper bounds), showed that the modeled daily ambient concentrations under rain conditions can differ by up to 10% for PM$_{2.5}$ and by up to 20% for PM$_{10}$.
- Not all models currently treat below-cloud scavenging of aerosol by snow; a scavenging coefficient approach is also commonly used for those that do include this process.
- Models vary in the representation of below-cloud scavenging of gases (by rain), from first-order scavenging coefficient approach, to Henry’s law equilibrium, to kinetic mass transfer.
- A few models do consider scavenging of gases (HNO$_3$ and NH$_3$) by snow.
Sensitivity test – 1
Aerosol activation (nucleation scavenging)
ICARTT: July & August 2004 (42- & 15-km)
Aerosol activation scheme in current AURAMS

- Jones et al. (1994): empirical relationship between droplet number concentration ($N_d$) and aerosol number concentration ($N_a$):

$$N_d = 375(1 - \exp(-2.5 \times 10^{-3} N_a))(cm^{-3})$$

\[\sum_{i=1}^{N_a} (i = nb, i_c, -1) = N_d\]

- The parameterization establishes a relationship between the maximum supersaturation ($S_{\text{max}}$) reached in updraft to an effective critical supersaturation ($S_e$), which in turn is determined by individual critical supersaturation of each sections ($S_i$):

$$S_{\text{max}} = \frac{S_e}{\left[0.5\left(\frac{\zeta}{\eta}\right)^{3/2} + \left(\frac{S_e^2}{\eta + 3\zeta}\right)^{3/4}\right]^{1/2}}$$

and

$$S_{e}^{2/3} = \frac{\sum_{i=1}^{nb} N_i S_i^{2/3}}{\sum_{i=1}^{nb} N_i}$$

where, $\zeta$ and $\eta$ are parameters dependant on updraft velocity, growth coefficient (accounting for diffusion of heat and moisture to particles), surface tension, etc.; $S_i$ depends on size, hygroscopicity, and surface tension characteristics of the particles in a given section/bin.

- Aerosol activation is determined by comparing the upper and lower bound of critical supersaturation of each size section/bin to the maximum supersaturation reached in the updraft; fractional activation is considered.

- Use of standard deviation of updraft $\sigma_w$ as characteristic updraft (Peng et al., 2005) in the calculation of $S_{\text{max}}$, parameterized here as a function of LWC (modelled), proposed by Hoose et al. (2010):

$$\sigma_w = w_t + 2 \left( \frac{m}{s} \right) \frac{k_{\text{air}}}{g_{\text{water}}} \cdot \text{LWC}$$

where $w_t$, the turbulence velocity scale, is set at 0.1 m s$^{-1}$ for this study.

- Good correlation between LWC and gust (updraft) velocity is also shown from the aircraft measurements during ICARTT-CTC; $\sigma_w$ derived from LWC is about 1/3 to 1/2 of the updraft velocity.
Impact of aerosol activation on droplet number

August 10, 2004 (24-hr average), 1235 m

- In comparison, modelled droplet number concentration from the Jones scheme is more homogenous, in part due to the cap at 375 (cm$^{-3}$).
- The Abdul-Razzak & Ghan scheme results in significantly higher peak values and more in-homogeneity corresponding to the variability in updraft.
Measurements show much greater droplet number concentration than 375 cm$^{-3}$!
Impact of aerosol activation on PM (sulphate) mass

base case, Jul 7 – Aug 31, 2004

\[
\frac{\text{sens} - \text{basecase}}{\text{basecase}} \times 100
\]

Greater impact on sulphate\textsubscript{1.0} than sulphate\textsubscript{2.5}
Impact of aerosol activation on PM (sulphate) size distribution (ave. Jul. 7 – Aug. 31, 2004)

Selected IMPROVE sites

Addison Pinnacle Park
Dolly Sods
Presque Isle
Acadia National Park
Impact of aerosol activation on AOD (preliminary)

Base case column AOD
(Averaged over July 7 – August 31, 2004)

Relative difference in averaged col. AOD
(sens - basecase) / basecase * 100

- Generally a reduction in modelled column AOD (at 550 nm) over the higher PM concentration region (eastern U.S.) with the AR&G scheme (note that the AR&G scheme results in activation of smaller aerosol particles and shifting mass to smaller sizes); the overall differences in AOD from the two different activation schemes are within +/-5%.
Sensitivity test – 2
Cloud processing of WSOC (an upper limit test)
*ICARTT*: July & August 2004 (42-km)
Assumptions and setup for the sensitivity run

• Three ADOM-II (lumped) water soluble species were considered: MGLY (C₂ – C₃ dicarbonyl), DIAL (larger dicarbonyls, from aromatic oxidation), CRES (aromatic alcohols, from aromatic oxidation and emission);

• A pseudo-first order uptake is used

\[
\frac{dC_g}{dt}\bigg|_{\text{uptake}} = -\frac{\gamma \nu A}{4} C_g
\]

\[
\frac{1}{\gamma} = \left( \frac{\nu a}{4D_g} - 0.5 \right) + \frac{1}{\alpha} + \frac{\nu}{4K_H RT \sqrt{k_{rxn} D_L}}
\]

assuming droplet diameter of 10 µm, max. pseudo 1st order OH-reaction rate, \(k_{rxn}\), of 10⁻⁴ s⁻¹ (modulated by cosine of solar zenith angle), etc..

• Aqueous-phase reactions were assumed to form non-volatile SOA mass with a yield of unity (upper limit).
Sensitivity run vs. base case

July 7 – August 31, 2004; 42-km resolution (sub-domain)
Comparison with observations (IMPROVE)

<table>
<thead>
<tr>
<th>Jul – Aug, 2004 (N = 54 sites)</th>
<th>Base case</th>
<th>Sensitivity run</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>-1.7</td>
<td>-0.83</td>
</tr>
<tr>
<td>NMB</td>
<td>-48%</td>
<td>-24%</td>
</tr>
<tr>
<td>( r )</td>
<td>0.81</td>
<td>0.77</td>
</tr>
<tr>
<td>RMSE</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Slope</td>
<td>0.56 ± 0.05</td>
<td>0.73 ± 0.08</td>
</tr>
<tr>
<td>Y-intercept</td>
<td>-0.13 ± 0.20</td>
<td>0.13 ± 0.31</td>
</tr>
</tbody>
</table>
Sensitivity test – 3
Below-cloud scavenging of aerosols
Sensitivity considerations

- scavenging coefficient ($\Lambda$) approach:
  \[ \frac{\partial C}{\partial t} = -\Lambda \cdot C \]
  \[ \Lambda(d_p) = \int_0^\infty \frac{\pi}{4} (D_p + d_p)^2 \left(V(D_p) - v(d_p)\right) E(d_p, D_p) N(D_p) dD_p \]
  \[ \Lambda(d_p) = f(P, D, V_t, E) \]

- Largest variability comes from the formulation of the collection efficiency ($E$).
- Sensitivity tests using two particular formulations based on Andronache et al. (2006) and Mircea et al. (2000):
  - **Mircea et al.** – considers the three most important collection processes, Brownian diffusion, interception, and inertial impaction (lower bound);
  - **Andronache et al.** - considers additional collection processes due to thermophoresis, diffusiophoresis, and electrostatic forces (upper bound).
- Two-day simulation (August 9 – 10, 2004) over the ICARTT 15-km domain.
Variability in scavenging rate due to different formulations of $\Lambda$

Wang et al. (2010, ACP)
Variability in scavenging rate due to different formulations of Λ

Vertical slice average and maximum scavenging rate statistics (AURAMS BAQSMet/ICARTT domain)
Impact on modelled PM$_{2.5}$ and PM$_{10}$ mass

August 10, 2004

Precipitation (daily mean)  Relative difference in daily mean PM$_{2.5}$  Relative difference in daily mean PM$_{10}$

- Bulk mass is dominated by large particles, and theoretical formulas agree well for large particles – hence limited sensitivity in PM mass;
- PM$_{2.5}$ is much less sensitive to scavenging process than PM$_{10}$ (see previous slide).
Recommendations

- Aerosol activation (or nucleation scavenging) has a profound impact on the size distribution of cloud processed aerosols. This process has not attracted much attention within the AQ modelling community due to its emphasis on bulk mass (so far). With emerging issues (e.g., health effect, air quality-climate interaction/feedback), there is a need to re-examine the representation of this process (in connection with size modification due to aqueous-phase secondary aerosol production) in AQ models.

- There is ample evidence, and the sensitivity test conducted in this study also demonstrate, that cloud processing of WSOC can contribute significantly to the overall atmospheric SOA formation particularly in locations with large isoprene emissions and high liquid water contents (clouds, high relative humidity).

- More investigation is needed to further understand the aqueous-phase organic oxidation products and the processes that occur as cloud droplets evaporate (e.g., complex radical and non-radical chemistry in concentrated solutions).

- Recommend the use of a theoretical parameterizations that gives highest \( \Lambda \) values for below-cloud scavenging of aerosol particles by rain.

- Areas (concerning wet deposition) still needing attention: scavenging of gases and particles by snow (parameterization and uncertainty assessment), tracer release during precipitation evaporation (below cloud).

- Modelling cloud remain to be a large source of uncertainty in modelling cloud processing of gases and aerosols.
Thank you!