Modelling Physical and Chemical Properties of Aerosols: A Challenge for Air Quality and Climate Change Research

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What is aerosol?
Aerosol sources
Aerosol processes

- condensation
- evaporation
- surface chemistry
- coagulation
- water uptake
- oxidation
- precursor emissions
- new particle formation
- aqueous chemistry
- scavenging
- activation
- subcloud scavenging
- diffusion
- evaporation
- primary emissions
- dry deposition
Aerosol models

Aerosol processes

Aerosol sources

Aerosol properties
Why is atmospheric aerosol so important?

Aerosol affects:
- air quality and health;
- climate changes;

and is used in:
- geoengineering experiments
M2M for air quality and climate change

Physical theories about:
- how air move
- how water behave
- how radiation transports energy.

and physical and chemical theories about:
- how gas and aerosol are transported, transformed and interact between them and with water and radiation.

The earth’s atmosphere is broken down into pieces-cells- and then it is computed what happens in each cell based on these physical theories. Cells exchange energy and matter with each other based on the physics of the transfer of matter and energy. The net results is a simulation of what the actual atmosphere might do.

Air quality and climate change have many overlapping and inter-linked problems.
Common issue between air quality and climate change with respect to aerosols

- at process level
- in model development, application and validation
- in measurement and monitoring strategies
Aerosol emissions have to be included in air quality (AQM) and climate models (CM) as process emission. Natural sources of aerosol depend on atmospheric conditions (wind speed, temperature, solar radiation, relative humidity, etc.), on surface type (soil, vegetation) and status (temperature, water content, etc.).

Both emission inventories and processes have to contain information not only on total mass or number of aerosol particles emitted, but on their size, chemical composition, state of mixing, solubility, etc.

Both emission inventories and processes have to describe the aerosol sources with much better temporal and spatial accuracy.

**Process emissions implemented in AQMs&CMs:**
- dust aerosol
- sea-salt aerosol
- biogenic VOC (aerosol precursors)

**Process emissions under implementation in AQMs&CMs:**
- primary organic marine aerosol
A combined organic-inorganic sub-micron sea spray source function for large-scale models

Requires only wind speed and surface ocean chlorophyll-a concentration as input parameters.

(O’Dowd et al., GRL 2008)
The combined source function was implemented in the REMOTE regional climate model and sea-spray fields are predicted over the North East Atlantic.
Formation of low-volatility (semivolatile and possibly nonvolatile) compounds is governed by a complex series of reactions of a large number of organic species.

Experimental characterization and theoretical description of SOA formation presents a substantial challenge.

SOA models, currently based on laboratory measurements, underestimate SOA production for two reasons:

- uncertainties in current treatments of SOA formation in models
- exist additional classes of SOA precursors that have yet to be studied in the laboratory or included in models.

- “two-product model” or “volatility basis set”
- the NOx dependence of SOA yields
- the effects of specific reaction conditions (RH, acidity, etc.)
- the effects of multigenerational chemistry
- cloud processing

- higher-volatility precursors (isoprene, acetylene), lower-volatility species “intermediate volatility” and semivolatile organics, such as those in diesel exhaust.
- a number of as-yet unidentified SOA precursors, with a wide range of volatilities.
Air Pollution in Pittsburgh

July 2, 2001

PM$_{2.5}$ = 4 $\mu$g m$^{-3}$

July 18, 2001

PM$_{2.5}$ = 45 $\mu$g m$^{-3}$

(from Spyros Pandis)
Process level: Aerosol water uptake

...humidification...mainly in the boundary layer...is source of inter-model variability...and...increases the range of modelled direct radiative forcing (RF)...(IPCC, 2007)

Aerosol water uptake

Aerosol physical and chemical properties

→ aerosol optical properties

→ aerosol sedimentation and dry deposition

→ aerosol wet removal

Need to know how aerosol water uptake depends on:
• size
• composition
• surface tension
• solubility
• mixing state
• shape
• gas condensation/dissolution
Process level: Aerosol interactions with clouds and precipitations

Need to know:

• the relationship between aerosol size/composition and drop/ice size distributions;

• the relationship between aerosol characteristics and cloud dynamics;

• the aerosol effects on the surface energy budget and, consequently, on convection, evaporation and precipitation and on biogeochemistry;

-0.7 W/m²
-0.3 - 1.8 W/m²
Outstanding research is needed:

• for understanding and parameterize the effect of particle size and composition on wet scavenging coefficient;
• for understanding the processes contributing to below-cloud wet removal (the effect of cloud entrainment for example);
• for understanding and parameterize the aerosol scavenging as a function of hydrometeor type
Process level: Aerosol nucleation

Nucleation mechanisms:

• condensation of a binary mixture of sulphuric acid and water;
• ternary nucleation of sulphuric acid, water and a third molecule, most likely ammonia;
• ion induced nucleation;
• secondary organic aerosol formation involving condensation of low- or non-volatile organic compounds;
• homogeneous nucleation of iodine oxides.

In addition, atmospheric particle formation events are significantly affected by environmental factors, such as temperature, humidity and the surface area of pre-existing particles.

Current problems in understanding particle formation and growth:
- inability to detect particles smaller than 3 nm
- inability to know in real time, in situ, composition of particles smaller than 200nm

(Hamed et al., 2007)
Process level: Aerosol heterogeneous and aqueous chemistry

Heterogeneous chemistry:
- clear evidences on gas scavenging (O3, HNO3, etc) via non-reactive processes and reactive heterogeneous chemistry on aerosol particles
- nitrate formation still a problem (size dependence, role of particles such as dust, sea-salt, etc)
- role of organics for aging (oxidation processes, oligomerization processes, etc.)

Aqueous chemistry:
- clear evidence of change in chemical composition due to sulfate oxidation, etc

Both these processes impact on particle composition and thus, on their further interactions with radiation and water.

Heterogeneous processes in troposphere are considerably less well understood than gas-phase chemistry for two reasons:

• detection of the effects of heterogeneous reactions are not easily observable because of the rapid mixing times in the troposphere and its chemical heterogeneity.

• the complexity that is observed in the chemical composition of the aerosol particles.
Dry deposition velocity of aerosol is quantified using resistance analogy approach:

\[ v_d(z) = \frac{1}{r_a(z) + r_b + r_c} + v_g, \]

- the aerodynamic resistance to transfer:
  \[ r_a = f \left( \frac{U}{u_*^2}, L \right) \]
- the resistance to transfer across the quasi-laminar surface layer:
  \[ r_b = f \left( \frac{1}{u_*}, D \right) \]
- the resistance to surface uptake:
  \[ r_c = f \text{ (surface structure, presence of water or films)} \]
- gravitational settling velocity \( v_g \)
- height \( z \)
- friction velocity \( u_* \)
- horizontal wind speed \( U \)
- Monin-Obukhov length \( L \)
- molecular diffusivity of \( C \) in air

Outstanding research needed:
- on assessing the magnitude and spatial extent of edge effects and landscape heterogeneity;
- on understanding and parameterization of particle size and composition effect on dry particle fluxes;
- on understanding the processes contributing to deposition efficiency (electro- and thermophoresis for example);
- on understanding and parameterization of re-suspension, saltation or other particle formation processes at or close to canopies.
Process level: Aerosol-radiation interactions

Dust-radiation interactions improve weather forecast

Table 3. Root Mean Square Error of the Mean Sea Level Pressure Forecasts at 12, 24, 36 and 48 Hours of the 0000 UTC Cycle on 12 April

<table>
<thead>
<tr>
<th>Experiment</th>
<th>12 Hours</th>
<th>24 Hours</th>
<th>36 Hours</th>
<th>48 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAD</td>
<td>1.93</td>
<td>1.52</td>
<td>2.29</td>
<td>1.76</td>
</tr>
<tr>
<td>CTR</td>
<td>1.95</td>
<td>1.83</td>
<td>2.73</td>
<td>2.09</td>
</tr>
</tbody>
</table>

(Perez et al., 2006)

Inadequate understanding of optical/radiative properties of aerosol.

(IPCC, 2007)
Heterogeneous chemistry

Gas Chemistry (SAPRC90/CBIV)

Emissions gas& aerosol

Dry and wet removal gas&aerosol

Winds, T, P, q, Clouds, Radiative Fluxes

aerosol optical properties, cloud condensation nuclei

Aerosol model M7

Heterogeneous chemistry

Meteorological Model (BOLAM)

Transport & diffusion

BOLCHEM Flow Chart
M7: size-resolved aerosol microphysical model
BOLCHEM: dry deposition and sedimentation

Dry deposition velocity of aerosol particles

\[ v_{d,p}(X) = (f_{snow} + f_{bs}) \times v_{d,p,sln}(X) \]
\[ + (1 - f_{snow})(1 - f_{ws})f_{veg} \times v_{d,p,veg}(X) \]
\[ + (1 - f_{snow})f_{ws} \times v_{d,p,veg}(X) \]
\[ + f_{ice} \times v_{d,p,sln}(X) \]
\[ + f_{wat} \times v_{d,p,wat}(X) . \]

Where \( f_{snow}, f_{bs}, f_{wat}, f_{veg}, f_{ws} \) and \( f_{ice} \) are the surface fractions of snow, bare soil, water, vegetation, wet skin and ice, respectively.

(Ganzeveld et al., 1995, 1998, 2006)
BOLCHEM: dust model

Dust emission depends on:

- Surface wind speed
- Vegetation type and cover
- Preferential source areas
- Soil particle granulometry (soil texture)
- Soil moisture, snow cover

(Tegen et al., 2002; Tegen et al., 2004)
BOLCHEM-dust simulations

Saharan Dust over Italy: July 16, 2003
Vertical distribution of dust concentrations (µg/m3) at Etna, from 14 to 19 July, for the cases S1 and S2. The results are in agreement with Tafuro et al. (2006), the dust layers are located below 6 km (ca. level 19). The simulations S1 and S2 were carried out with threshold wind velocity lowered by a factor of 0.50 and 0.75 with respect to the values calculated according with Marticorena and Bergametti (1995).
Source emissions model for sea-salt:

1) Moanhan et al. (1986) adapted for M7 by P. Stier

2) Gong (2003) adapted for M7 by E. Viganti

16 July 2003, 12 UTC – sea salt model 2

These results are similar to the results of Langmann et al. (2008) for June 2003.
BOLCHEM: aerosol wet removal

The aerosol is removed:

- with different scavenging coefficients for **convective** and **stratiform** precipitations
- with different scavenging coefficients for **in-cloud** and **below-cloud** in case of stratiform precipitations.

The scavenging coefficient is computed as a function of rain intensity.

The amount of aerosol removed in a grid box is also a function of the cloud fraction contained in it.

The present implementation considers only the removal by liquid precipitations.

The scavenging coefficients are size and compound dependent.

(Mircea et al., 2000)
BOLCHEM: aerosol wet removal simulations

**Stratiform precipitation:** 26 September 2007 at 19:00
- precipitation
- aerosol without wet removal
- aerosol with wet removal

**Convective precipitations:** 12 June 2007 at 16:00
- precipitation
- aerosol without wet removal
- aerosol with wet removal
BOLCHEM: aerosol wet removal simulations
BOLCHEM: anthropogenic aerosol
BOLCHEM: gas phase photochemistry

http://gems.ecmwf.int/d/products/raq/forecasts/plot_RIU/
BOLCHEM: gas phase photochemistry

GEMS-RAQ Verification
Surface Ozone [µg/m³]
Mean error forecast
Europe
Date: 20080916 00UTC to 20080922 00UTC

http://gems.ecmwf.int/d/products/raq/forecasts/plot_RIU/
BOLCHEM: gas phase photochemistry

GEMS-RAQ Verification
Surface Ozone [µg/m³]
Root mean square error forecast
Europe
Date: 20080916 00UTC to 20080922 00UTC

http://gems.ecmwf.int/d/products/raq/forecasts/plot_RIU/
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Grazie!
Thank you!
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