Combustion related nanoparticle formation in the atmosphere

Frank Arnold

Max-Planck-Institut für Kernphysik (MPIK), Heidelberg (Germany)

Talk given at 11th ETH conference on Combustion Generated Nanoparticles, 13-15 August 2007 (Zuerich, Switzerland)

Atmospheric aerosol particles are of considerable current concern as they influence climate and human health. Particles scatter sunlight and if sufficiently large may also serve as water condensation nuclei in cloud formation and freezing nuclei in cloud droplet freezing. The atmosphere contains primary and secondary aerosol particles. Primary particles are introduced into the atmosphere by external sources. Examples are soot from combustion, mineral dust from deserts, and sea salt from the oceans. Secondary particles are formed in the atmosphere by gas-to-particle conversion. Nascent secondary particles are initially very small (diameters around 1 nm) and hereafter may grow by condensation and mutual coagulation.

An important if not the most important gaseous precursor of secondary particles is sulphuric acid (H2SO4). It is formed by photochemical conversion of the atmospheric trace gas SO2 which in turn stems mostly from combustion. Gaseous H2SO4 induces new particle formation by nucleation and contributes to new particle growth by condensation.

It is presently thought that sulphur containing aerosol particles have a strong influence on climate. They tend to increase the planetary albedo and thereby cool the planet. Hence they counteract the warming induced by anthropogenic greenhouse gases. Interestingly both SO2 and anthropogenic greenhouse gases stem mostly from combustion. Recently a climate engineering method has been proposed as an “ultima ratio therapy” of climate in case of a greenhouse warming disaster. The climate engineering method generates sulphur containing stratospheric aerosol particles in order to cool the planet and damp anthropogenic greenhouse warming. This proposal builds on the experience with the two recent major volcanic eruptions (1982, 1992) which have cooled the planet by about 0.4 degrees for about 1-2 years.

This contribution reports on measurements of the atmospheric nano particle precursor gases H2SO4 and SO2. The measurements employed novel analytical tools (mass spectrometry-based) and have been made in a close cooperation between our MPIK-Heidelberg group and DLR-IPA (Deutsches Zentrum für Luft- und Raumfahrt-Institut für Physik der Atmosphäre). Measurements took place at altitudes between ground-level and 13000 m. Data have been obtained from various campaigns made in different parts of the globe including the northern and southern hemispheres, middle latitudes, the subtropics, the tropics, and the Arctic. Mass spectrometric instruments were deployed at ground-level, at high-altitude mountain sites, on a research ship, and on a research air craft (FALCON; operated by DLR).

Strong SO2 pollution has been observed at all heights covered by our measurements (0-13000 m). This implies that efficient vertical SO2 – transport takes place, particularly by convection in spite of some SO2 removal by clouds usually accompanying convection. Even long-range SO2 transport over thousands of kilometres has been observed particularly in the middle and upper troposphere where winds are very fast and within only about 7 days may transport SO2 around the globe. For example SO2 plumes released by fossil fuel combustion in China (where particularly sulphur-rich coal is burnt) have been observed over Europe.

This implies that photochemical SO2 conversion to gaseous H2SO4 followed by the formation and growth of nano particles can take place even thousands of kilometres downstream of major SO2 source regions.
Combustion related nano particle formation in the atmosphere

Frank Arnold
Max-Planck-Institut für Kernphysik Heidelberg

Talk given at 11th ETH conference on *Combustion Generated Nanoparticles*, 13-15 August 2007
Opening remarks

- Thanks to organizers of ETH conference
- Great pleasure to attend conference again
- 2005 air craft
- 2006 Diesel car
- 2007 Ocean ships and stationary sources
  (details of molecular processes can be found in power point hand out)
Perspective
Combustion related aerosol particle formation in the atmosphere

- influences **climate**
- potential adverse **health** effects
oceans black
clouds white

Aerosols
reflect → cooling
absorb → warming
An important if not the most important aerosol precursor gas is sulfuric acid

H₂SO₄
H2SO4

- Photochemically formed from SO2 which stems mostly from combustion
- Induces new aerosol particle formation
H2SO4

- Photochemically formed from SO2 which stems mostly from combustion
- Induces new aerosol particle formation
- In upper troposphere (UT): SO2 conversion fast; H2SO4/H2O nucleation efficient; horizontal long – range transport fast
H2SO4

- Photochemically formed from SO2 which stems mostly from combustion
- Induces new aerosol particle formation
- In upper troposphere (UT): SO2 conversion fast; H2SO4/H2O nucleation efficient; horizontal long-range transport fast
- But vertical SO2 transport from ground level SO2 sources to UT hindered by cloud processes?
Atmospheric Gaseous Sulfuric Acid
Sources and Sinks of Atmospheric H2SO4
Atmospheric H2SO4 Variations

which processes are controlling H2SO4

?
### Atmospheric Gaseous Sulfuric Acid Sources and Sinks

<table>
<thead>
<tr>
<th>SO2-Sources (mT/a)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil Fuel combustion</td>
<td>78.1</td>
</tr>
<tr>
<td>Oceanic Plankton</td>
<td>15.4</td>
</tr>
<tr>
<td>Volcanism</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Clouds can act as a source and sink for SO2.

Deposition processes are also important in the sulfur cycle.
Anthropogenic sulfur emissions

Emission rate: red (high), blue (very high)
Anthropogenic sulfur emissions

substantial SO2 pollution by ocean ships!
Ocean ship Diesel engines

• Are strong SO2 emitters
• Combust sulfur rich Diesel fuel
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

\[ \text{SO}_2 \xrightarrow{\text{OH}} \text{HSO}_3 \xrightarrow{\text{O}_2} \text{SO}_3 \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{SO}_4 \]
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

SO₂ → OH → HSO₃

H₂SO₄ → H₂O → PAP → HONO

SO₃ → HONO

IONS → PAP

PAP → SAP
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

Measured by MPIK-Heidelberg

SO2 → OH → HSO3

O2 → HO2 → H2O → H2SO4

SO3 → HSO3 → H2SO4

UV → O3 → UV

UV → (CH3)2CO

PAP → IONS → SAP → PAP
Measurements of Atmospheric Gaseous Sulfuric Acid
by MPIK Heidelberg
Atmospheric gaseous H$_2$SO$_4$ measured by MPIK

Composite of MPIK Data

marine PBL
Atmospheric gaseous H2SO4 measured by MPIK

Composite of MPIK Data

PBL:
Finland (Hy)
Germany (HD)
Atmospheric gaseous H$_2$SO$_4$ measured by MPIK

Composite of MPIK Data

FT:
Mt Zugspitze
Atmospheric gaseous H$_2$SO$_4$ measured by MPIK

Composite of MPIK Data
Atmospheric gaseous H$_2$SO$_4$ measured by MPIK

Composite of MPIK Data

Stratosphere: balloon and rocket
Atmospheric gaseous H$_2$SO$_4$ measured by MPIK
Atmospheric gaseous H2SO4 measured by MPIK
Composite of MPIK Data

Atmospheric gaseous H$_2$SO$_4$ measured by MPIK

sulfuric acid aerosol
and
sulfate aerosol
layer 0 – 30 km
Composite of MPIK Data

Atmospheric gaseous $\text{H}_2\text{SO}_4$ measured by MPIK

sulfuric acid aerosol
and
sulfate aerosol
layer 0 – 30 km
impact on climate!
OH and H2SO4 measurements

On Mount Zugspitze
Mount Zugspitze SFH 2300 m altitude
H2SO4 measurements

In ground-level air in Finland
Fiedler et al., 2004

H$_2$SO$_4$ concentration
inverse H$_2$SO$_4$ lifetime CS
Number concentration $N_3$ of particles with diameters $> 3$ nm

$N_3 \times 10^4$ # cm$^{-3}$

$H_2SO_4$ # cm$^{-3}$
H2SO4 variability is to a large part due to SO2 variability
Air craft-based SO2 measurements

cooperation MPIK/ DLR
Research aircraft FALCON (DLR)
Research air craft FALCON (DLR)
SO2 Measurements
(MPIK/DLR-IPA cooperation)

Atmospheric mole fraction ranges
(schematic)
Atmospheric sulfur dioxide measured by MPIK-DLR

- Mid-latitude remote atmosphere

Graph showing log SO2 mole fraction (ppt) vs. altitude (km).
Atmospheric sulfur dioxide measured by MPIK-DLR

- Mid-latitude remote atmosphere
- Tropical Remote atmosphere
Atmospheric sulfur dioxide measured by MPIK-DLR

log SO2 MOLE FRACTION (ppt)

ALTITUDE (km)

Mid-latitude remote atmosphere

Remote marine PBL
Atmospheric sulfur dioxide measured by MPIK-DLR

Mid-latitude remote atmosphere

Polluted continental PBL
Atmospheric sulfur dioxide measured by MPIK-DLR

Long-range transport
Pollution plume
Atmospheric sulfur dioxide measured by MPIK-DLR

Polluted marine atmosphere in ship corridor
Atmospheric **sulfur dioxide** measured by MPIK-DLR
Atmospheric **sulfur dioxide** measured by MPIK-DLR

Composite of previous figures
Aircraft Campaigns 2005-2007

CIMS measurements (cooperation MPIK/DLR)
Bio mass burning plume measurements

colaboration MPIK/ DLR
MODIS fire map: 22 – 31 Mar 06

MODIS fire map: 01 - 10 May 06

Fires indicated by red and yellow
Bio mass burning plume measurements

colaboration MPIK/ DLR
Absorbing aerosol measured by OMI (on AURA satellite)
Absorbing aerosol measured by OMI (on AURA satellite)
ATMOSPHERIC SULFUR DIOXIDE

Composite of MPIK Data

ALTITUDE (km)

log SO2 MOLE FRACTION (ppt)

Bio mass burning plume
Biomass burning plume

- Efficient NOx conversion to HNO3
- Suggests high OH
- appreciable SO2 conversion to gaseous H2SO4
- H2SO4 coating of soot → hygroscopcity increases
Aerosol model simulations

AEROFOR model (cooperation with L. Pirjola, UH)
AEROFOR model: 10 day simulation of number concentrations $N_x$ of particles with diameters $> x$ nm

F. Arnold, L. Pirjola, et al. 2007
AEROFOR model: 10 day simulation of number concentrations $N_x$ of particles with diameters $>x$ nm

F. Arnold, L. Pirjola, et al. 2007
Conclusions

• Aerosol precursor gas SO2 (main sources: combustion and smelters; other sources: plankton and volcanoes) can be efficiently transported vertically and horizontally
• Rapid long – range transport in UT
• Rapid photochemical conversion to gaseous H2SO4 in UT
• Efficient formation of nanoparticles by H2SO4 nucleation in UT
• Growth of nanoparticles to CCN size by H2SO4 condensation followed by coagulation is possible
Acknowledgements

• Organizers of ETH conference
• Cooperation partners
  (DLR, MAN, UH, NILU, ....)
Thank you for your interest