Combustion Generated Aerosol Precursors

Frank Arnold
Max-Planck-Institut für Kernphysik Heidelberg

Talk given at 9th ETH workshop on Combustion Generated Nanoparticles, 15-17 August 2005
Combustion Related Aerosol Particles are important due to their

- Health effects
- Climate effects
Climate Effects of Combustion Related Aerosol Particles

• direct effect: scattering and absorption of sunlight
• indirect effect: particles act as CCN and CFN
• particles tend to increase planetary albedo
• albedo increase counteracts additional greenhouse warming
• albedo increase is not well quantified

Æ large uncertainties in climate model predictions
Climate Effects of Combustion Related Aerosol Particles

- **direct effect**: scattering and absorption of sunlight
Climate Effects of Combustion Related Aerosol Particles

- **direct effect**: scattering and absorption of sunlight
- **indirect effect**: particles act as CCN and CFN

Æ

large uncertainties in climate model predictions
Climate Effects of Combustion Related Aerosol Particles

- **direct effect**: scattering and absorption of sunlight
- **indirect effect**: particles act as CCN and CFN
- particles tend to increase planetary albedo
Climate Effects of Combustion Related Aerosol Particles

- **direct effect**: scattering and absorption of sunlight
- **indirect effect**: particles act as CCN and CFN
- particles tend to **increase planetary albedo**
- albedo increase **counteracts** additional greenhouse warming
Climate Effects of Combustion Related Aerosol Particles

- direct effect: scattering and absorption of sunlight
- indirect effect: particles act as CCN and CFN
- particles tend to increase planetary albedo
- albedo increase counteracts additional greenhouse warming
- albedo increase is not well quantified → large uncertainties in climate model predictions
clouds contribute most to planetary albedo
oceans covering 70% of planets surface do not contribute much
Visual Manifestations of Combustion Effects on the Atmosphere
Indirect effect of carbonaceous particles: Ship tracks

Ship tracks on the East Atlantic. Aerosol particles emitted by ships (soot particles with a high sulfur content) act as CCN and form clouds and enhance cloud reflectivity.
Combustion Generated Aerosol Precursors

- **NUCLEATING GASES:**
- **CHEMIIONS:**
- **CONDENSING GASES:**
- **GASEOUS PRECURSORS of NUC. and COND. GASES:**
Combustion Generated Aerosol Precursors

- **NUCLEATING GASES:**
  - H$_2$SO$_4$

- **CHEMIIONS:**
  - HSO$_4$-(H$_2$SO$_4$)$_a$(H$_2$O)$_w$

- **CONDENSING GASES:**
  - H$_2$SO$_4$, organics

- **GASEOUS PRECURSORS of NUC. and COND. GASES:**
  - SO$_2$
Focus of present talk

nucleating and condensing gas

H2SO4
Aerosol Precursor Measurements:

Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)
- Air Craft Engine Exhaust (at ground level)
- Ship Plumes
- Automobile Exhaust
- Burner Exhaust (laboratory)
- Flow Reactor (laboratory)
Aerosol Precursor Measurements: Environments

- Free Atmosphere
- Atmospheric Boundary Layer
- Air Craft Wakes (in flight)
- Air Craft Engine Exhaust (at ground level)
- Ship Plumes
- Automobile Exhaust
- Burner Exhaust (laboratory)
- Flow Reactor (laboratory)
Atmospheric Gaseous Sulfuric Acid
SULFURIC ACID MOLECULE
H2SO4

- Most important property: large GA
  - proton transfer to other molecule with large PA
    (Atmosphere: H2O)
  - Gas-Phase Hydrates: H2SO4(H2O)n
**SULFURIC ACID MOLECULE**

\[ \text{H}_2\text{SO}_4 \]

- Most important property: large $\text{GA}$
  - proton transfer to other molecule with large $\text{PA}$
    (Atmosphere: $\text{H}_2\text{O}$)
  - Gas-Phase Hydrates $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$

- Atmosphere:
  - **Secondary H$_2$SO$_4$:** formed in Atmosphere from SO$_2$
  - **Primary H$_2$SO$_4$:** released from combustion

**Example:** Aircraft
Sources and Sinks of Atmospheric H2SO4
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

SO2
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

SO2

SO2-Sources (megatons per year):
- Fossil Fuel combustion : 78.1
- Oceanic Plankton : 15.4
- Volcanism : 9.4
SO2-Sources (megatons per year):
Fossil Fuel combustion : 78.1
Oceanic Plankton : 15.4
Volcanism : 9.4
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

**SO2-Sources (megatons per year):**
- Fossil Fuel combustion : 78.1
- Oceanic Plankton : 15.4
- Volcanism : 9.4
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

SO₂ → OH → HSO₃

O₂ → SO₃

SO₃ + H₂O → H₂SO₄
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

SO₂ → OH → HSO₃ → NO → H₂SO₄

O₂ → HO₂ → SO₃ → H₂O
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

- \( \text{SO}_2 \) → \( \text{HSO}_3 \) → \( \text{H}_2\text{SO}_4 \)
- \( \text{OH} \) → \( \text{HSO}_3 \)
- \( \text{O}_2 \) → \( \text{SO}_3 \) → \( \text{H}_2\text{SO}_4 \)
- \( \text{H}_2\text{O} \) → \( \text{PAP} \)
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

- **SO₂**
- **OH** → **HSO₃**
- **O₂** → **SO₃**
- **H₂O** → **H₂SO₄**

**Sources**:
- **SO₂**
- **O₂**
- **H₂O**

**Sinks**:
- **OH**
- **PAP** → **IONS**
- **PAP** → **SAP**
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

- SO₂
- OH
- H₂SO₄
- H₂O
- PAP
- SAP
- IONS
- HONU
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

- SO₂
- OH
- HSO₃
- O₂
- SO₃
- H₂O
- H₂SO₄
- PAP
- IONS
- HONU
- SAP
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

- SO2 → OH
- HSO3
- O2 → HO2
- H2SO4 → SO3
- H2O
- PAP
- IONS
- HONU
- (CH3)2CO
- UV → O3
- UV

Chemical reactions involved in the formation and decay of atmospheric gaseous sulfuric acid.
Atmospheric Gaseous Sulfuric Acid Sources and Sinks

Measured by MPIK-Heidelberg

SO₂ → OH

HSO₃ → NO

O₂ → HO₂

SO₃ → H₂SO₄

H₂O → IONS

PAP → SAP

(CH₃)₂CO → UV

O₃ → UV
Measurements of Atmospheric Gaseous Sulfuric Acid by MPIK Heidelberg
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

PBL:
Finland (Hy)
Germany (HD)
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

FT:
Mt Zugspitze
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

UT/LS: aircraft
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

Stratosphere:
balloon and rocket
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

equilibrium saturation
H2SO4 concentration
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

Supersaturated-Layer

[Graph showing atmospheric gaseous sulfuric acid data with labeled axes and data points]
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

sulfuric acid aerosol and sulfate aerosol layer 0 – 30 km
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

sulfuric acid aerosol
and
sulfate aerosol
layer 0 – 30 km
impact on climate!
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

altitudes (km)

Log ($\text{H}_2\text{SO}_4$)$_{\text{GAS}}$ (cm$^{-3}$)

aircraft
ATMOSPHERIC GASEOUS SULFURIC ACID

Composite of MPIK Data

![Graph showing atmospheric gaseous sulfuric acid levels]

- altitude (km)
- Log (H₂SO₄)₆GAS (cm⁻³)

- aircraft
- automobile
Atmospheric Gaseous Sulfuric Acid Measurements made by MPIK at ground level during projects SCAVEX and QUEST in close collaboration with University of Helsinki and DLR
Mount Zugspitze SFH  2300 m altitude

![Graph showing OH, H2SO4, and Sunlight concentrations over Local Time (h) with corresponding Solar Radiation (W per m2).]
Conclusions

• particle formation triggered by H2SO4
• only about 5% of particle growth is due to H2SO4/H2O condensation
• particle growth probably due to condensable organics
• see our recent papers
  Fiedler et al (2005)
  Boy et al (2005)
Atmospheric Sulfuric Acid Measurements made by MPIK in Aircraft Exhaust

measurements made in close collaboration with DLR
**EMISSION INDEX (mg / kg)**
for modern engine and **FSC=400 (100-3000) ppmM**

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_4$ - CONDENSATE</td>
<td>73</td>
<td>(18 - 550)</td>
</tr>
<tr>
<td>SOOT</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>COND. HC.</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

• about 2 - 4 % of fuel sulfur undergoes conversion to gaseous H2SO4
• most of the aerosol mass in an aircraft exhaust plume is due to H2SO4/H2O
• see our publications (following slide)
SO2 Measurements made by MPIK in Oceanship Exhaust during project ITOP (in close collaboration with DLR)
Indirect effect of carbonaceous particles: Ship tracks on the East Atlantic. Aerosol particles emitted by ships (soot particles with a high sulfur content) act as CCN and form clouds and enhance cloud reflectivity.
Conclusions

• strong SO2 pollution in marine boundary layer near ship traffic ways
• sounding individual ship tracks is feasible
• next step H2SO4 and OH measurements in marine boundary layer and ship exhaust
Gaseous Sulfuric Acid Measurements made by MPIK in Automobile Exhaust in close collaboration with University of Helsinki
Conclusions from automobile measurements

• particle formation is induced by $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ nucleation

• less than 10% of particle growth is due to $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ condensation

• particle growth is probably mostly due to condensable organics
Acknowledgements

- DLR
- University of Helsinki
- IFT Leipzig
- Members of our MPIK-Heidelberg group
MEMBERS OF MPIK HEIDELBERG GROUP

SCIENTISTS
Prof. F. Arnold, Dr. H. Aufmhoff, Dr. B. Umann, Dr. E. Katragkou,
Dr. S. Wilhelm, Dr. M. Hanke, Dr. J. Ücker, Dr. A. Kiendler,
Dr. S. Eichkorn, Dr. J. Curtius

PHD STUDENTS
M. Speidel, T. Schuck, V. Fiedler, R. Nau, G. Eerdekens,
H. Aufmhoff, B. Umann, E. Katragkou, S. Wilhelm, J. Ücker, S. Eichkorn,
M. Hanke, A. Kiendler,

DIPLOMA STUDENTS
A. Kuhlmann, V. Fiedler, R. Nau, J. Hoffmann,
S. Scholz, K. Gerlinger, H. Haverkamp, J. Reimann, D. Wiedner, CH. Schaal,
S. Wilhelm, H. Aufmhoff, B. Umann

VISITING SCIENTISTS
Dr. L. Pirjola, Dr. A. Sorokin, Dr. K. Sellegri

TECHNICIANS
B. Preissler, R. Zilly, U. Schwan, A. Jung