Primary and Secondary Organic Aerosol from Diesel Engines

Urs Baltensperger
Paul Scherrer Institut, Villigen, Switzerland

12th ETH-Conference on Combustion Generated Nanoparticles
Zurich, June 23-25, 2008
Primary versus secondary aerosol

- **Primary particles**: directly emitted to the atmosphere

- **Secondary particles**: formed in the atmosphere by condensation (nucleation and growth) after chemical transformation
Secondary aerosol can make up to 75% of PM1. Gaseous aerosol precursors (like NOx) should be included in considerations.

Source attribution of PM1 in Switzerland in winter.
Secondary aerosol appears to be also involved in health effects: higher slope in summer than in winter

Nawrot et al., Journal of Epidemiology and Community Health (2006)
Worldwide AMS measurements show the abundance of organics in the atmospheric aerosol

Zhang et al., GRL 2007
Traditional ways of determining primary and secondary organic aerosol (POA and SOA) A: OC/EC ratio

Castro et al., AE 1999
Traditional ways of determining primary and secondary organic aerosol (POA and SOA)

B: Tracers

\[ c_i = \sum_k \alpha_{i,k} S_k + e_i \]

Critical issues

- Atmospheric stability
- Source completeness
- Representative source profiles
- Analytical accuracy and precision

Subramanian et al., 2005
Applying partitioning theory to primary emissions results in much smaller primary fraction than classical OC/EC ratios suggest, because emission factors are not constant, but decrease with increasing dilution, due to evaporation.

Robinson et al., Science 2007

Donahue et al., Environ. Sci. Technol. 2006
The partitioning coefficient $\xi$ for a compound $i$ with an effective saturation concentration $C_i^*$

$$\xi_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

Donahue et al., 2006
Mass increase on aging much higher than explained with traditional SOA precursors

Mass estimates based on SMPS (density 1) Robinson et al., Science 2007
Revised approach (less POA because of dilution, more SOA than from traditional precursors) results in much higher SOA fraction, which matches field data.

Robinson et al., Science 2007
Carbon-14 analysis suggests that Zurich’s SOA is mainly biogenic (in winter: substantial biomass burning)

Szidat et al., JGR (2006)
Paradox:
- Correlation of WSOC with CO suggests anthropogenic origin
- $^{14}$C analysis finds 70-80% of WSOC to be biogenic
  (in Zurich we find 80-90% of WSOC biogenic, Szidat et al., 2006)

Weber et al.,
JGR 2007
Mass increase on aging much higher than explained with traditional SOA precursors

Done with a small power generator: how representative for diesel cars on the roads?

Mass estimates based on SMPS (density 1)  

Robinson et al., Science 2007
Aging of diesel exhaust in the PSI smog chamber
Aging of diesel exhaust in the PSI smog chamber

Euro 3 diesel car running at 60 km per hour

Filling the chamber in ~15 min
Diesel and wood combustion aerosol generators for the PSI smog chamber
EC project POLYSOA:
Exposure of various biological systems to SOA, in collaboration with Marianne Geiser Univ. Bern and Markus Kalberer, highly interesting findings, first results in Baltensperger et al., JAM 2008
Instrumentation

- **Size distribution:** SMPS
- **Black carbon concentration:** aethalometer
- **Organic mass, size+ chem.:** aerosol mass spectrometer
- **Hygroscopic growth factor:** Hygroscopicity tandem differential mobility analyzer
The Aerodyne aerosol mass spectrometer (AMS)

- Particle Inlet (1 atm)
- Aerodynamic Lens (2 Torr)
- Chopper
- TOF Region
- Turbo Pump
- Thermal Vaporization & 70 ev EI Ionization
- MCP
- Signal to ADC
- MCP
Comparison of AMS measurements in Gubrist tunnel (June 2008) and EURO III car in PSI smog chamber

\[ R^2 = 0.9324 \]
Instrumentation – and related problems

• Size distribution: SMPS
  Effective density?

• Black carbon concentration: aethalometer
  Mass absorption efficiency?

• Organic mass, size+ chem.: aerosol mass spectrometer
  Collection efficiency?

• Hygroscopic growth factor: Hygroscopicity tandem differential mobility analyzer
  Restructuration?
Technological difficulties

Diesel

Wood combustion
Technological differences

When just turning on the lights: nothing happens:
NO + O₃ → NO₂ and O₂
Solution: adding ozone to achieve a more realistic NO/NO₂ ratio
After addition of 660 ppb ozone: still nothing happens (except wall losses)
After addition of 660 ppb ozone: still nothing happens (except wall losses)

\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \]
After addition of 570 ppb ozone and 1800 ppb propene: SOA formation
Wood combustion aerosol: immediate SOA formation after turning on the lights; no addition of ozone or propene needed
The ToF-AMS allows for discrimination of mass fragments with m/z 57
m/z 57 (C₄H₉⁺) used as marker of vehicle primary emissions

57.074 (C₄H₉⁺)

POA MS (fresh diesel soot) ➔ pure HOA
The ToF-AMS allows for discrimination of mass fragments with m/z 57

57.038 (C$_3$H$_5$O$^+$)  57.074 (C$_4$H$_9$$^+$)

Aged POA MS (diesel soot after 2 hours of aging) ➔ 50% OOA
Hygroscopic growth factor increases with time; little restructuration for diesel soot particles see more on poster by Torsten Tritscher
Conclusions

- Secondary aerosol is an important aerosol fraction
- SOA typically far more abundant than POA, needs to be included in an overall assessment of PM
- Big debate currently going on about importance of anthropogenic SOA (mainly traffic)
- Diesel exhaust typically produces less SOA than wood combustion; the latter forms SOA immediately after turning on the lights
- More experiments are needed (and planned) to assess the SOA formation potential of these sources
Thank you for your attention

Acknowledgments
People:


Funding:
- Competence Centre for Energy and Mobility
- Competence Centre for Environment and Sustainability
- Swiss National Science Foundation
- BAFU
- EC projects ACCENT, EUCAARI, EUROCHAMP, POLYSOA

http://www.psi.ch/lac
Aerosols affect our health and have an impact on climate

Affect our health; in order to reduce this adverse effect we need to know the sources contributing to the total aerosol load

- a health hazard

Source: www.ecocouncil.dk

Affect our climate by exerting a cooling; in order to better quantify this effect we need to know more about climate relevant aerosol properties

http://saga.pmel.noaa.gov/aceasia/
Set-up experiments

PM Target conc = 20 ug/m3

(Adapted from Brit A. Holmén et al., 2005)
Aerosol number distribution close to a highway

Condensation particles

Soot particles

Condensation particles are formed within ~1 sec after emission, but without chemical transformation → primary particles
Primary versus secondary organic aerosol

• Primary organic aerosol (POA): directly emitted to the atmosphere in particulate form

• Secondary organic aerosol (SOA): formed in the atmosphere by condensation (nucleation and growth), after chemical transformation *

• Primary particles that undergo chemical reactions: ➔ aged primary
Key organic mass fragments originally used for source apportionment

“Hydrocarbon”: HOA

\[ \text{e}^- \]

\[ \text{C}_n\text{H}_m \rightarrow \text{C}_n\text{'H}_m'^+ \]

\[ 27, 29, 41, 43, 55, 57, 69, 71, \ldots \]

“Oxygenated”: OOA

\[ \text{e}^- \]

\[ \text{C}_n\text{H}_m\text{O}_y \rightarrow \text{HCO}^+ \text{ CO}_2^+ \text{ H}_3\text{C}_2\text{O}^+ \text{ HCO}_2^+ \text{ C}_n\text{'H}_m'^+ \]

\[ 29, 44, 43, 45, 55, 57, \ldots \]

\[ m/z \ 44 \text{ is a measure of degree of oxidation} \]
AMS summer data for Zurich

Zurich, Summer
19 $\mu$g m$^{-3}$

OM: 13 $\mu$g/m$^3$

Org 69%
NO$_3$ 8%
SO$_4$ 8%
NH$_4$ 15%

OM: 13 $\mu$g/m$^3$