Properties of aged combustion aerosols
First results from smog chamber experiments

T. Tritscher*, M. Heringa, R. Chirico, M. Steiger, J. Duplissy, M. Gysel, P. DeCarlo, J. Dommen, E. Weingartner, U. Baltensperger

Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
*contact: Torsten Tritscher, torsten.tritscher@psi.ch, http://lac.web.psi.ch/

Aerosols from combustion processes are made up of soot mainly; but they also contain a certain fraction of organic matter and inorganic salts. In the atmosphere, volatile organic species can condense on the soot particles. This results in complex mixtures of black carbon and organic species (secondary organic aerosols – SOA) in the particle phase. Their hygroscopic properties and the contribution to cloud formation are still largely unknown and less understood than those of inorganic mixtures.

The aging of combustion aerosols is analyzed under almost atmospheric conditions at the PSI smog chamber. The 27 m^3 Teflon bag in a wooden housing of the smog chamber is temperature and RH (relative humidity) controlled. The chamber is equipped with 4 Xenon lamps to simulate sunlight and several gas instruments (NO/NO_x, O_3, CO, CO_2). The particle number size distribution (SMPS), the total particle number (CPC), the chemical composition (AMS, Aerosol mass spectrometer) and black carbon (BC) concentration (Aethalometer). In addition a new version of the Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA) measures the hygroscopic growth of the aged soot particles and their SOA coating.
Two different sources of soot aerosols from a diesel passenger car (without particle filter) and a wood stove are introduced to the chamber. The combustion sources were connected to the chamber via heated tubing and a dilution unit.

The characterization of the hygroscopic properties is done with the H-TDMA, which analyzes the hygroscopic growth of aerosols. The hygroscopic growth depends on humidity (RH), particle size and chemical composition. The hygroscopic growth factor is defined as:

$$\text{Growth factor (GF)} = \frac{\text{wet particle diameter } (D_{wet})(RH)}{\text{dry particle diameter } (D_{dry})}$$

First results from freshly emitted diesel soot and wood stove particles show that the hygroscopic growth of these particles is quite small due to the high hydrophobic soot content. The restructuring of the soot particles from larger agglomerates to more compact particles needs to be taken into account and influences the hygroscopic growth measurements.

Organic matter (OM), measured by the AMS, increases strongly after lights on, caused by SOA formation. The level it reaches is different between experiments. Black carbon (BC) is very high after injection and decreases due to wall losses in the chamber. The SMPS derived mass can be quite different between experiments (diesel/wood) and indicates different effective densities (high BC fraction) or restructuring of the soot agglomerates (high BC fraction).
After several hour of photochemical aging a GF at RH=90% up to 1.10 is reached for diesel particles, for wood burning experiments the corresponding GF increases up to 1.14.

Summarizing, freshly emitted soot particles are characterized by low hygroscopicity, but they experience increasing hygroscopic growth caused by photochemical aging. There are no

significant differences between GF of wood and diesel emissions so far. A constant GF is not yet reached after 6-7 hours of aging. The size dependence is not clear in all experiments; smaller particles tend to show a faster increase in GF, due to a higher SOA uptake. Restructuring of the soot particles is found to be relatively small: a GF of ~0.98 is measured after the particles experience high RH and were subsequently dried. The comparison of SMPS derived mass and OM plus BC mass shows significant discrepancies, which is due to the fact that the particles are not spherical.
Further experiments will prove the consistency of these results and help characterize atmospheric aging processes of the combustion particles in terms of a change in size, hygroscopicity and volatility.

Acknowledgements
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Introduction

Aerosols from combustion processes are made up of soot mainly; they contain also a fraction of organic matter and salts. Volatile organic species can condense on the soot particles. This results in complex mixtures of black carbon and organic species (secondary organic aerosols – SOA) in the particle phase.

The hygroscopic properties and the contribution to cloud formation of these organic mixtures are still largely unknown and less understood than those of inorganic mixtures.

Atmospheric aging of combustion aerosols is studied at the PSI smog chamber with emissions from a diesel passenger car and a wood stove.

A new version of the Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) measures the hygroscopic growth of the aged diesel and wood soot particles and their SOA coating.

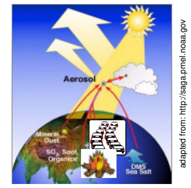


Figure 1: Aerosols in atmosphere

PSI smog chamber

- $27\ m^3$ teflon bag in wooden housing
- 4 Xenon lamps to simulate sunlight
- Gas phase instruments: NO/NO_x, O_3, CO, CO_2
- Particle number size distribution, total number
- Chemical composition (Aerosol mass spectrometer), black carbon (Aethalometer)
- Hygroscopic properties of aerosols (H-TDMA)

- Combustion source connected to the chamber via heated tubing and dilution unit:
  - biomass burning emissions, wood stove
  - diesel exhaust passenger car (without particle filter)

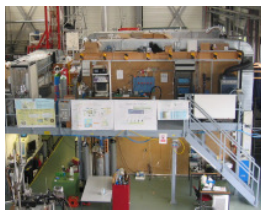
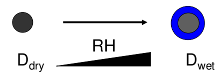


Figure 2: View on the PSI smog chamber with instrumentation

Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA)

- Analyzes the hygroscopic growth of aerosols
- Hygroscopic growth depends on humidity (RH), particle size and chemical composition
- Definition of hygroscopic growth factor:



$$\text{Growth factor (GF)} = \frac{\text{wet particle diameter } (D_{wet})(RH)}{\text{dry particle diameter } (D_{dry})}$$

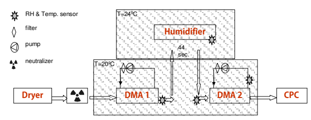


Figure 3: Sketch of the H-TDMA

Figure 4: H-TDMA instrument

Diesel emission aging

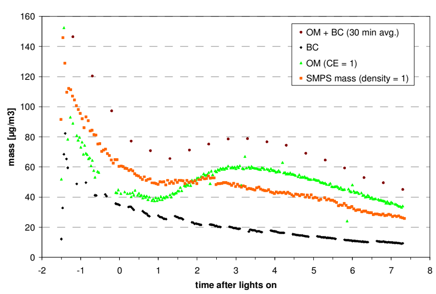


Figure 5: Mass evolution during a diesel exhaust experiment (9.4.2008). Organic matter (OM) increases strongly after lights on, caused by SOA production. Black carbon (BC) decreases due to wall losses. SMPS derived mass indicates different effective densities (high BC fraction).

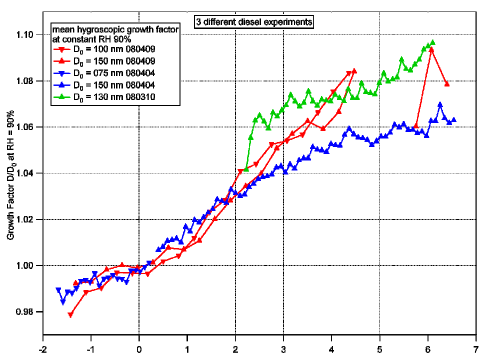


Figure 6: Evolution of the particle's hygroscopicity for 3 different diesel aging experiments. Start values GF <1 indicate slightly restructuring before lights are on. GF up to 1.1 are reached. Different experiments agree very well.

Wood combustion aging

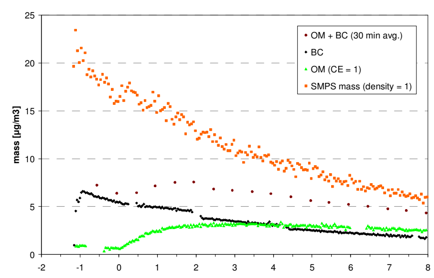


Figure 7: Mass evolution during a wood combustion experiment (14.4.2008). Organic matter (OM) increases after lights on, but reaches only the level of black carbon (BC). SMPS derived mass indicates restructuring of the soot agglomerates (high BC fraction).

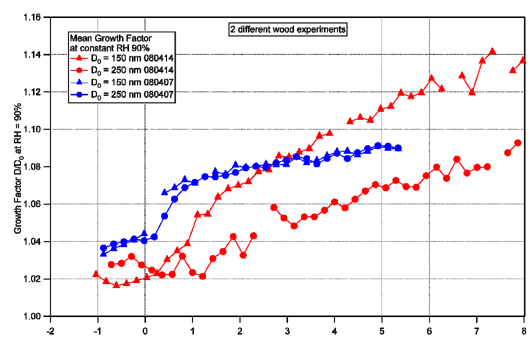


Figure 8: Time series of hygroscopic growth factors of 2 different wood aging experiments. GF is already before lights on >1, increases up to GF 1,14. Experiments agree well, only one experiment shows size depend differences

Conclusions

- Fresh soot emissions are characterized by low hygroscopicity, but they experience increasing hygroscopic growth under high RH conditions during photochemical aging.
- There are no significant differences between GF of wood and diesel emissions, a constant GF after 6-7 hours of aging is not yet reached.
- Size dependence is not clear in all experiments, smaller particles tend to show a faster increase in GF, more uptake of SOA.
- Restructuring of the soot particles needs to be taken into account, but the experiments with pre-humidifier showed no or very small influences on the hygroscopic growth measurements.
- Further experiments will prove the consistency of the results and help to work out more physical properties like volatility, size dependence or difference between wood and diesel in hygroscopicity.

Contact
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