

# Change of physical aerosol properties during aging of combustion emissions in a smog chamber

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Combustion emissions from natural or anthropogenic sources are a complex mixture of black carbon (BC), organics, and other compounds such as inorganic salts. They contribute in several areas to an important fraction of the total aerosol mass. Secondary organic aerosol (SOA) in our atmosphere originates from the photochemical transformation of primary volatile organic compounds over a wide volatility range. The hygroscopicity and other physical aerosol properties (e.g. volatility and light scattering) change during atmospheric aging. The magnitude of these effects and the influence on cloud formation, which is relevant for the global climate change, are still largely unknown.

The photochemical aging of combustion aerosols was analyzed under almost atmospheric conditions at the Paul Scherrer Institut (PSI) smog chamber (27 m<sup>3</sup>). Combustion aerosols from different sources including a Euro 3 diesel passenger car (without particle filter), a log wood oven, and a pellet burner were introduced via heated injection system into the chamber. A hygroscopicity tandem differential mobility analyzer (H-TDMA) measured the hygroscopic properties during photochemical aging, complemented by further aerosol instrumentation for chemical composition, size distribution, volatility and light scattering. The hygroscopic growth factor (GF) depends on relative humidity (RH), chemical composition and particle size and is defined as the ratio of the wet particle mobility diameter  $D$  to dry mobility diameter ( $D_0$ ).

Figure 1 shows the temporal evolution of the particle's mean GFs at 90% RH, the black carbon (BC) to organics (org.) ratio and the O to C ratio from aerosol mass spectrometer (HR-ToF-AMS) and aethalometer for different log wood burning experiments. GFs measured during the experiments investigating starting phase emissions showed an increasing trend up to values of about 1.20 at 90% RH. Particles emitted during some burning experiments exhibited a lower GF (1.02 at 90% RH) and no trend with photochemical aging. Generally spoken photo-chemical aging of wood oven emissions impacts on O to C and BC to organics ratios and on hygroscopic growth. The variation between the experiments is not fully understood, yet. However there is a clear link between the O to C ratio (increasing with aging time) and hygroscopicity, while the BC to organics ratio seems to be less important for determining the hygroscopicity.

Biomass burning aerosols from a pellet oven showed much higher hygroscopicity with GFs up to 1.90 at 95% RH during stable phase burning experiments. A more complete combustion process resulted in lower emissions of total organics and soot, leaving inorganic salts as a major component. Photochemical aging resulted in the formation of additional secondary organic aerosol and the mean GF decreased with time to values of about 1.4 (at 95% RH). The hygroscopicity of diesel aerosols from the Euro 3 passenger car was generally lower and remained constant with photochemical aging in most experiments (GF  $\approx$  1.00 at RH = 90 - 95%) or increased slightly in a few experiments to a GF of at most 1.1.

The light scattering under humidified conditions showed a similar trend of only slightly increased scattering enhancement ( $f(\text{RH } 80\%) = 1.0\text{-}1.3$ ) during diesel experiments and relatively high light scattering enhancement ( $f(\text{RH } 80\%) = 2.0\text{-}3.5$ ) during the aging of emissions from the wood pellet oven.

Summarising, distinct differences in hygroscopicity and other aerosol properties were observed for different combustion experiments. The aged soot-rich diesel car emissions show the lowest hygroscopicity and the salt-rich pellet burner emissions the highest. Aged emissions from a traditional log wood oven are intermediate. Further experiments will proof the consistency of those first findings and give further information for instance about the mixing state (internal/external) of the aerosols.

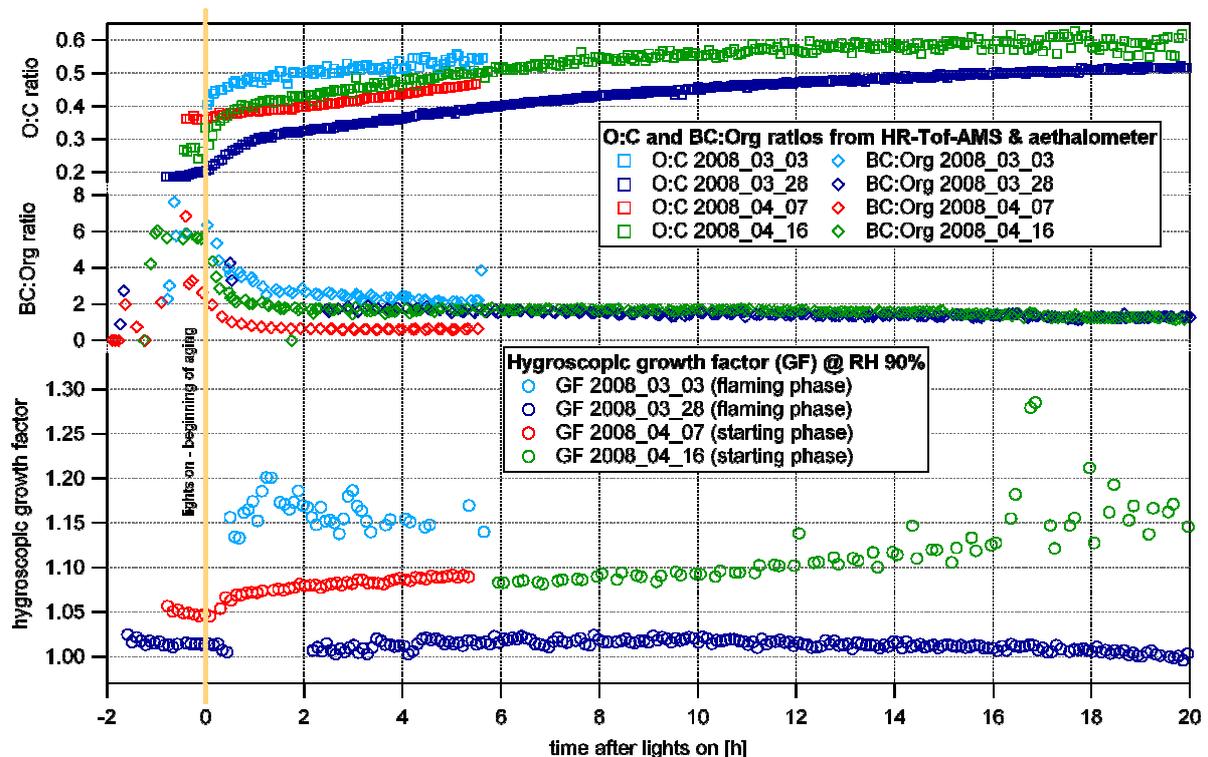


Figure 1: Temporal evolution of the particle's mean hygroscopic growth factors at 90% RH for different log wood oven experiments (lower panel) and corresponding BC to organics ratio (middle panel) and O to C ratio (upper panel) calculated from aerosol mass spectrometer (HR-ToF-AMS) and aethalometer.

#### 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 inorganic salts.

Volatile organic compounds from biogenic (e.g.  $\alpha$ -pinene) or anthropogenic (e.g. combustion aerosol) sources can form secondary organic aerosols (SOA) e.g. under the influence of light. This results in complex mixtures of organic species (and other compounds) in the particle phase.

Atmospheric aging and SOA formation of particles from different combustion sources are studied at the Paul Scherrer Institut (PSI) smog chamber.

## Facility

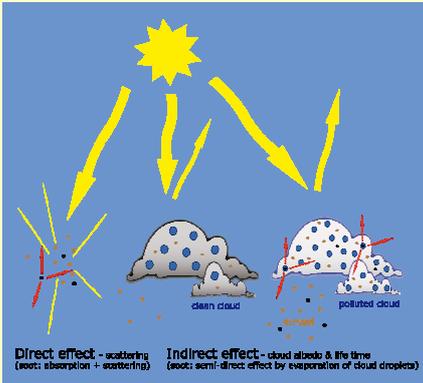
Several gas phase and aerosol instruments are connected to the 27 m<sup>3</sup> Teflon bag in the PSI chamber. Four Xenon lamps simulate sunlight.

Primary aerosol emissions from a EURO 3 diesel passenger car (without particle filter), a log wood oven and a pellet burner were exposed to photo-chemical aging and possible SOA formation in the smog chamber.



Fig. 1: View on the PSI smog chamber with instrumentation

## Motivation



Aerosols particles interact in several ways with the climate system.

Two main aerosol effects are defined. The direct effect is the light scattering and absorption by particles. The indirect effect describes the cloud-aerosol interaction (micro-physical cloud properties) and includes cloud albedo, cloud lifetime and other effects (IPCC 2007).

The hygroscopic properties of combustion aerosols and their contribution to cloud formation are still quite unknown and less understood than those of inorganic mixtures.

Fig. 2: Direct and indirect aerosol effect on climate (adapted from IPCC 2007)

## Instrumentation for measurement of ...

hygroscopic properties		chemical composition	
H-TDMA	WetNeph	HR-ToF-AMS	AE-31
Hygroscopicity Tandem Differential Mobility Analyzer	Humidified Nephelometer (3 wavelengths: 450, 550, 700 nm)	High-resolution time-of-flight aerosol mass spectrometer	Aethalometer
Hygroscopic growth factor: $GF(RH) = \frac{D_{wet}(RH)}{D_{dry}}$ <i>D</i> =diameter <i>RH</i> =relative humidity	Light scattering enhancement factor: $f(RH) = \frac{\sigma_s(RH)}{\sigma_s(dry)}$ $\sigma_s$ = scattering coefficient	Mass of organics and other refractory compounds	Attenuation of light → black carbon
GF @ RH 90-95%	f(RH) @ RH 80%	Org.	BC

## Aging of diesel car and pellet burner emissions

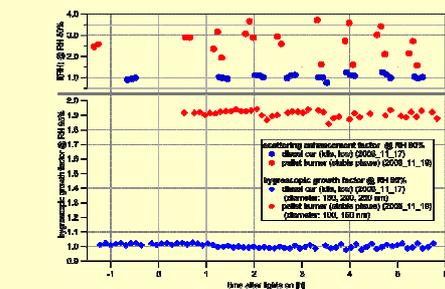


Fig. 3: Time series of hygroscopicity (lower panel) and scattering enhancement (upper panel) at high relative humidity.

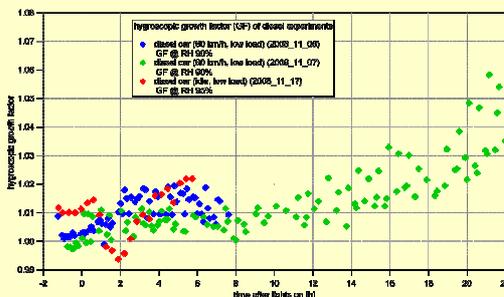


Fig. 4: Hygroscopic growth factor versus aging time in the smog chamber for three diesel experiments.

The hygroscopicity increases only slightly to max. GF of 1.06 at RH 90 - 95%.

## Conclusion

- Distinct differences between soot-rich diesel car and salt-rich pellet burner emissions in hygroscopicity (GF ~1.01 and 1.90) and scattering enhancement (f(RH) 1 and ~3), respectively (fig. 3)
- Hygroscopicity of diesel car aerosols generally low and remained fairly constant with photochemical aging in most experiments (fig. 4)
- Aerosols from pellet burner sometimes externally mixed (soot and salt mode)

## Aging of log wood oven emissions

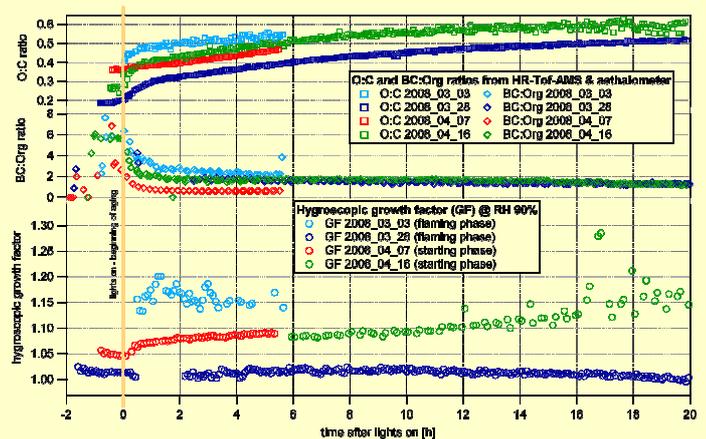


Fig. 5: Temporal evolution of the particle's mean hygroscopic growth factors at 90% RH for different log wood oven experiments (lower panel) and corresponding BC:organics ratio (middle panel) and O:C ratio (upper panel) calculated from HR-ToF-AMS and aethalometer.

## Conclusion

- Photo-chemical aging of wood oven emissions impacts on O:C and BC:organics ratios and on hygroscopic growth.
- Clear link between O:C ratio (increasing with aging time) and hygroscopicity
- BC:organics ratio seems to be less important for determining the hygroscopicity (differences in mixing state of the aerosol?)
- Variations between different log wood oven experiments – more experiments needed, but difficult to reproduce exactly the same conditions

## References

Denman, K.L. et al., 2007: Couplings Between Changes in the Climate System and Biogeochemistry. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

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