Primary and Secondary Organic Aerosol from Diesel Engines

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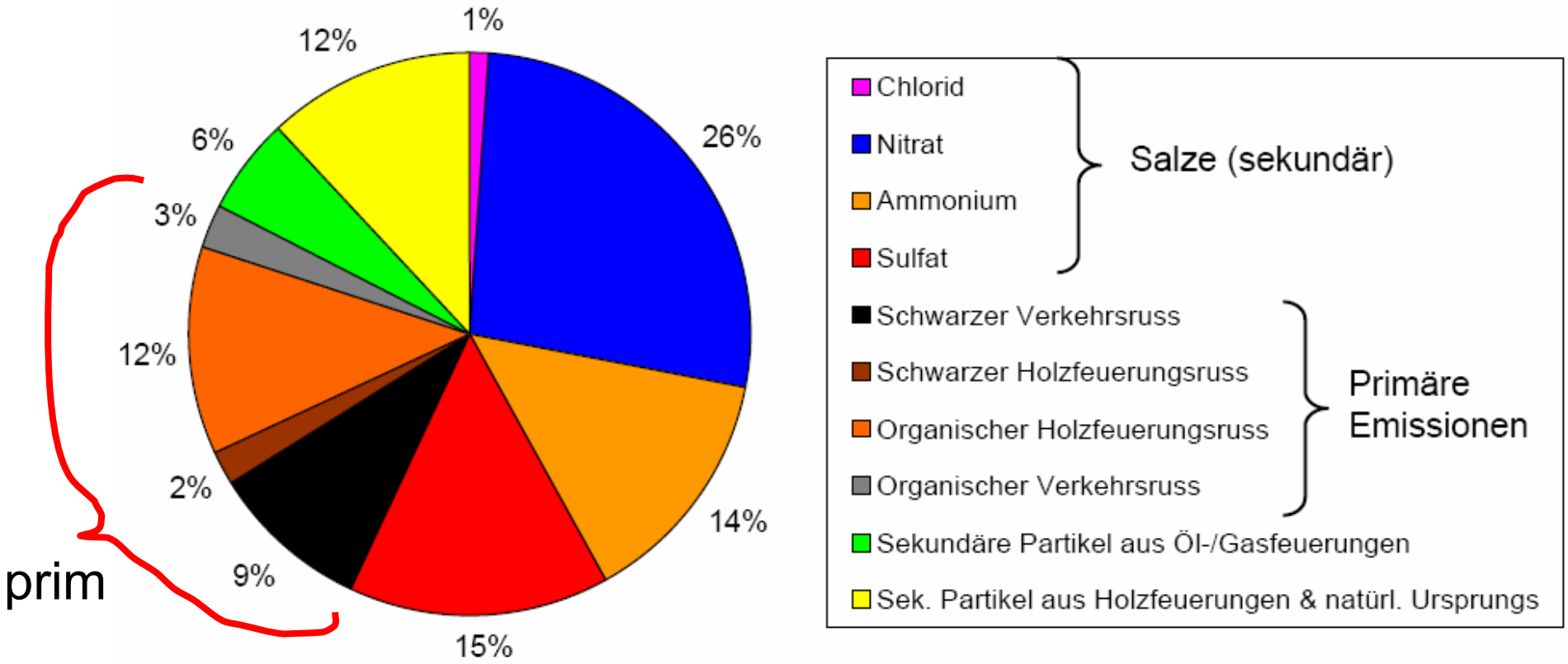
Primary versus secondary aerosol

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

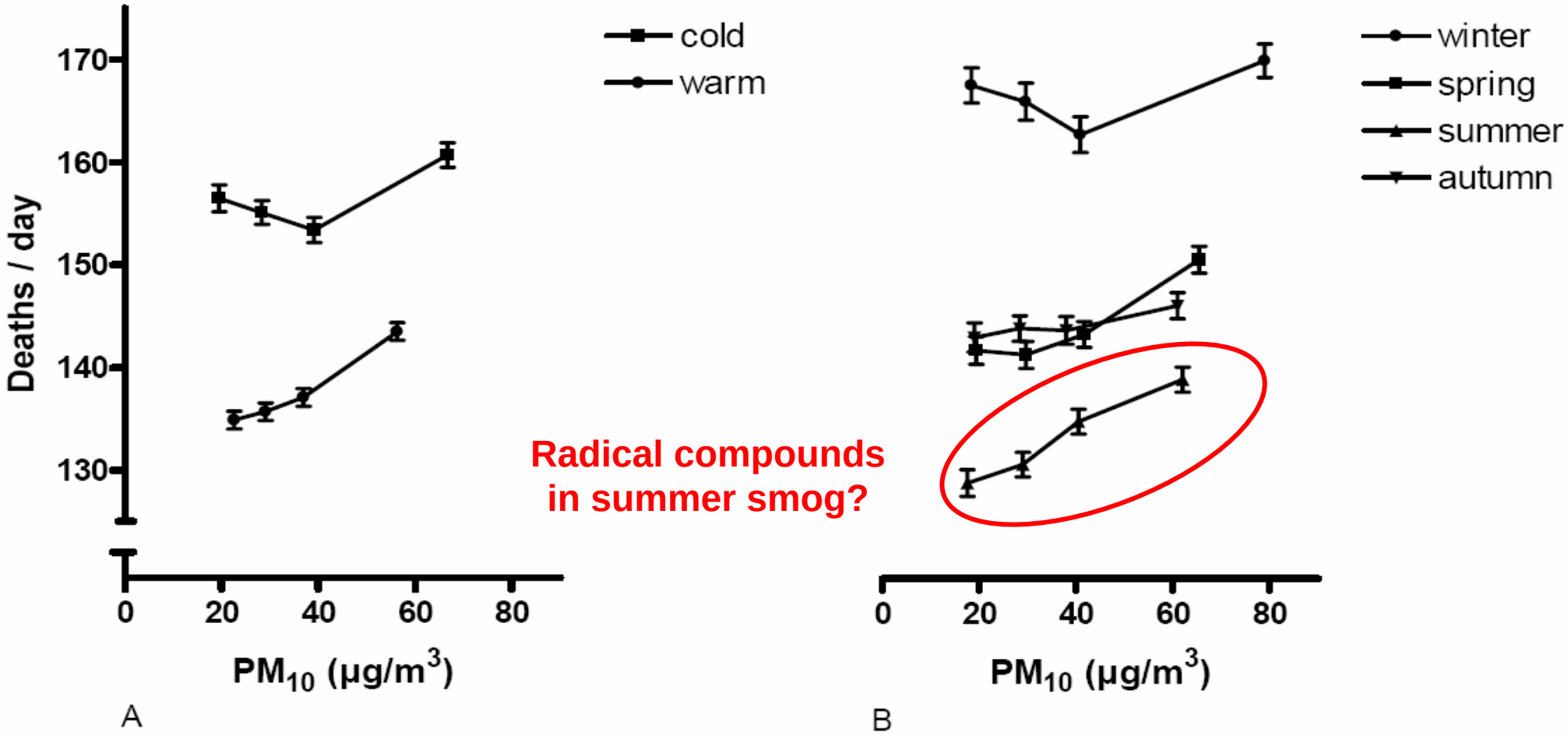
- **Secondary particles: formed in the atmosphere by condensation (nucleation and growth) after chemical transformation**

Secondary aerosol can make up to 75% of PM1 ➔ gaseous aerosol precursors (like NOx) should be included in considerations



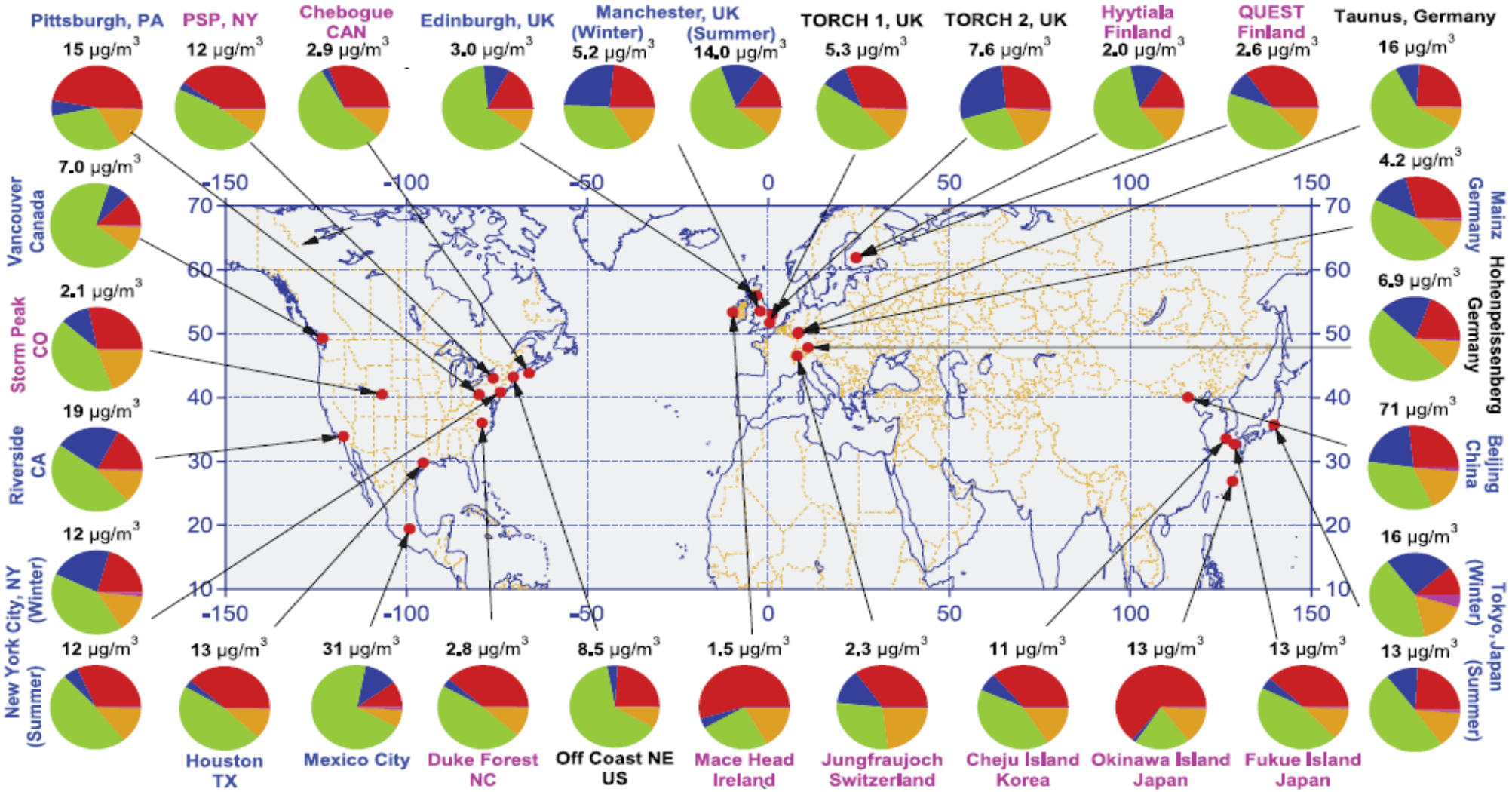
Source attribution of PM1 in Switzerland in winter

Secondary aerosol appears to be also involved in health effects: higher slope in summer than in winter



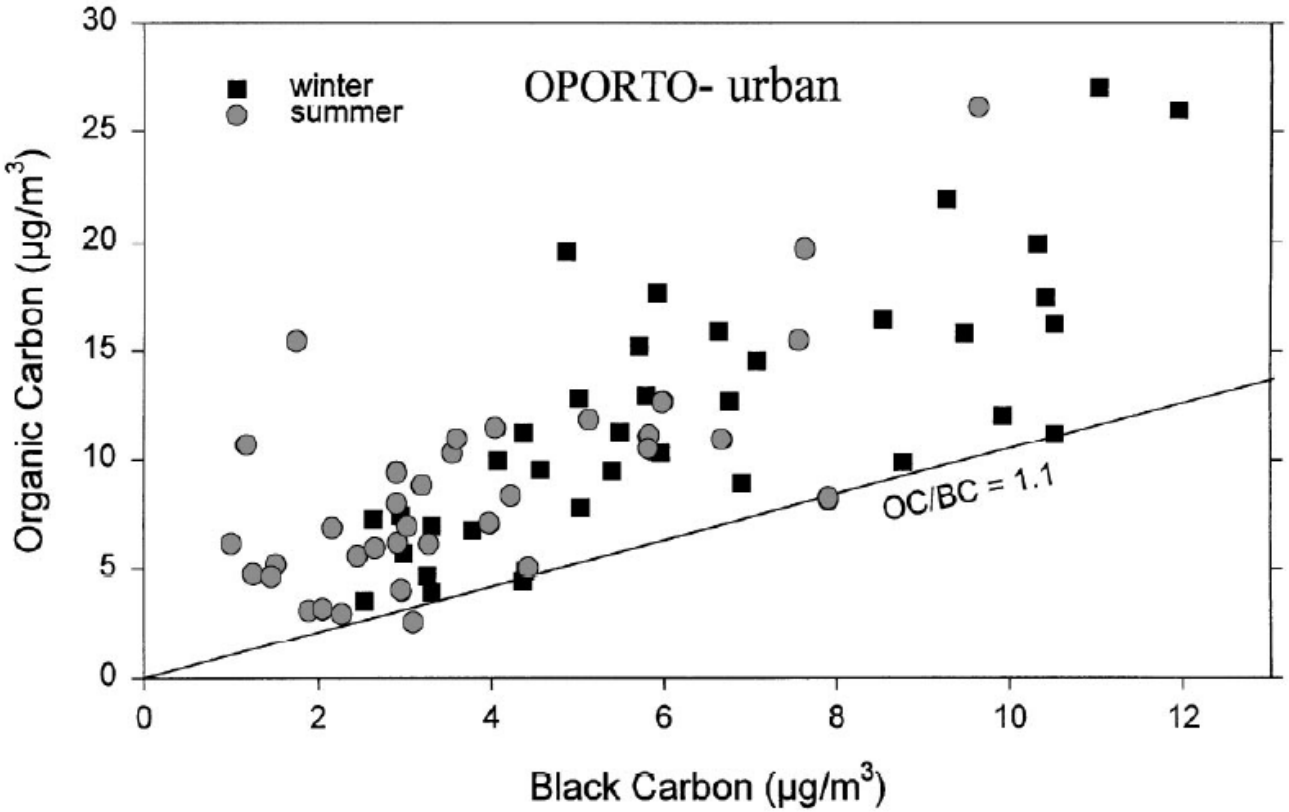
Nawrot et al., Journal of Epidemiology and Community Health (2006)

Worldwide AMS measurements show the abundance of organics in the atmospheric aerosol



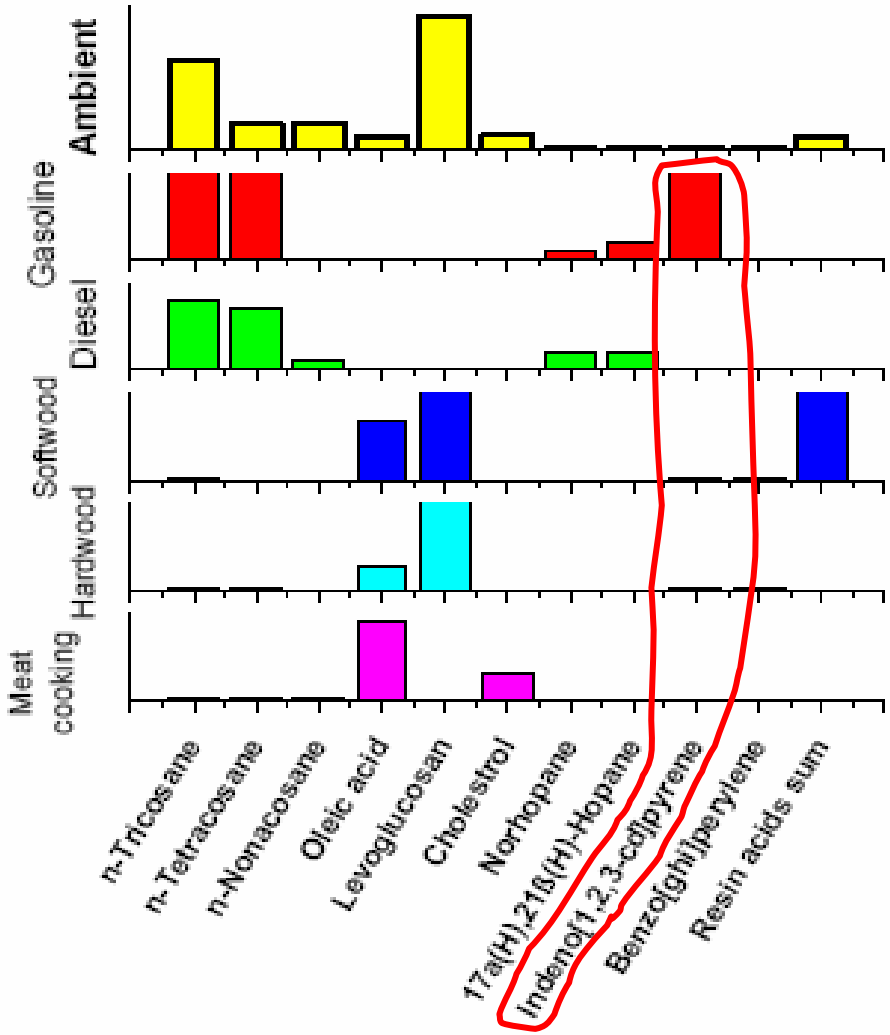
Zhang et al., GRL 2007

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



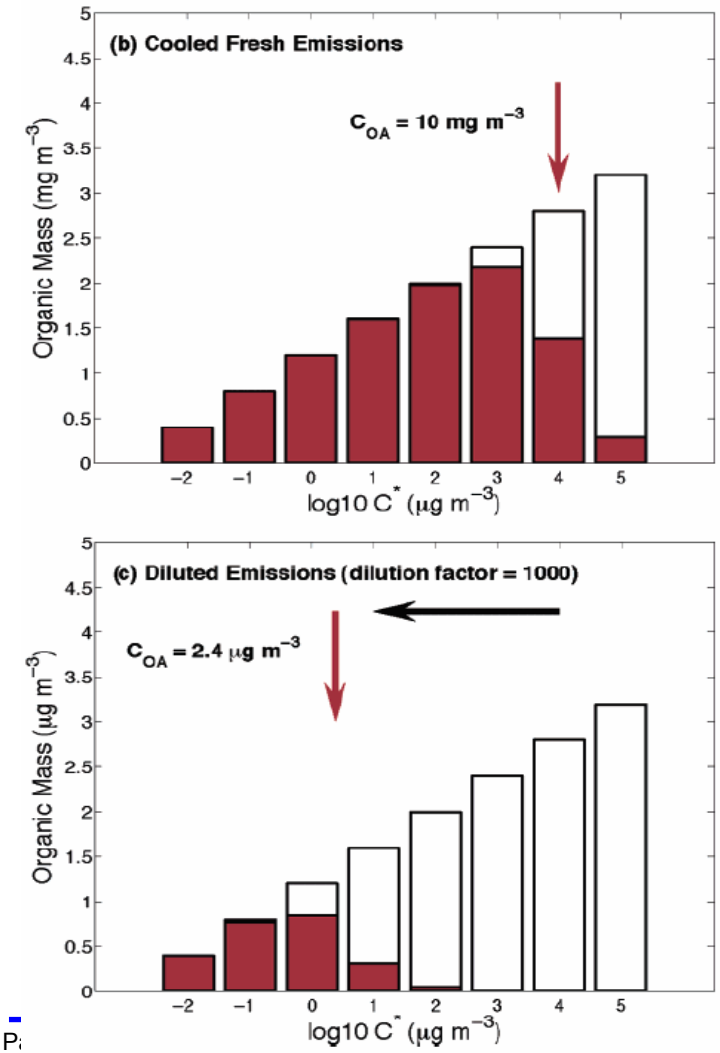
$$c_i = \sum_k \alpha_{i,k} S_k + e_i$$

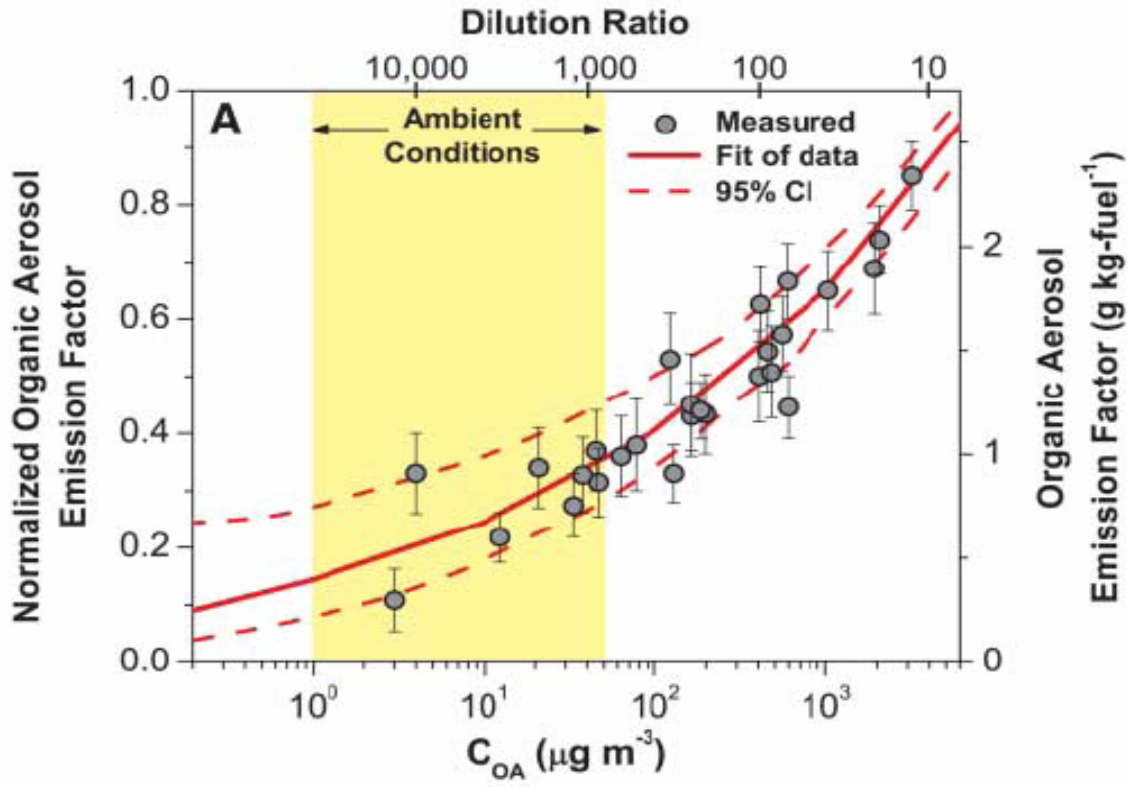
Critical issues

- 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



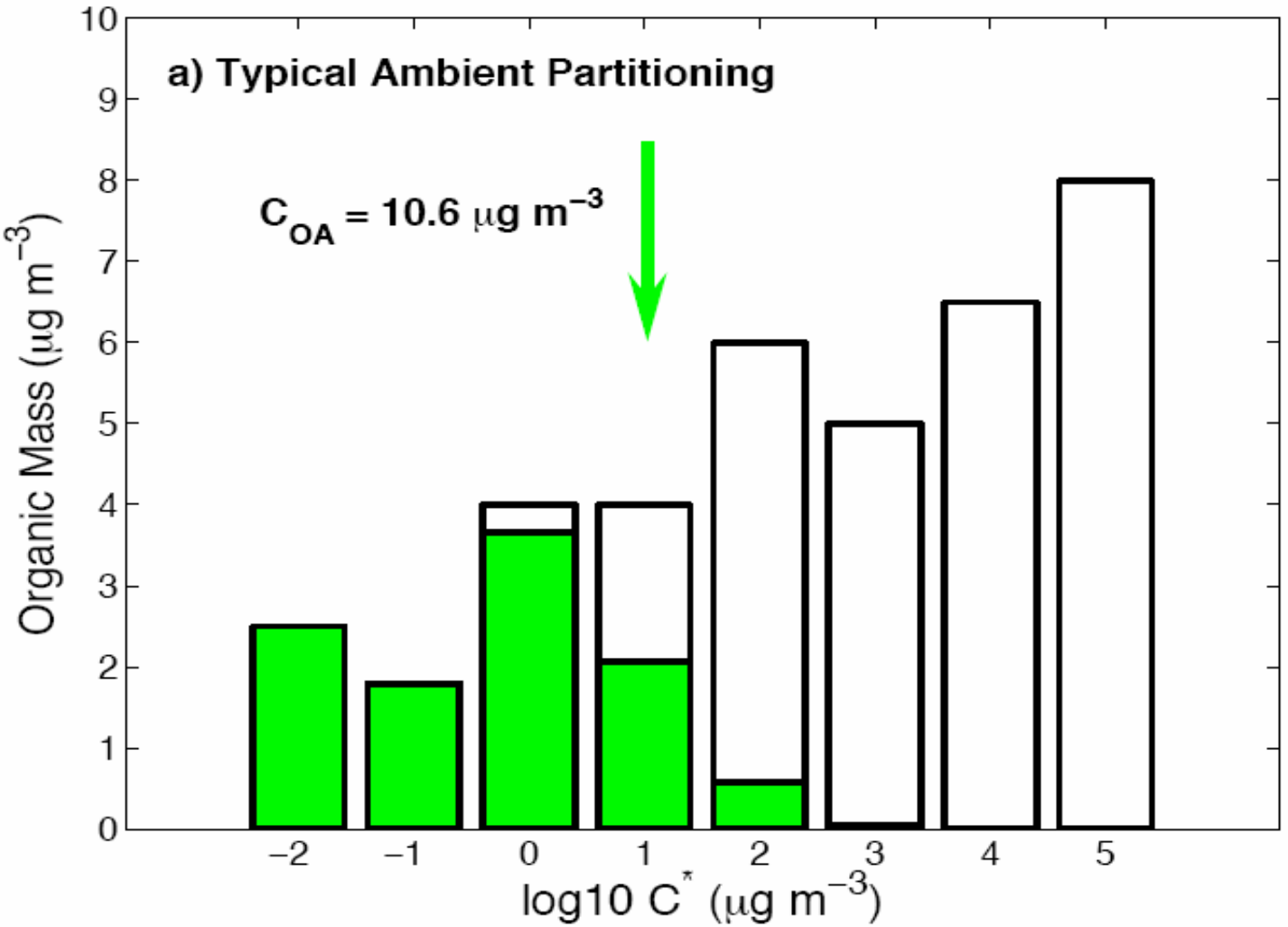


Robinson et al., Science 2007

Donahue et al., Environ. Sci. Technol. 2006

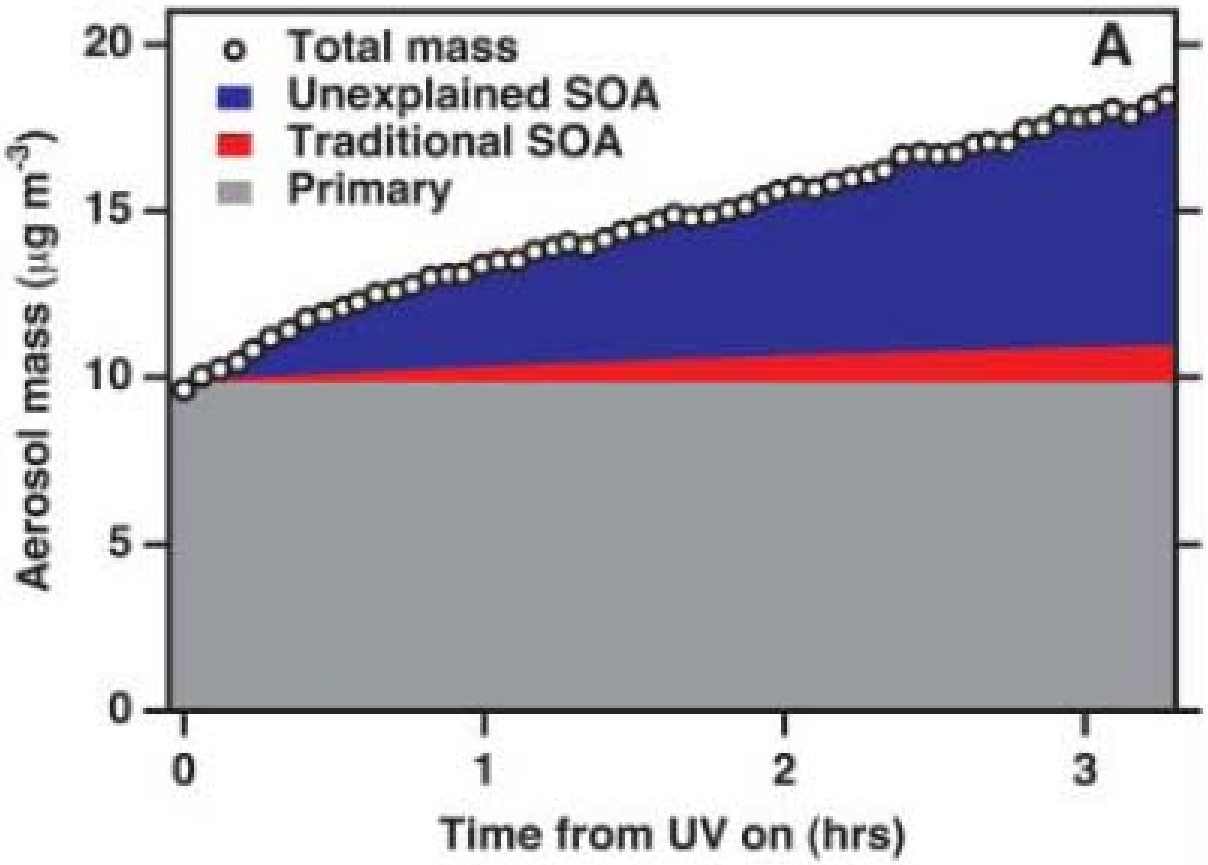
The partitioning coefficient ξ for a compound i with an effective saturation concentration C_i^*

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



Donahue et al., 2006

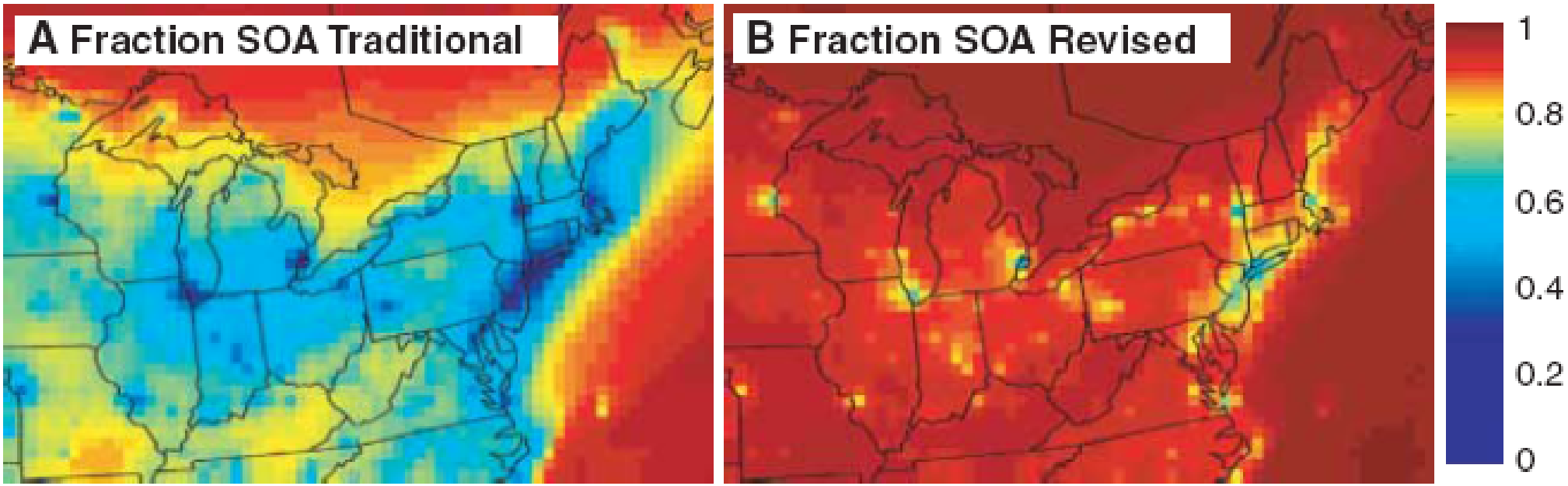
Mass increase on aging much higher than explained with traditional SOA precursors



Mass estimates based on SMPS (density 1)

Robinson et al., Science 2007

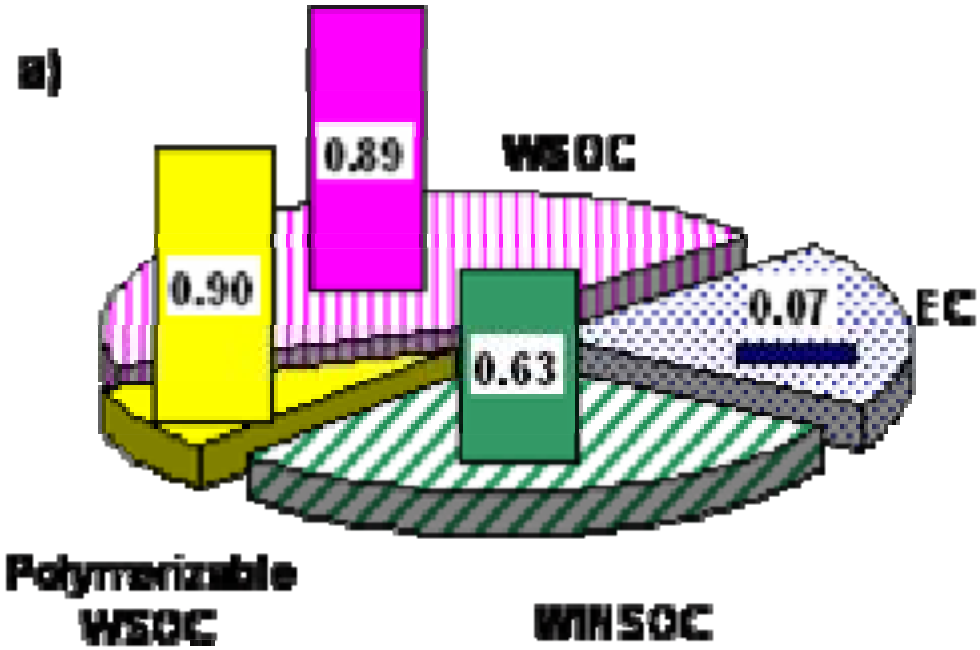
Revised approach (less POA because of dilution, more SOA than from traditional precursors) results in much higher SOA fraction, which matches field data



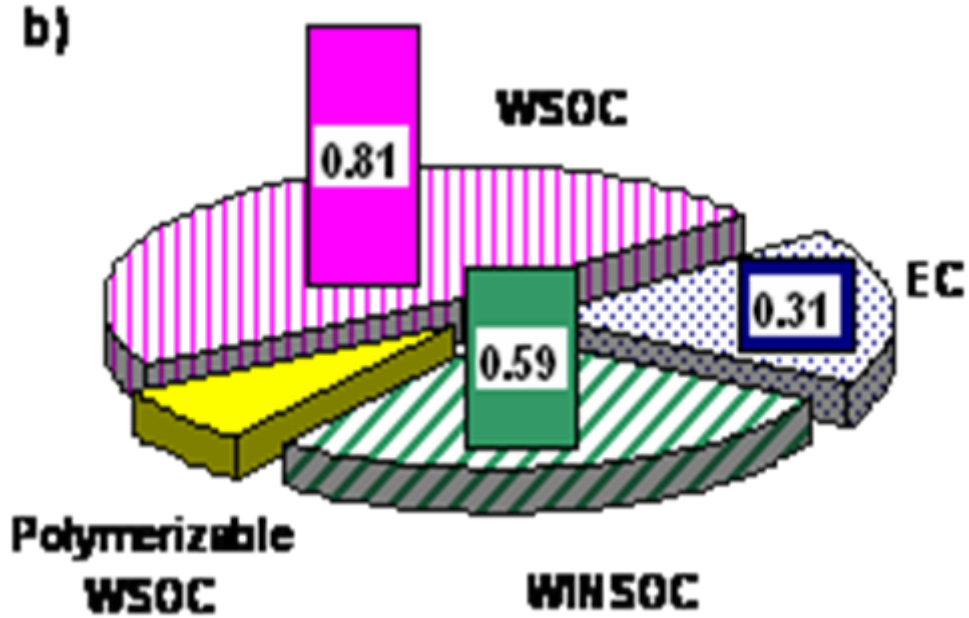
Robinson et al., Science 2007

Carbon-14 analysis suggests that Zurich's SOA is mainly biogenic (in winter: substantial biomass burning)

Summer



Winter

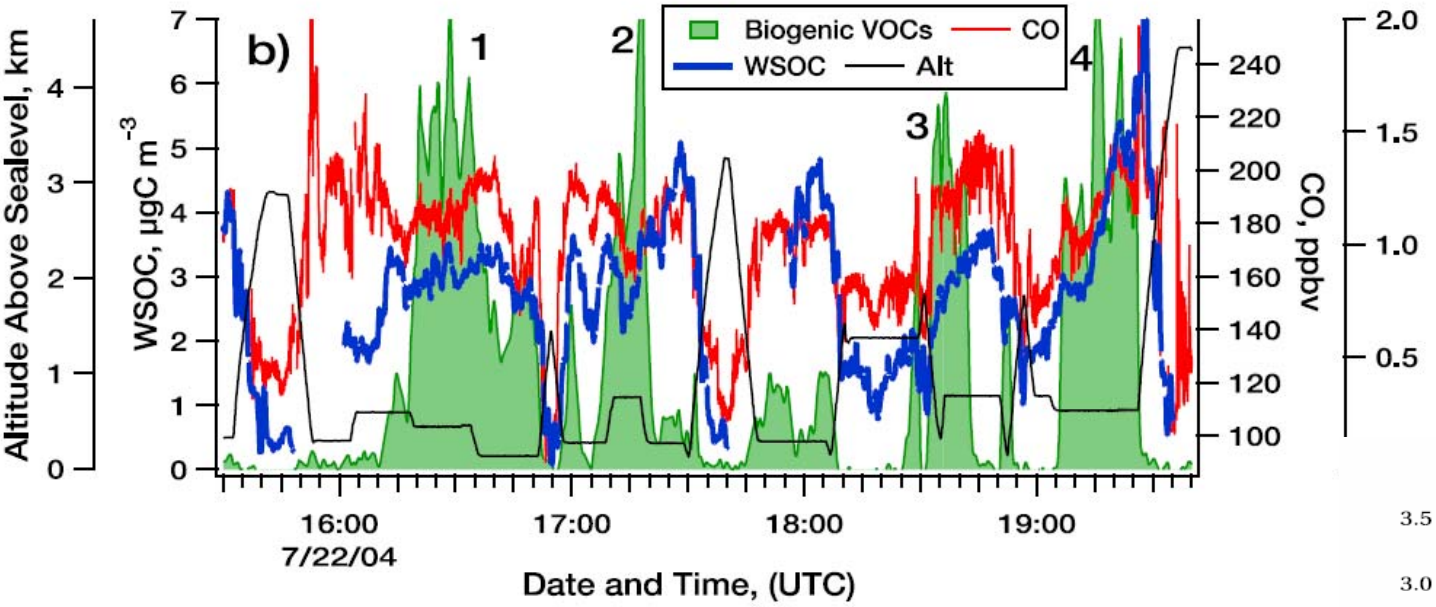


Szidat et al., JGR (2006)

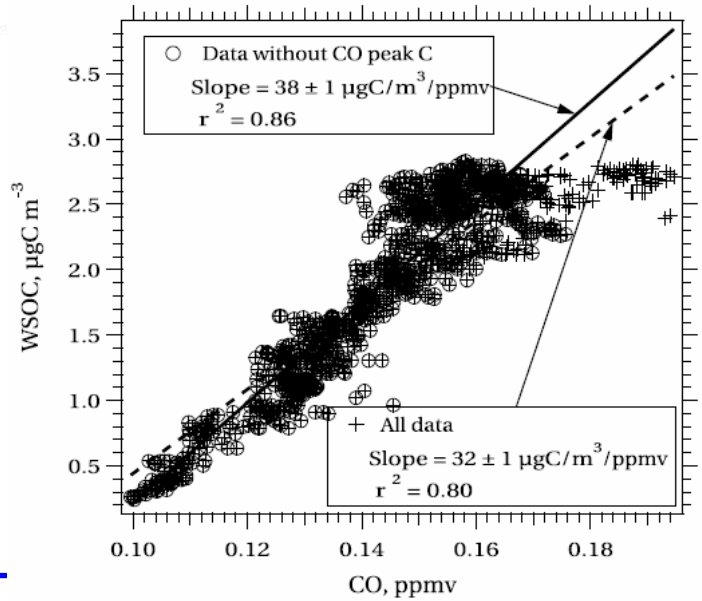
Paradox:

- 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)

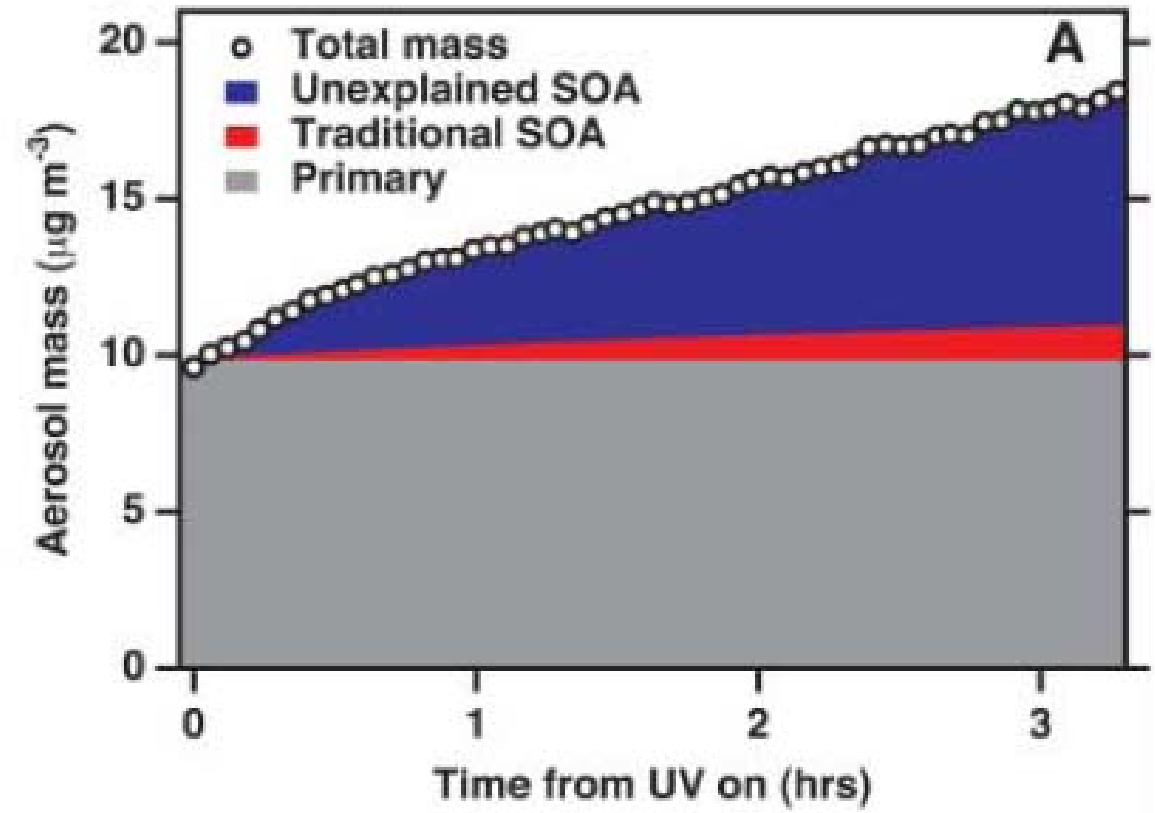


Weber et al., JGR 2007



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

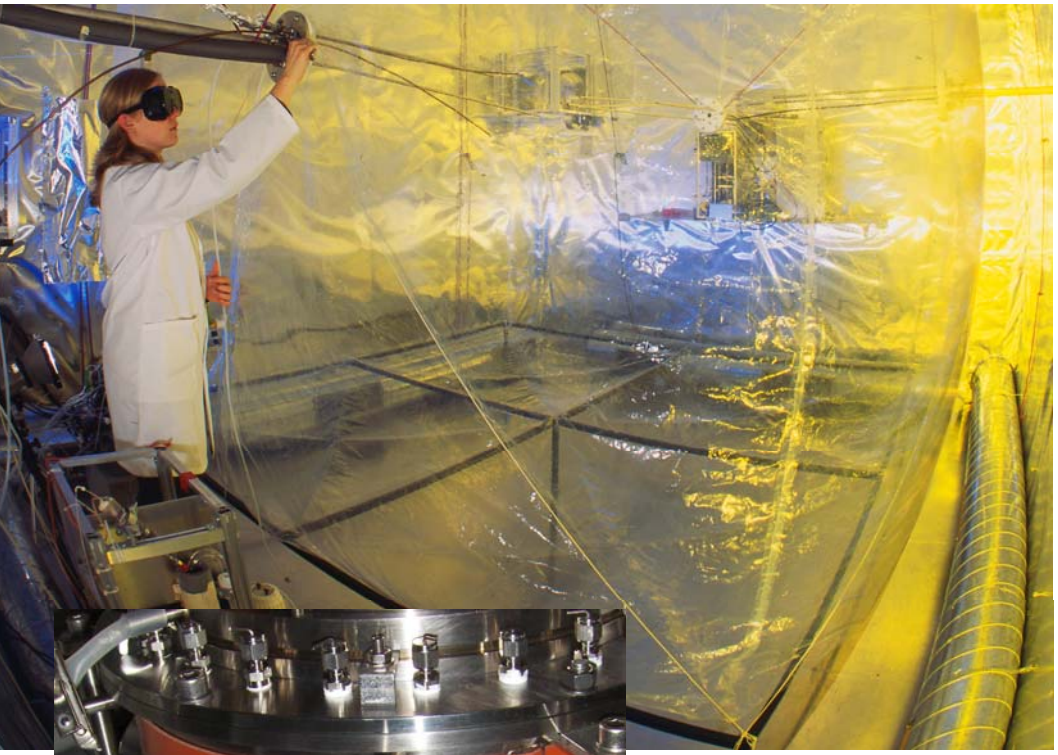
Aging of diesel exhaust in the PSI smog chamber

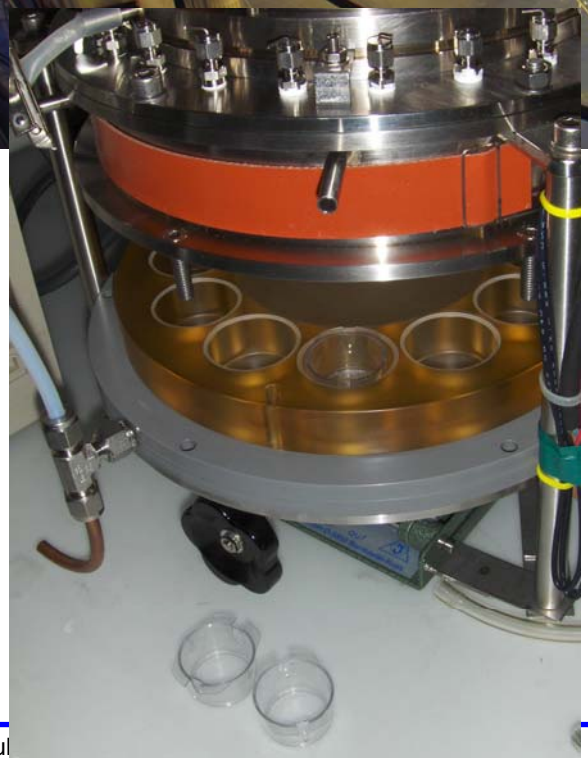
Euro 3 diesel car running at 60 km per hour

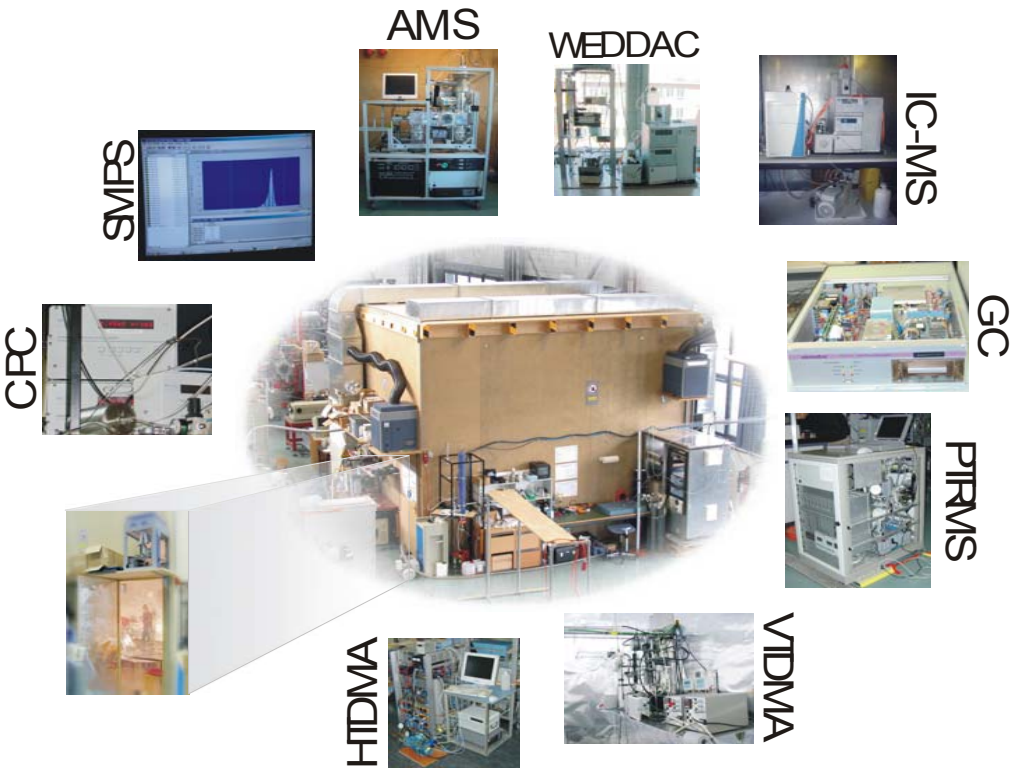
Filling the chamber
in ~15 min

Diesel and wood combustion aerosol generators for the PSI smog chamber

The PSI smog chamber





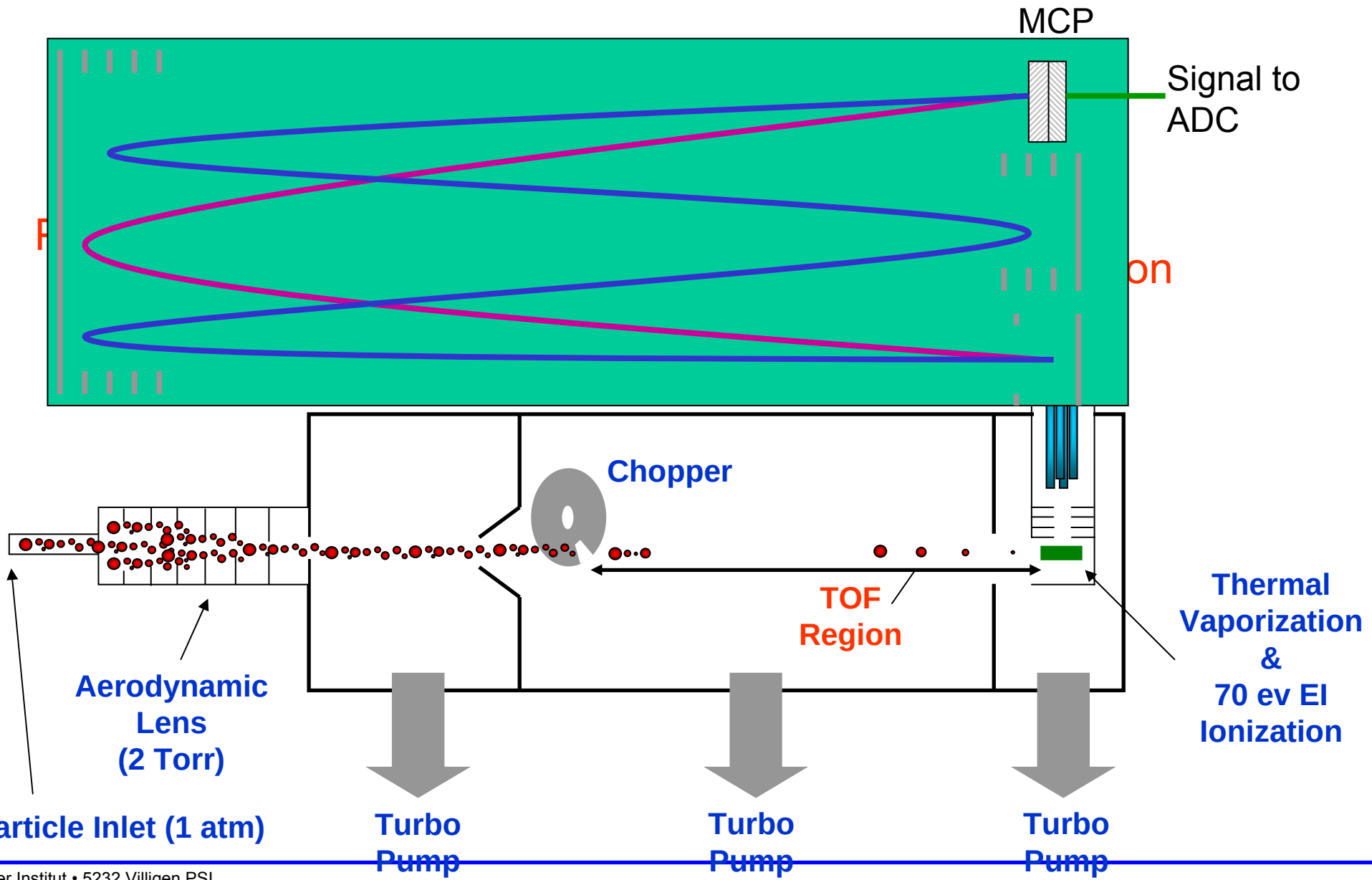


EC project POLYSOA:
Exposure of various biological systems to SOA, in collaboration with Marianne Geiser Univ. Bern and Markus Kalberer, highly interesting findings, first results in Baltensperger et al., JAM 2008

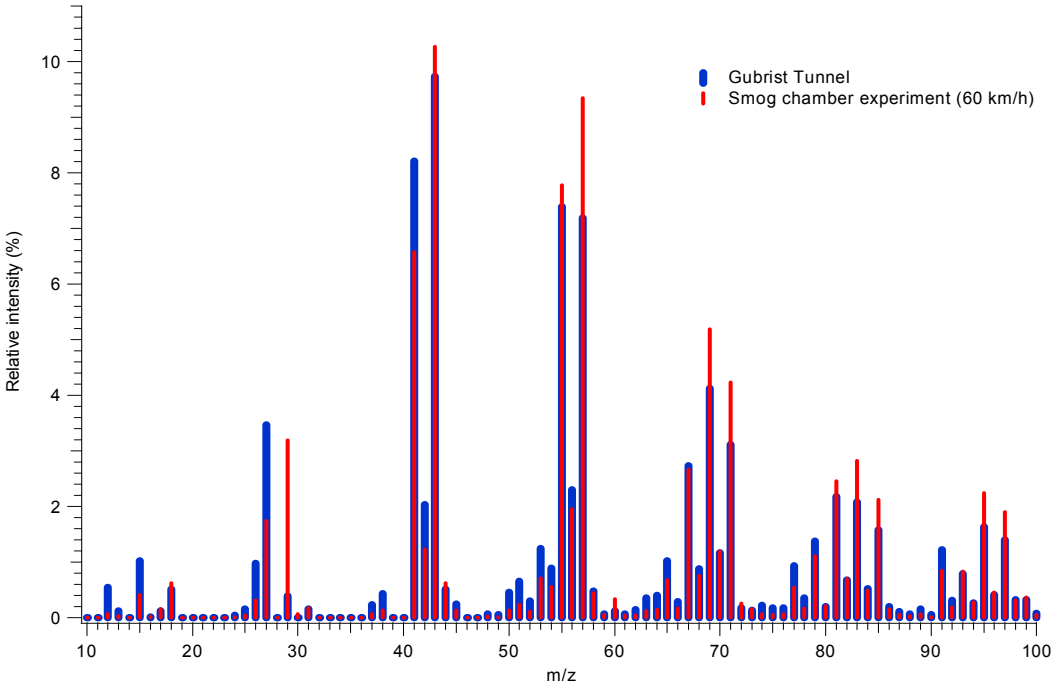
Instrumentation

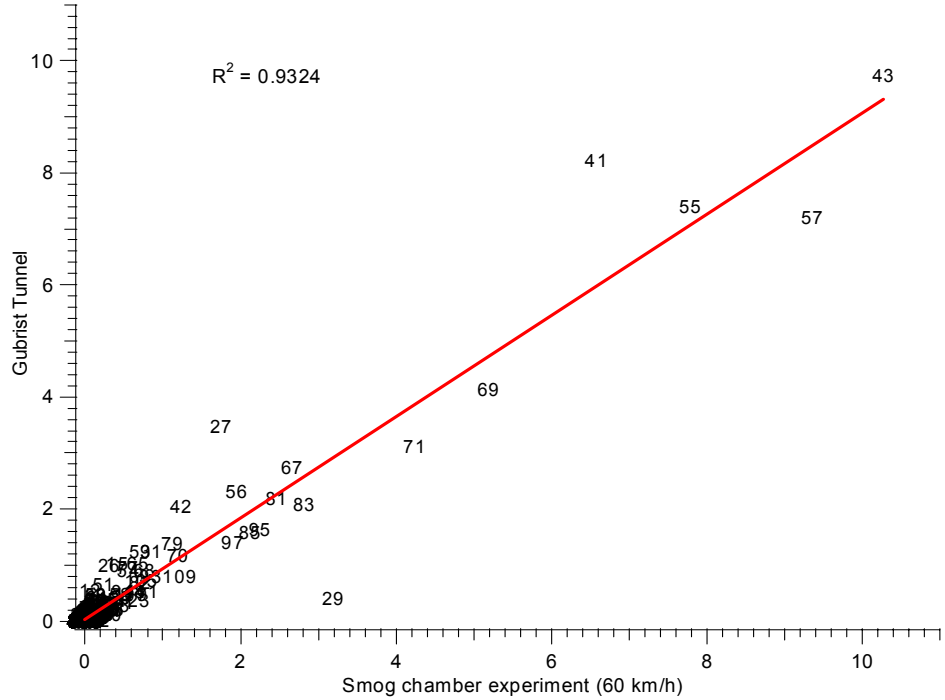
- **Size distribution: SMPS**
- **Black carbon concentration: aethalometer**
- **Organic mass, size+ chem.: aerosol mass spectrometer**
- **Hygroscopic growth factor: Hygroscopicity tandem differential mobility analyzer**

The Aerodyne aerosol mass spectrometer (AMS)



Comparison of AMS measurements in Gubrist tunnel (June 2008) and EURO III car in PSI smog chamber



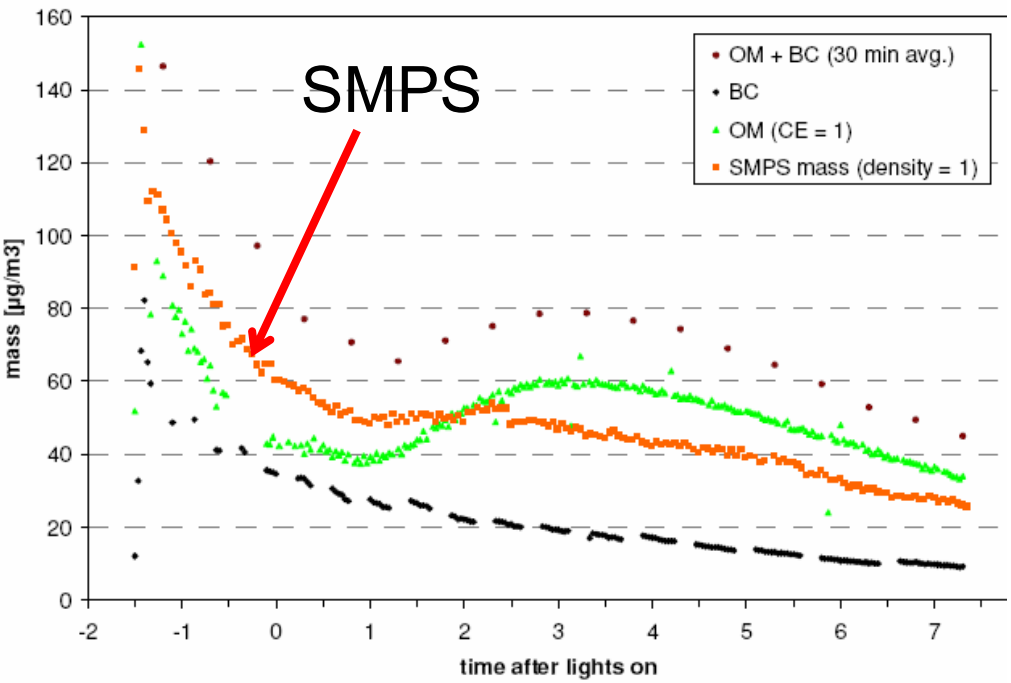


Instrumentation – and related problems

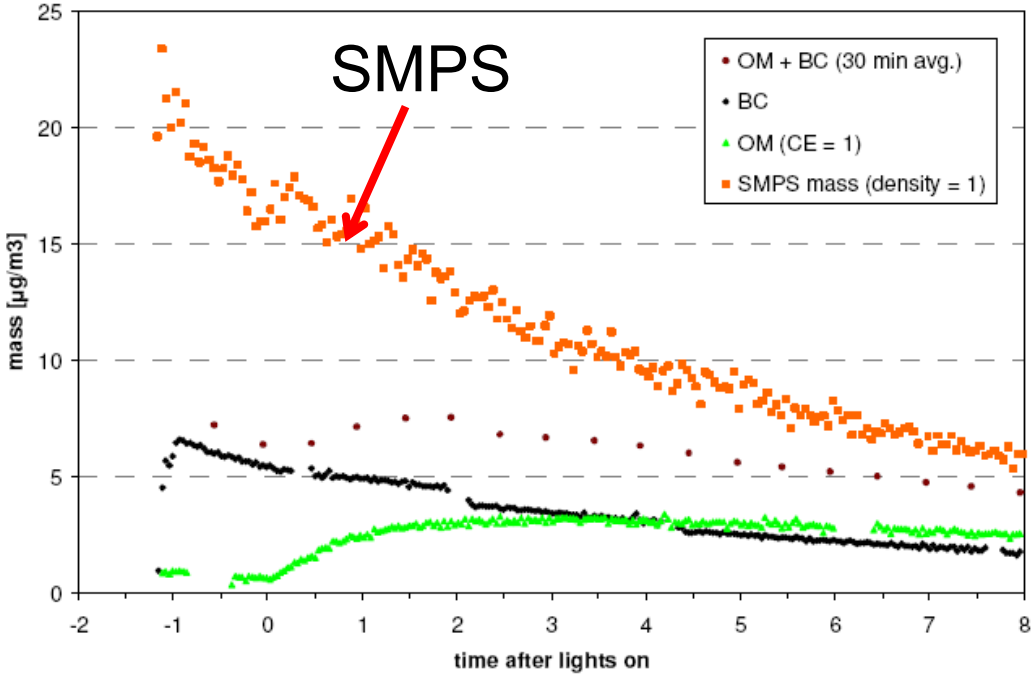
- **Size distribution: SMPS** — **Effective density?**
- **Black carbon concentration: aethalometer** — **Mass absorption efficiency?**
- **Organic mass, size+ chem.: aerosol mass spectrometer** — **Collection efficiency?**
- **Hygroscopic growth factor: Hygroscopicity tandem differential mobility analyzer** — **Restructuration?**

Technological difficulties

Diesel



Wood combustion



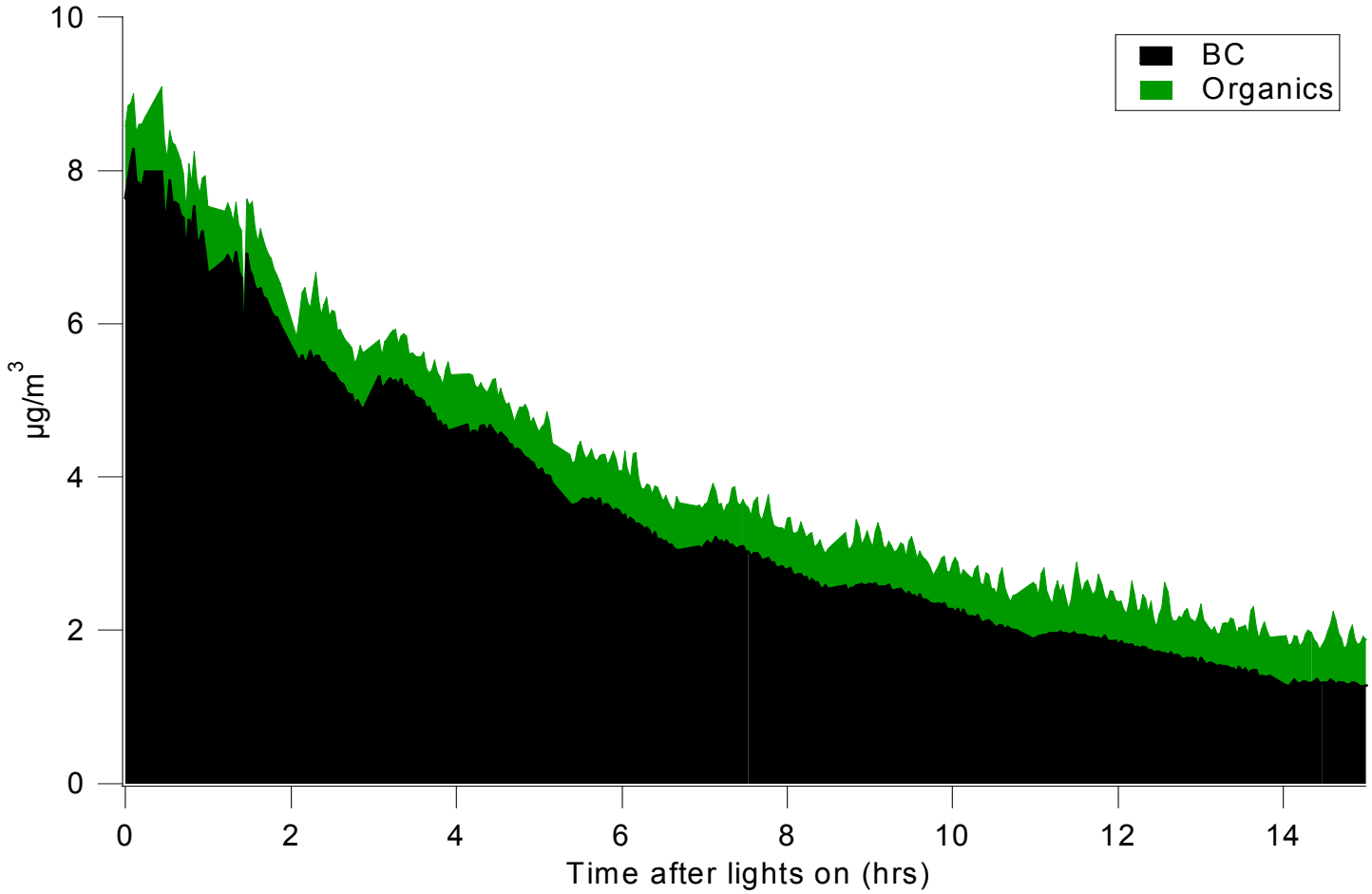
Technological differences

When just turning on the lights: nothing happens:

$NO + O_3 \rightarrow NO_2$ and O_2

Solution: adding ozone to achieve a more realistic NO/NO_2 ratio

After addition of 660 ppb ozone: still nothing happens (except wall losses)



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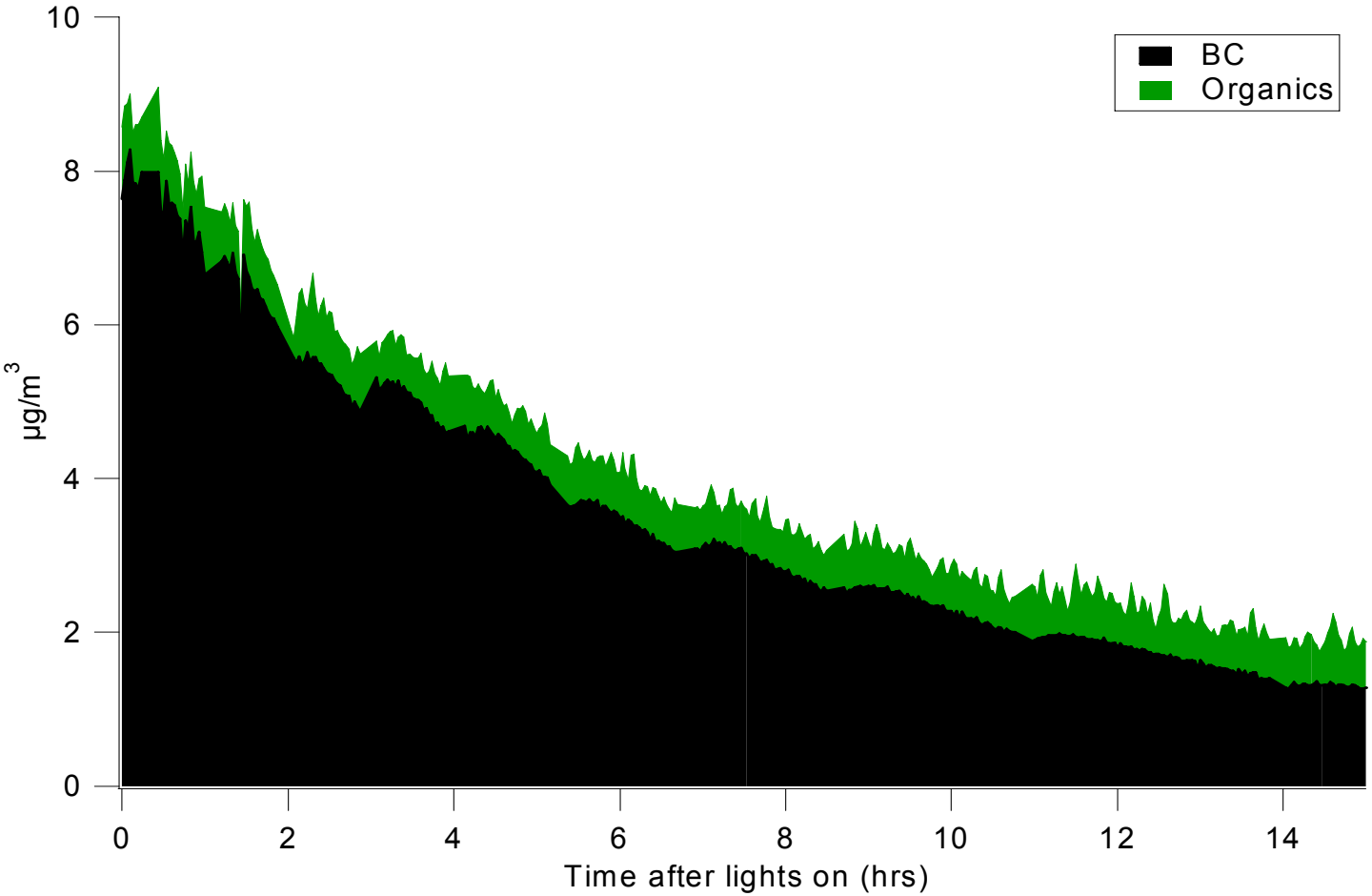
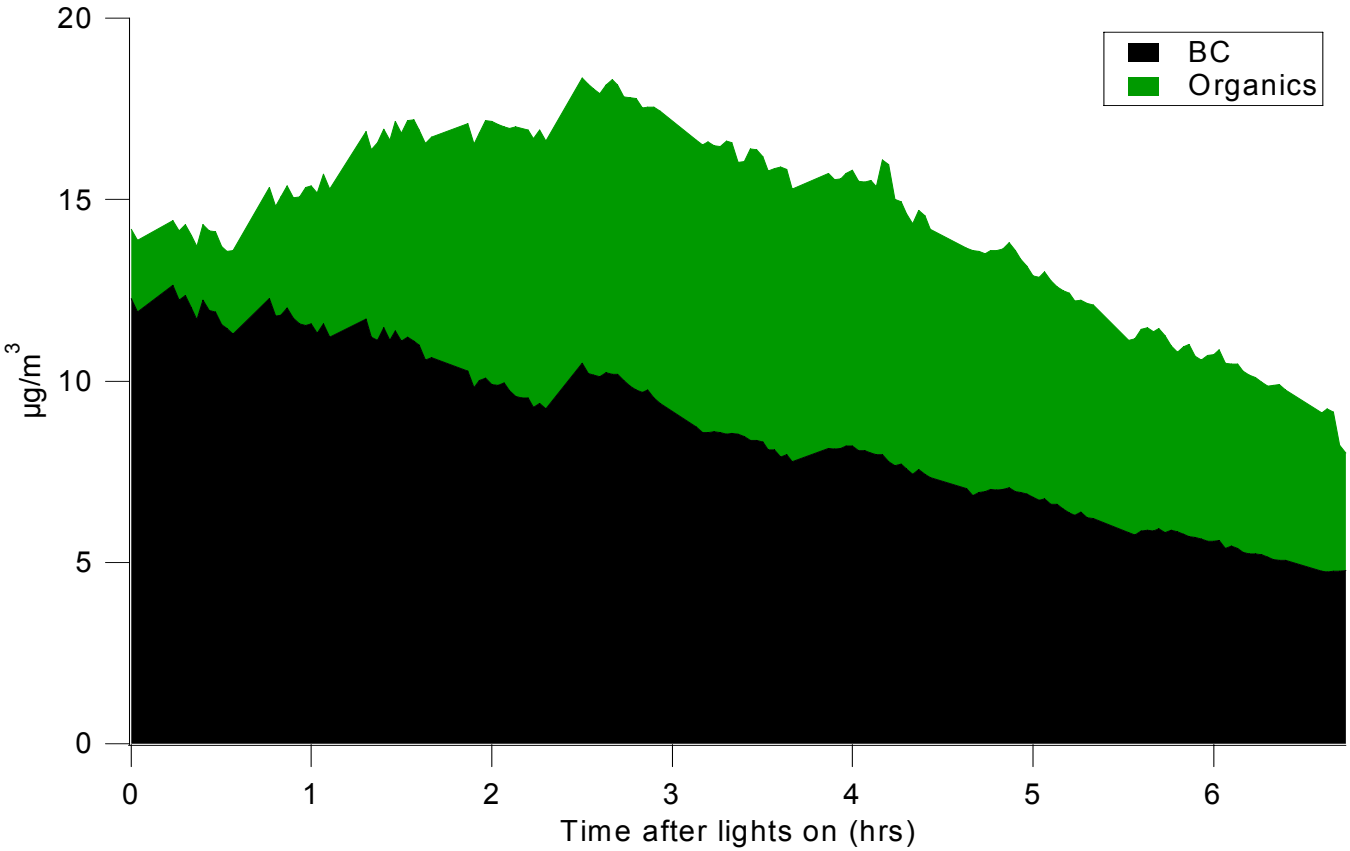
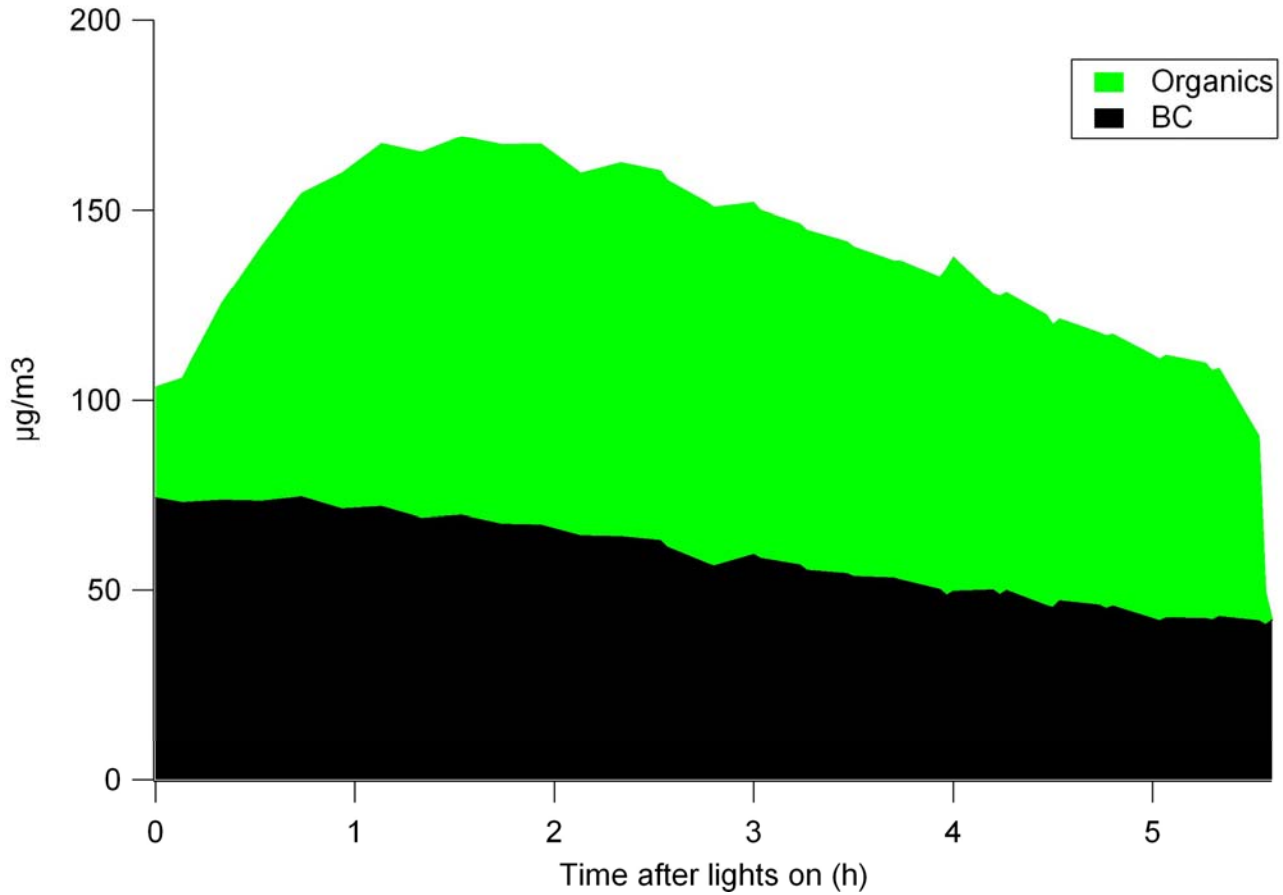


$$NO_2 + OH \rightarrow HNO_3$$

After addition of 570 ppb ozone and 1800 ppb propene: SOA formation

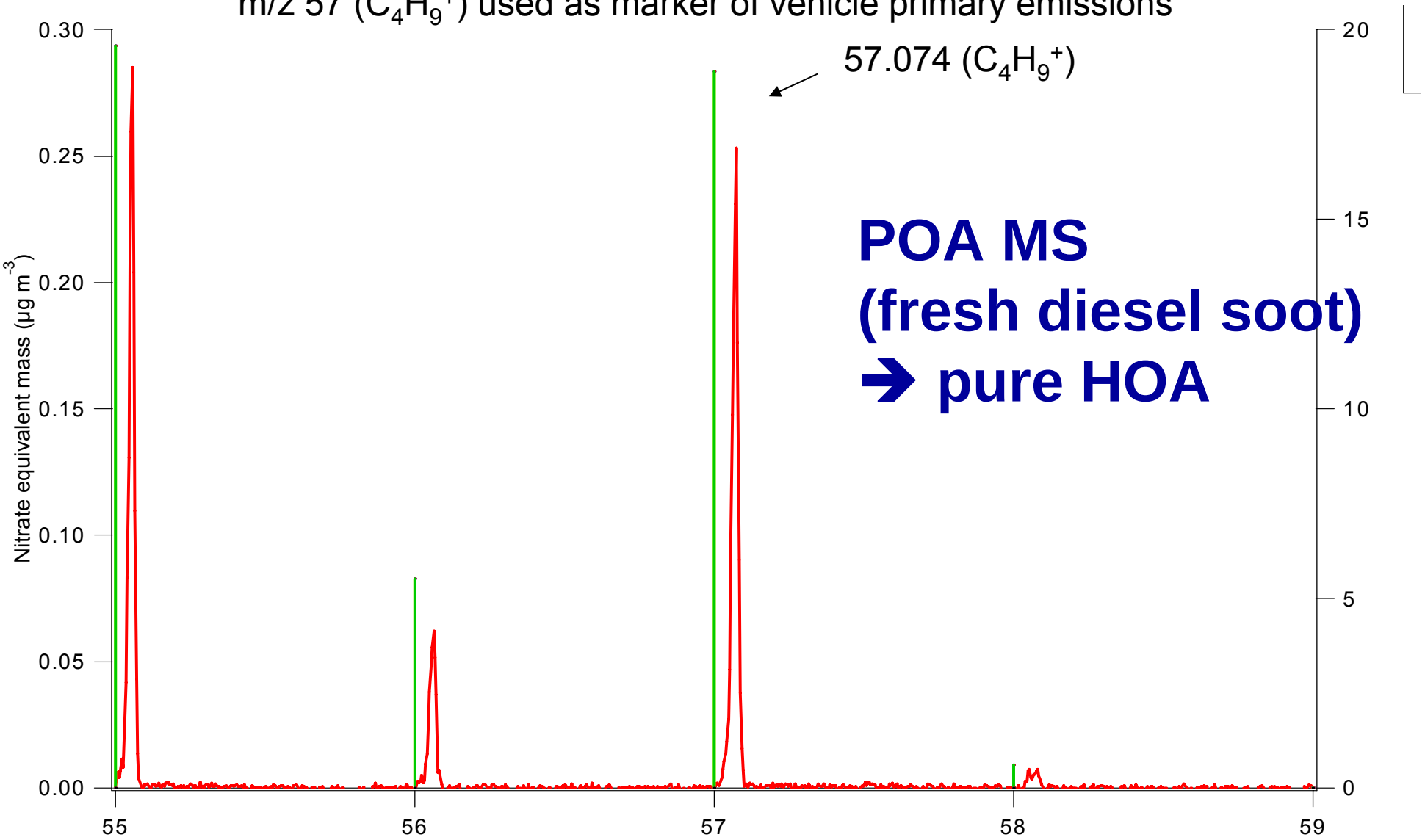


Wood combustion aerosol: immediate SOA formation after turning on the lights; no addition of ozone or propene needed



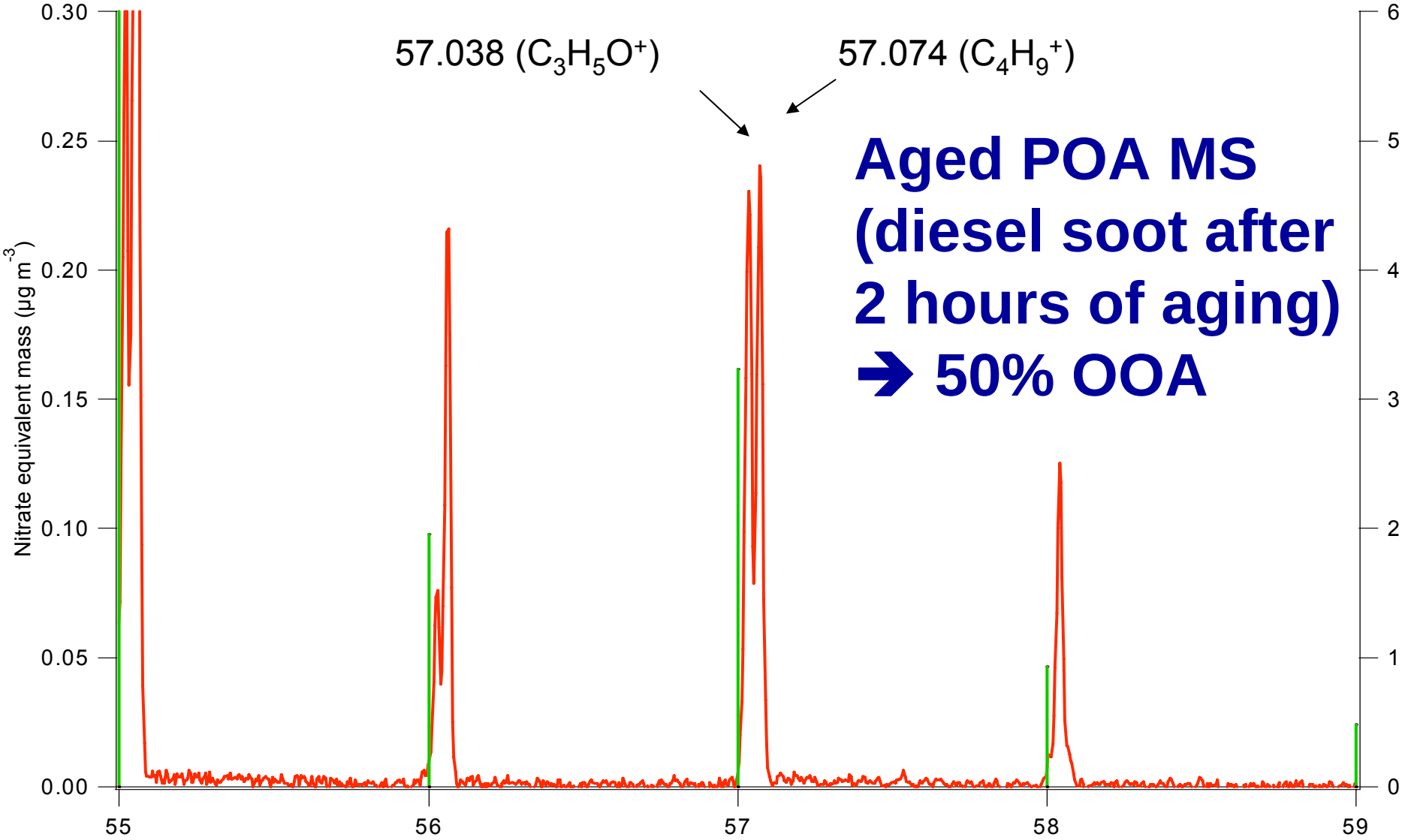
The ToF-AMS allows for discrimination of mass fragments with m/z 57

m/z 57 ($C_4H_9^+$) used as marker of vehicle primary emissions



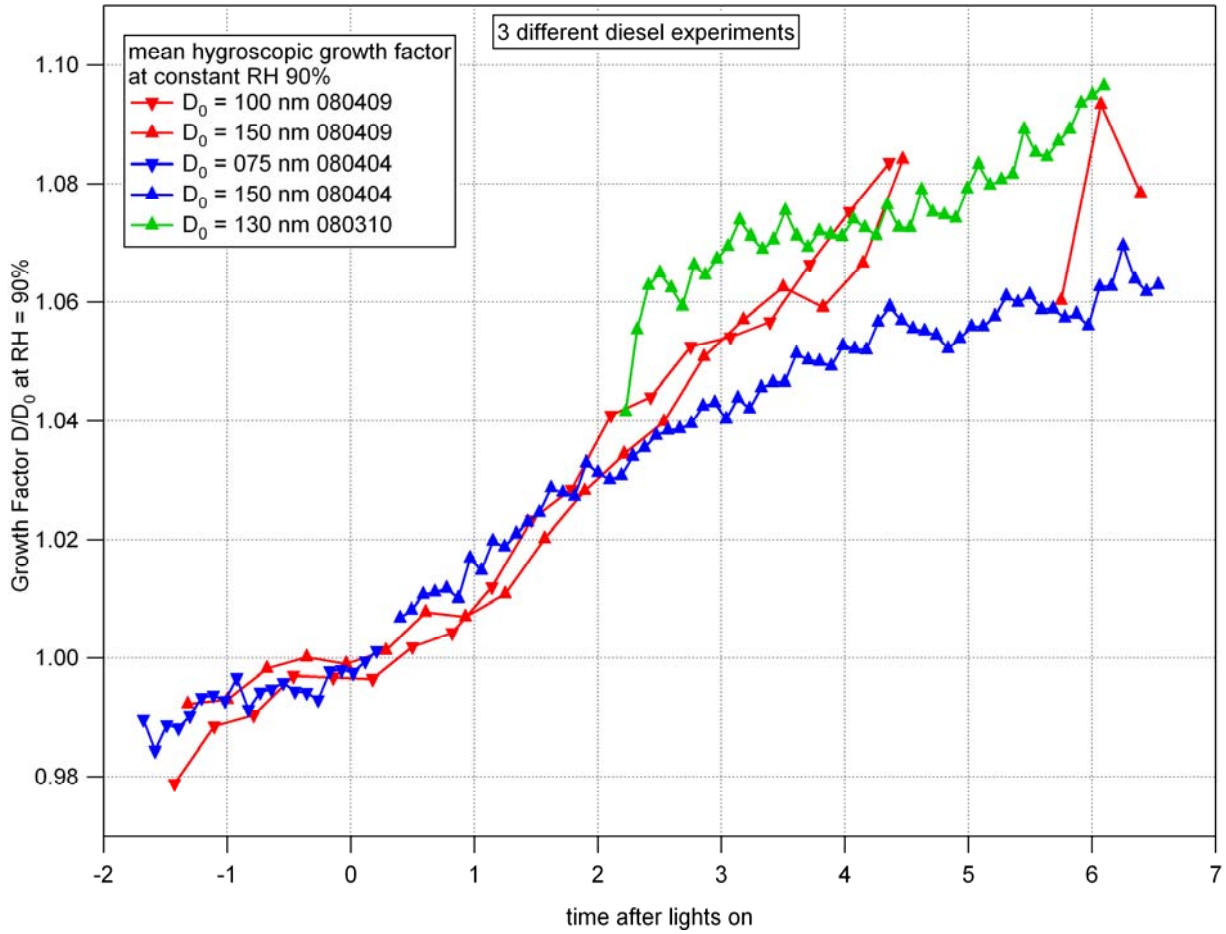
POA MS (fresh diesel soot) ➔ pure HOA

The ToF-AMS allows for discrimination of mass fragments with m/z 57



Hygroscopic growth factor increases with time; little restructuration for diesel soot particles

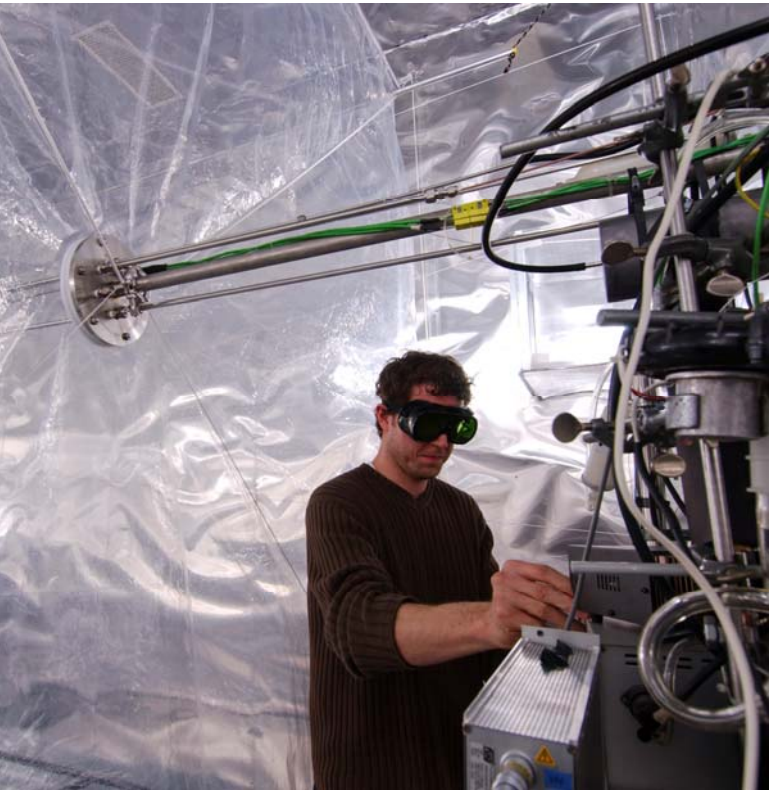
see more on poster by Torsten Tritscher



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



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

http://www.psi.ch/lac

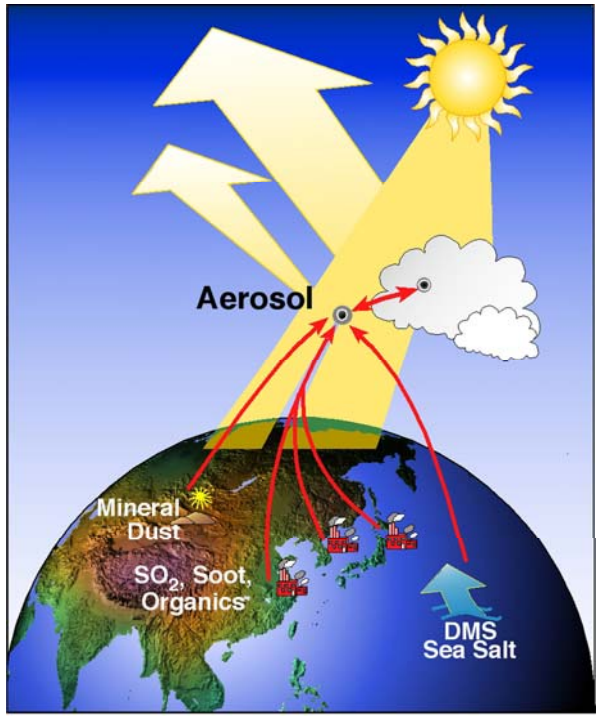
Aerosols affect our health and have an impact on climate

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

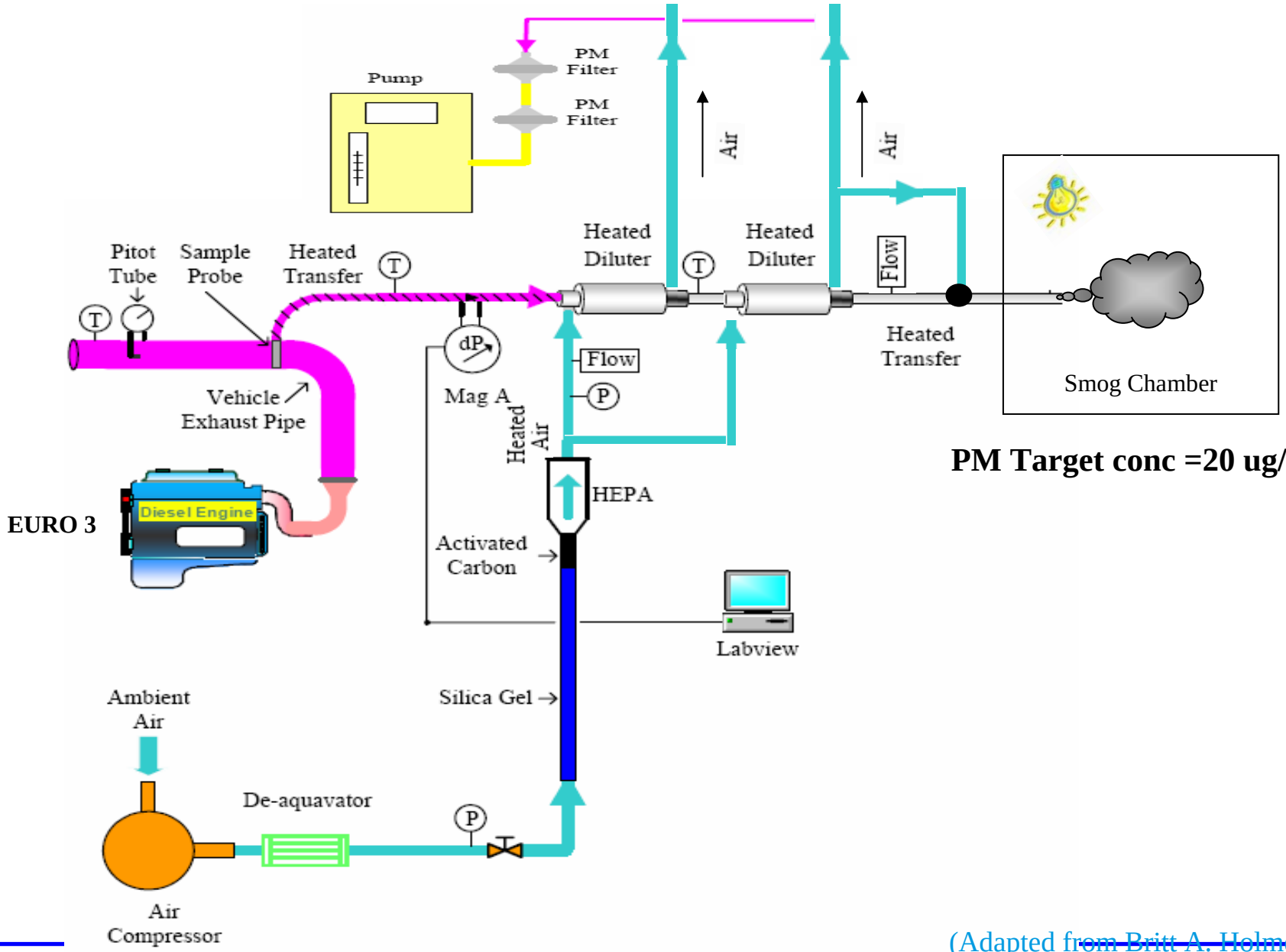
Source: www.ecocouncil.dk

Affect our climate by excerting 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

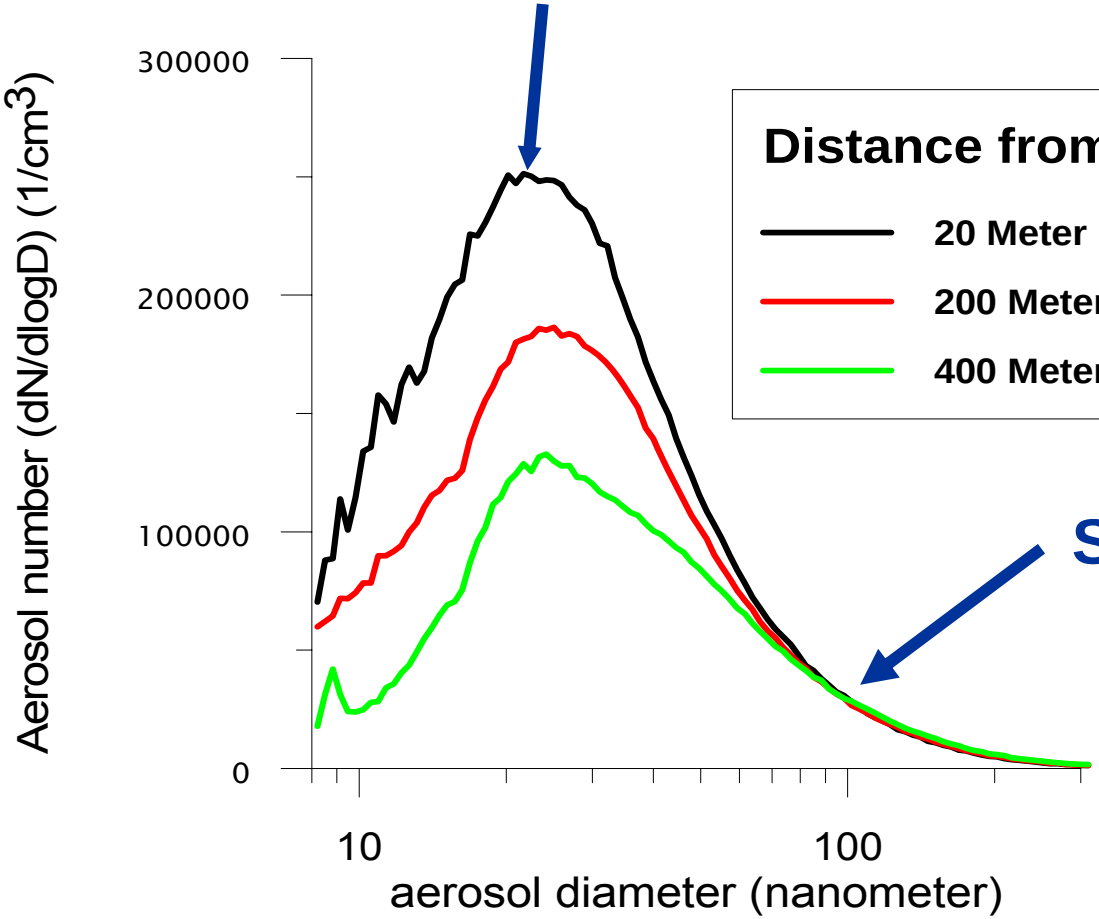


PM Target conc =20 ug/m3

(Adapted from Britt 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

$$C_nH_m \xrightarrow{e^-} C_{n'}H_{m'}^+$$

27, 29, 41, 43, 55, 57, 69, 71, …

"Oxygenated": OOA

$$C_nH_mO_y \xrightarrow{e^-} HCO^+ \; CO_2^+ \; H_3C_2O^+ \; HCO_2^+ \; C_{n'}H_{m'}^+$$

29 ***44*** ***43*** ***45*** ***55, 57, ...***

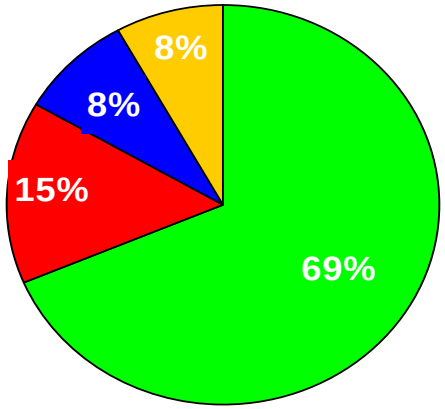
m/z 44 is a measure of degree of oxidation

AMS summer data for Zurich

Zurich, Summer

19 μg m^{-3}

OM: 13 μg/m^3



Org
NO3
SO4
NH4