Secondary organic aerosol formation in a smog chamber and its link to source apportionment in the real atmosphere

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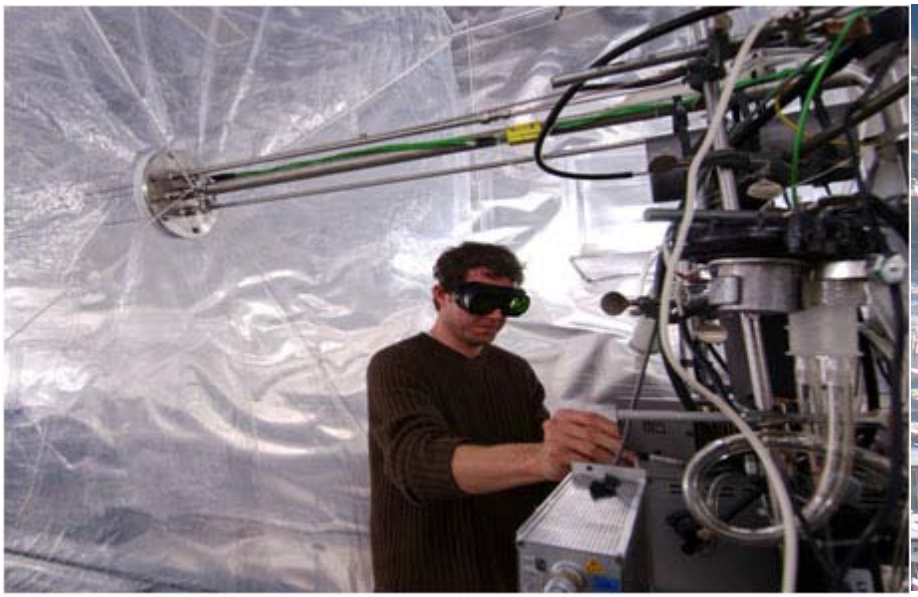
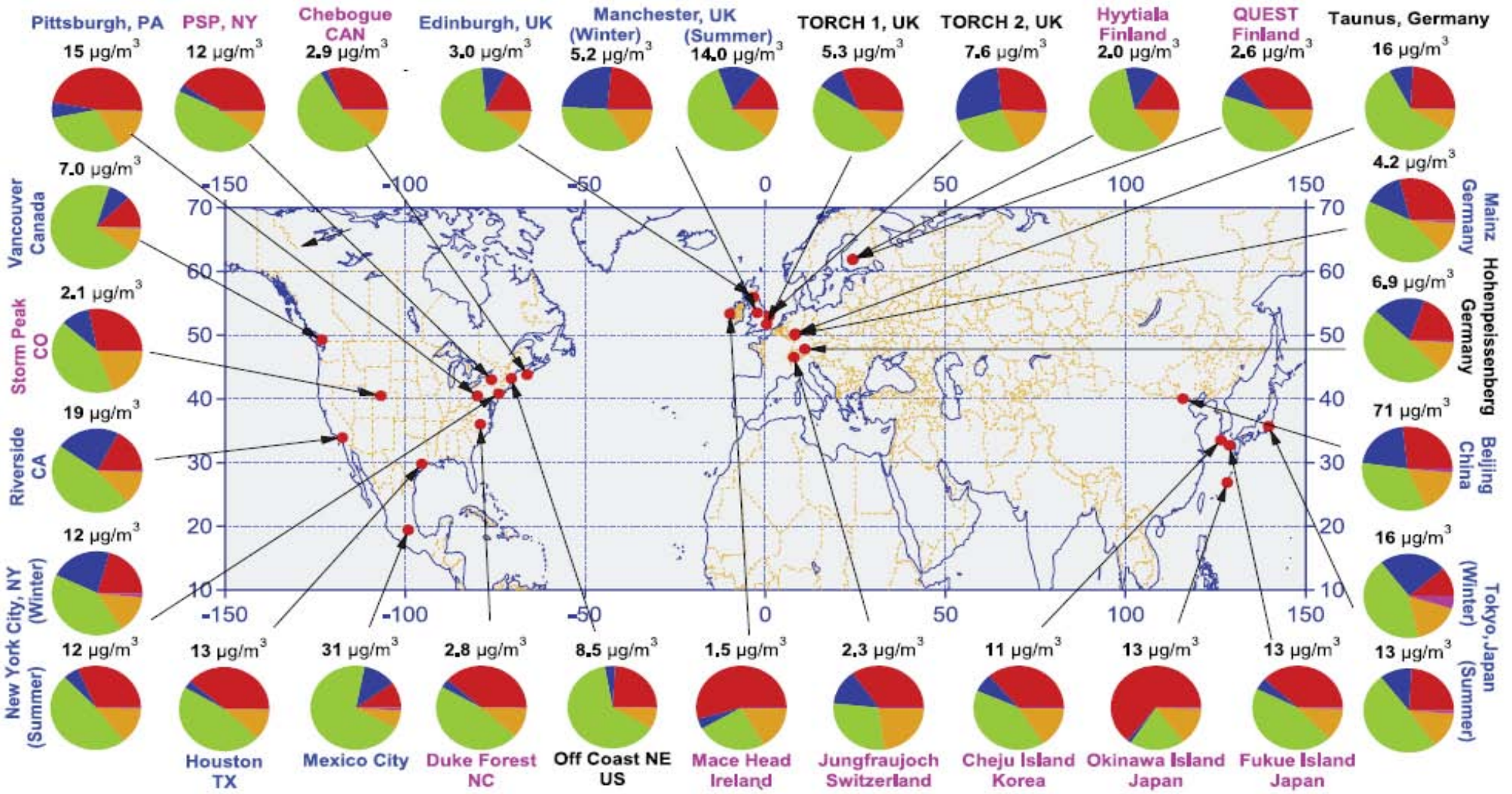


9th Int. Conf. on Carbonaceous Particles in the Atmosphere
Berkeley, CA, August 12-14, 2008

Worldwide AMS measurements of the chemical composition: the importance of organic aerosol



Sources of this OA?

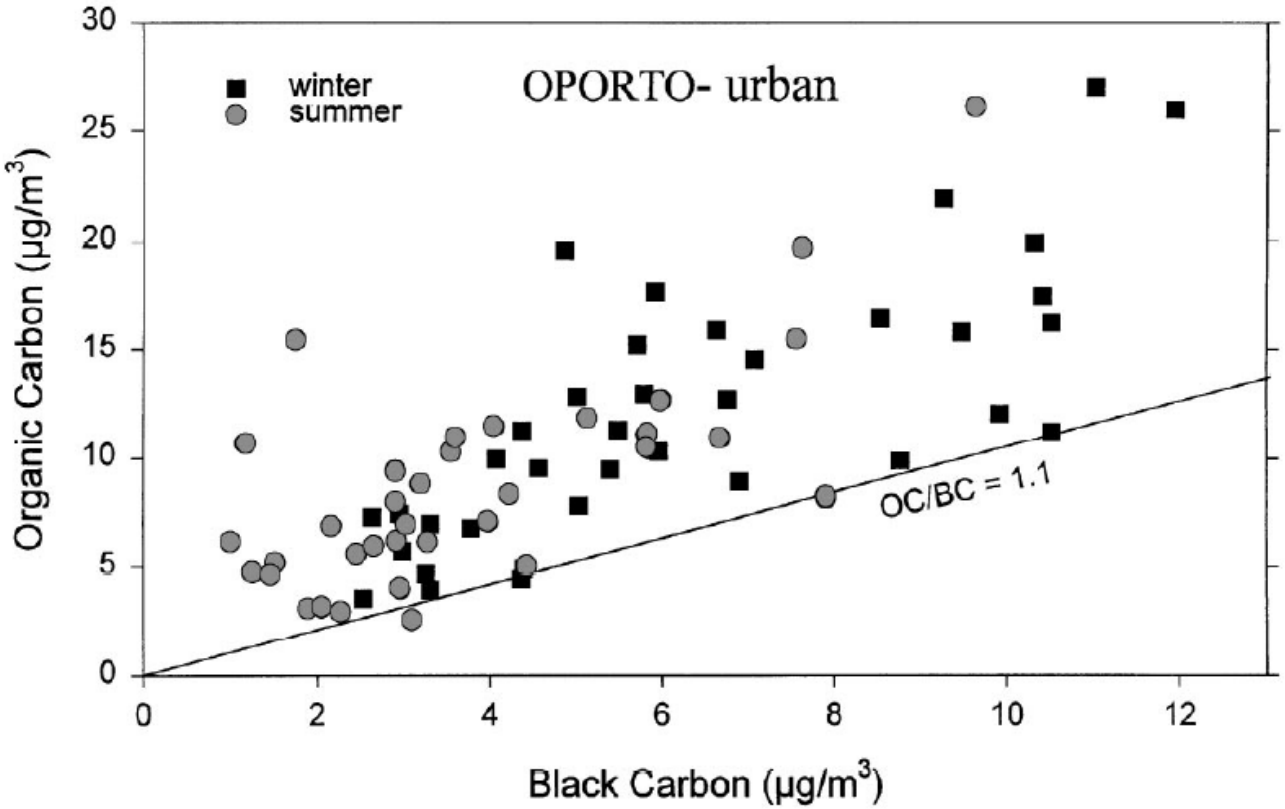
Zhang et al., GRL 2007

Sources of that organic aerosol? Which fraction is primary, which secondary?

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

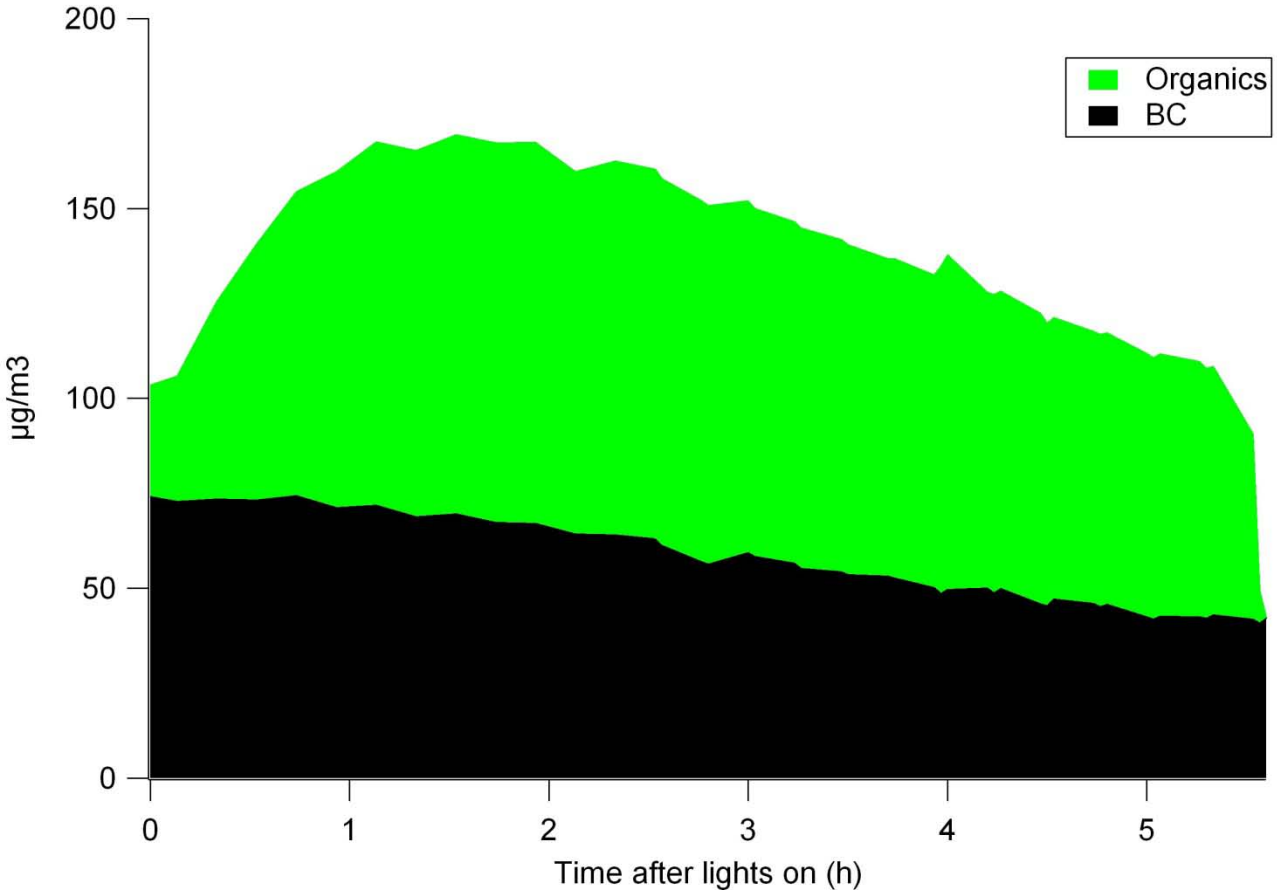
- **Secondary particles: formed in the atmosphere by condensation (nucleation and growth) after chemical transformation**

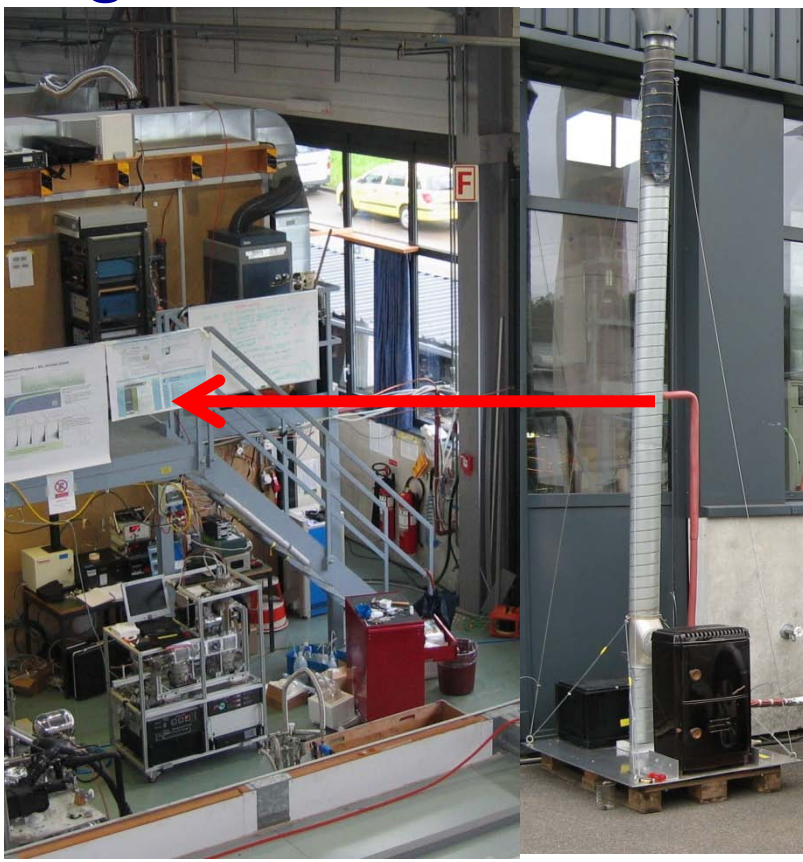
Traditional ways of determining primary and secondary organic aerosol (POA and SOA)
A: OC/EC ratio



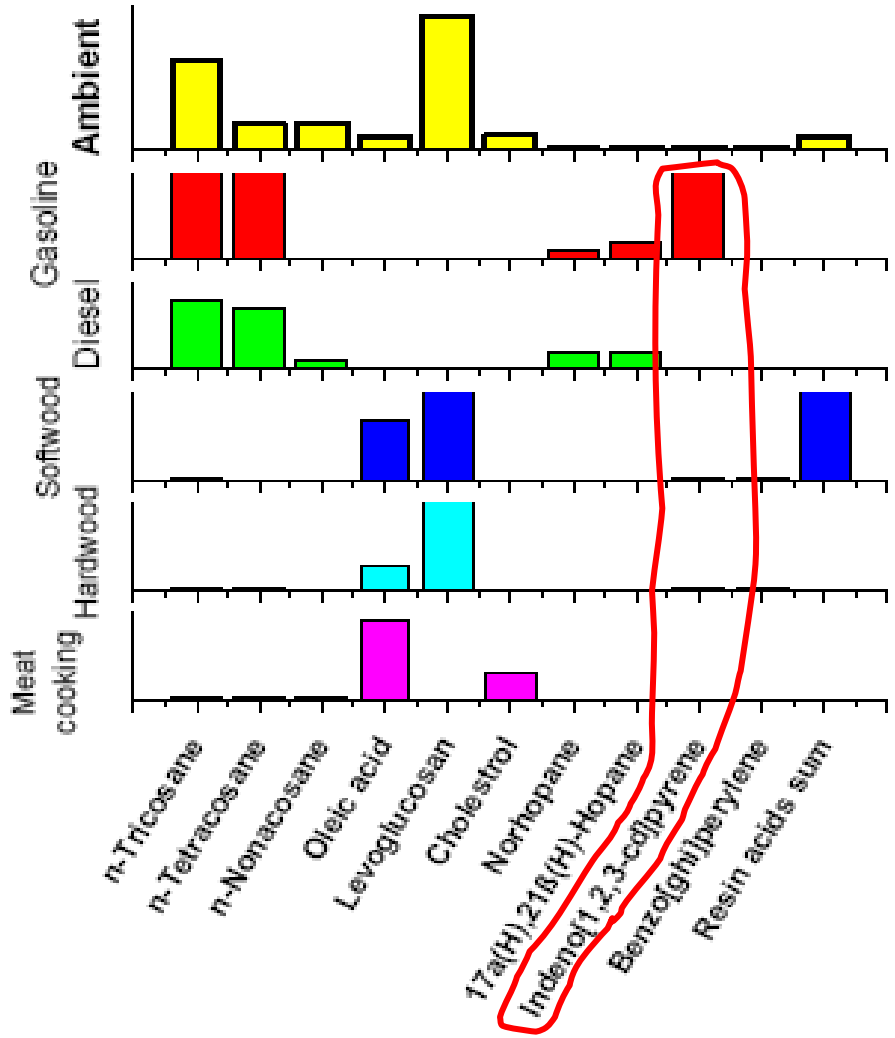
Castro et al., AE 1999

But: SOA may be formed nearly instantaneously; Example: Wood combustion aerosol shows immediate SOA formation after turning on the lights in a chamber





Traditional ways of determining primary and secondary organic aerosol (POA and SOA)
B: Tracers



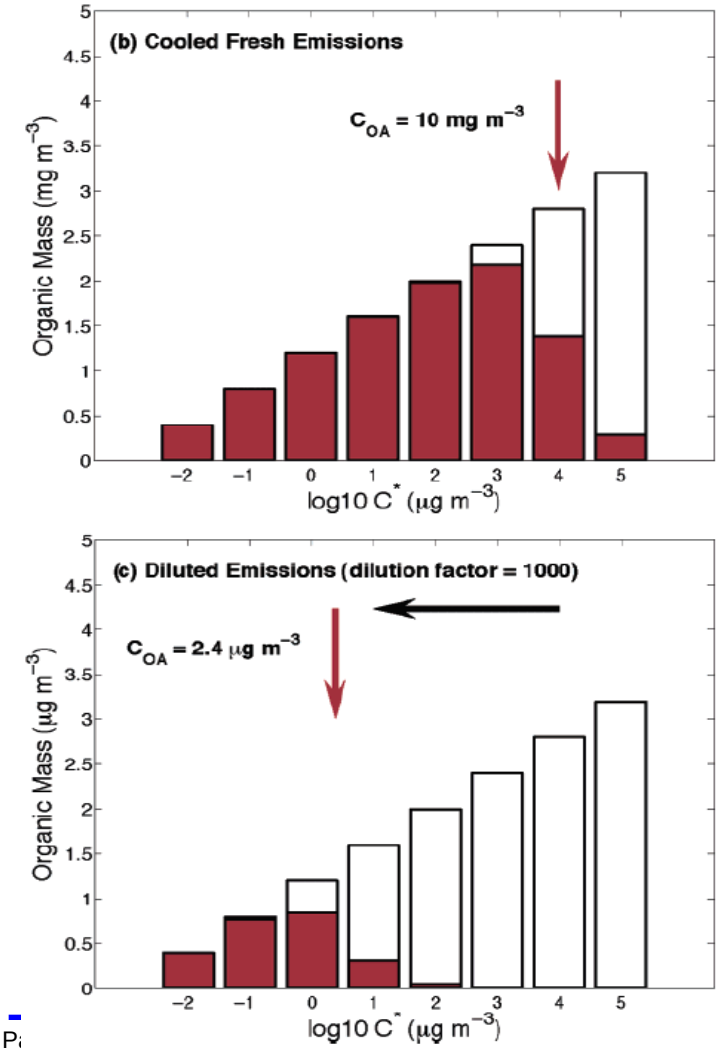
$$c_i = \sum_k \alpha_{i,k} S_k + e_i$$

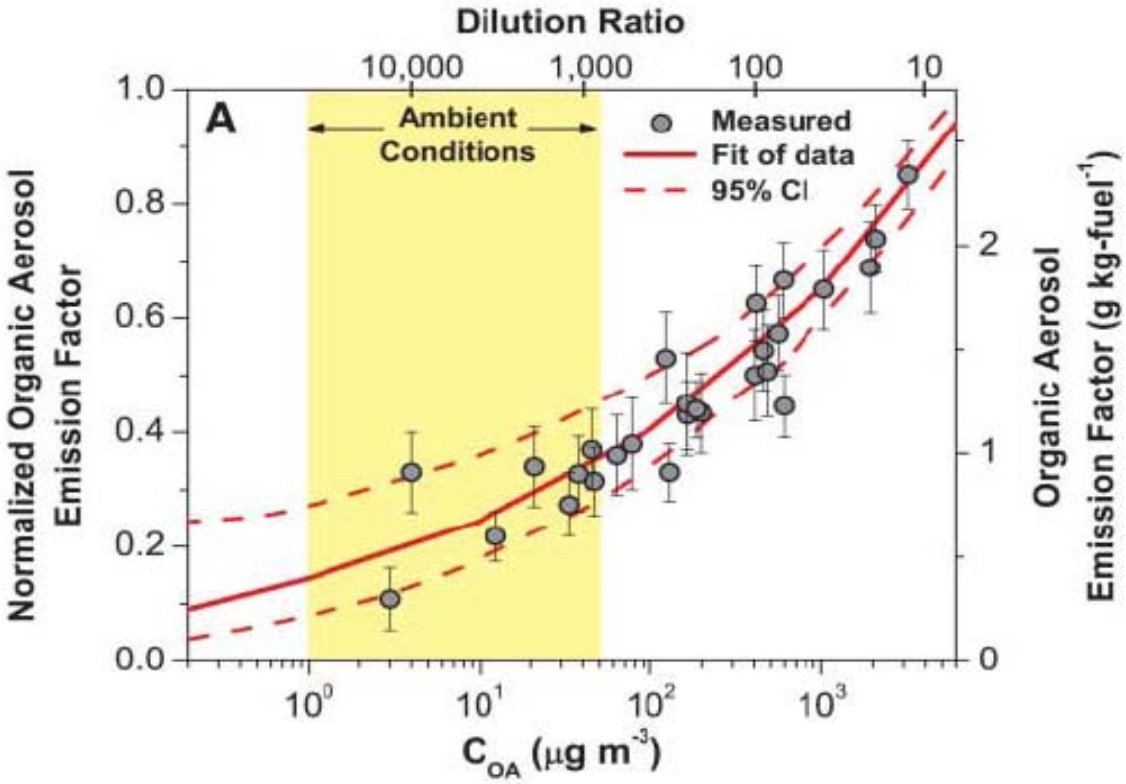
Critical issues

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

Subramanian et al., 2005

Dilution results in decrease of semivolatile OC in aerosol
➔much smaller primary fraction than expected from tracer ratios





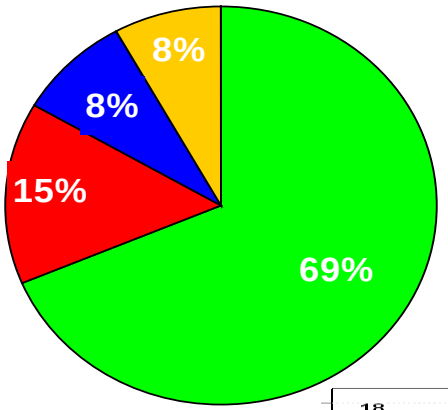
Robinson et al., Science 2007

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

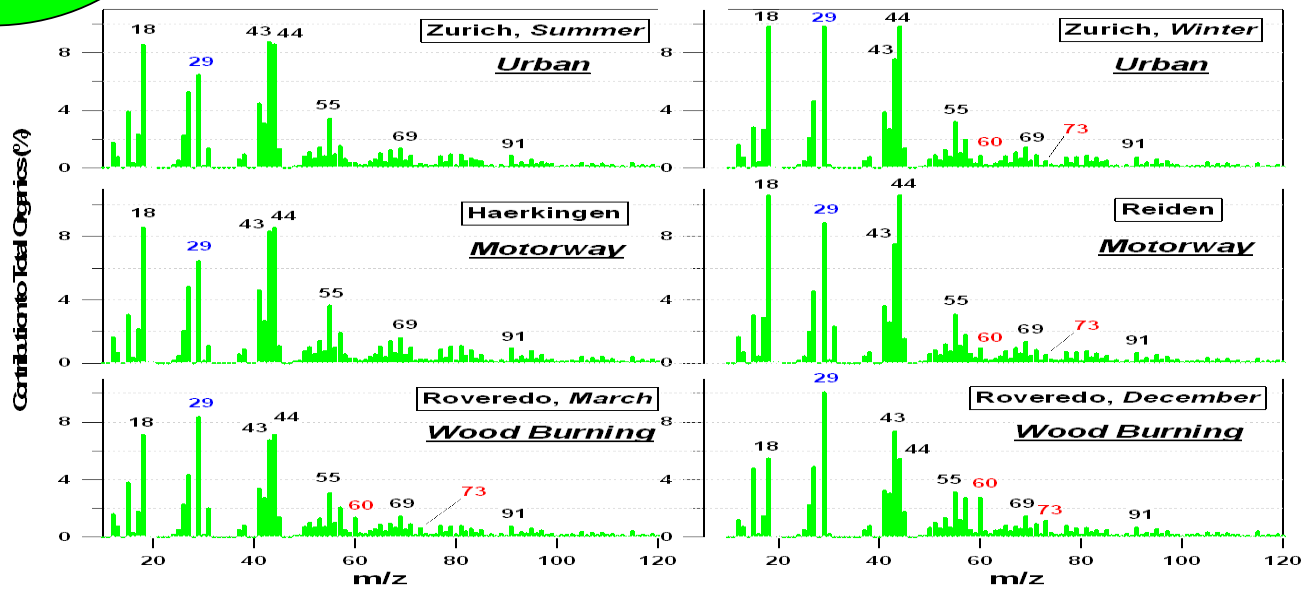
An alternative approach:
Use the full (organic) spectra of an aerosol mass spectrometer to retrieve source contributions

Example:
Zurich, Summer
AMS mass:
19 μg/m³

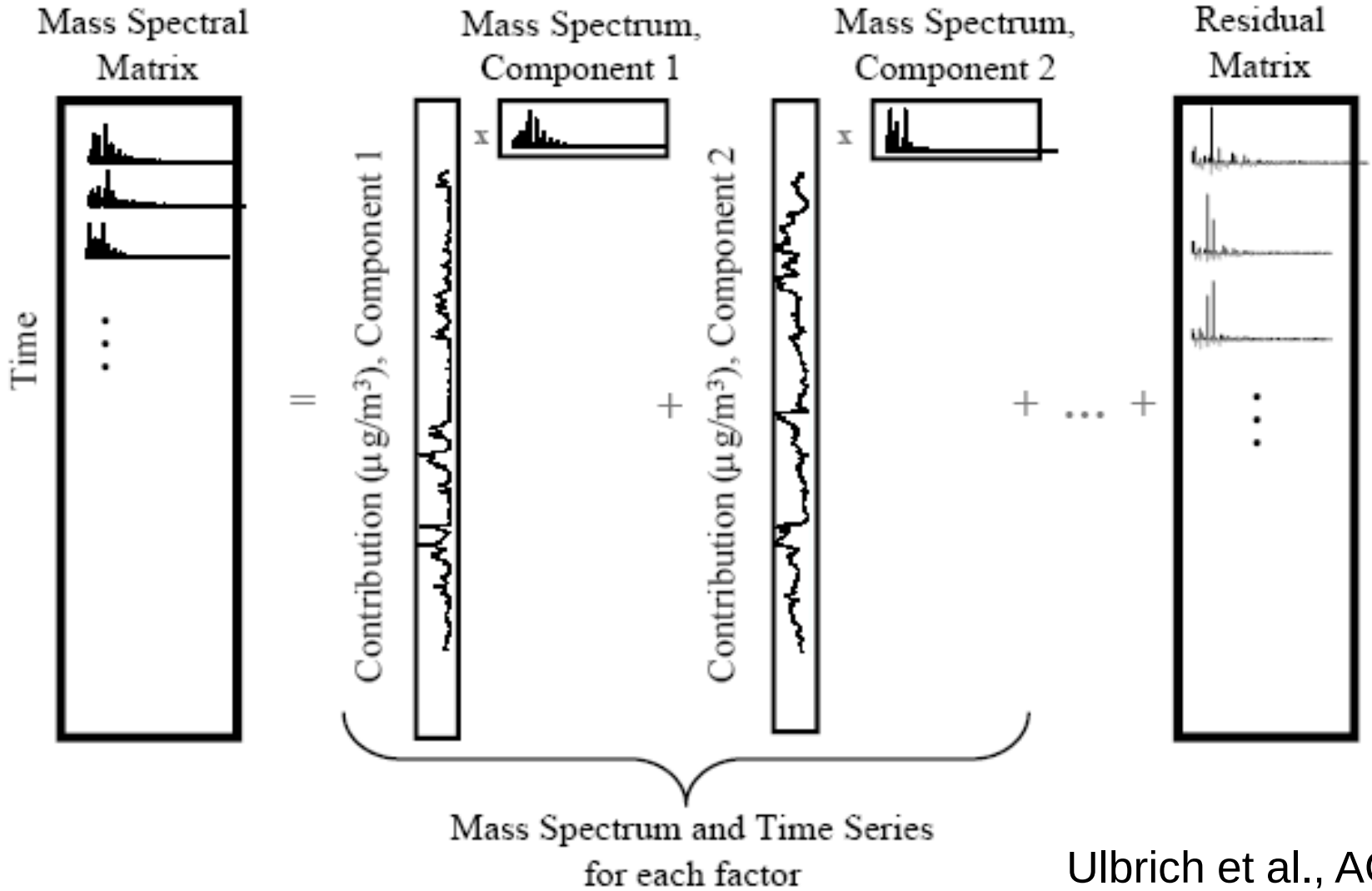
OM: 13 μg/m³



Org
NO3
SO4
NH4

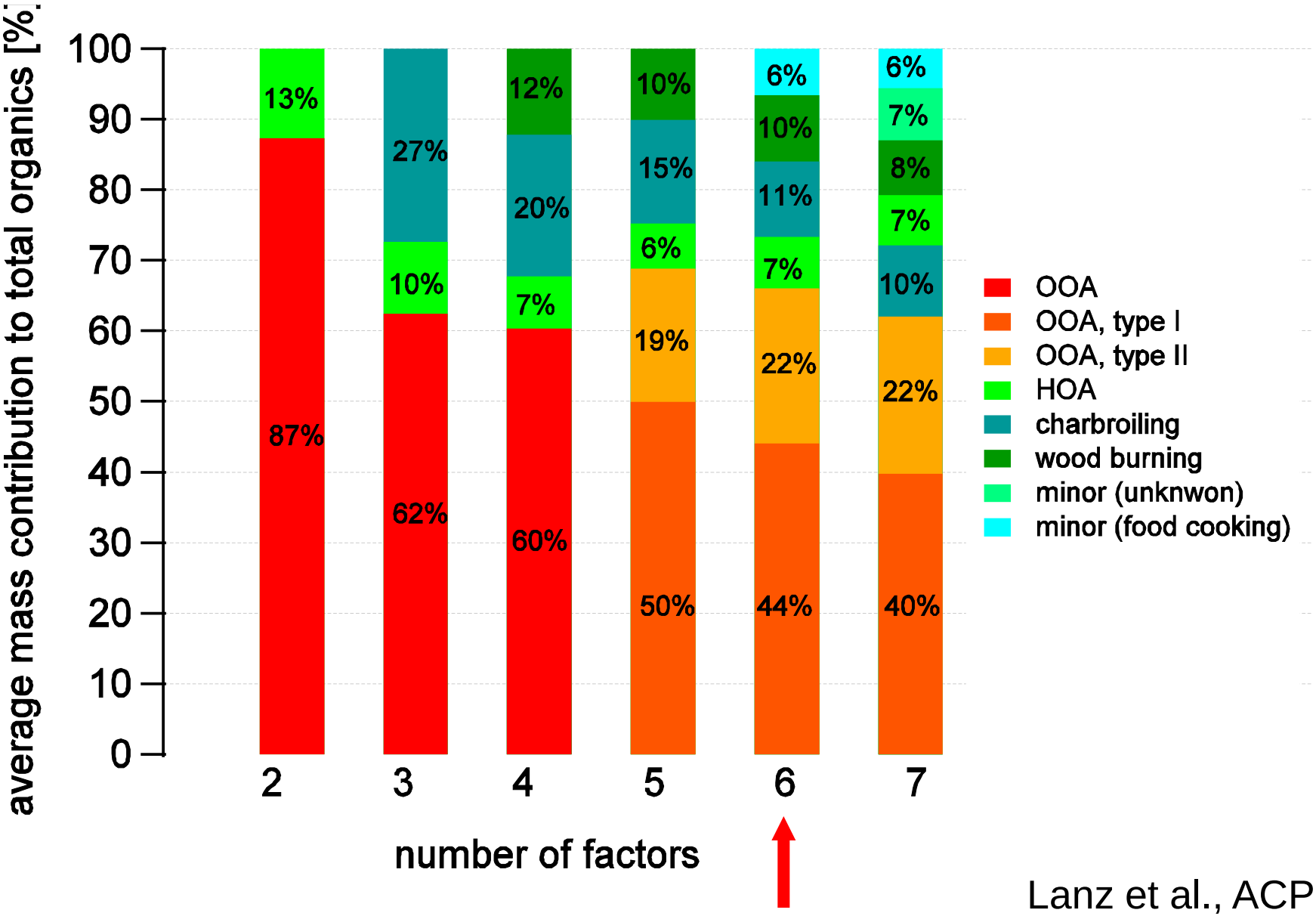


Positive Matrix Factorization (PMF) of full OM spectrum for source identification and attribution



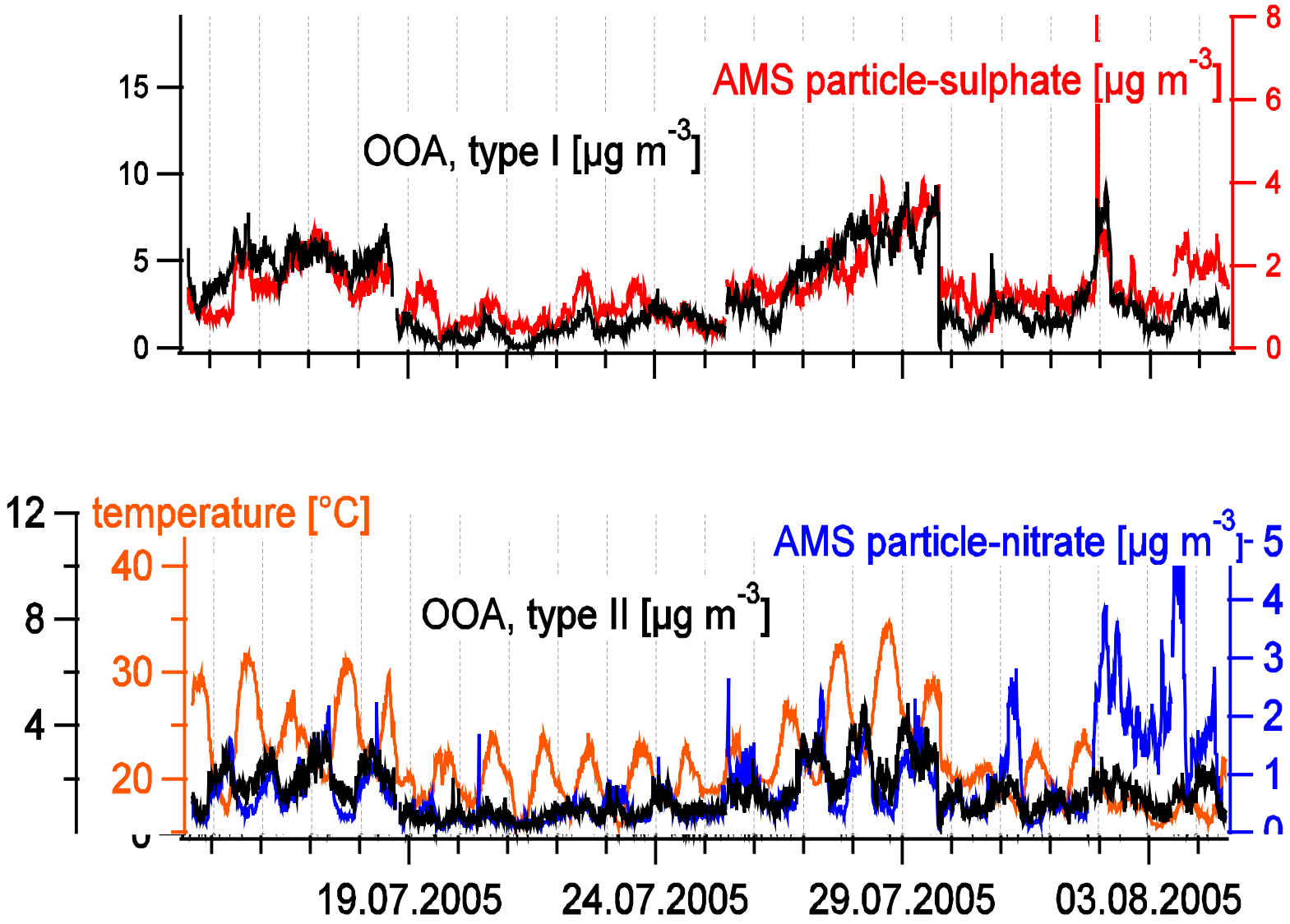
Ulbrich et al., ACPD 2008

The result of PMF



Lanz et al., ACP (2007)

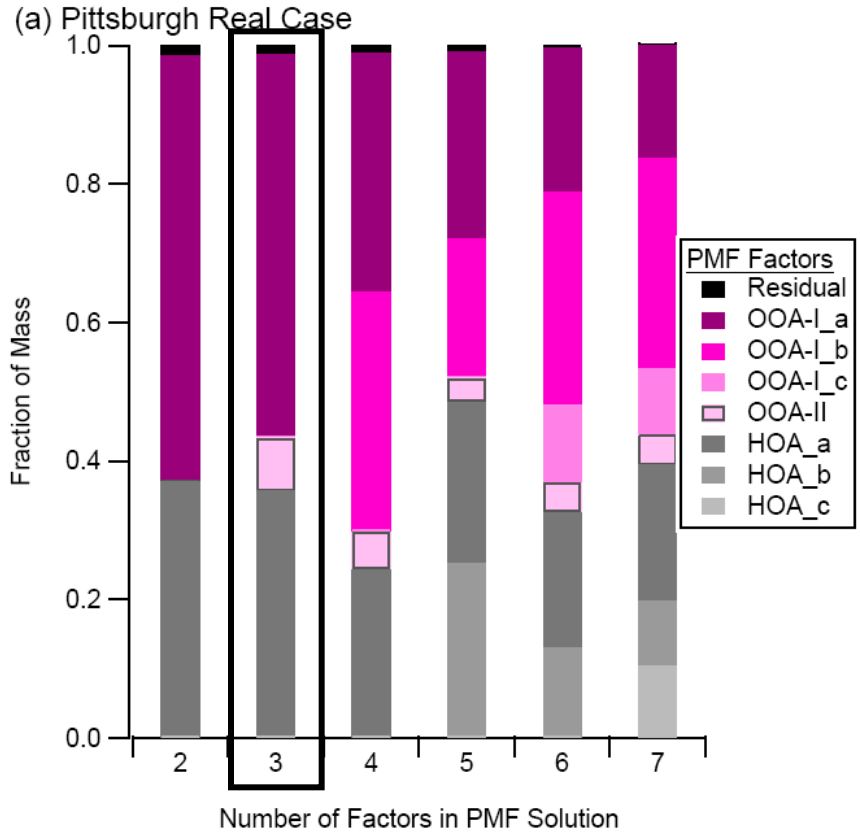
The two different types of OOA behave differently



Lanz et al., ACP (2007)

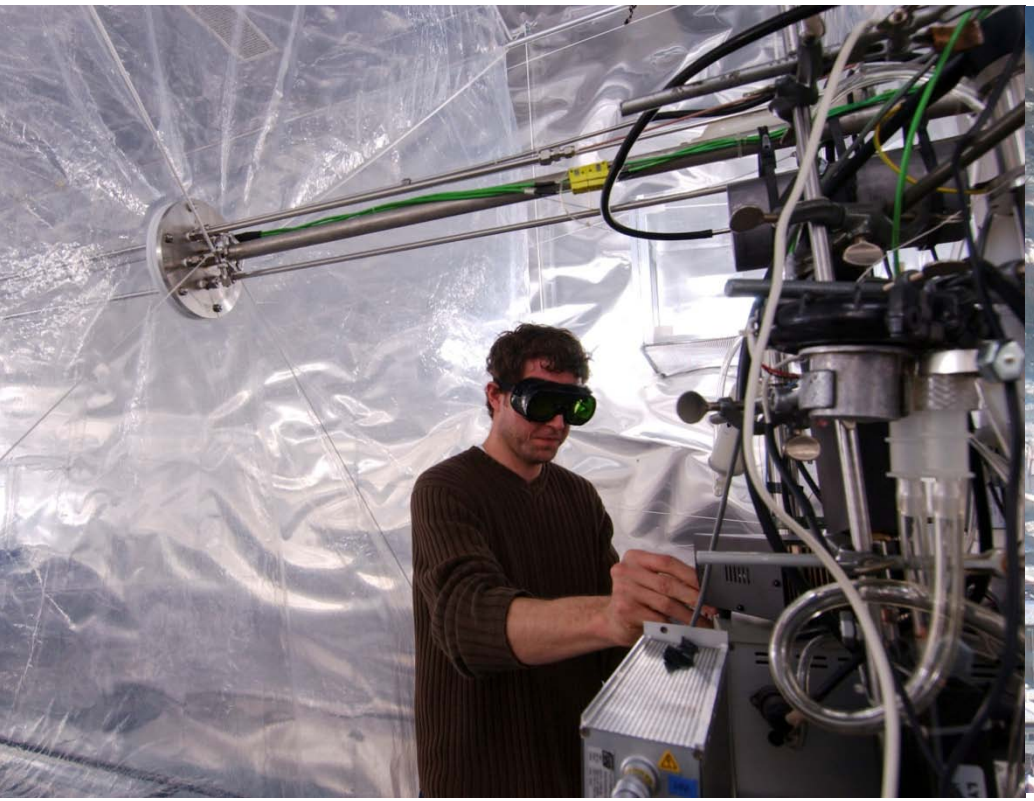
OOA-I and OOA-II now found at many other sites

- Zurich summer
- Pittsburgh (left)
- Japan
- Mexico City
- UK
- Jungfraujoch
- many other sites in Switzerland
- …
- not in Zurich winter (too little temperature variation)



Three sources for Pittsburgh
Ulbrich et al., ACPD (2008)

How does this OOA compare to secondary organic aerosol?



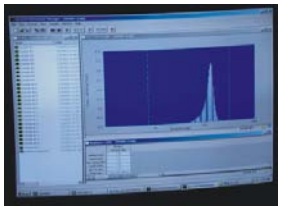
The PSI smog chamber

AMS

WEDDAC

IC-MS

SMPS



CPC

GC

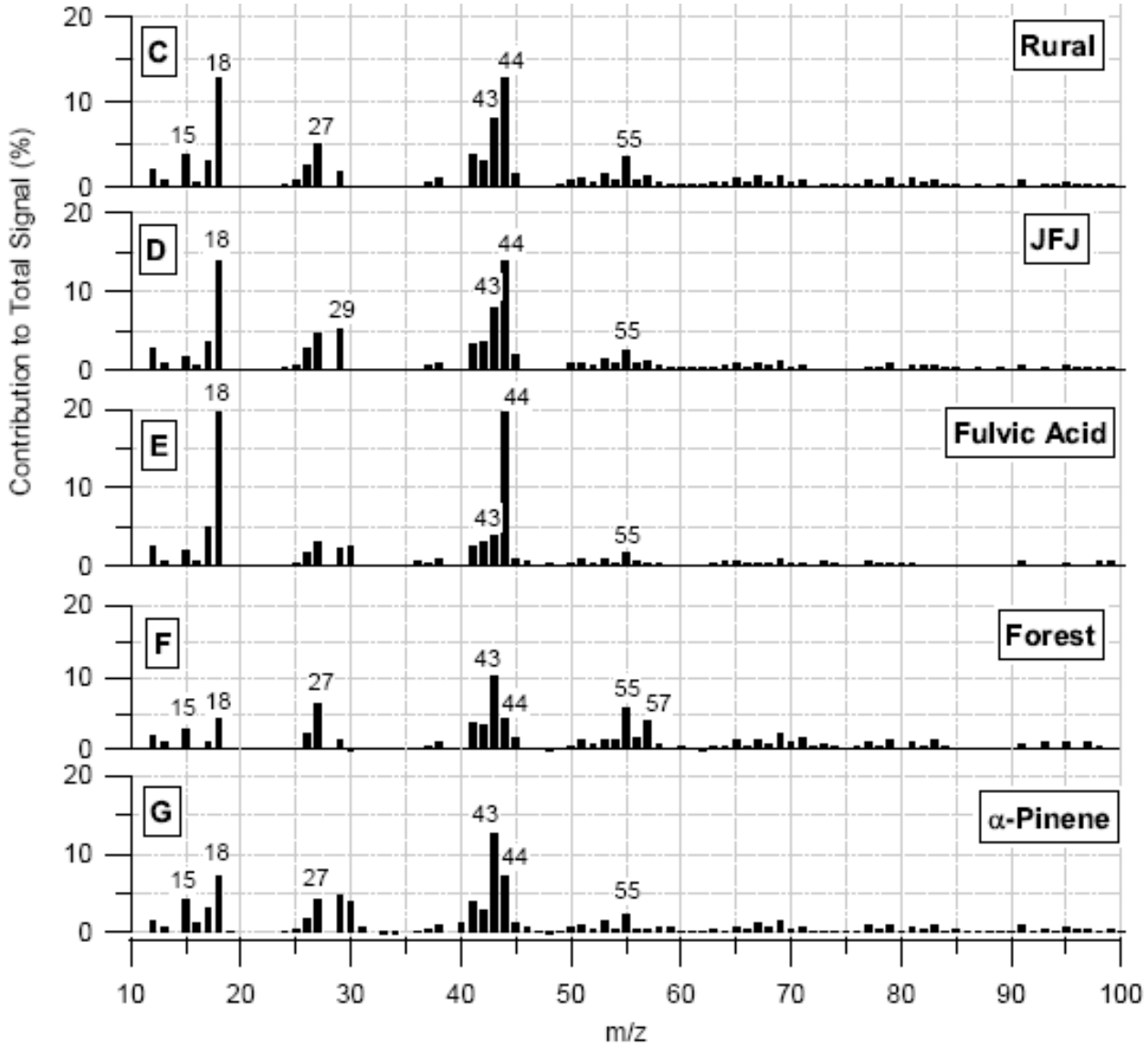
PTRMS

HTDMA

VTDMA

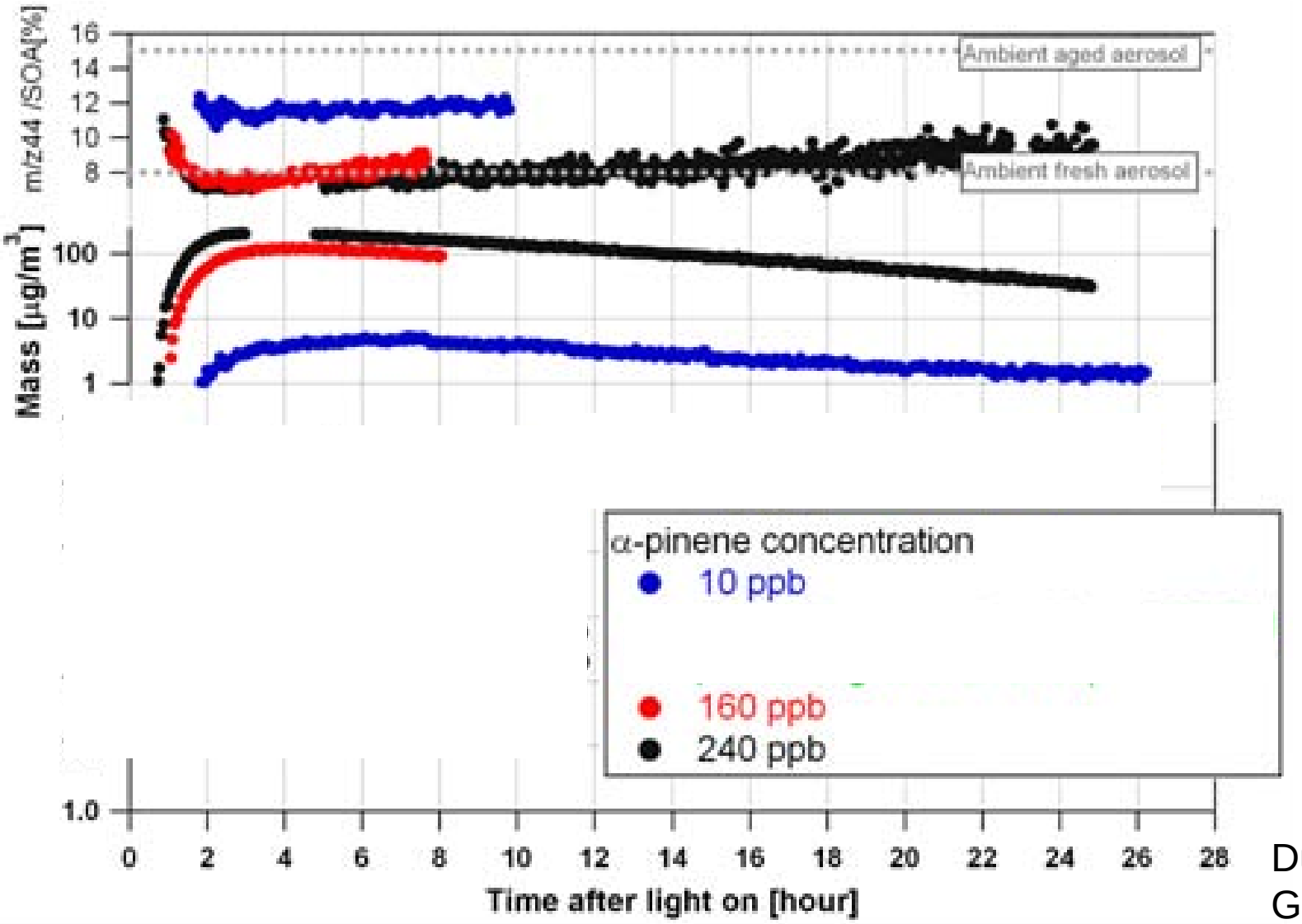
Paulsen et al.,
ES&T (2005)

Early AMS smogchamber spectra e.g. of α-pinene did not match aged ambient spectra ➔ why?



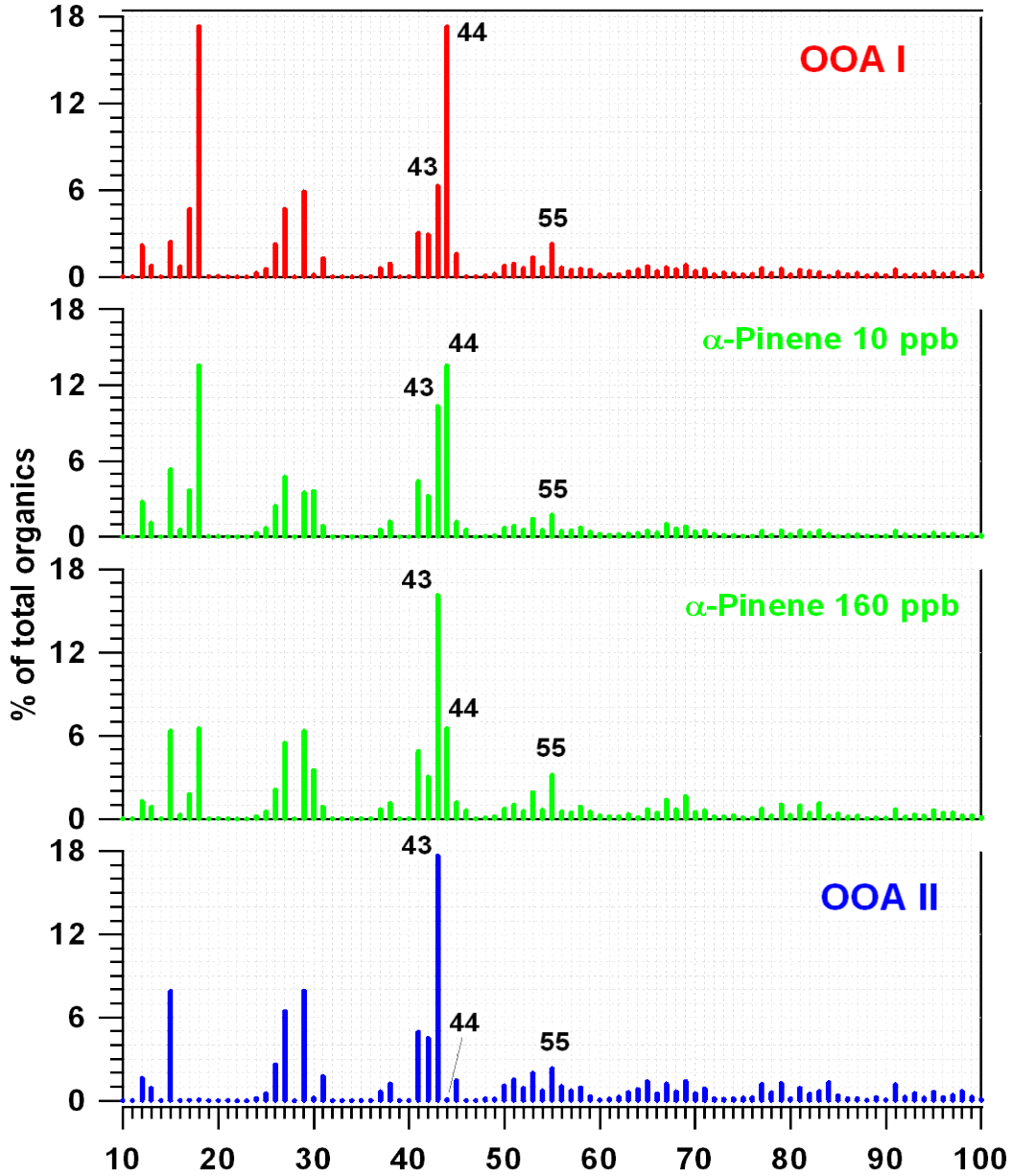
Alfarra et al., ACP 2006

AMS m/z 44 gets close to ambient only at low precursor concentration

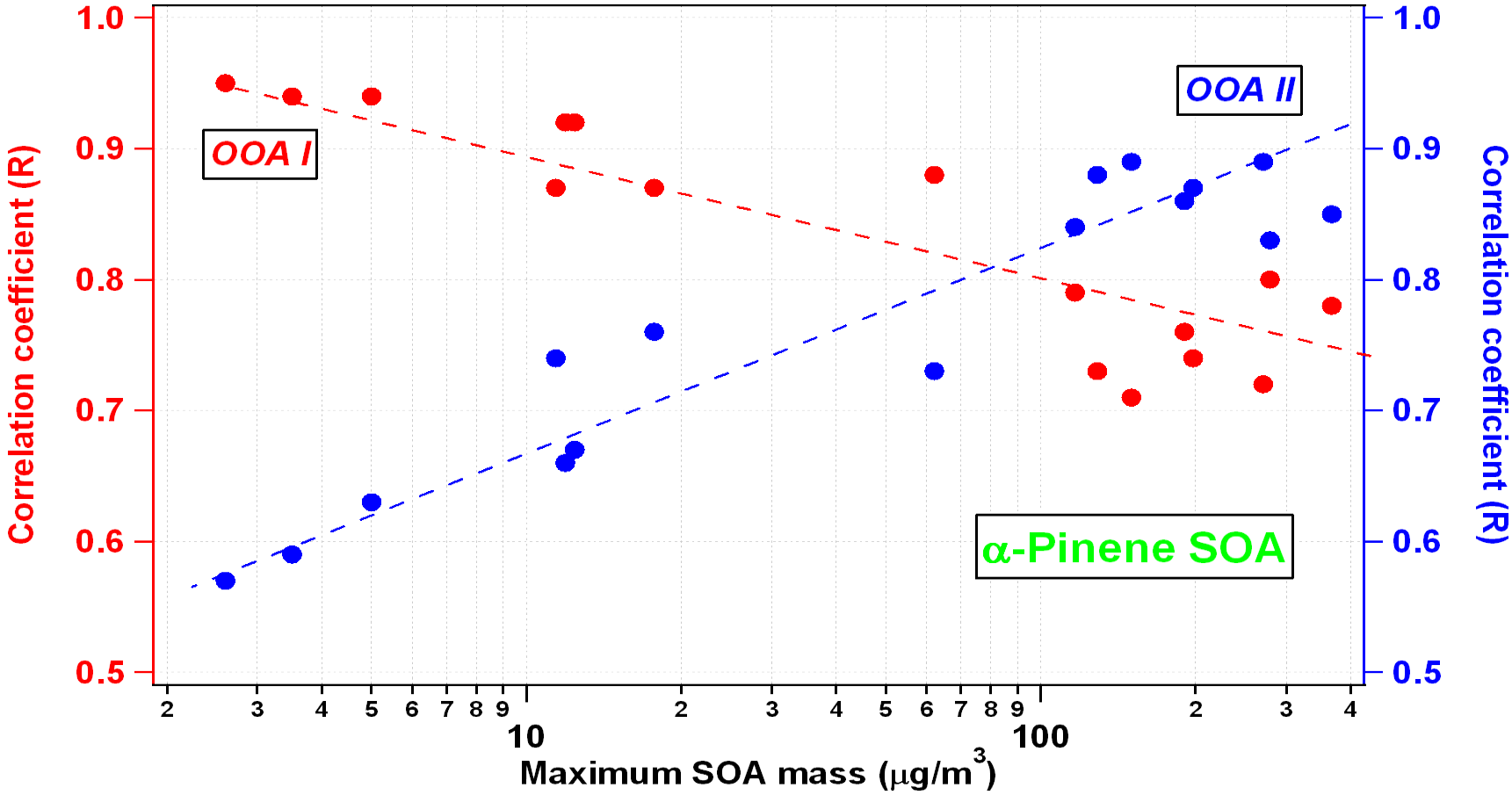


Duplissy et al., GRL, 2008

Smog chamber SOA vs. ambient OOA I & OOA II



Smog chamber SOA from α-pinene vs. ambient OOA I & OOA II from Zurich

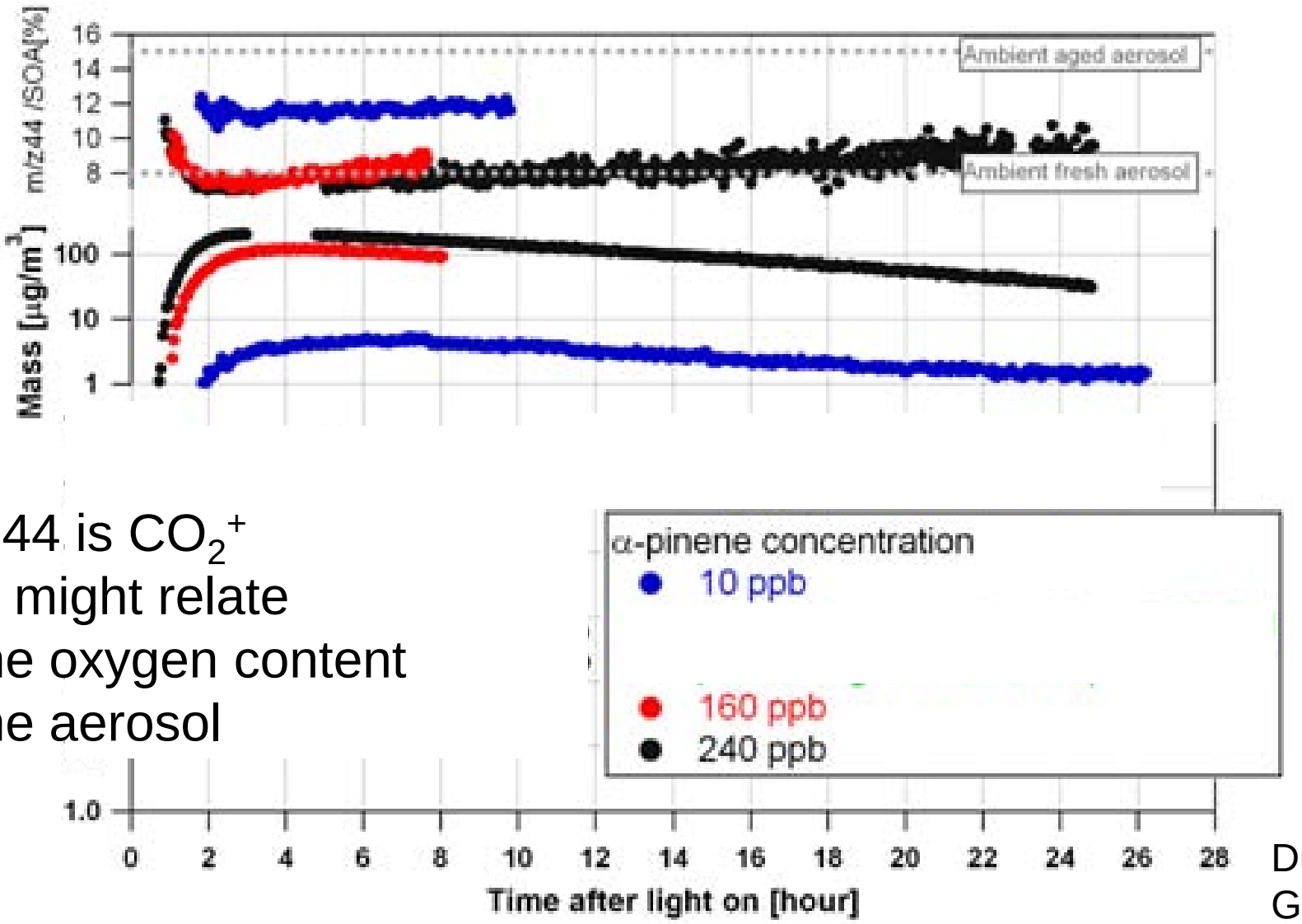


Lower VOC concentration = lower SOA mass = more oxidized and less volatile SOA

Higher VOC concentration = higher SOA mass = less oxidized and more volatile SOA

Alfarra et al., submitted

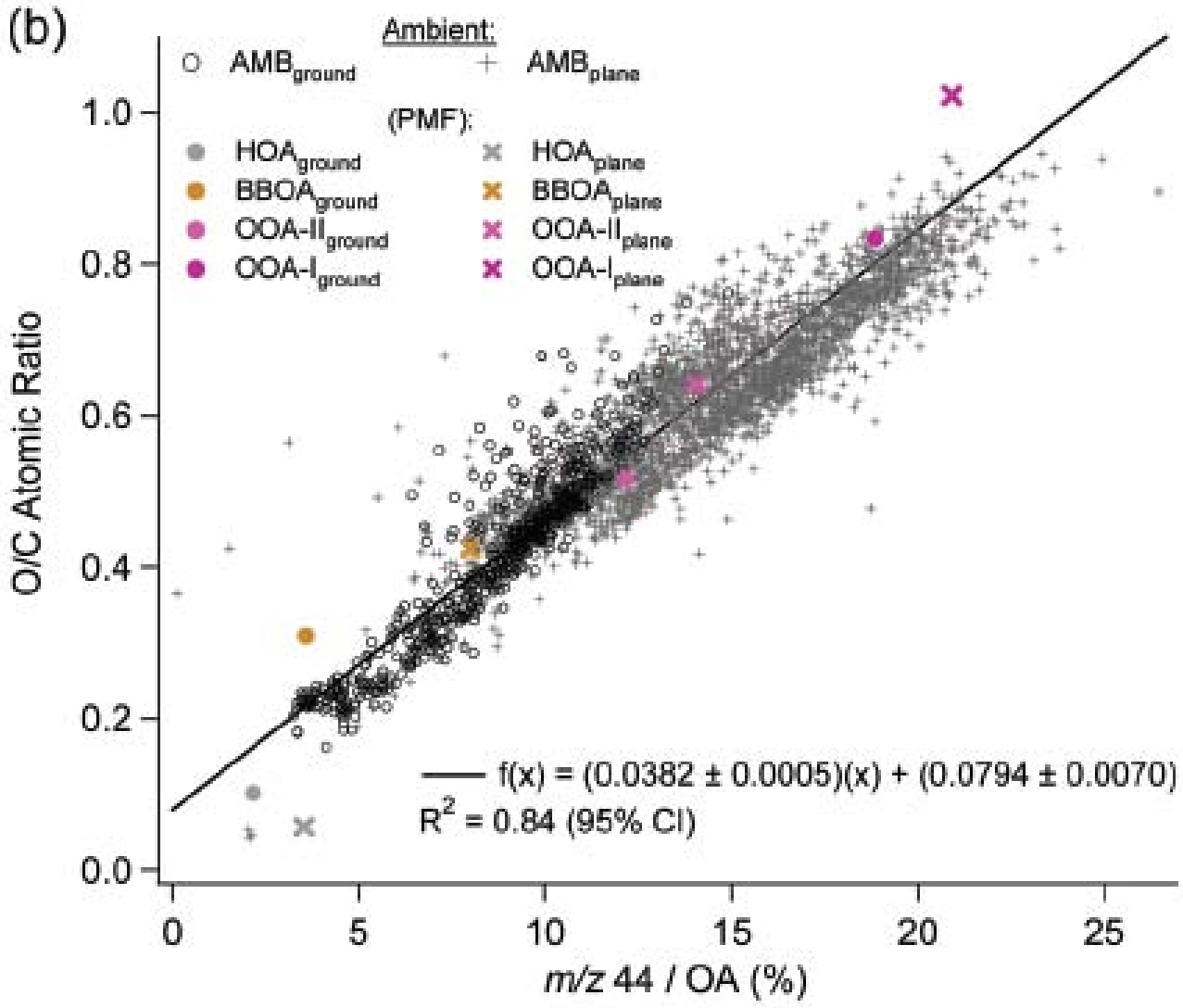
What does AMS m/z 44 mean at all?



m/z 44 is CO_2^+
so it might relate
to the oxygen content
of the aerosol

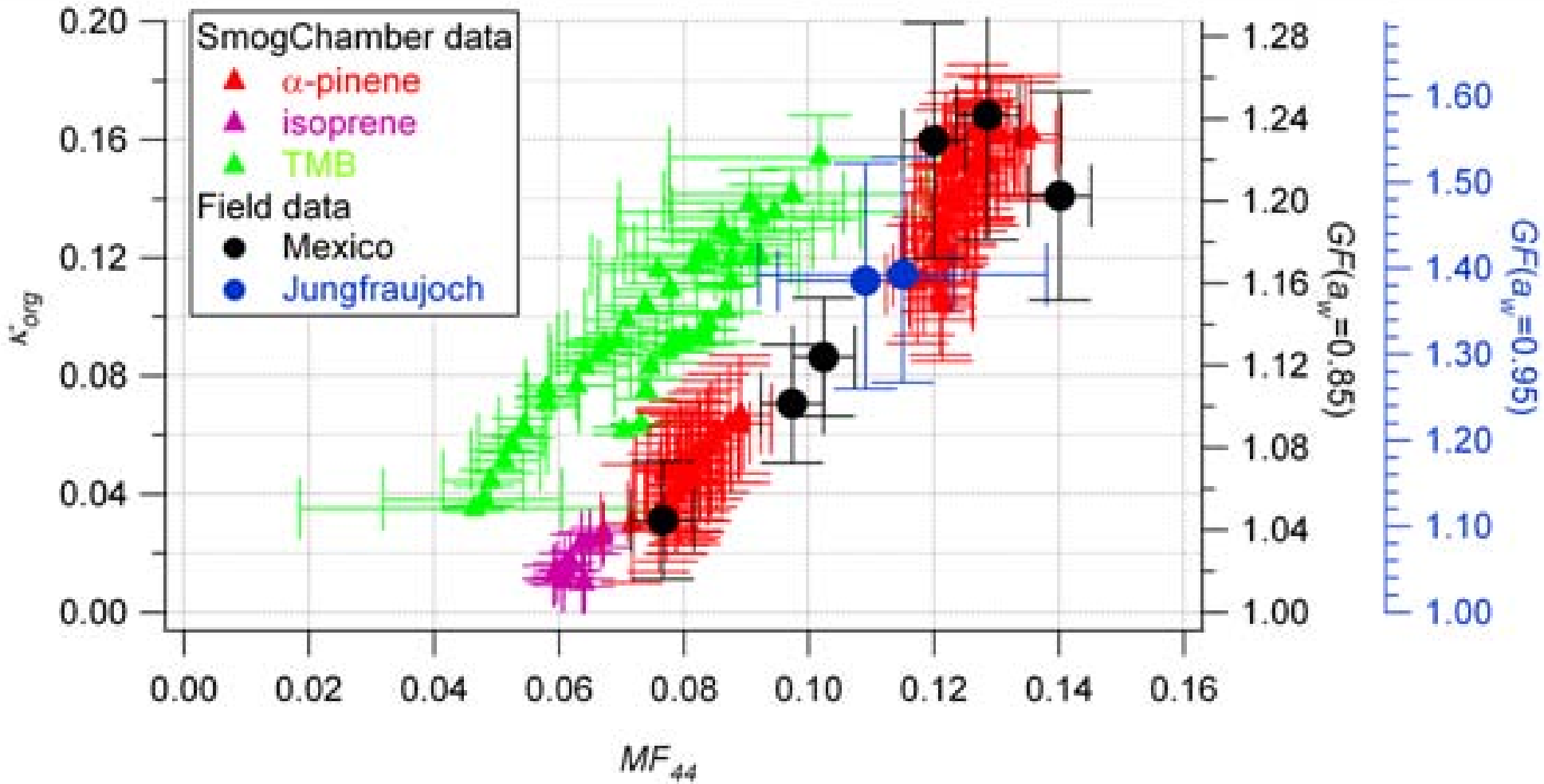
Duplissy et al., GRL, 2008

The link between m/z44 and the O/C ratio



Aiken et al., ES&T 2008

m/z44 is also correlated with hygroscopic growth



Duplissy et al., in preparation

Conclusions

- **PMF of AMS data provides a highly suitable means to identify sources of organic aerosol; both primary and secondary**
- **Smog chamber results are representative of the real atmosphere if you do it right (low concentrations)**
- **AMS features can be related to fundamental chemical signatures of the aerosol**

Thank you for your attention

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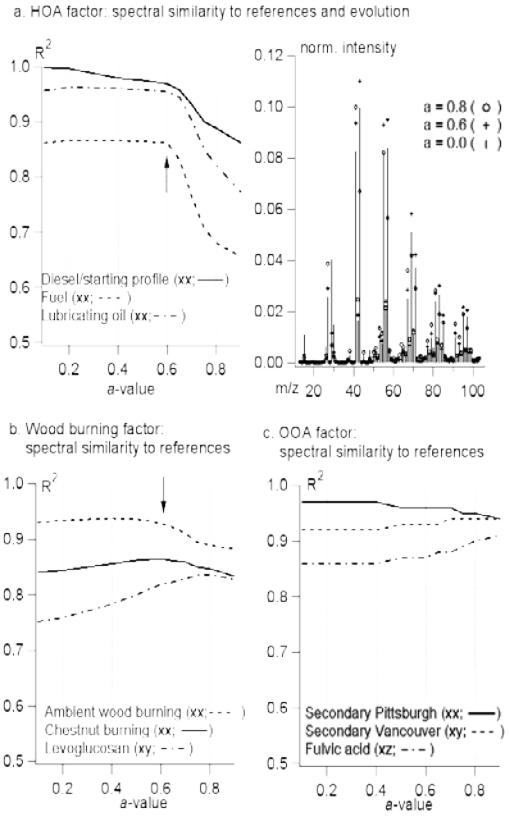
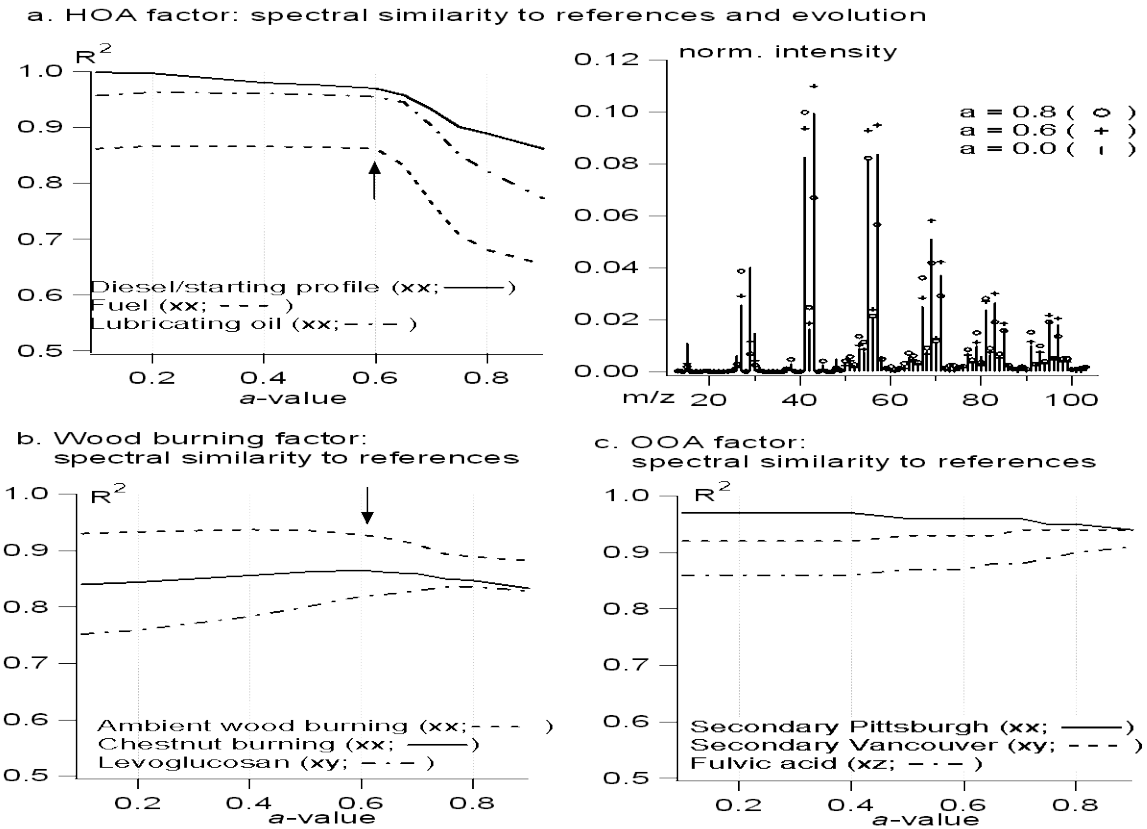
http://www.psi.ch/lac

The use of a Multilinear Engine (ME-2) instead of PMF





a-value = 0: profile fixed a-value = 1: intensities can evolve from 0 to 200%
Additional constraints by other methods (e.g. radiocarbon analysis): a-value cannot be higher than 0.8 (otherwise HOA overestimated (fossil SOA negative)

Lanz et al., ES&T, 2008