Speciation / Source Apportionment of PM

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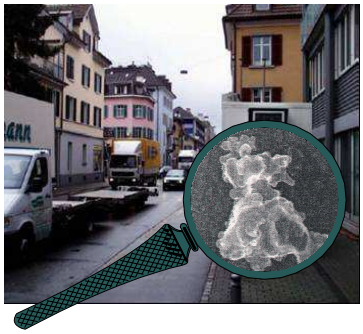
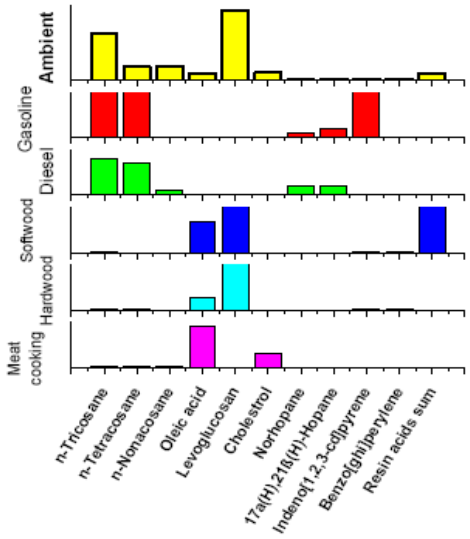


10th Task Force on Measurement and Modeling Meeting
Paris, 15-17 June, 2009

The traditional approach for source apportionment: use of specific tracers



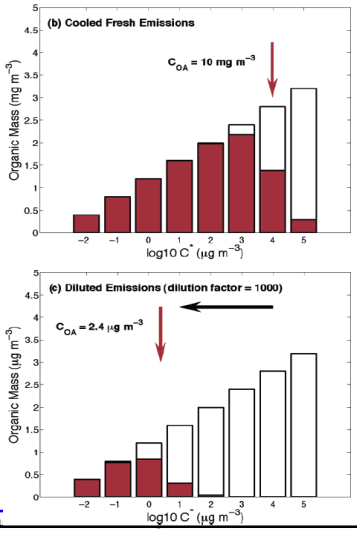
$$c_i = \sum_k \alpha_{i,k} S_k + e_i$$

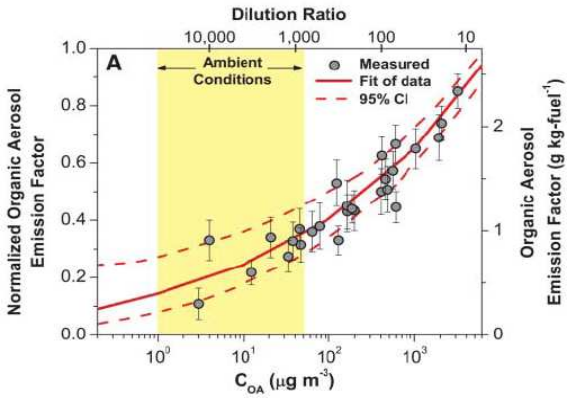
Critical issues

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

R. 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

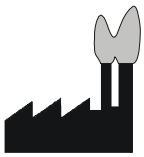
Donahue et al., Environ. Sci. Technol. 2006

Our approach: Combination of

- **Carbon-14 analysis**
- **PMF (Positive Matrix Factorization) of organic aerosol mass spectra**
- **PMF of elemental spectra from rotating drum impactors**

Fossil vs. non-fossil carbonaceous aerosol: Source apportionment by $^{14}C/^{12}C$

Anthropogenic Emissions



Biogenic Emissions

^{14}C decayed

^{14}C modern

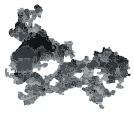
Flux $F_a = dm_a/dt$

$f_M = 0$

Flux $F_b = dm_b/dt$

$f_M = 1$ in reference year 1950

Carbonaceous aerosol

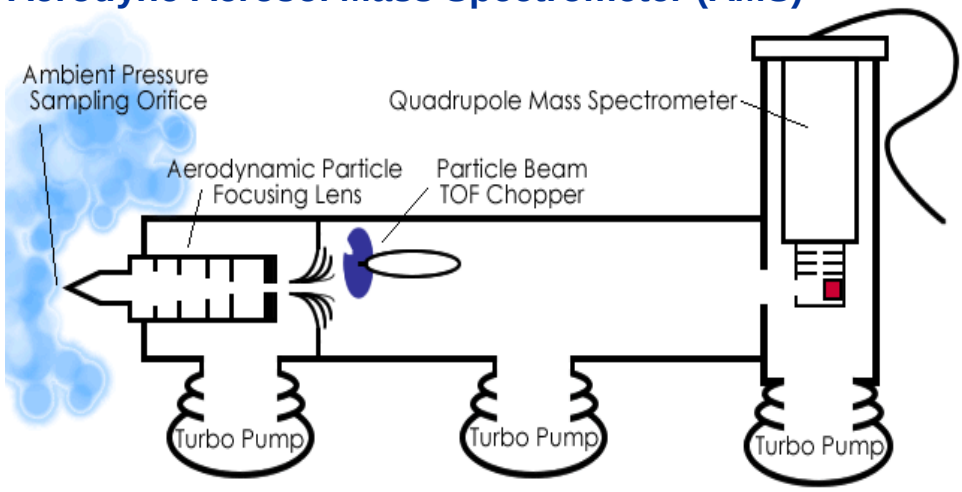


$$f_M = \frac{F_b}{F_a + F_b}$$

Important: discriminate OC and EC (EC mainly fossil, OC mainly recent)

Fraction of modern: $f_M = (^{14}C/^{12}C_{Sample}) / (^{14}C/^{12}C)_{Current\ Biomass}$

Non-refractory aerosol mass spectra with the Aerodyne Aerosol Mass Spectrometer (AMS)



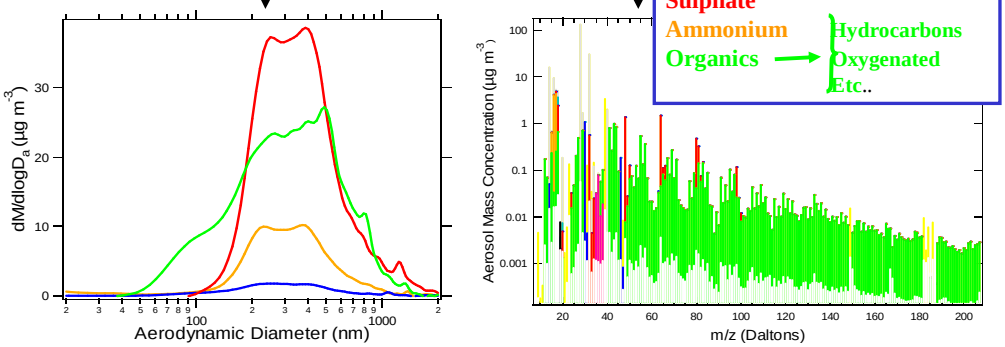
Matt Thyson (Lexington, Massachusetts)

Output of AMS: particle size and mass spectra (high time res.)

Aerosol Sampling

Real-time measurement → **AMS**

Nitrate
Sulphate
Ammonium
Organics → Hydrocarbons, Oxygenated, Etc..

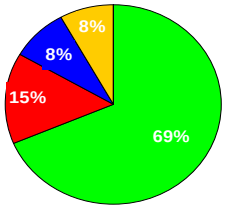


Mass Size distribution ***Chemical composition***

AMS summer data for Zurich

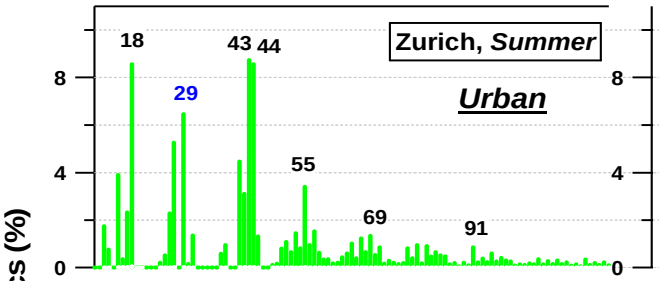
➔ how can we retrieve source contributions from this?

Zurich, *Summer*
19 µg m^{-3}

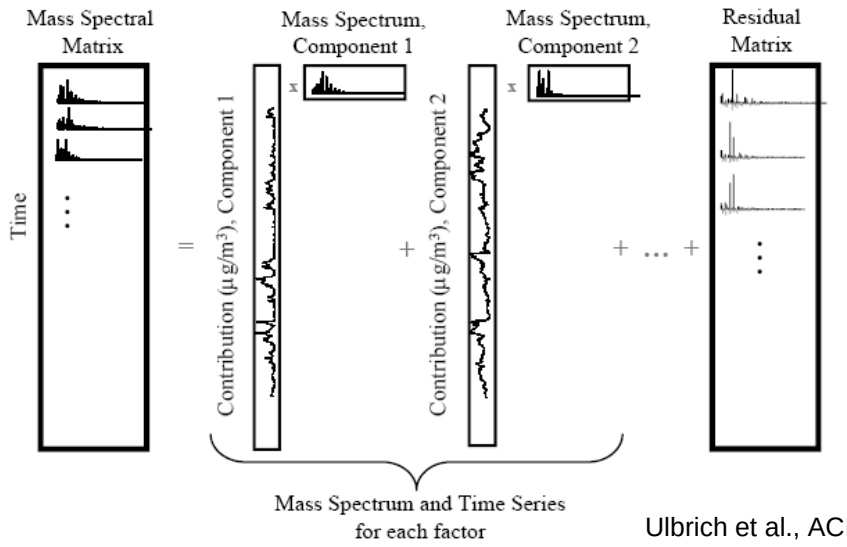


Org
NO3
SO4
NH4

OM: 13 µg/m³

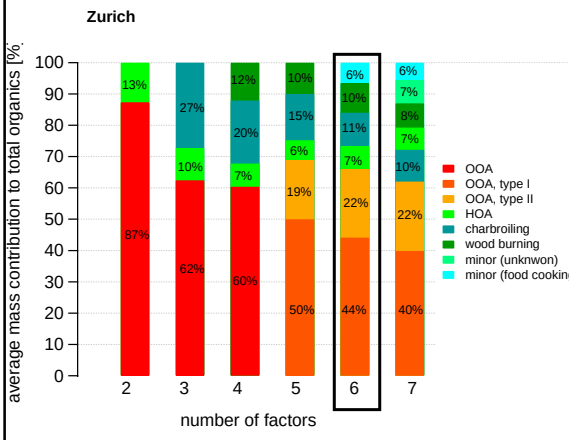


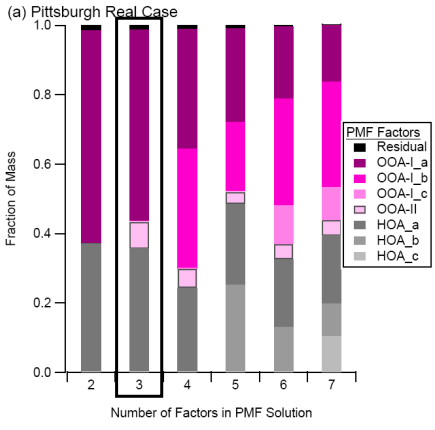
Positive Matrix Factorization (PMF) of full OM spectrum for source identification and attribution



Ulbrich et al., ACP 2009

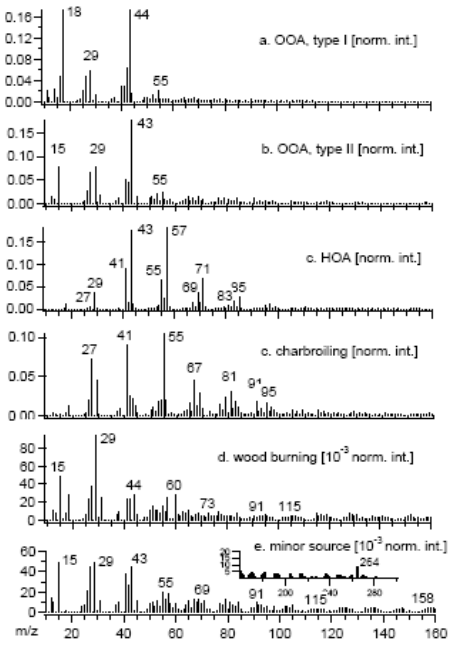
Results of PMF for Zurich and Pittsburgh





Six sources found for Zurich, Lanz et al., ACP (2007)

Three sources for Pittsburgh Ulbrich et al., ACP (2009)

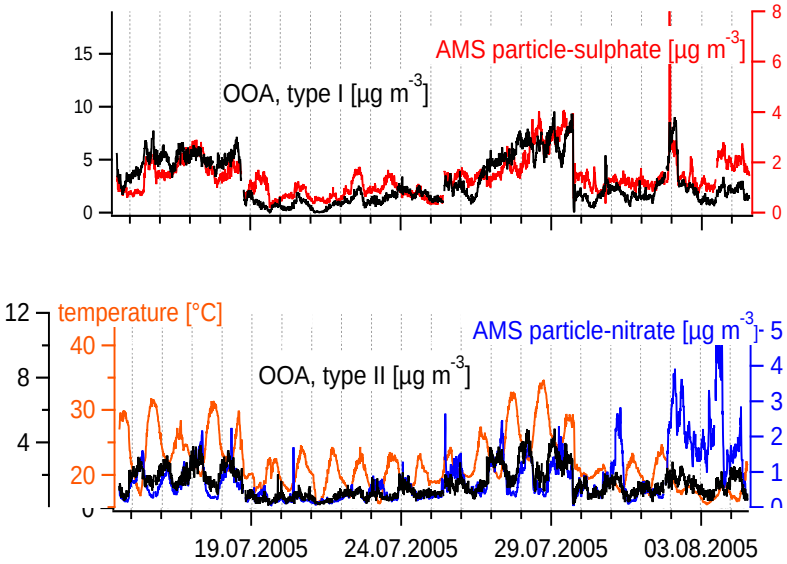


Check of spectral similarity of retrieved spectra with measured spectra from sources

Lanz et al., ACP (2007)

PAUL SCHERRER INSTITUT

There are two different types of OOA



Lanz et al., ACP (2007)

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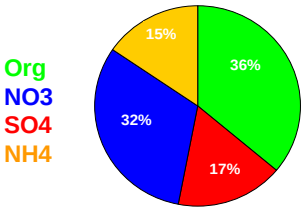
The situation in winter is different:

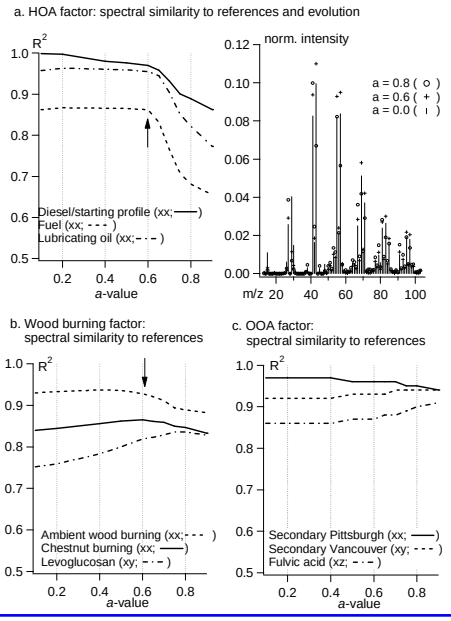
Concentrations mainly driven by meteorology
➔ high correlation between the time patterns from the different sources
➔ Traditional factor analysis fails



Zurich, *Winter*
44 µg m^{-3}

OM: 16 µg/m^3

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

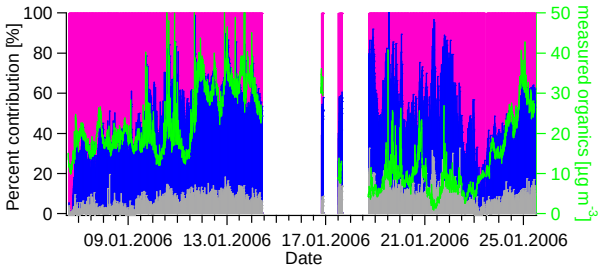


a-value = 0: profile fixed
a-value = 1: intensities can evolve from 0 to 200%

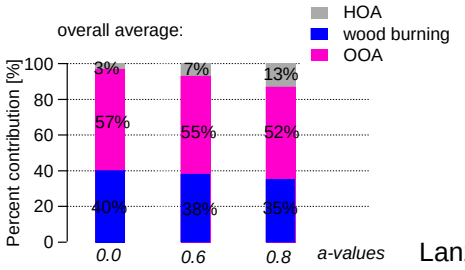
Additional constraints by radiocarbon analysis: a-value cannot be higher than 0.8 (otherwise HOA overestimated (fossil SOA negative)

Lanz et al., ES&T 2008

ME-2 result for OA in Zurich during winter

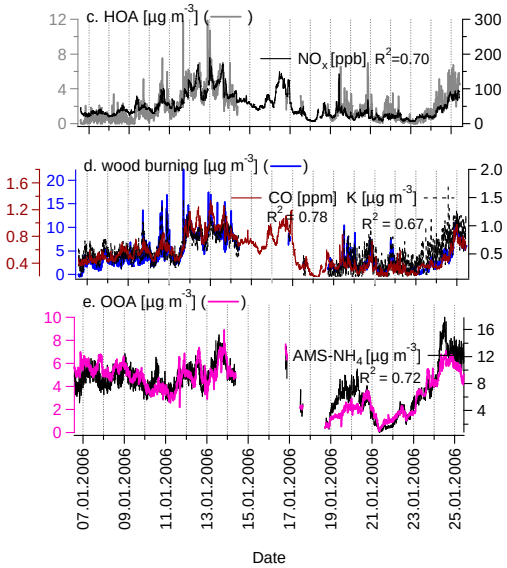


From C-14 analysis:
69% of OOA non-fossil
➔ Sources?



Lanz et al., ES&T 2008

Temporal evolution of the three components

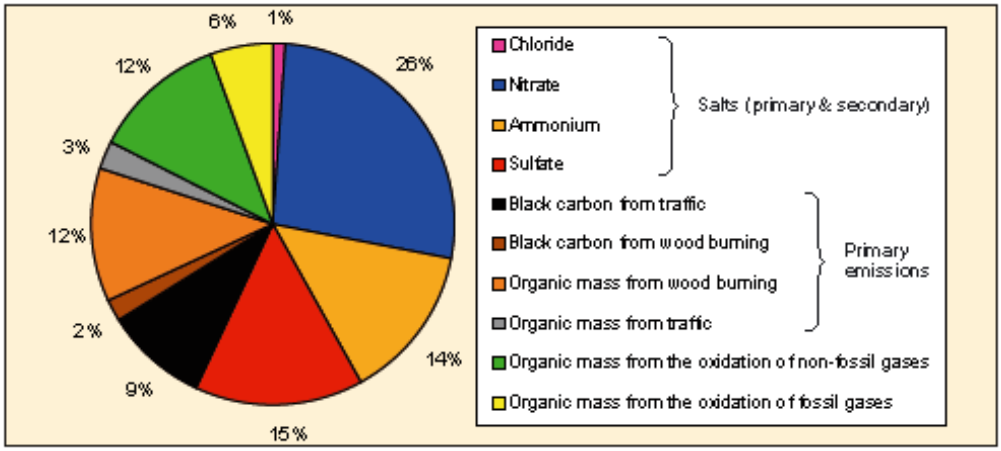


Comparison of sum of these 3 components with orginal data yields slope of 1.00 and R^2 of 0.99

No split into OOA1 & OOA2

Lanz et al., ES&T 2008

Chemical composition of PM1 in Zurich in winter: >50% secondary



Energiespiegel 19/2008
http://gabe.web.psi.ch/pdfs/Energiespiegel_19d.pdf

How about refractory material?
➔ RDI aerosol sampling

RDI: Rotating Drum Impactor

- **Size fractionation in 3 classes based on rectangular jet impaction**
- **Rotating substrate ➔ flexible time resolution using a step motor**

PM10 Inlet:

16.6 L/min (1 m³/h)

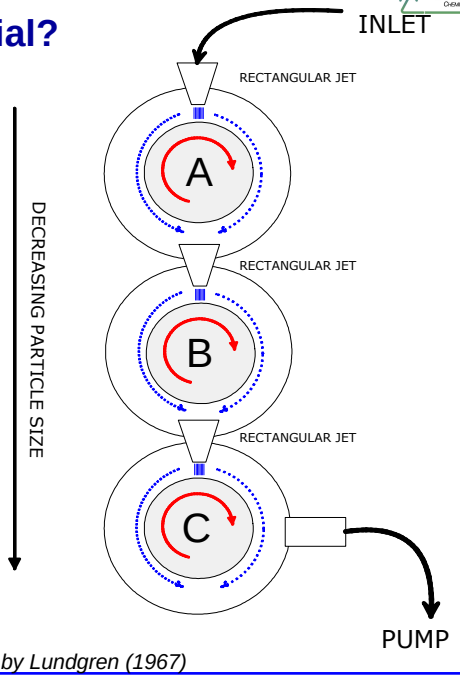
1h – steps!

3 size fractions:

A: 10 – 2.5 µm

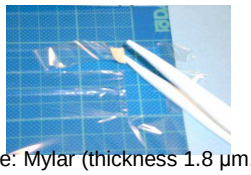
B: 2.5 – 1 µm

C: 1 - 0.1 µm

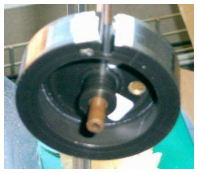


Modified design of the original impactor by Lundgren (1967)

RDI sample handling

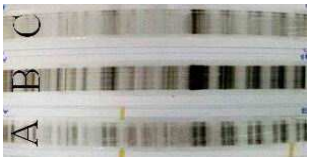


Substrate: Mylar (thickness 1.8 µm, greased with APIEZON L)



RDI impactor wheels

RDI aerosol sampling



Aerosol covered Mylar films

Sample holder for SR-XRF analysis

Elemental time series

Size fractionation

+

High time resolution

+

Low elemental detection limit

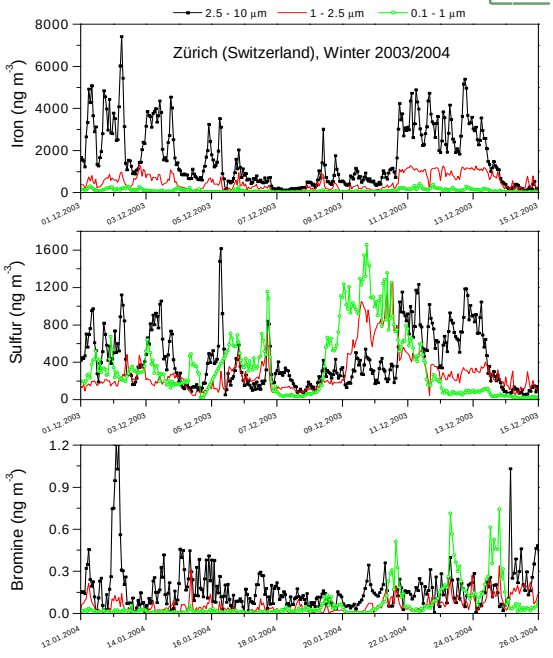
+

Broad range of elements

=

New insight into short-term dynamics of atmospheric pollution by trace elements

Bukowiecki et al., ES&T, 2005

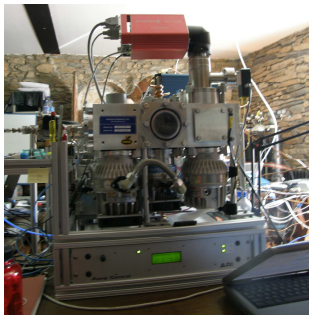


Conclusions

- PMF is a powerful means for source apportionment (needs to be used with care!)
- Can be applied to organics and inorganics
- The combination with C-14 analysis adds much additional strength
- Wood burning OA much higher than expected
- SOA often dominating, also high in winter
- We cannot (yet) discriminate between SOA from different sources

Is this of any help for the air quality authorities?

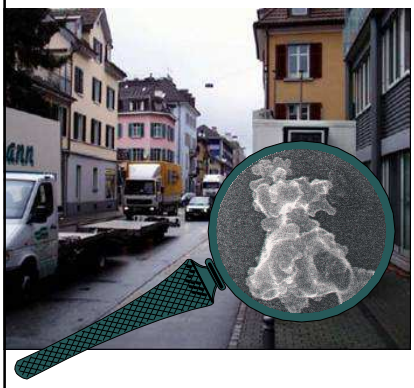
- Yes, e.g. Swiss project: temporal evolution of fossil/non-fossil carbonaceous aerosol at ~10 sites over the next 5 years
- Not yet for AMS: too expensive; may change in near future with introduction of new ‚Mini-AMS'



Conclusions on PM source apportionment / short

+ We know how to do it
- It‘s expensive

Thank you for your attention



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http://www.psi.ch/lac