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The high PM10 episode in January / February 2006

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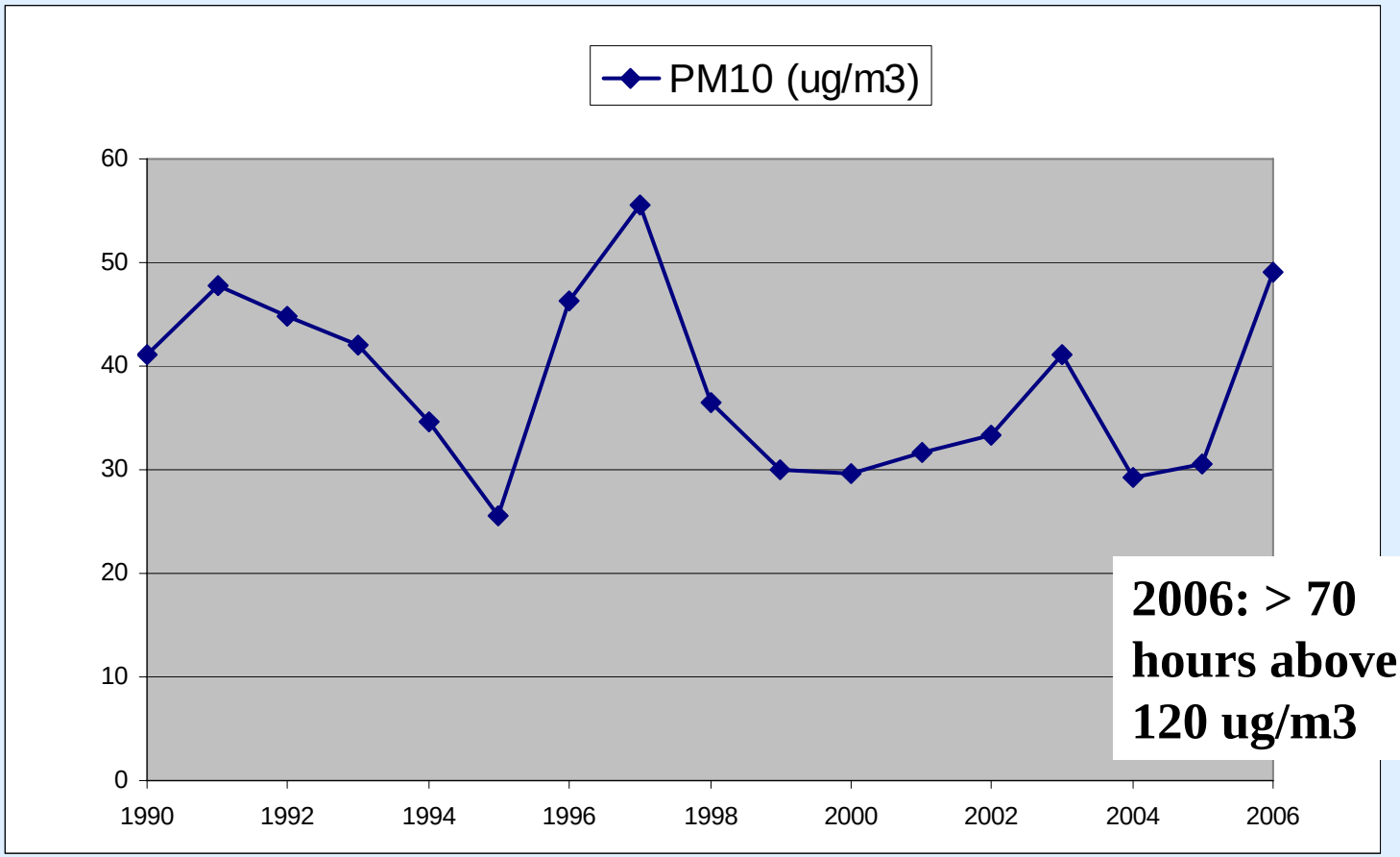
- Overview over PM10 data
- Methods (Aerosol mass spectrometer, ^{14}C method)
- First assessment of contributing sources
- Conclusions

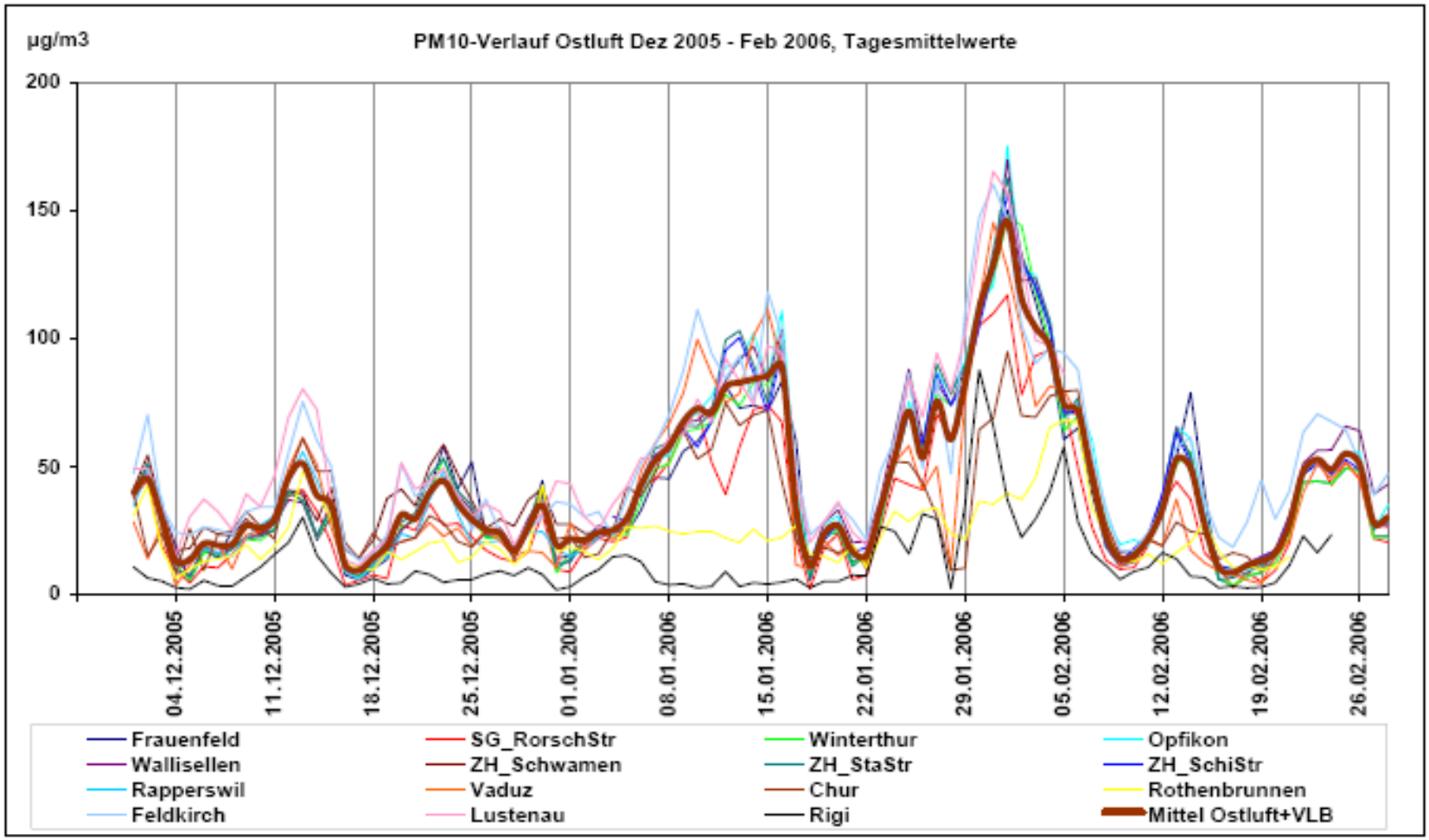
Thanks to BAFU, Kantons Lucerne, Graubünden, Tessin, Zürich, Oekoscience

PM10 concentration development in Zürich



2006: > 70 hours above 120 ug/m3

PM10 episode in eastern Switzerland



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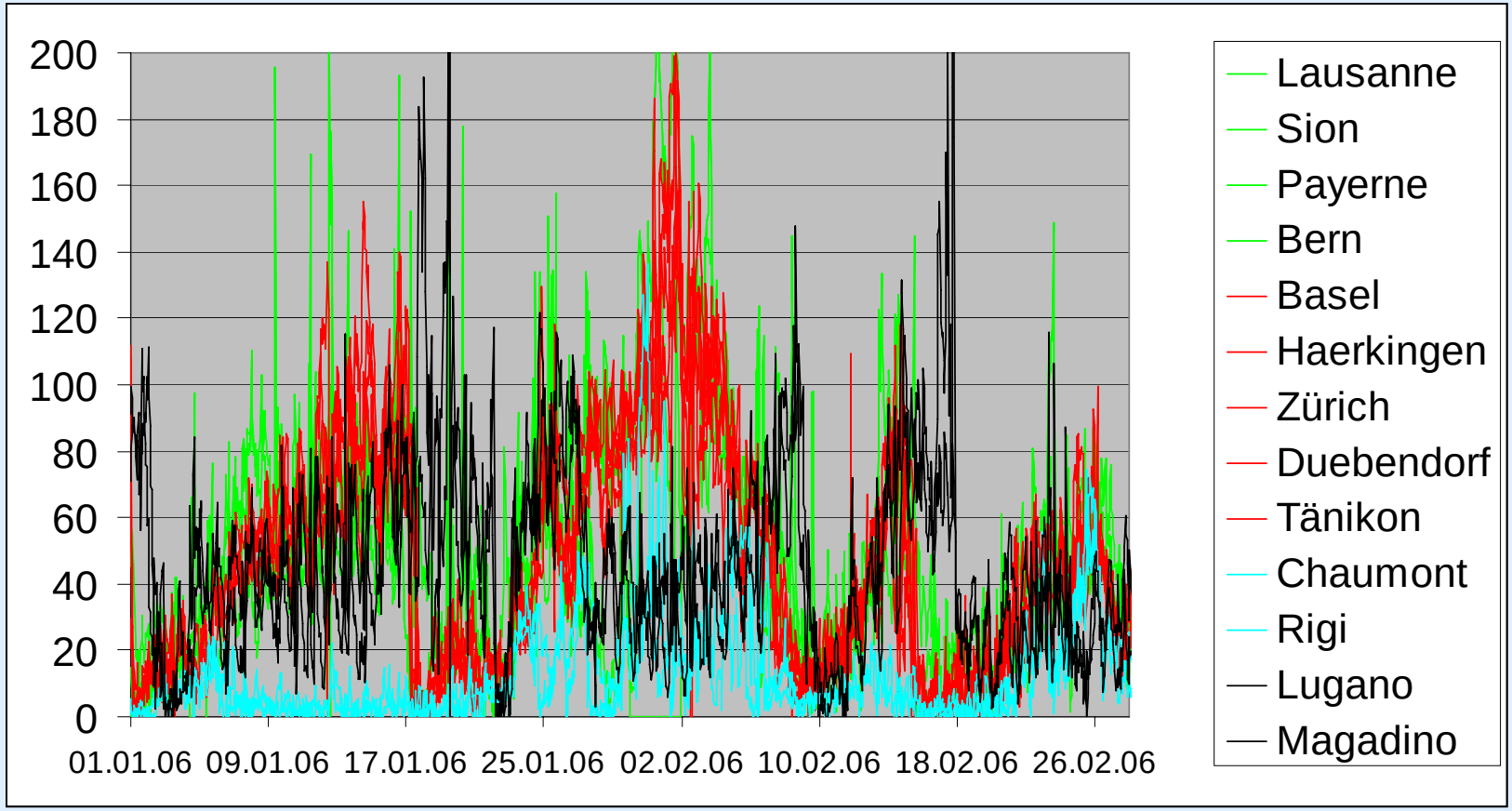
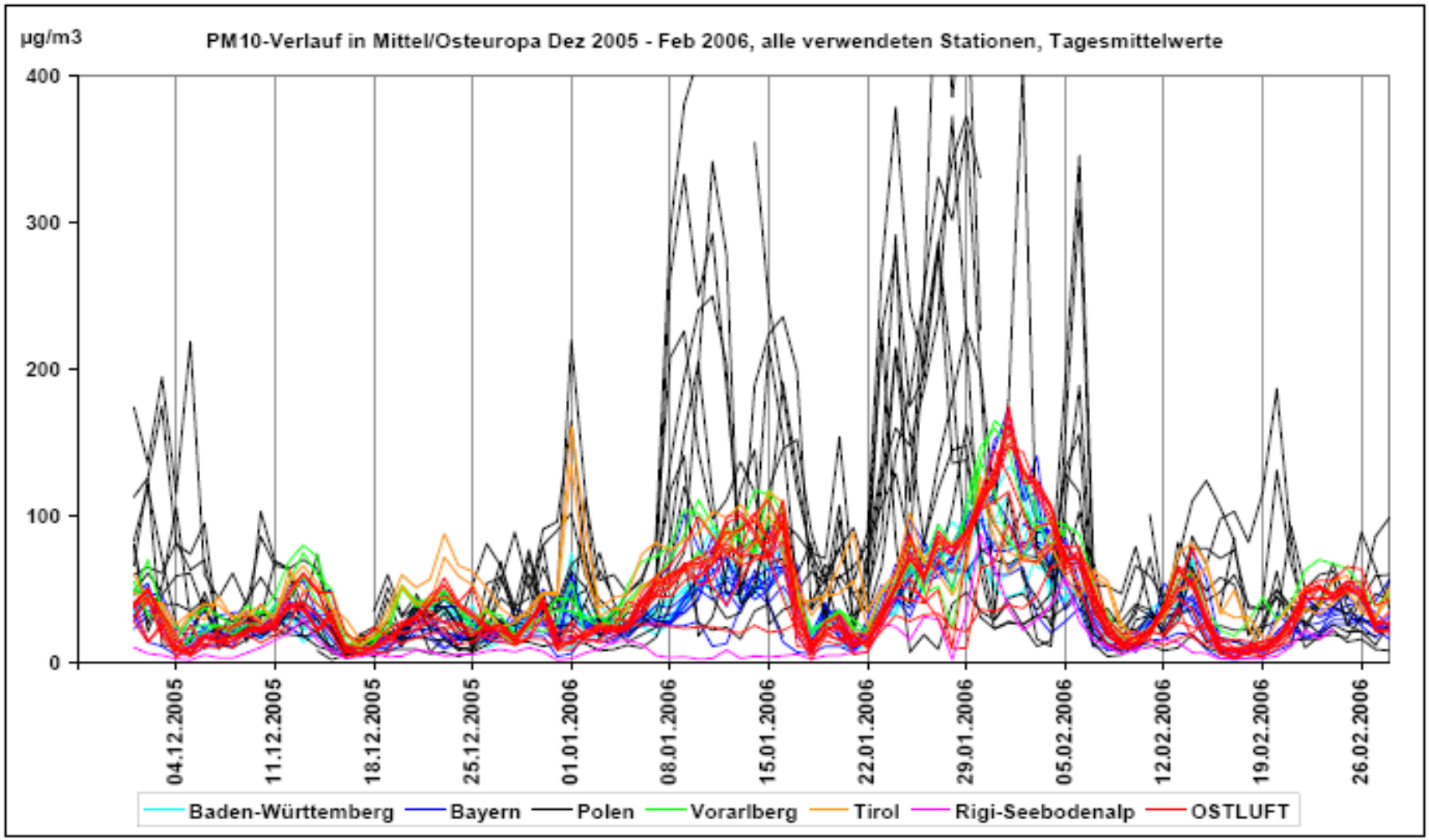
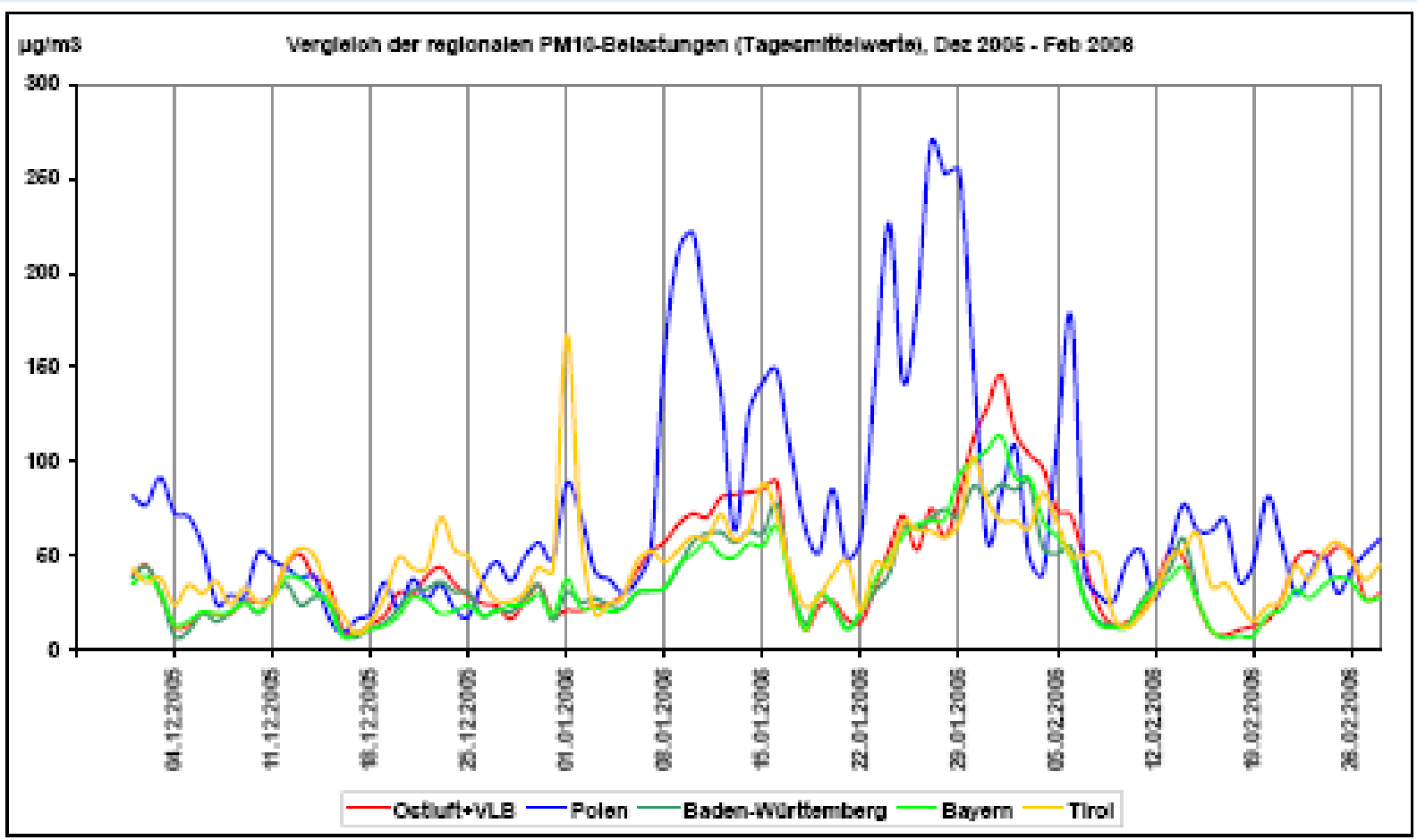
PM10 episode in Switzerland



PM10 episode in Poland, southern Germany, western Austria and eastern Switzerland



PM10 episode in Poland, southern Germany, western Austria and eastern Switzerland



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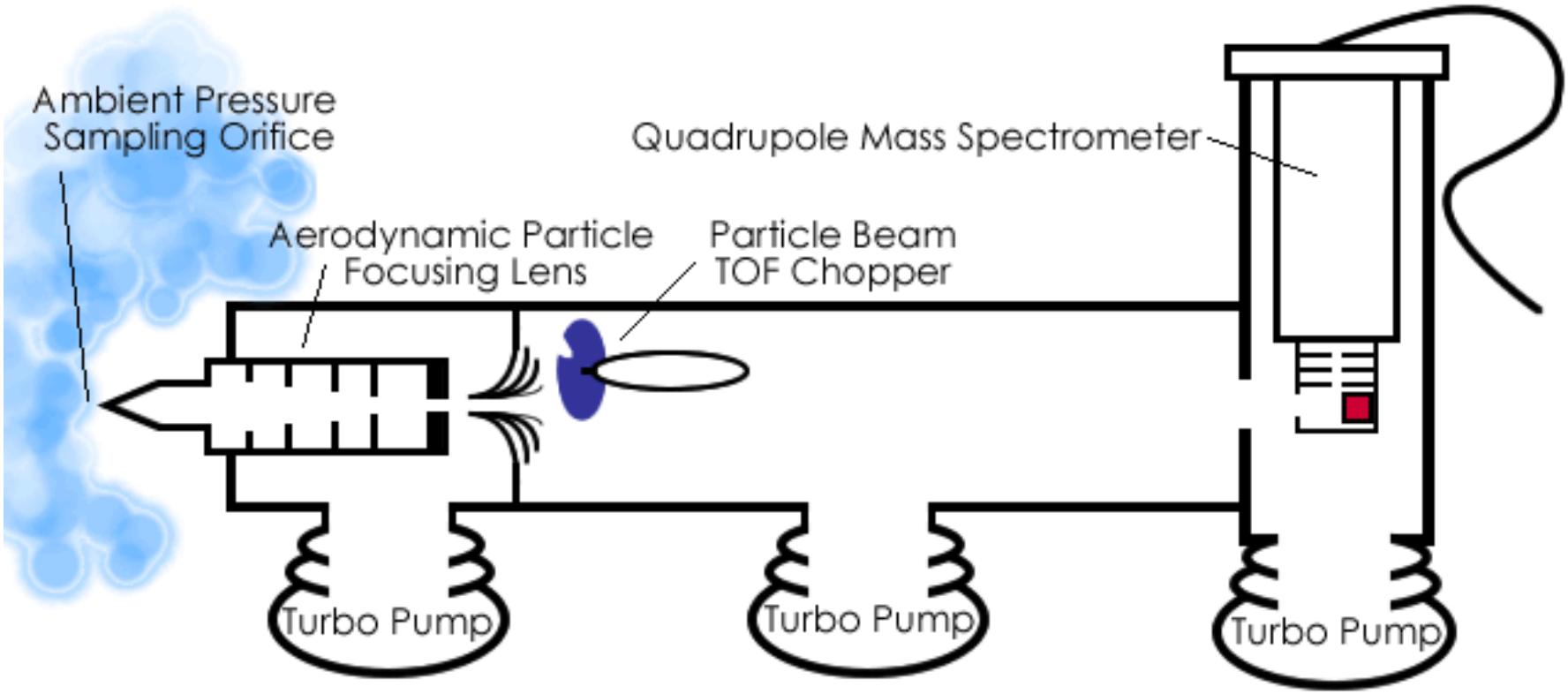
Locations in Switzerland with ^{14}C and/or AMS measurements

The aerodyne aerosol mass spectrometer



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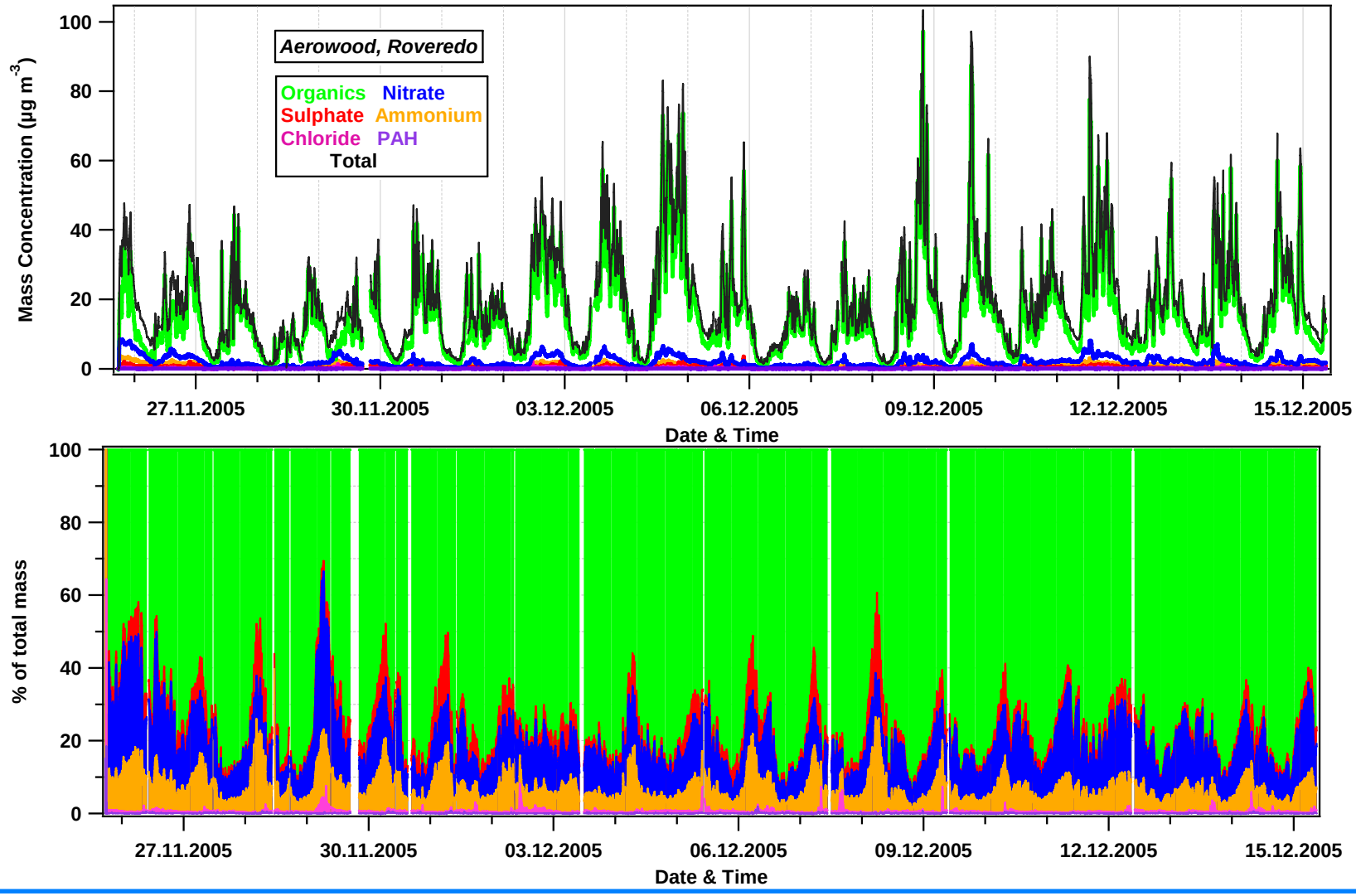
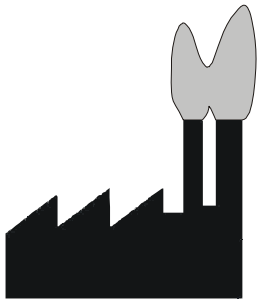
AMS measurements in Roveredo in November/December 2005



Simplified source apportionment by $^{14}C/^{12}C$

Anthropogenic Emissions



Biogenic Emissions

^{14}C decayed

^{14}C modern

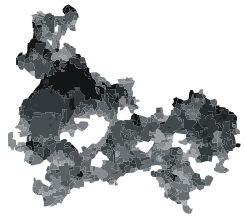
Flux $F_a = \mathrm{d}m_a/\mathrm{d}t$

$f_M = 0$

Flux $F_b = \mathrm{d}m_b/\mathrm{d}t$

$f_M = 1$

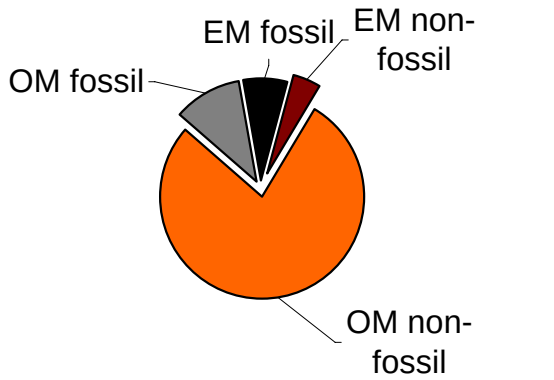
Carbonaceous aerosol

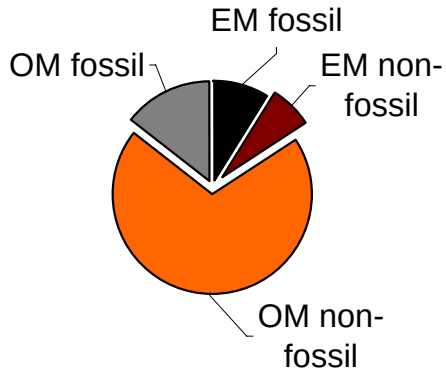


$$f_M = \frac{F_b}{F_a + F_b}$$

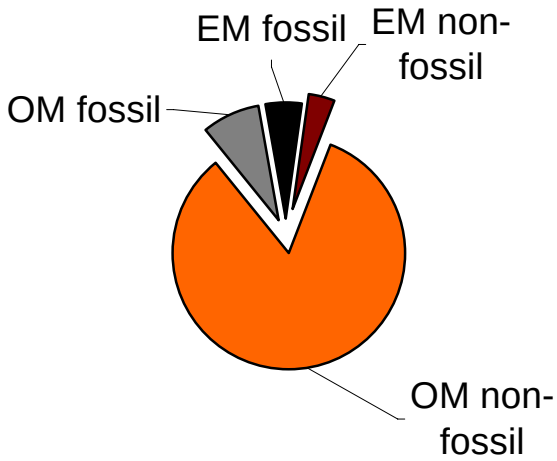
Fraction of modern: $f_M = (^{14}C/^{12}C_{Sample}) / (^{14}C/^{12}C)_{Current\ Biomass}$

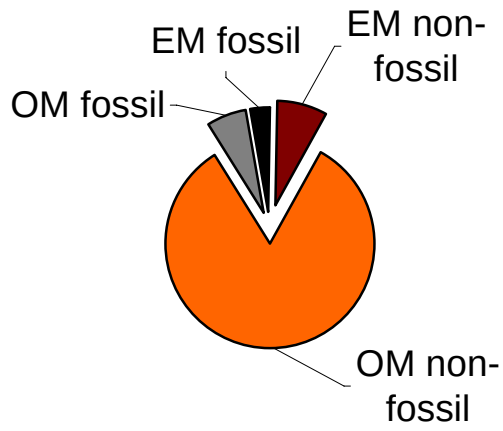
Fossil and non-fossil elemental and organic carbon mass (EM, OM) in Roveredo





mornings





evenings

Fossil: mostly traffic; Non-fossil: mostly wood burning in these conditions

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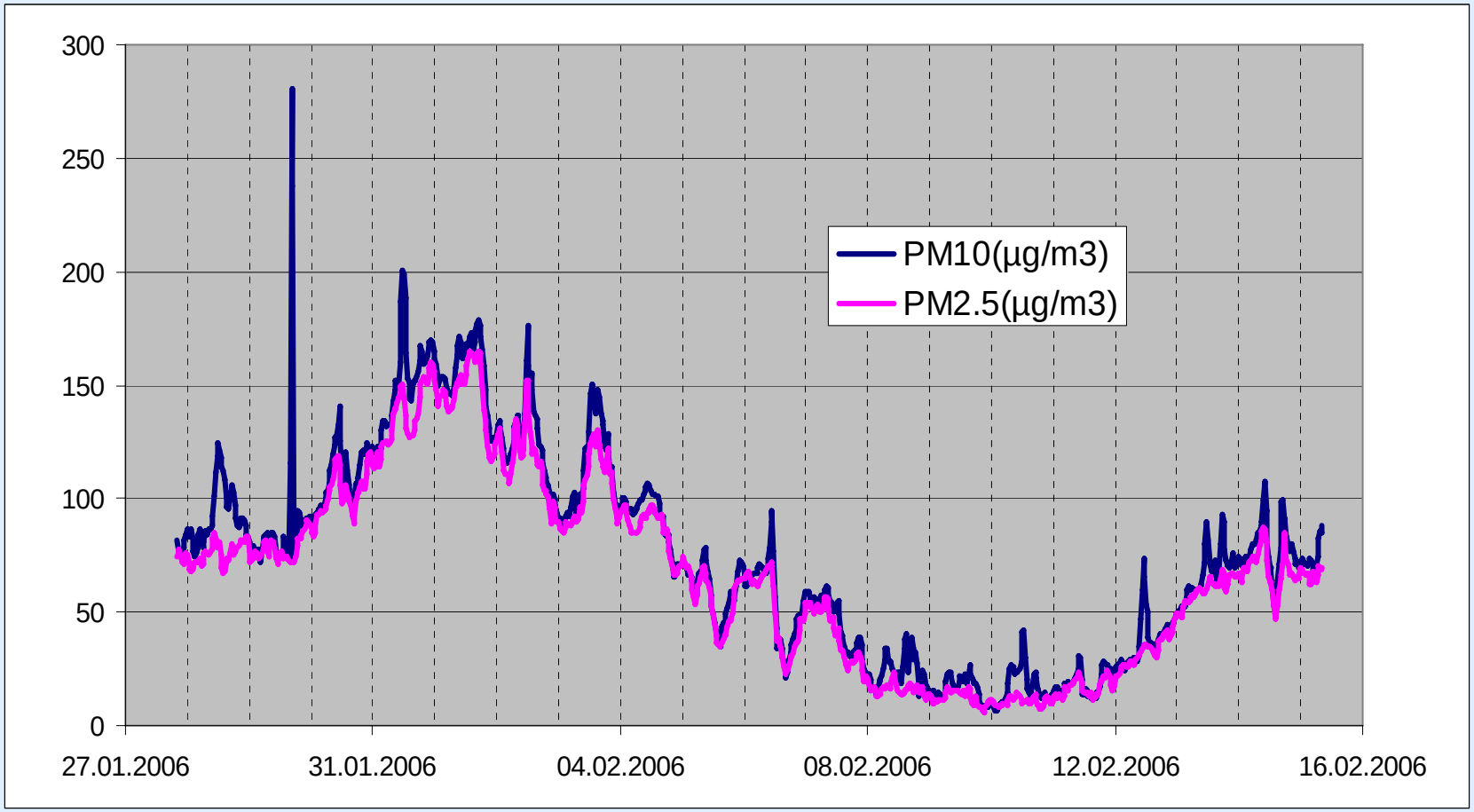
PM10 and PM2.5 in Reiden (Kt. Lucerne)



PM2.5/PM10 on average 0.9

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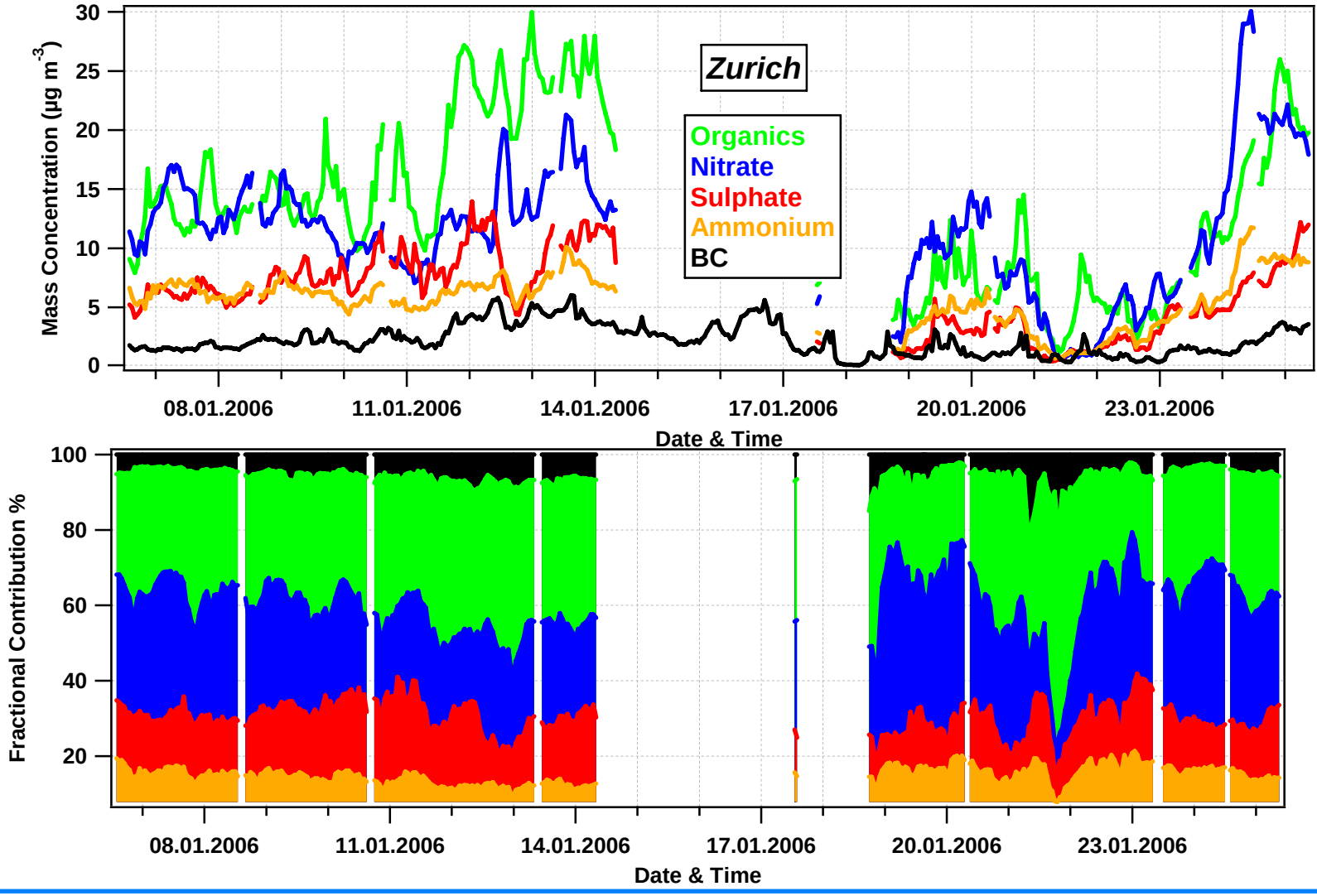
AMS and black carbon measurements in Reiden (Kt. Lucerne)



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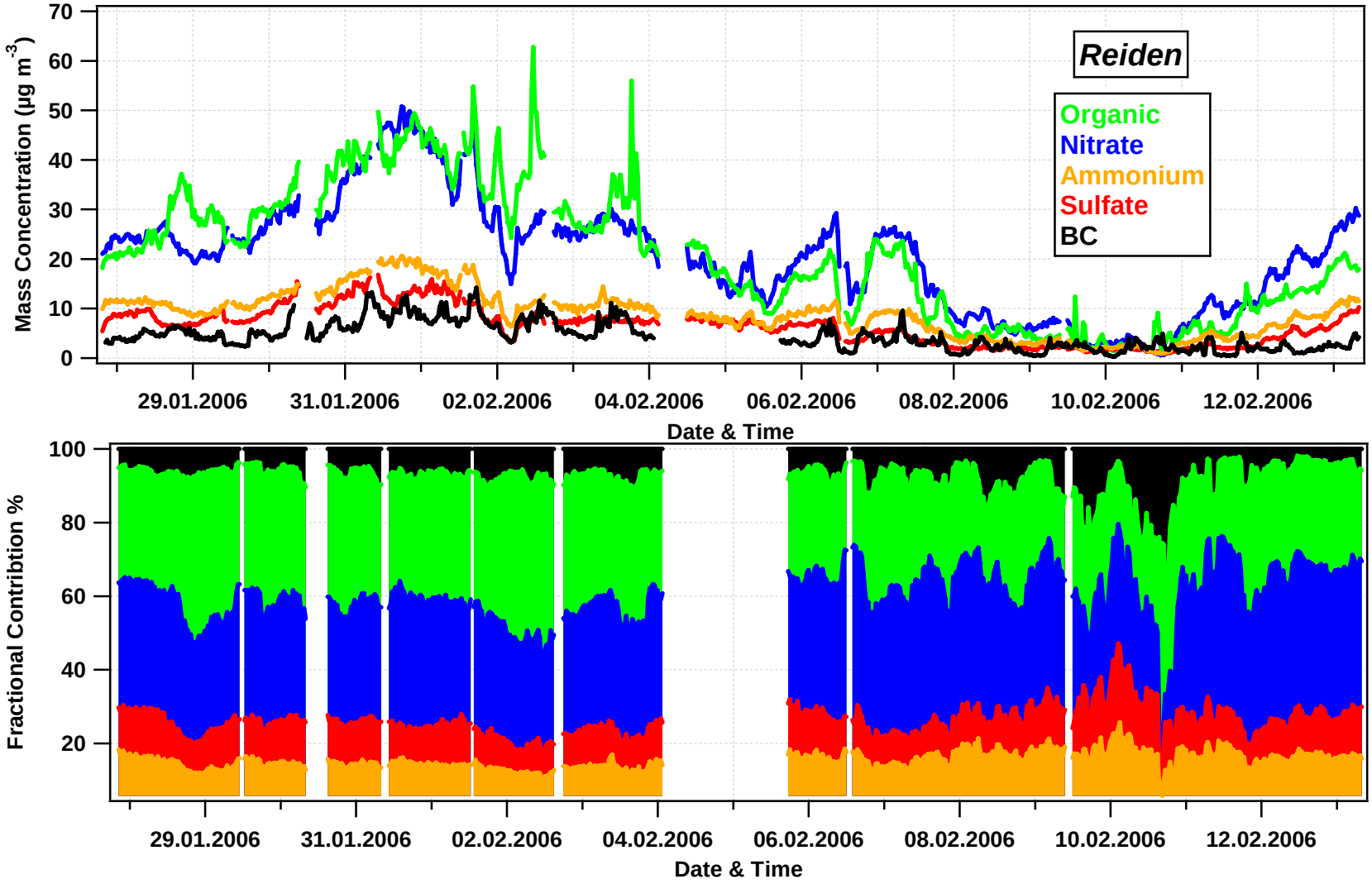
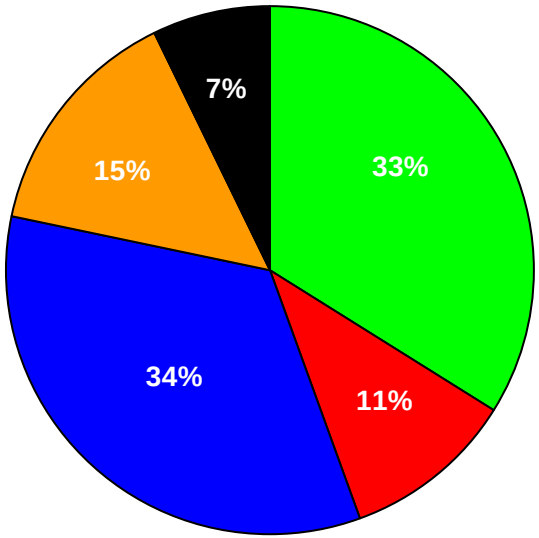
AMS and black carbon measurements in Reiden (Kt. Lucerne)



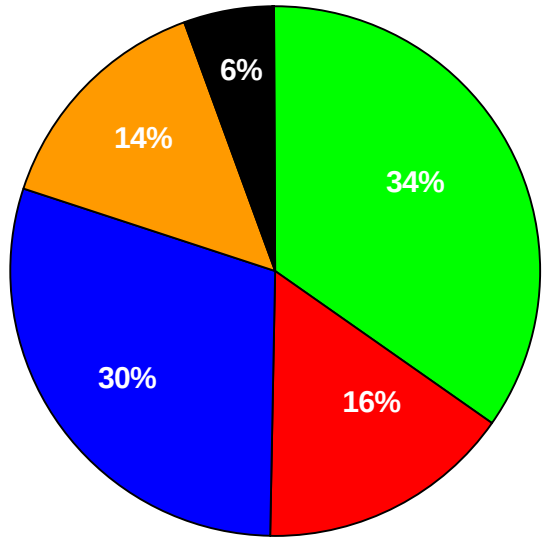
Relative contributions of BC, OM, NO_3, SO_4, NH_4 in Reiden and Zürich

Reiden



Black Carbon
Organic mass
Nitrate
Sulfate
Ammonium

Zürich



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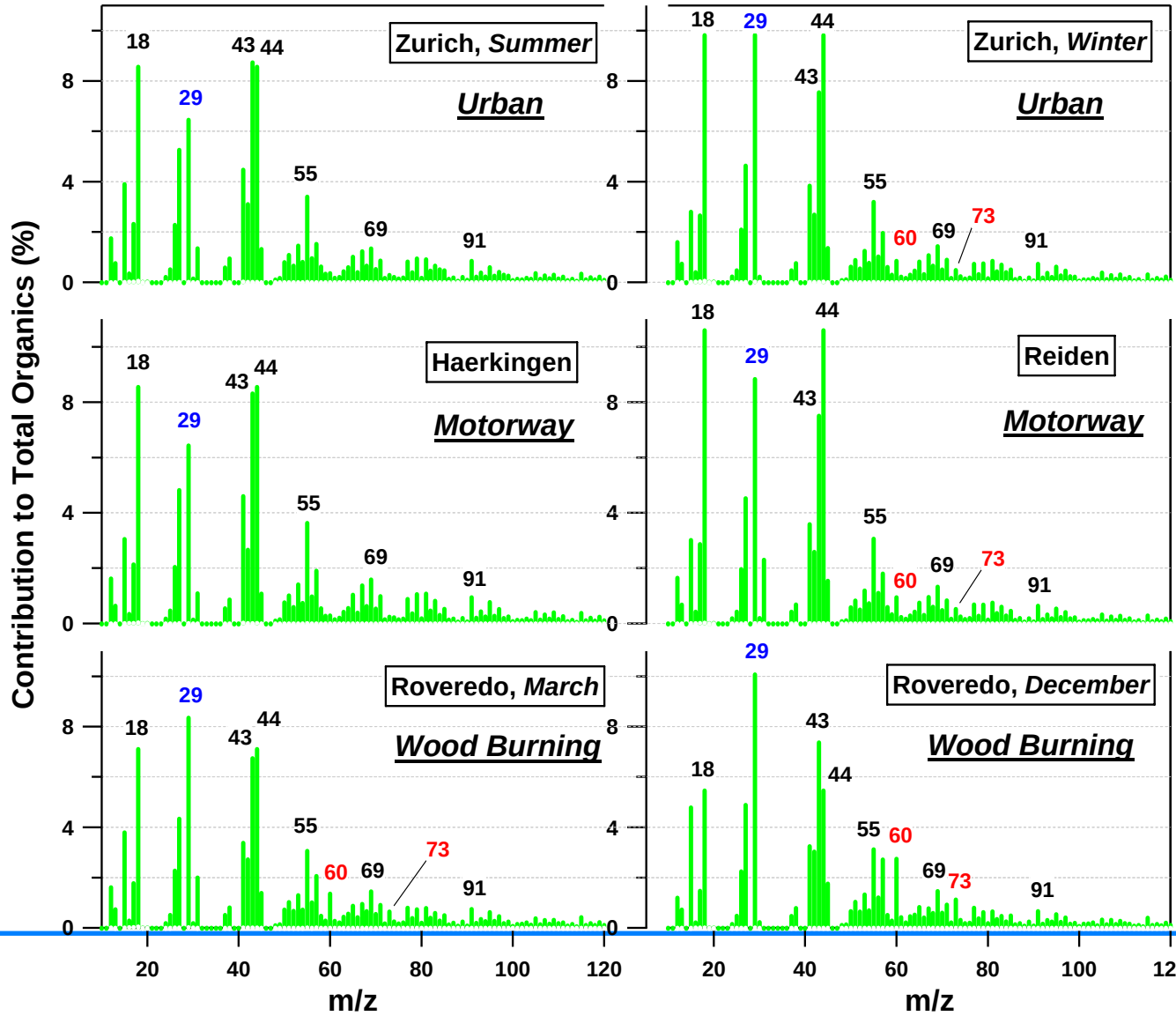
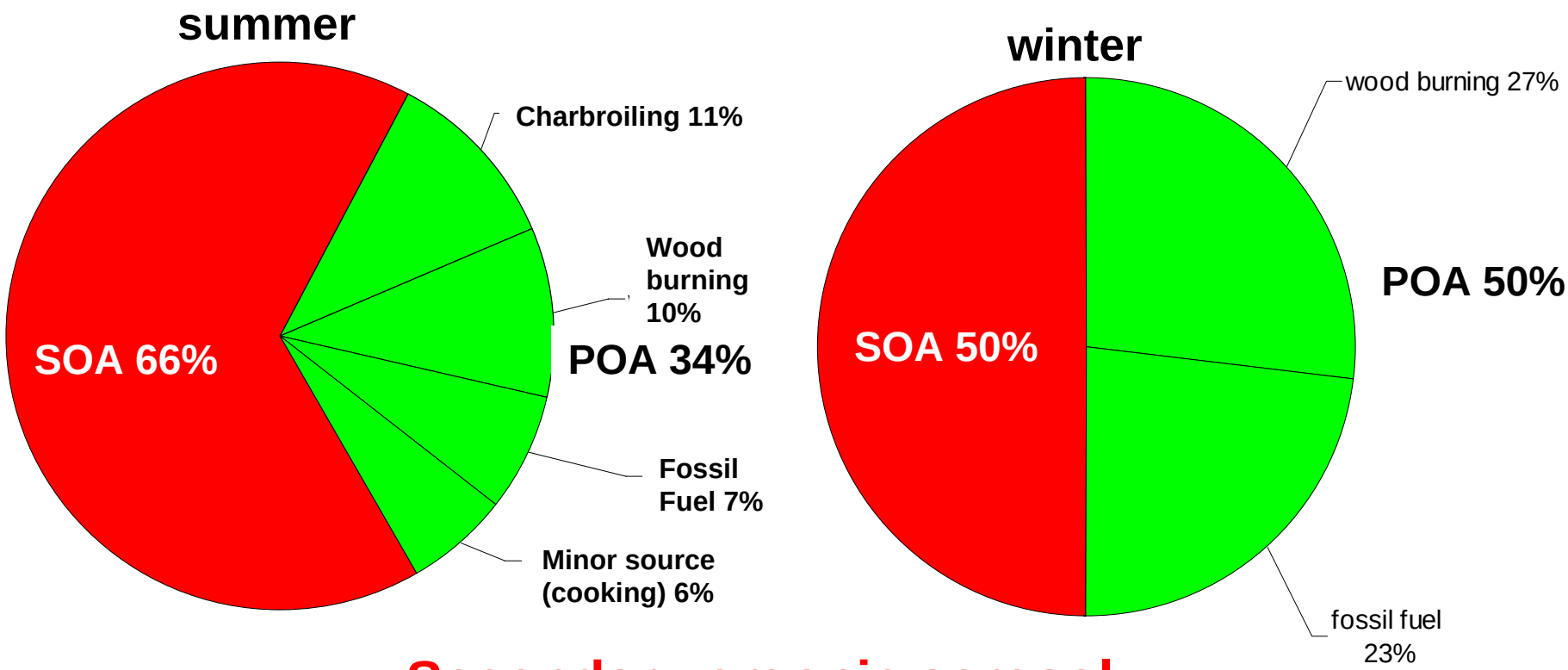
Mass spectra of organic aerosols in Switzerland



Use of positive matrix factorization and a chemical mass balance method for the source apportionment of the organics in Zürich

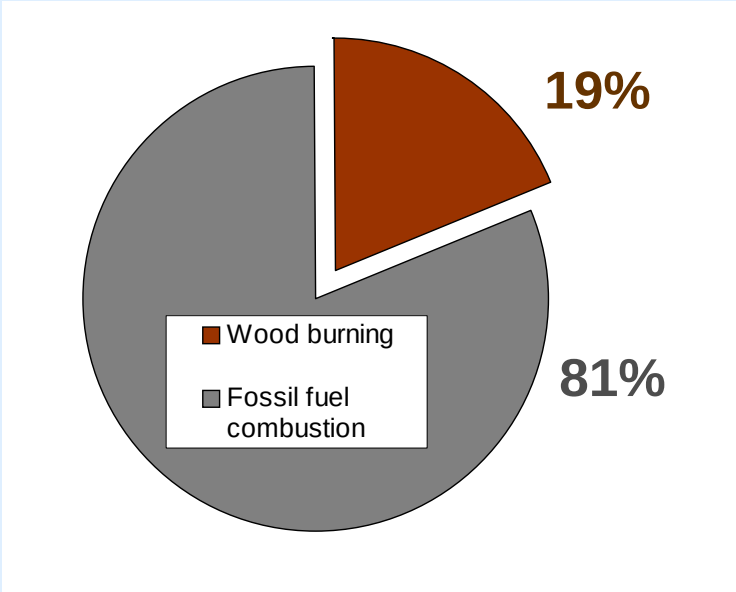


Secondary organic aerosol

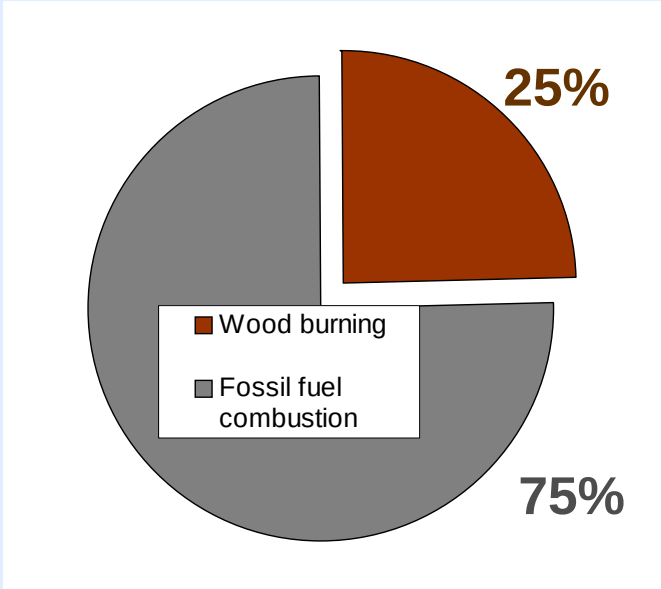
Primary organic aerosol

Average ^{14}C results for black carbon

Zürich



Reiden



Estimation of wood burning contribution to organic mass :

$OM_{wood\ burning} = EC_{wood\ burning} * OC/EC_{wood\ burning}$ (6) * $OM/OC_{wood\ burning}$ (2)

$OM_{wood\ burning}$ (Zürich) : 40% compared to 27% from multi-variate statistics

Summary of PM10 sources in January/February 2006

10(-40)% Coarse particles : dust, tire wear, resuspension

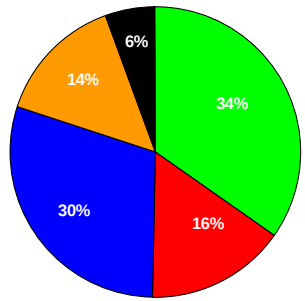
15% Ammonium : mostly from agricultural ammonia

30-35% Nitrate : secondary from nitrogen oxides oxidation from traffic (+industry)

11-16% Sulfate : mostly secondary from sulfur dioxide oxidation
(industry, heating, traffic)

6-7% Black carbon : 4-6% traffic exhaust; 1-2% wood burning

35% Organics : 15-20% secondary (from biogenic (terpenes) and anthropogenic emissions (e.g. aromatics))
7-15% wood burning
6-10% traffic exhaust



Black Carbon
Organic mass
Nitrate
Sulfate
Ammonium

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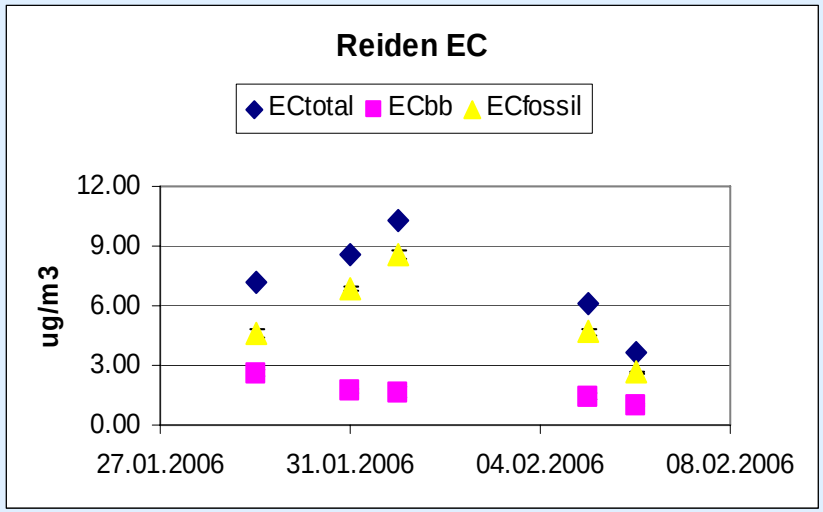
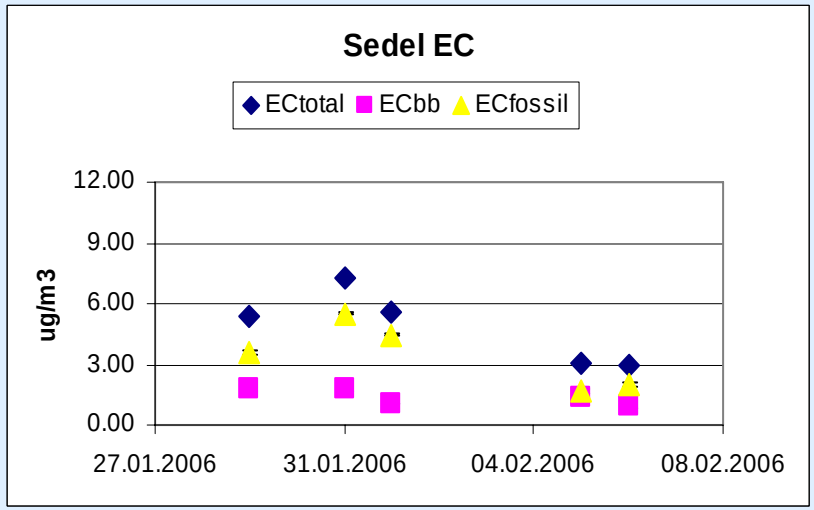
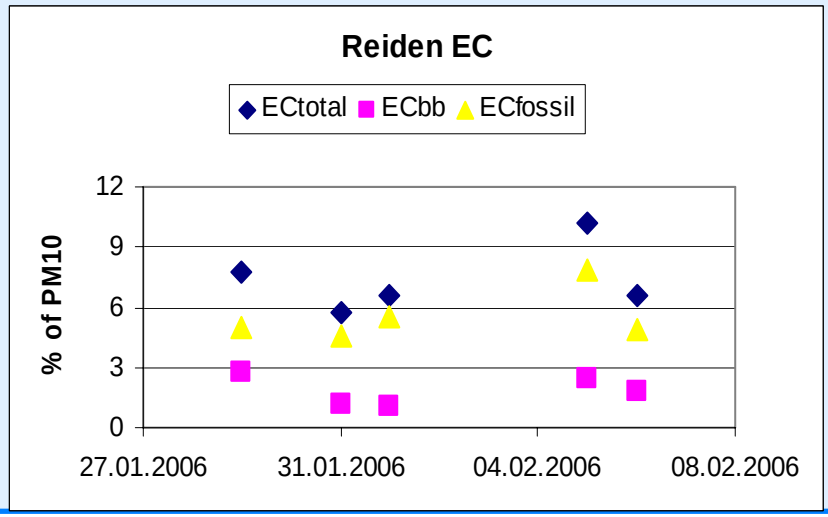
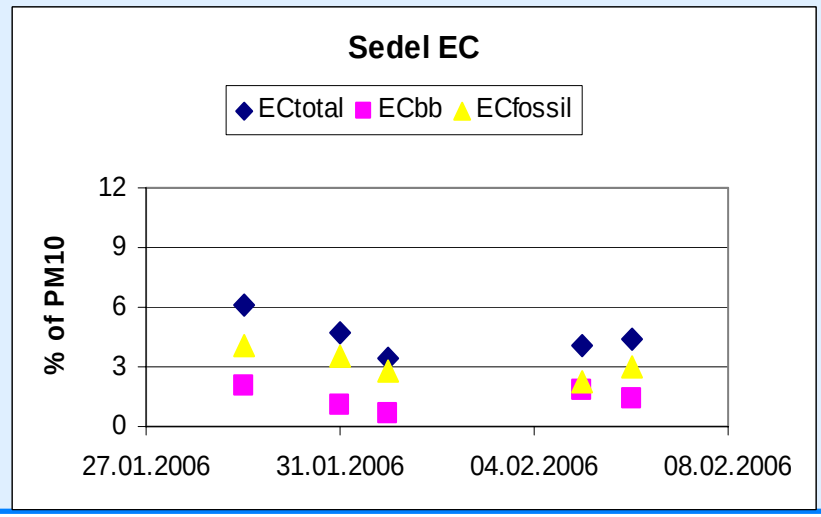
Soot from traffic and wood burning









Source Identification and Attribution : Postive Matrix Factorization

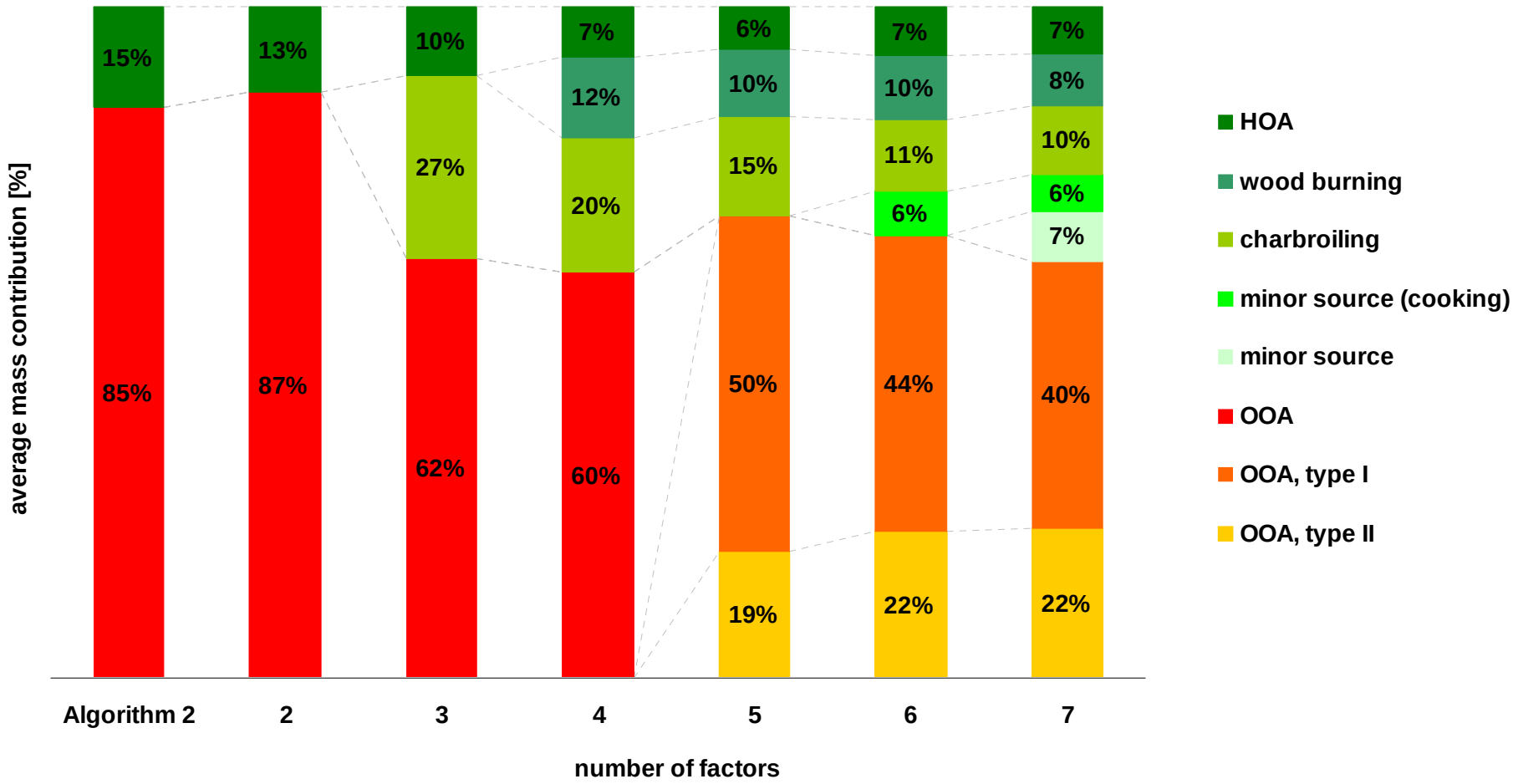
$$X_{nm} = G_{np} F_{pm}$$

X: measured organics
G: source strengths (scores), calculated time series in [mg m^{-3}]
F: source profile (loadings), calculated MS in [1]

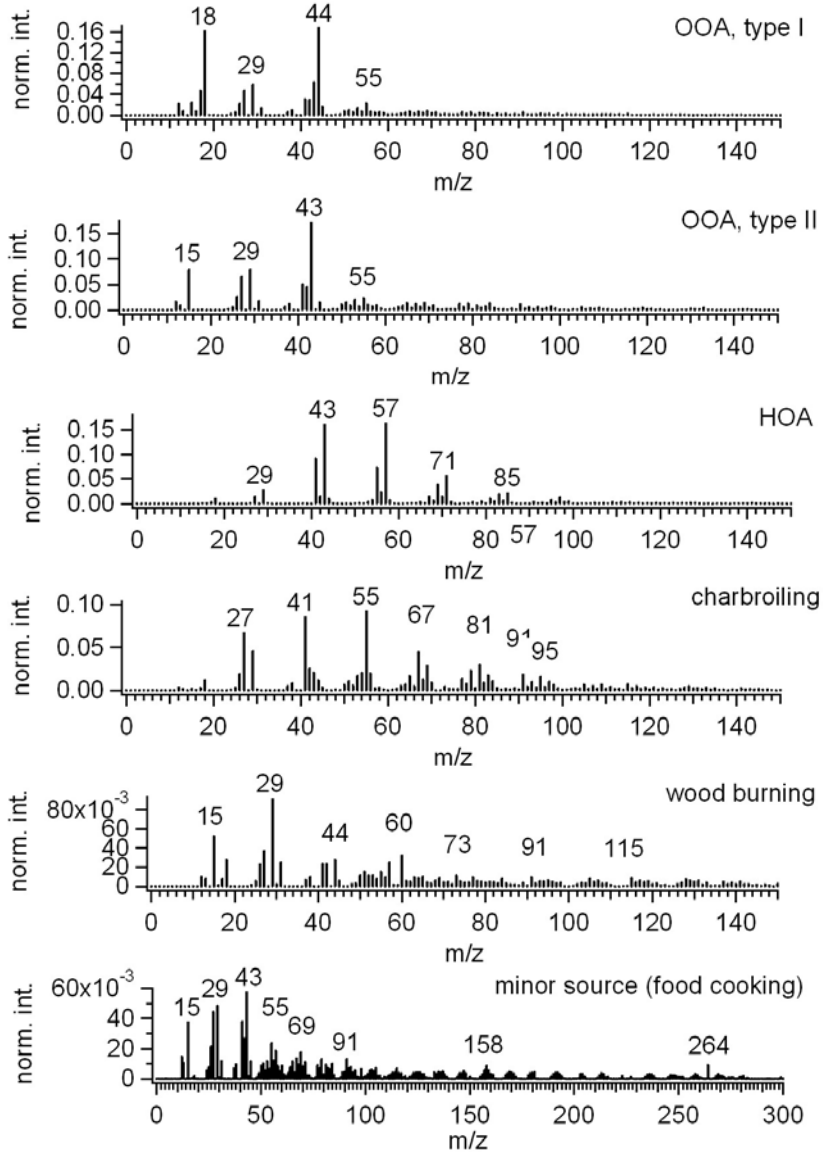
n: samples in time (15000)
m: species (270)
p: number of assumed sources

interpretation of G and F

G: correlation with indicative species (*e.g.* particle-phase nitrate)
F: spectral similarity to AMS reference spectra (*e.g.* diesel exhaust)

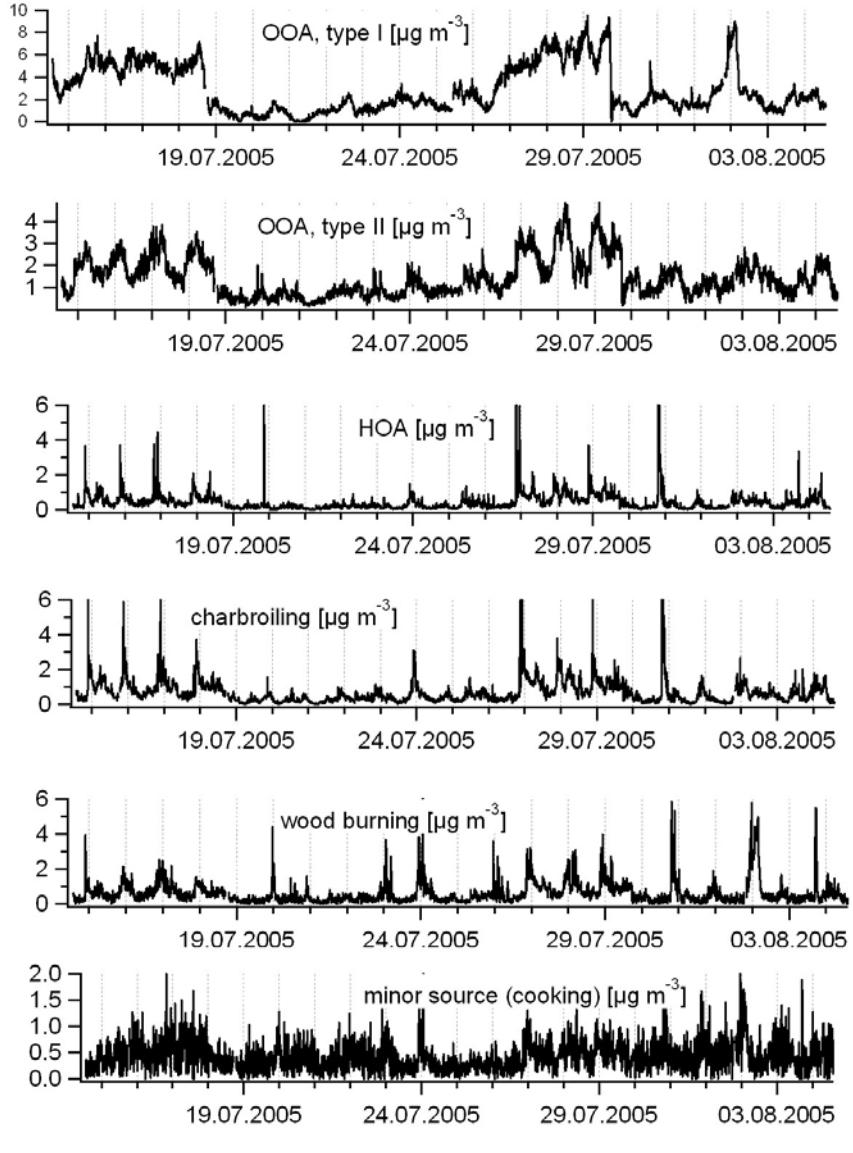

average mass contribution [%]
15%
85%
13%
87%
10%
27%
62%
7%
12%
20%
60%
6%
10%
15%
50%
19%
7%
10%
11%
6%
44%
22%
7%
8%
10%
6%
7%
40%
22%
Algorithm 2
2
3
4
5
6
7
number of factors
HOA
wood burning
charbroiling
minor source (cooking)
minor source
OOA
OOA, type I
OOA, type II

4. Calculated G and F factors

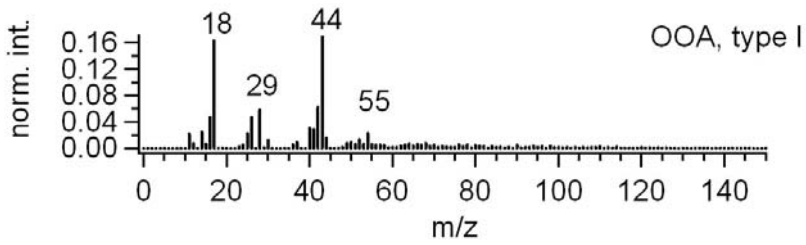


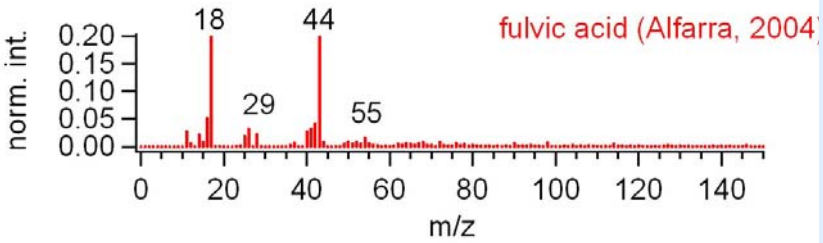
F factors: source profiles

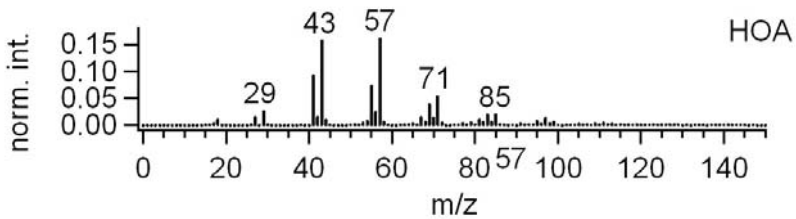
G factors: source strengths

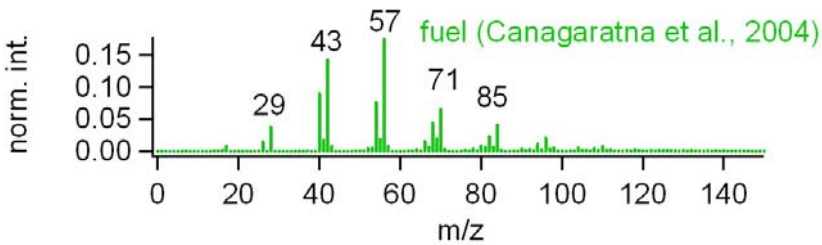


4. interpretation of F factors









calculation of **spectral similarity** to **reference mass spectra**

spectral similarity:

R^2: correlation of all m/z's

$R_{m/z>44}^2$: correlation m/z larger 44

reference spectra:

mass spectra from lit. (AMS measurements)

example 1:

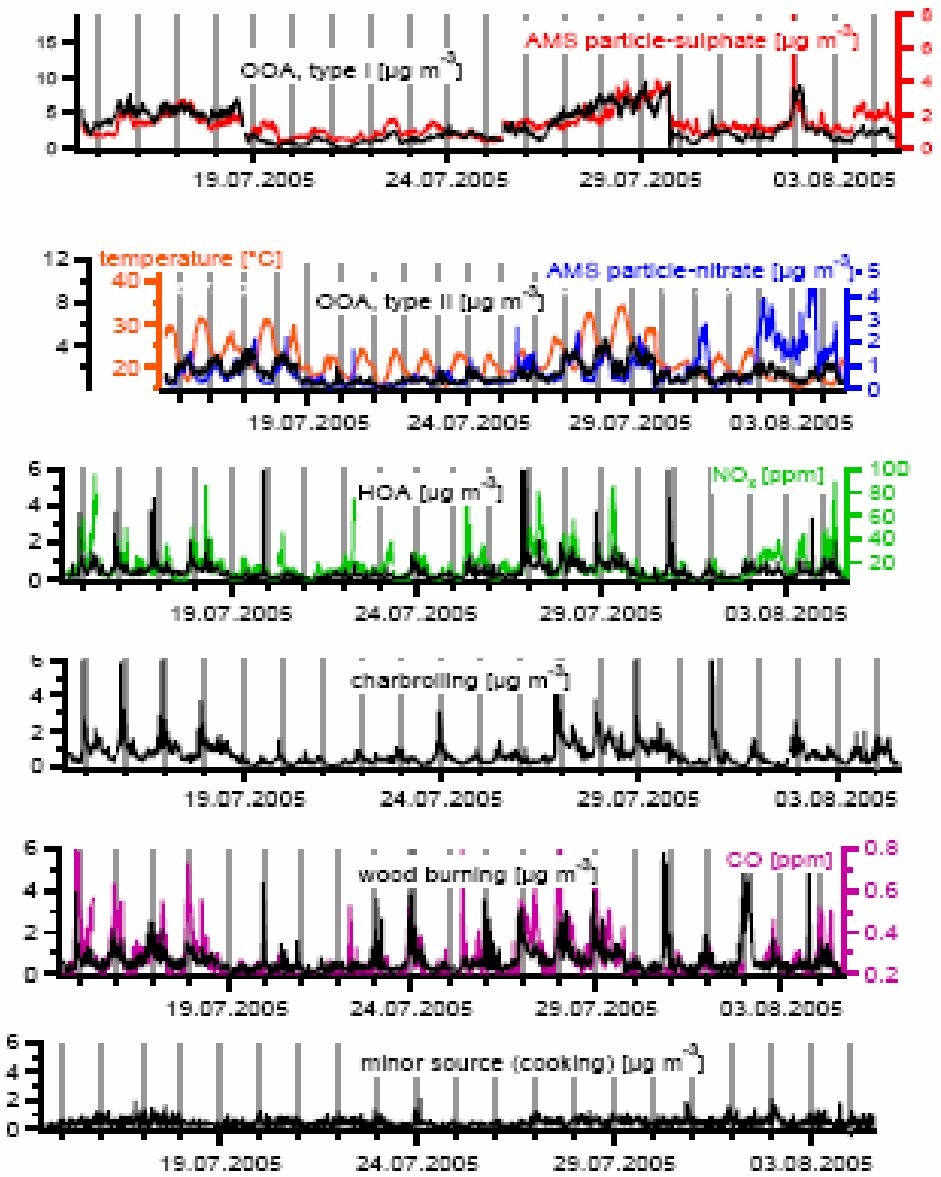
1st F factor is very similar to fulvic acid

(R^2=0.96; $R_{m/z>44}^2$=0.83)

example 2:

3rd F factor is very close to fuel

(R^2=0.99; $R_{m/z>44}^2$=0.99)


OOA, type I [µg m-3]
AMS particle-sulphate [µg m-3]
19.07.2005
24.07.2005
29.07.2005
03.08.2005
temperature [°C]
OOA, type II [µg m-3]
AMS particle-nitrate [µg m-3]
HOA [µg m-3]
NOx [ppm]
charbroiling [µg m-3]
wood burning [µg m-3]
CO [ppm]
minor source (cooking) [µg m-3]

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Global source strengths (10^{12} g a^{-1}) of fine PM

	Natural emissions		*Anthropogenic emissions*	
Primary OC	Forest fires	4 (2-8)	Biomass burning	50 (10-110)
	Emissions of plants (e.g. abrasion, debris)	56 (0-90)	Fossil-fuel burning	42 (10-120)
	Marine sources	small		
Secondary OC	Partially oxidized VOC, primarily terpenes	28 (14-56)	Partially oxidized VOC, from fossil-fuel burning	8 (3-14)
EC	Natural fires	0.4 (0.2-0.8)	Biomass burning	12 (2-20)
			Fossil-fuel burning	6 (1-10)

Values according to: Penner, 1994

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Global source strengths (10^{12} g a^{-1}) of fine PM: contemporary vs. fossil carbon

	Natural emissions		*Anthropogenic emissions*	
Primary OC	Forest fires	4 (2-8)	Biomass burning	50 (10-110)
	Emissions of plants (e.g. abrasion, debris)	56 (0-90)	Fossil-fuel burning	42 (10-120)
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EC	Natural fires	0.4 (0.2-0.8)	Biomass burning	12 (2-20)
			Fossil-fuel burning	6 (1-10)

Values according to: Penner, 1994

Microanalytical sample preparation and ^{14}C measurement methods

1. Two-step heating combustion of samples on quartz fibre filters

$$\text{"C}_{\text{sample}}\text{"} + \text{O}_2 \xrightarrow[2.)\ 650°C]{1.)\ 340°C} \text{CO}_2$$

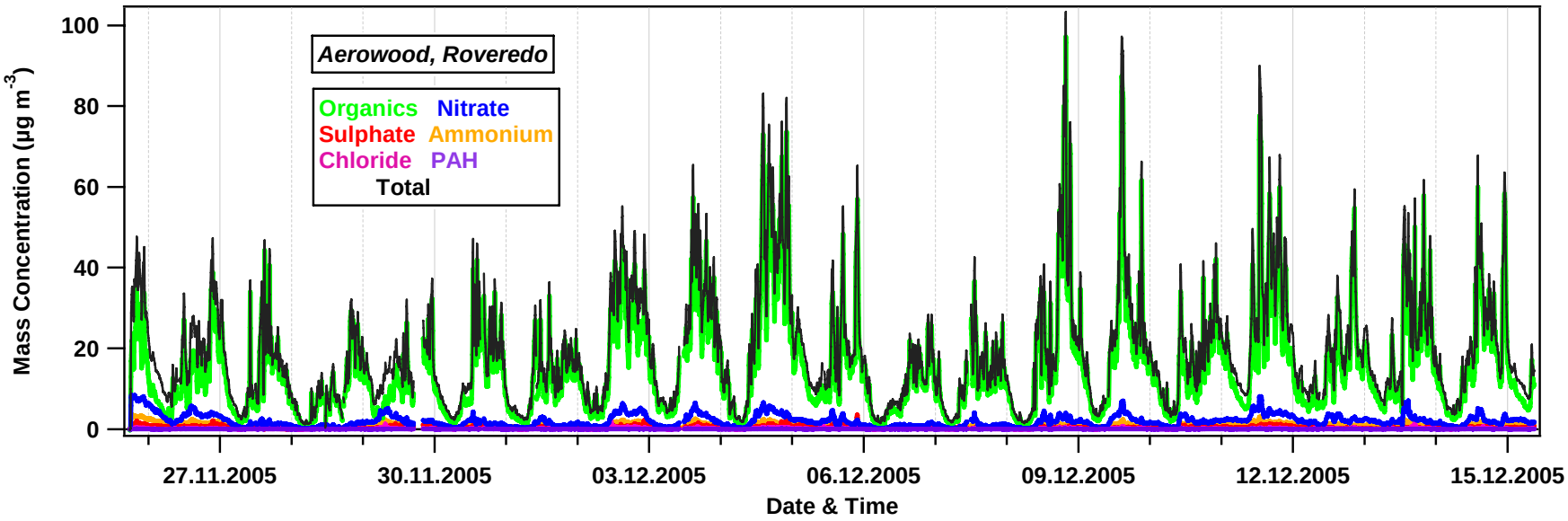
2. Reduction to filamentous carbon, the target material for accelerator mass spectrometry (AMS) measurements

$$\text{CO}_2 + 2\ \text{Mn} \xrightarrow{650°C,\ \text{Co}} \text{C}_{\text{filamentous}} + 2\ \text{MnO}$$

3. Sub-milligram ^{14}C measurements at the PSI/ETH compact Accelerator Mass Spectrometric system in Zürich, based on a 500 kV pelletron accelerator

Szidat et al., Radiocarbon, 2004

Aerodyne aerosol mass spectrometer output : quantitative data



- High time resolution seconds to minutes of organics, sulphate, nitrate, ammonium, and at least qualitative results on chloride and PAHs
- Less problems with sampling artifacts as filter samples

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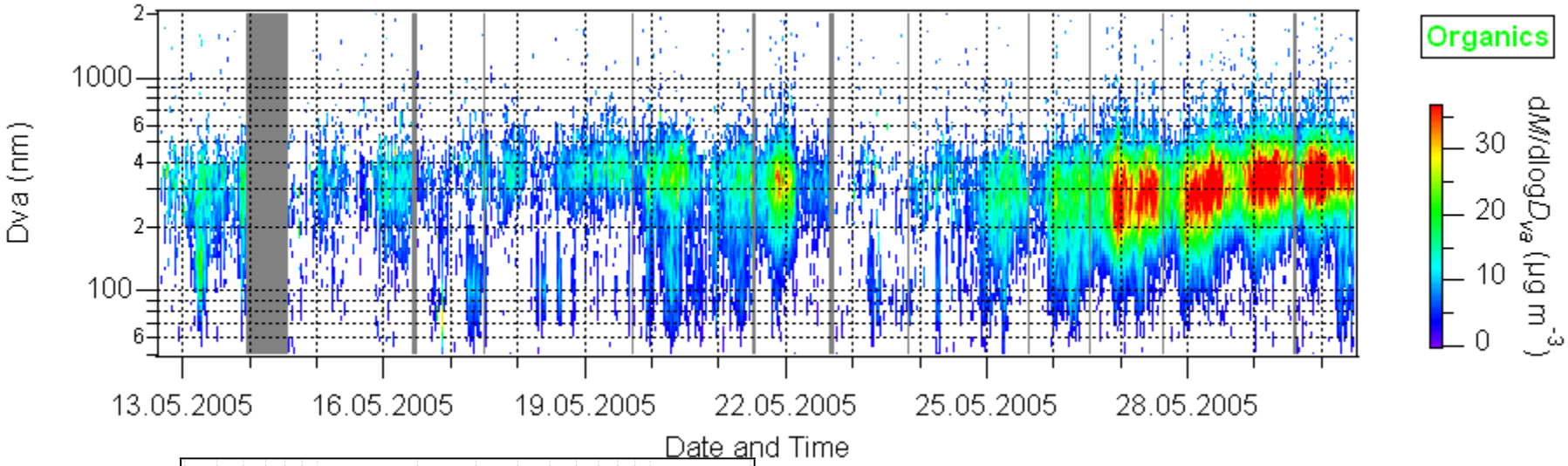
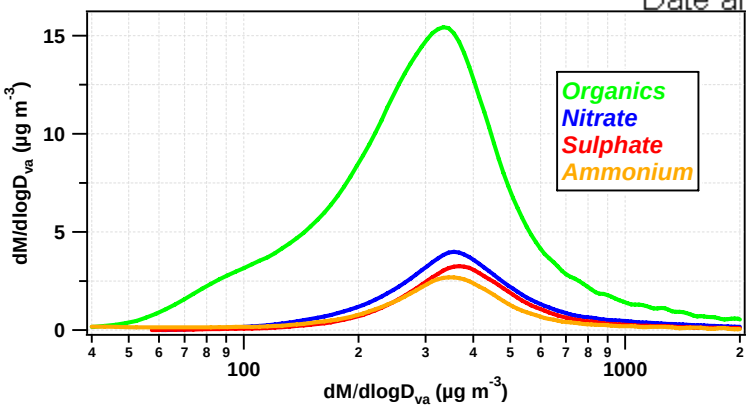
Aerodyne aerosol mass spectrometer output: size distribution





- Aerosol mass size distributions

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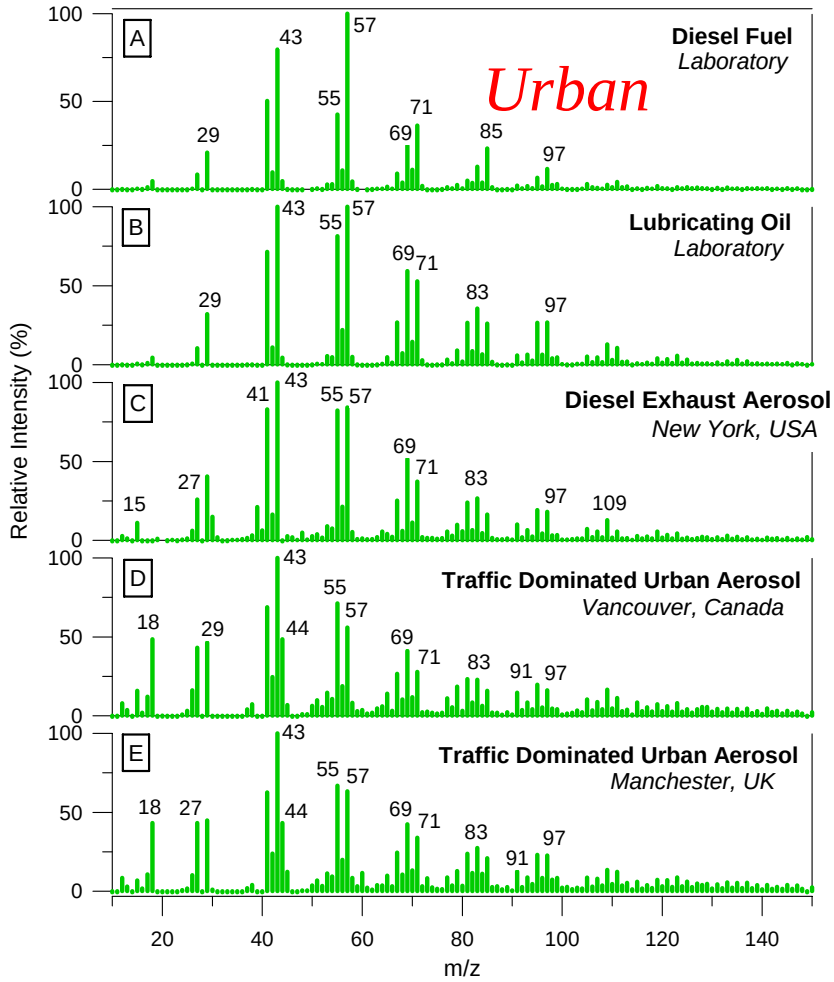
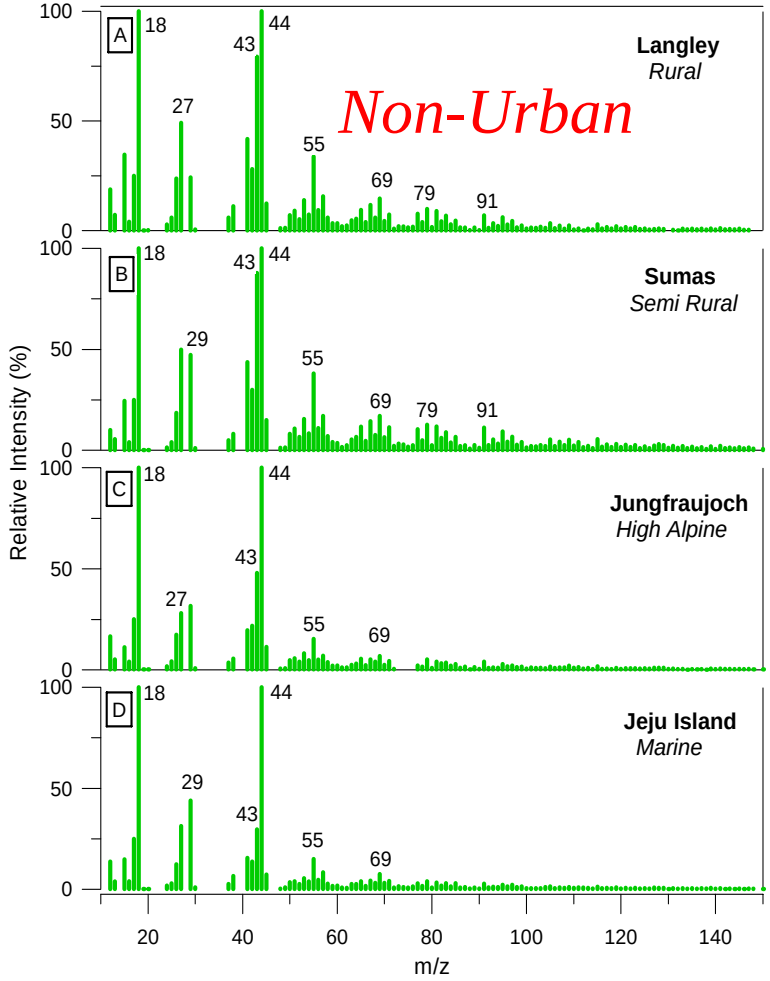
Aerodyne aerosol mass spectrometer output: organic aerosol mass spectra

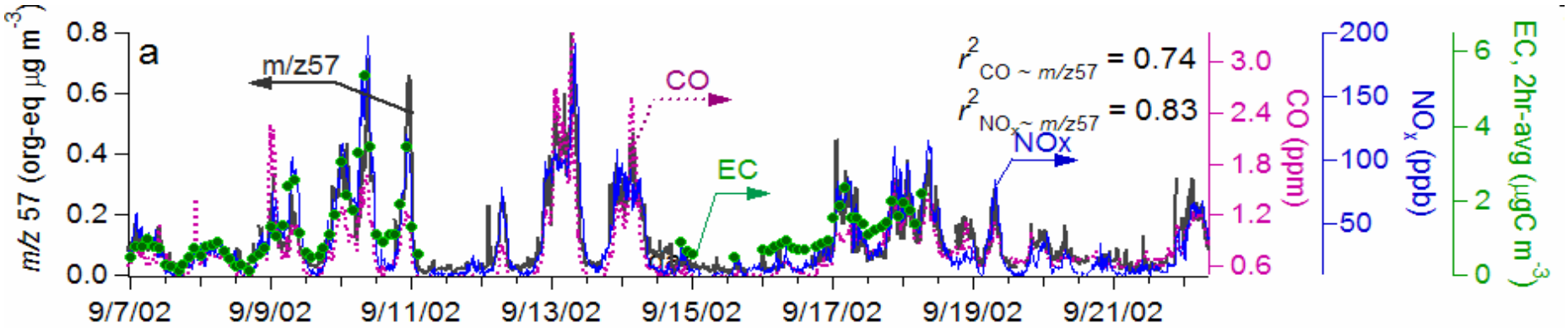




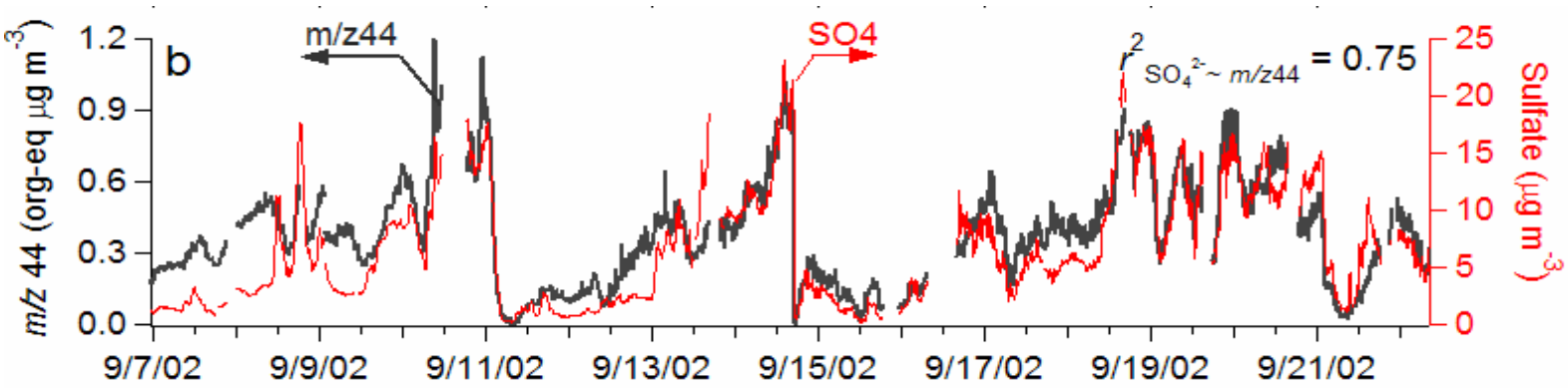
McFiggans, Alfarra et al., Faraday Discussions, 2005

MS (m/z) Tracers for Organic Components

m/z 57 (mostly $C_4H_9^+$): Hydrocarbon-based Organic Aerosol (**HOA**)



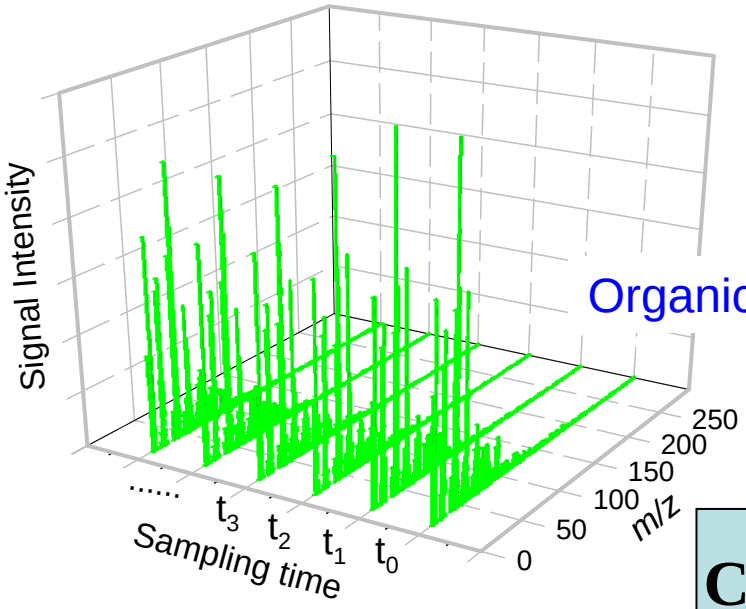
m/z 44 (mostly CO_2^+): Oxygenated Organic Aerosol (**OOA**)



Zhang, Alfarra et al., ES&T 2005

Deconvolution of HOA and OOA Components

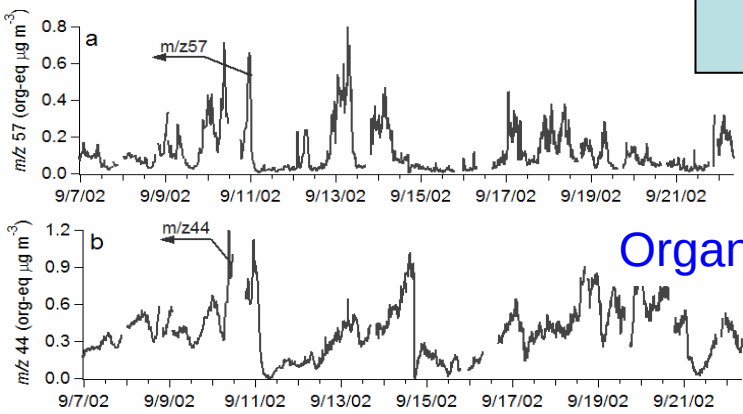
Zhang et al., *Environmental Science and Technology*, 2004

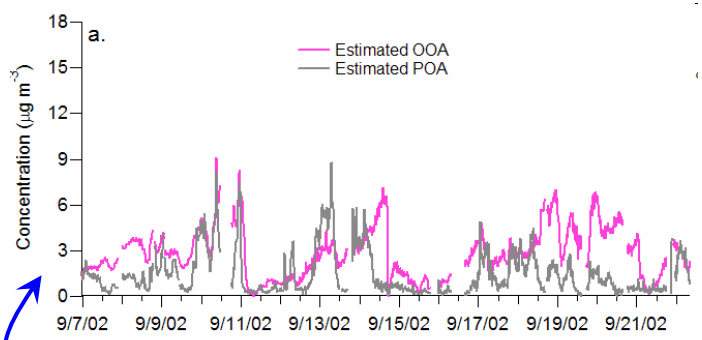


Organic Mass Spectra

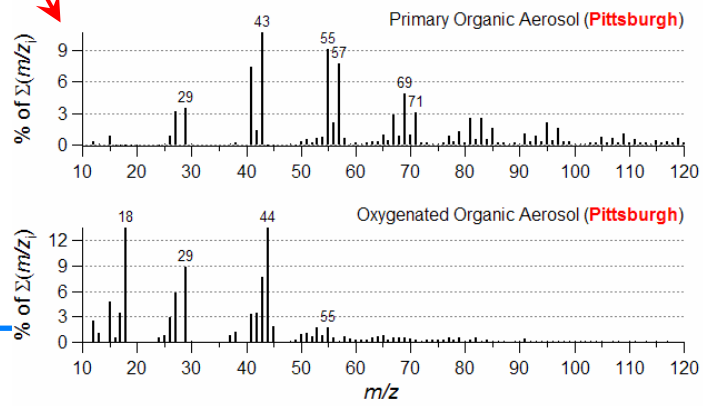
Custom *Iterative* Principal Component Analysis

Organic MS Tracers

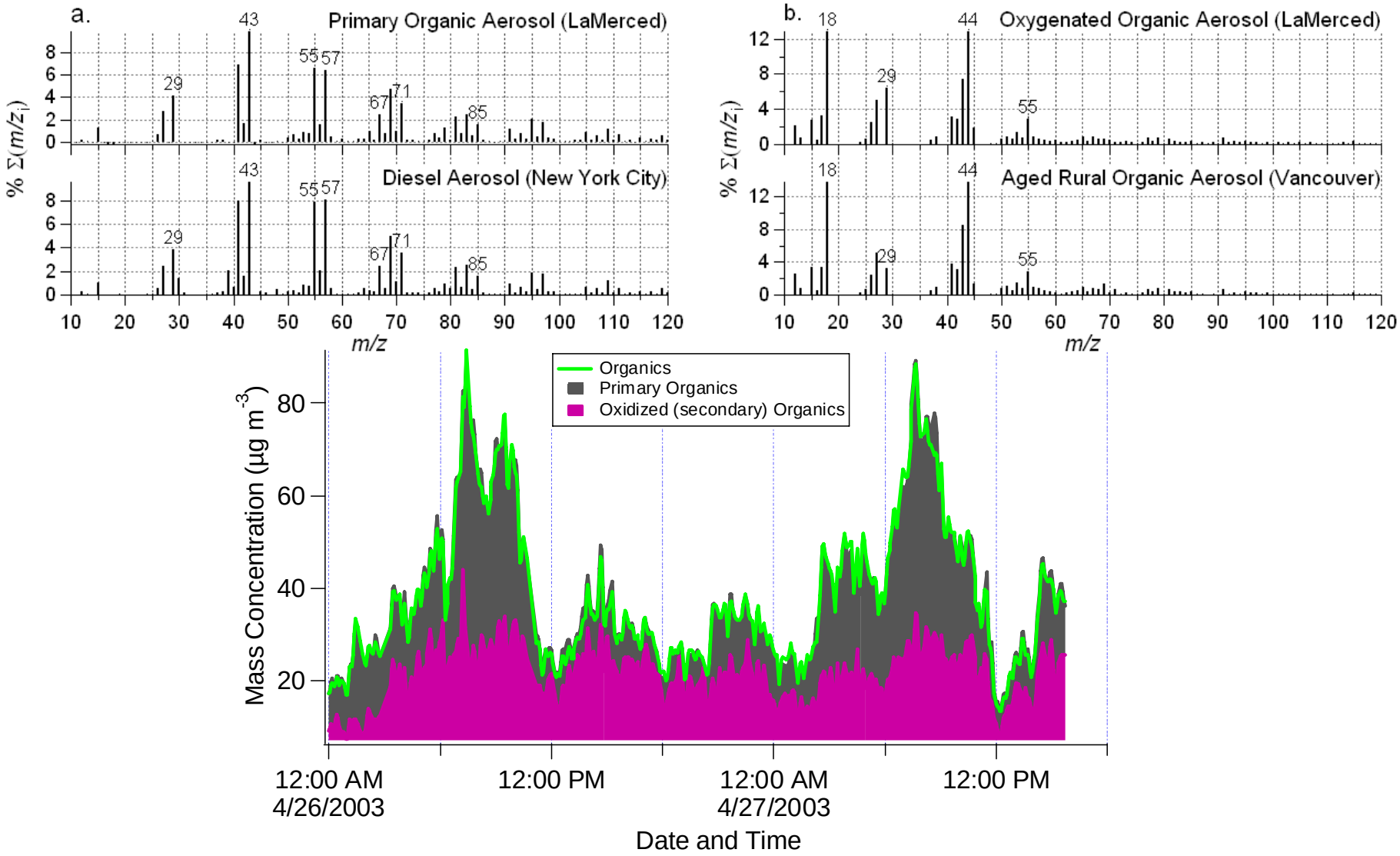




Time series & **mass spectra** of HOA and OOA



Primary vs. Oxidized Organics



Zhang et al., *Environmental Science and Technology*, 2004.

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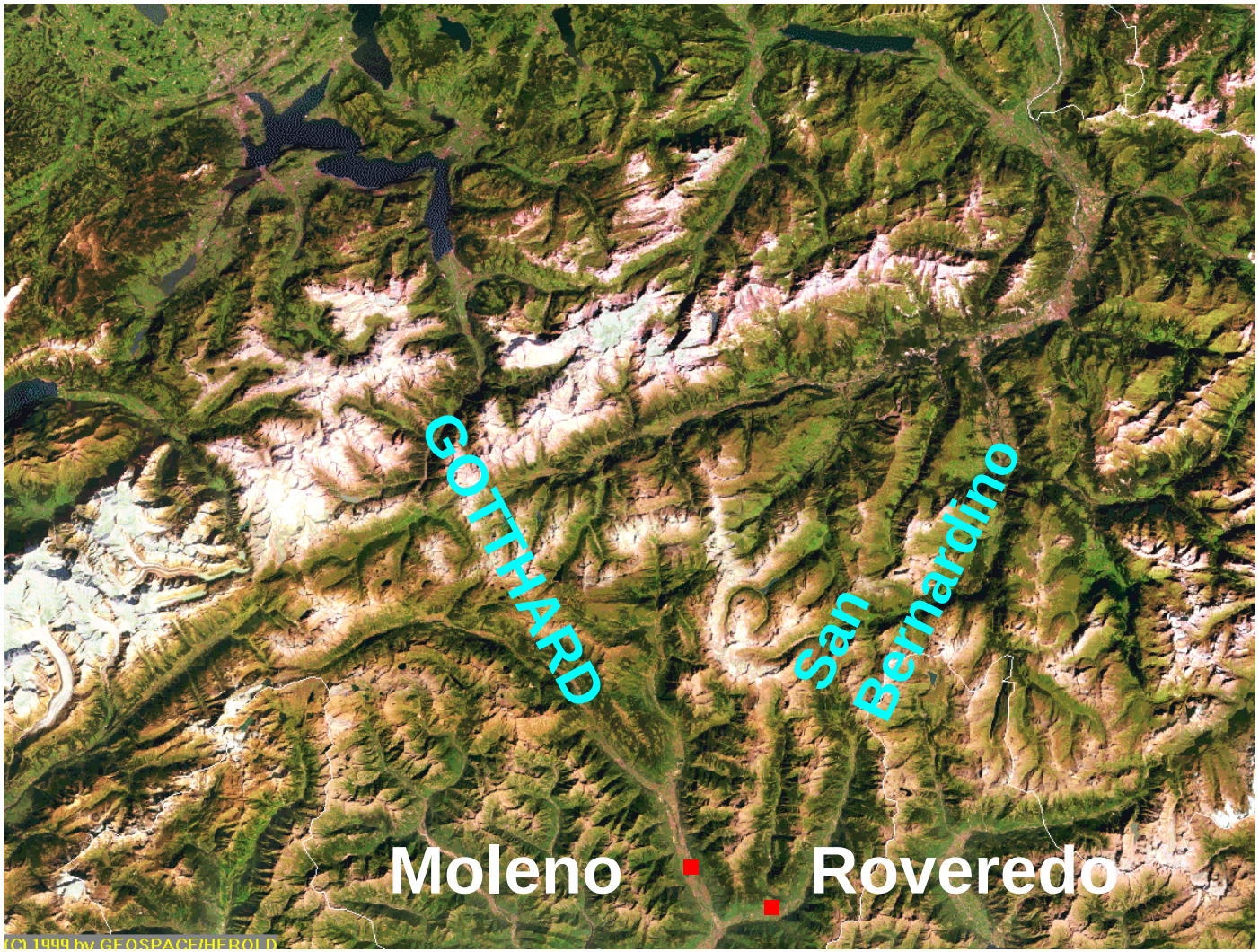
Roveredo, a nice place to study aerosols

Sites during the AEROWOOD study



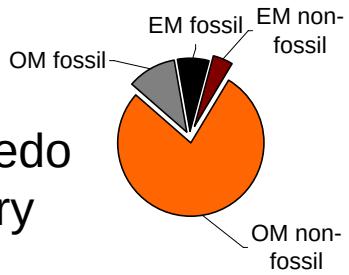
Campaigns:

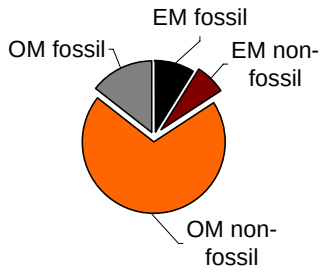
December 2004-March2005

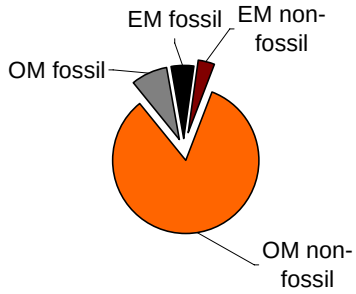
November-December 2005

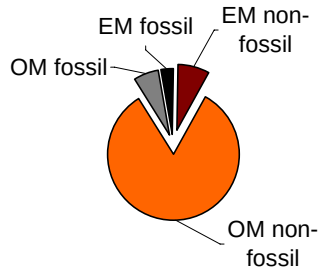
Partitioning of fossil and non-fossil elemental and organic carbon mass (EM, OM)

Roveredo
January









Moleno
February

mornings

evenings

Roveredo
March

Fossil: mostly traffic; Non-fossil: mostly wood burning in these conditions

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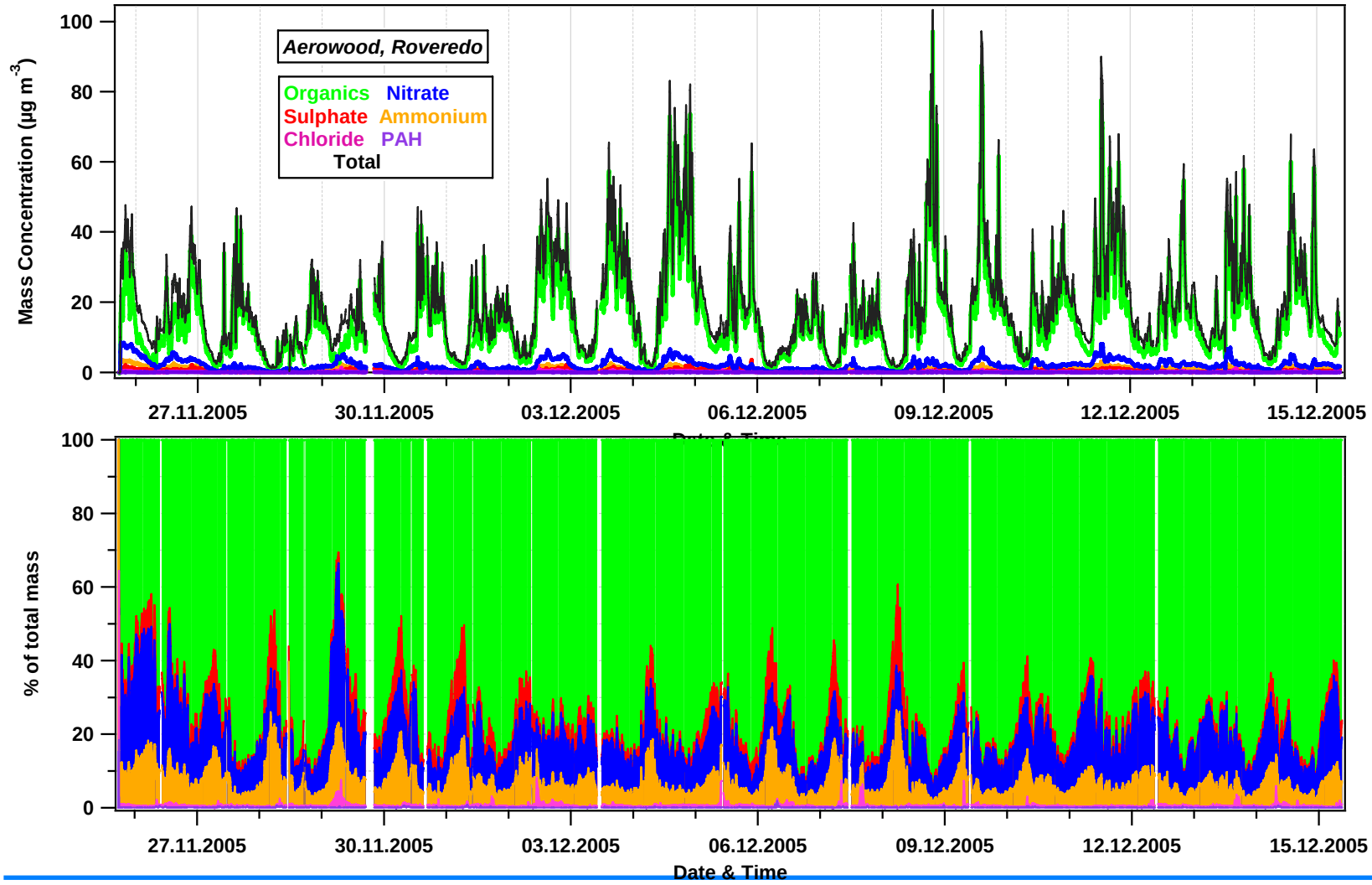
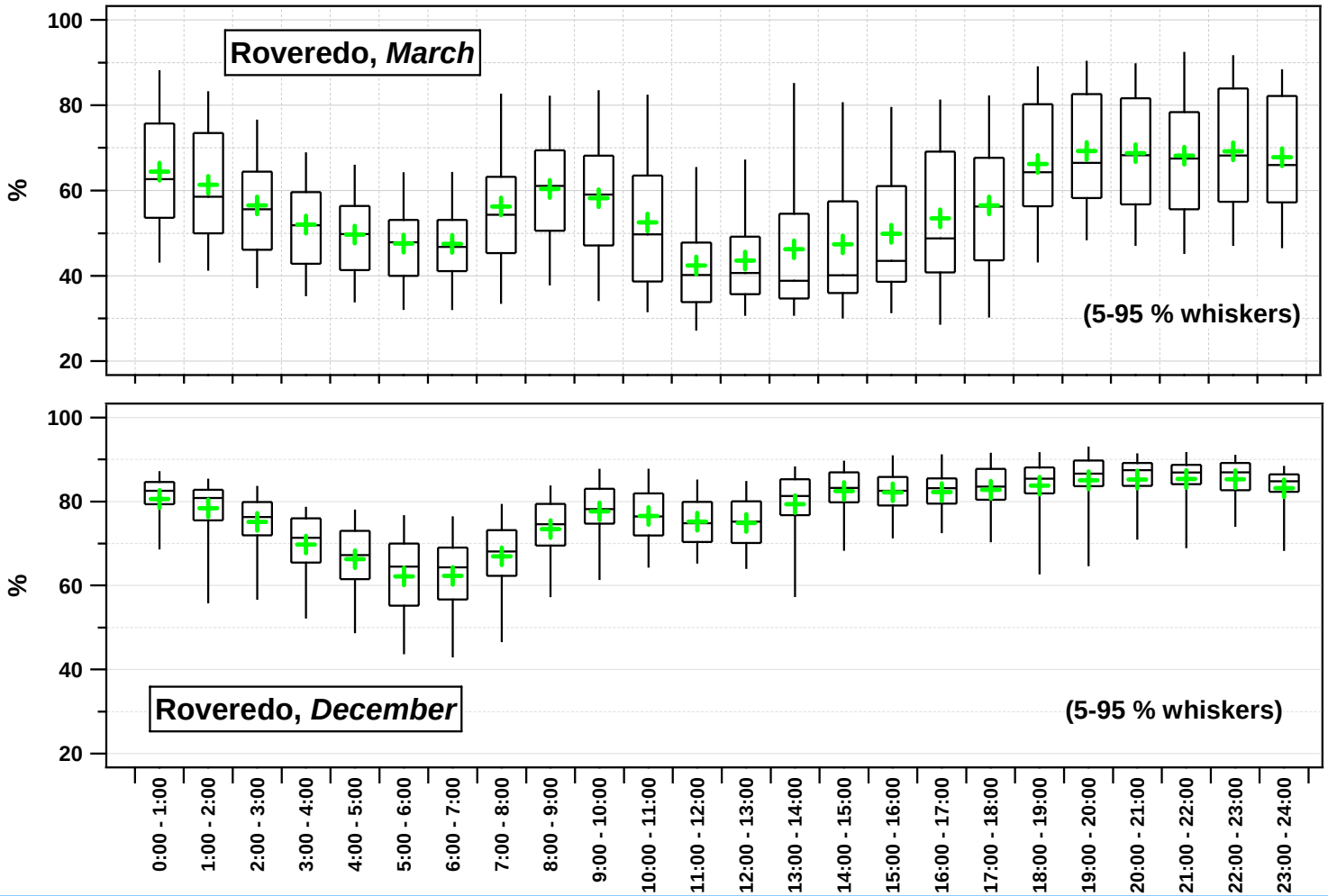
AMS measurements in Roveredo in November/December 2005



Organic contribution to total AMS mass in Roveredo



Aerosol mass spectra

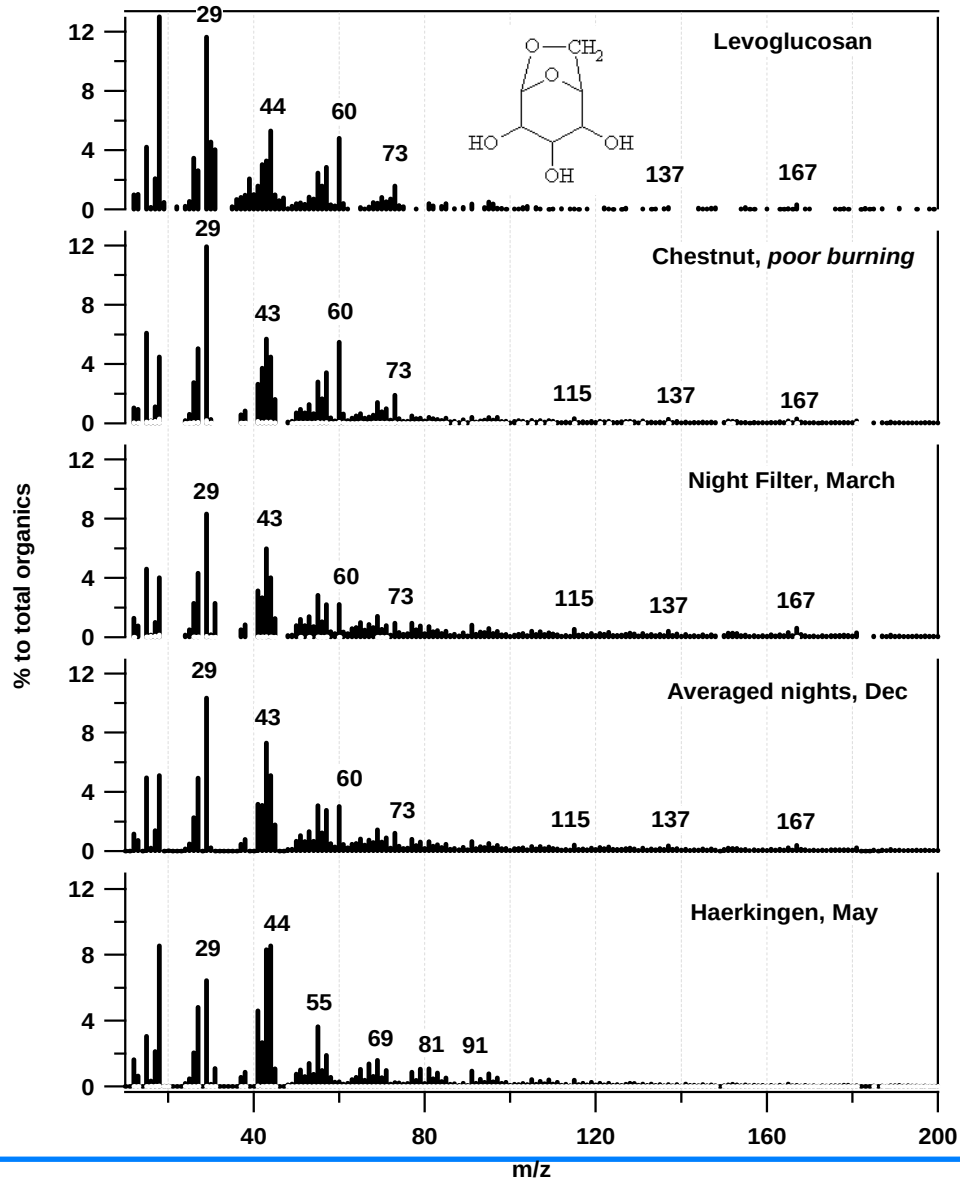
Levoglucosan

Wood burner (emissions) chestnut, very inefficient burning

Night period in Roveredo in March, more than 80% of OC non-fossil

Average in Roveredo over the whole December

Mass spectra from a Motorway site in May



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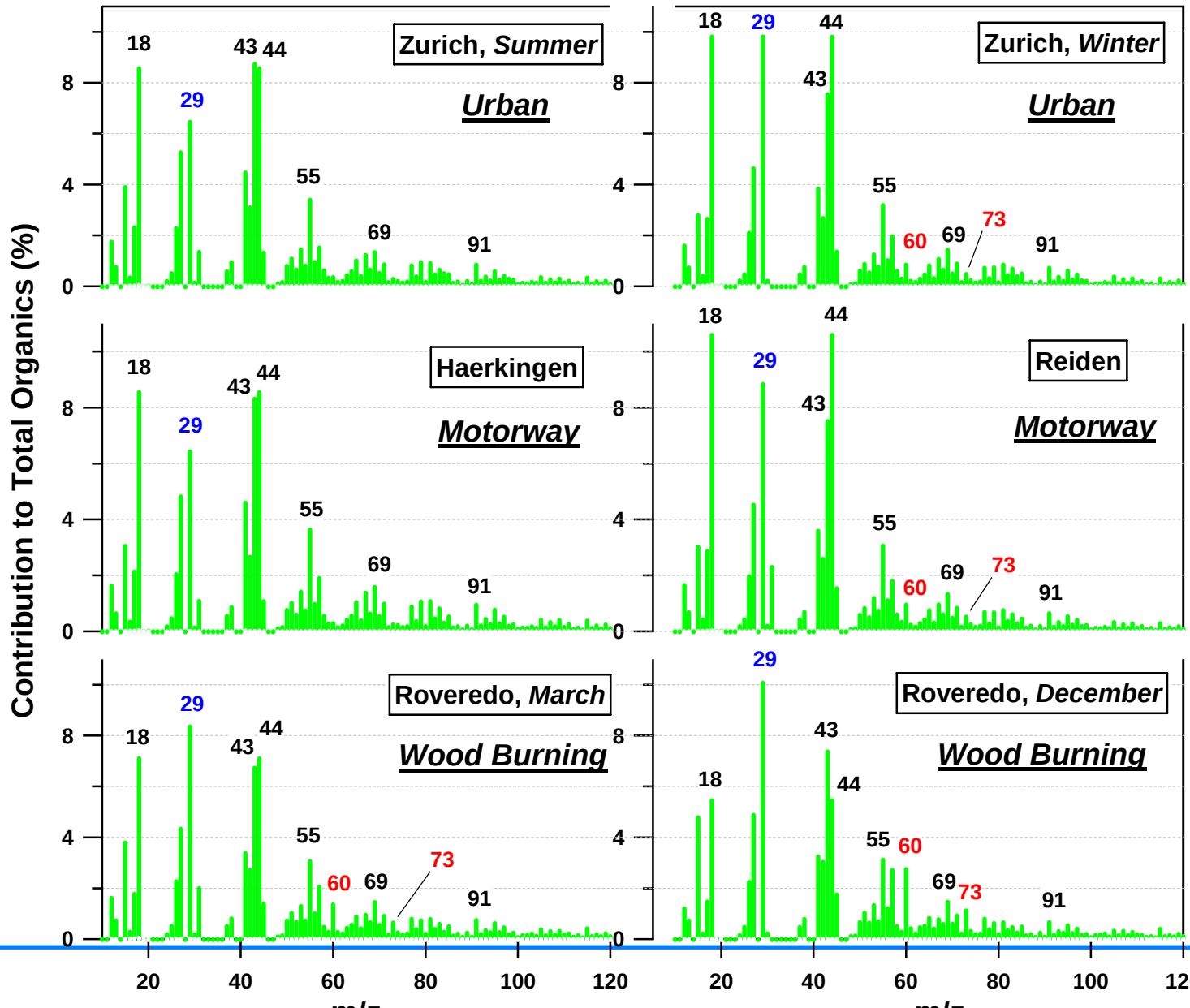
Mass spectra of organic aerosols in Switzerland



2006

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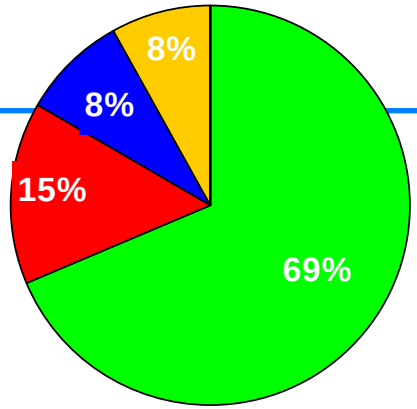
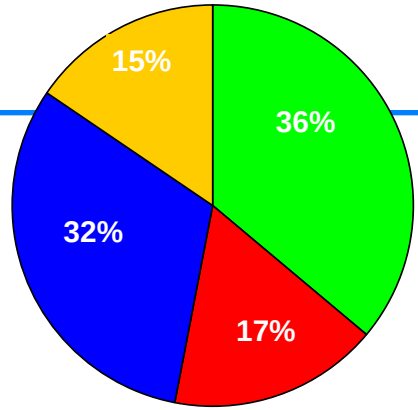
PSI

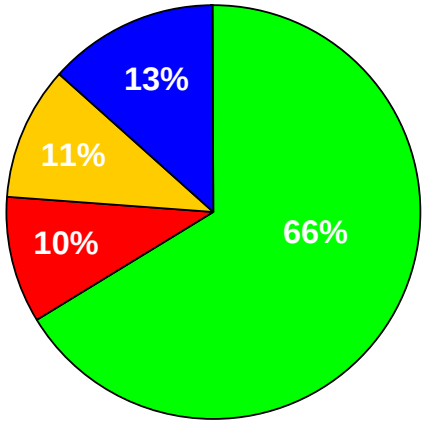
Zurich, *Summer*
Urban
19 µg m^{-3}



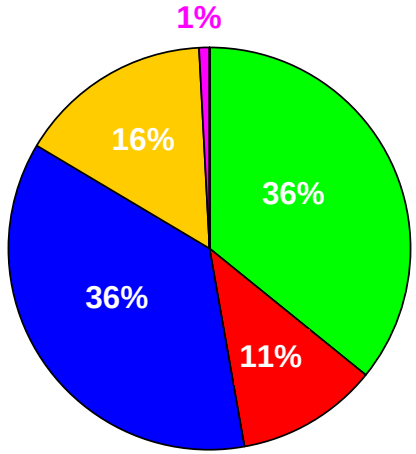


Zurich, *Winter*
Urban
44 µg m^{-3}

Haerkingen
Motorway
25 µg m^{-3}

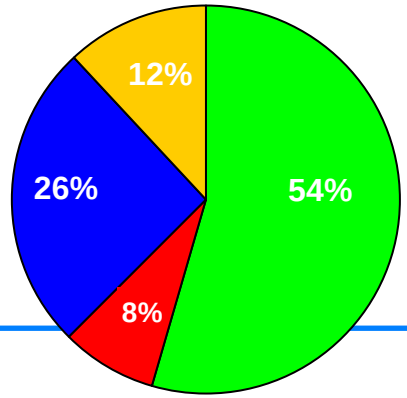


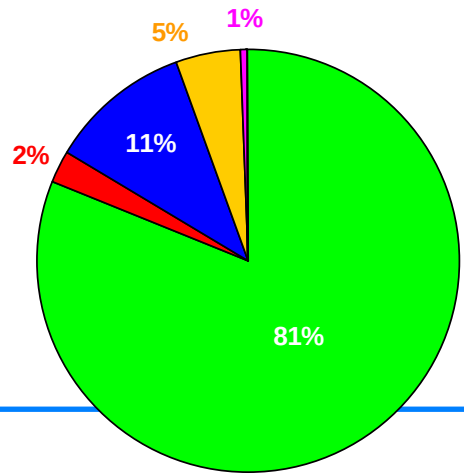
Org
NO3
SO4
NH4
Chl



Reiden, *Winter*
Motorway
56 µg m^{-3}

Roveredo, *March*
Wood Burning
17 µg m^{-3}





Roveredo, *December*
Wood Burning
39 µg m^{-3}

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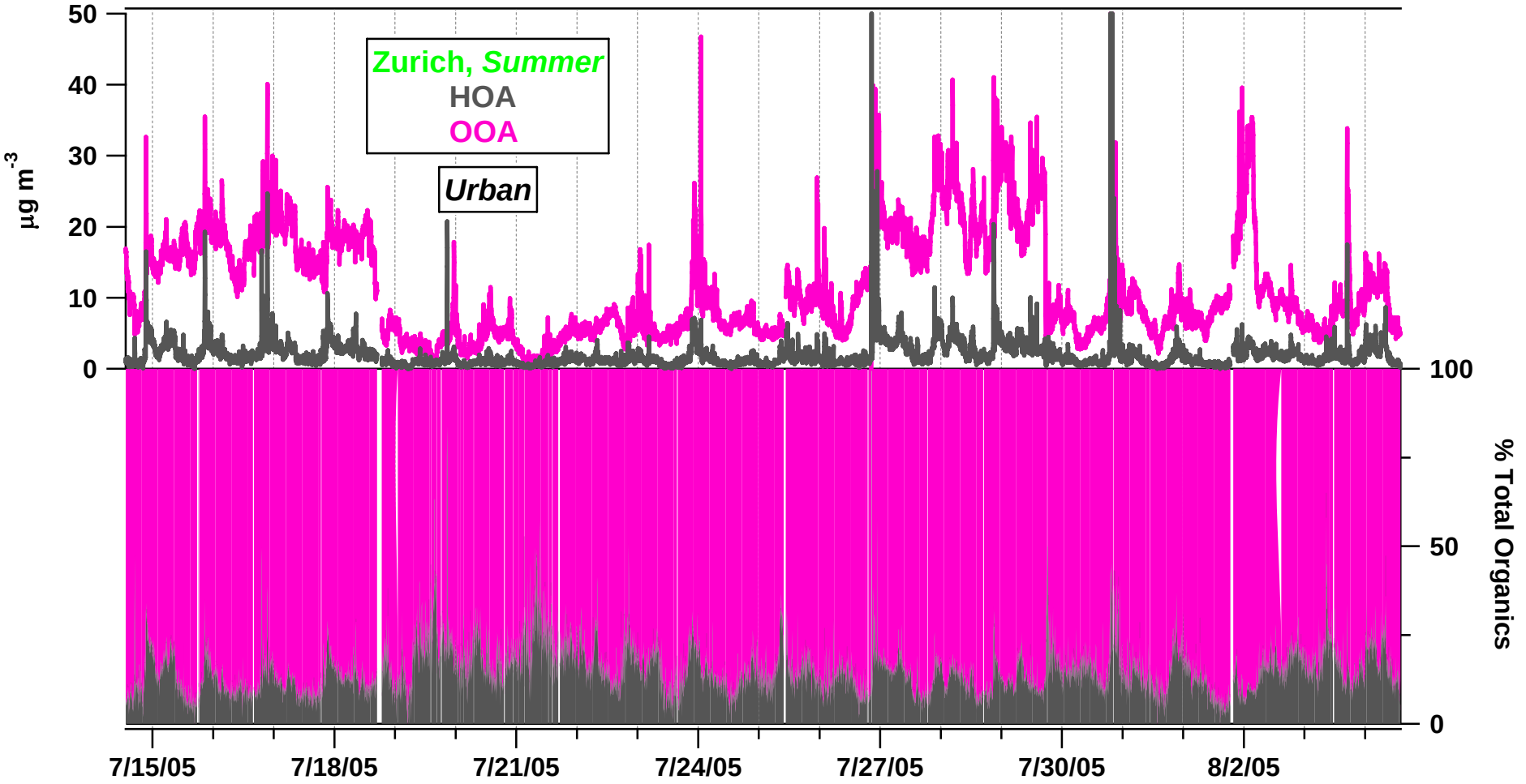
Hydrocarbon-like and oxygenated organic aerosols in Zurich



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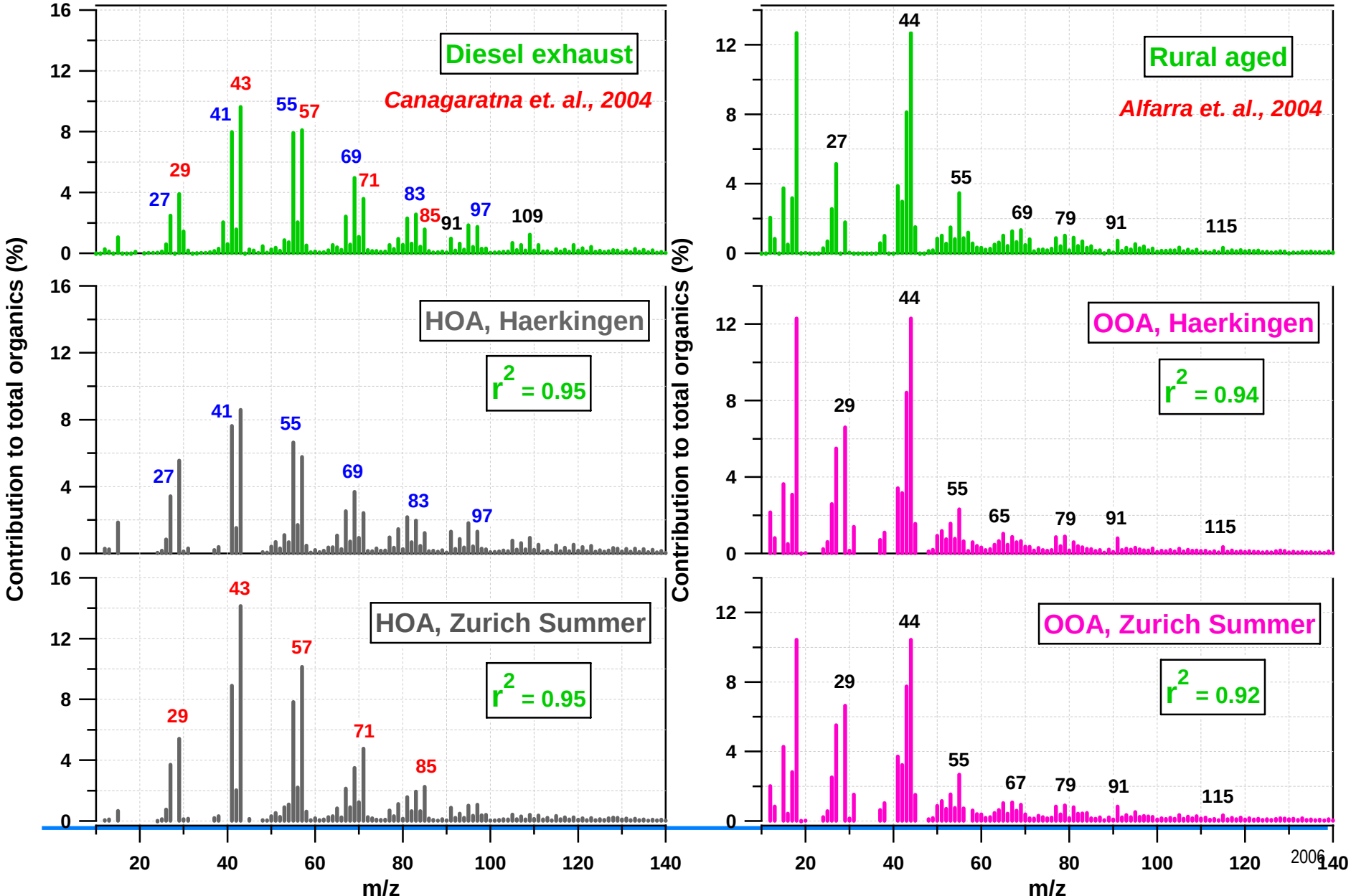
Insights into organic aerosols in Switzerland



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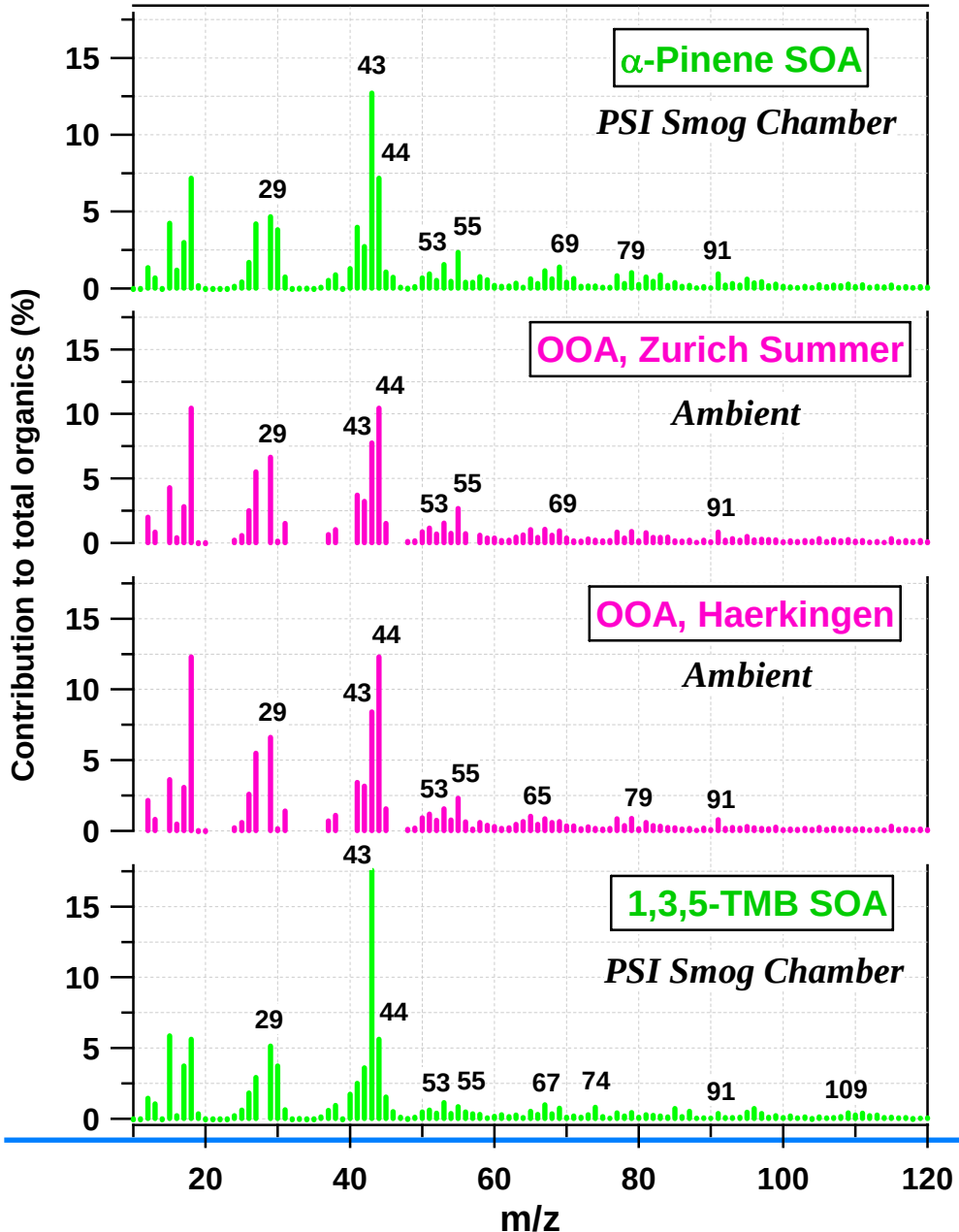
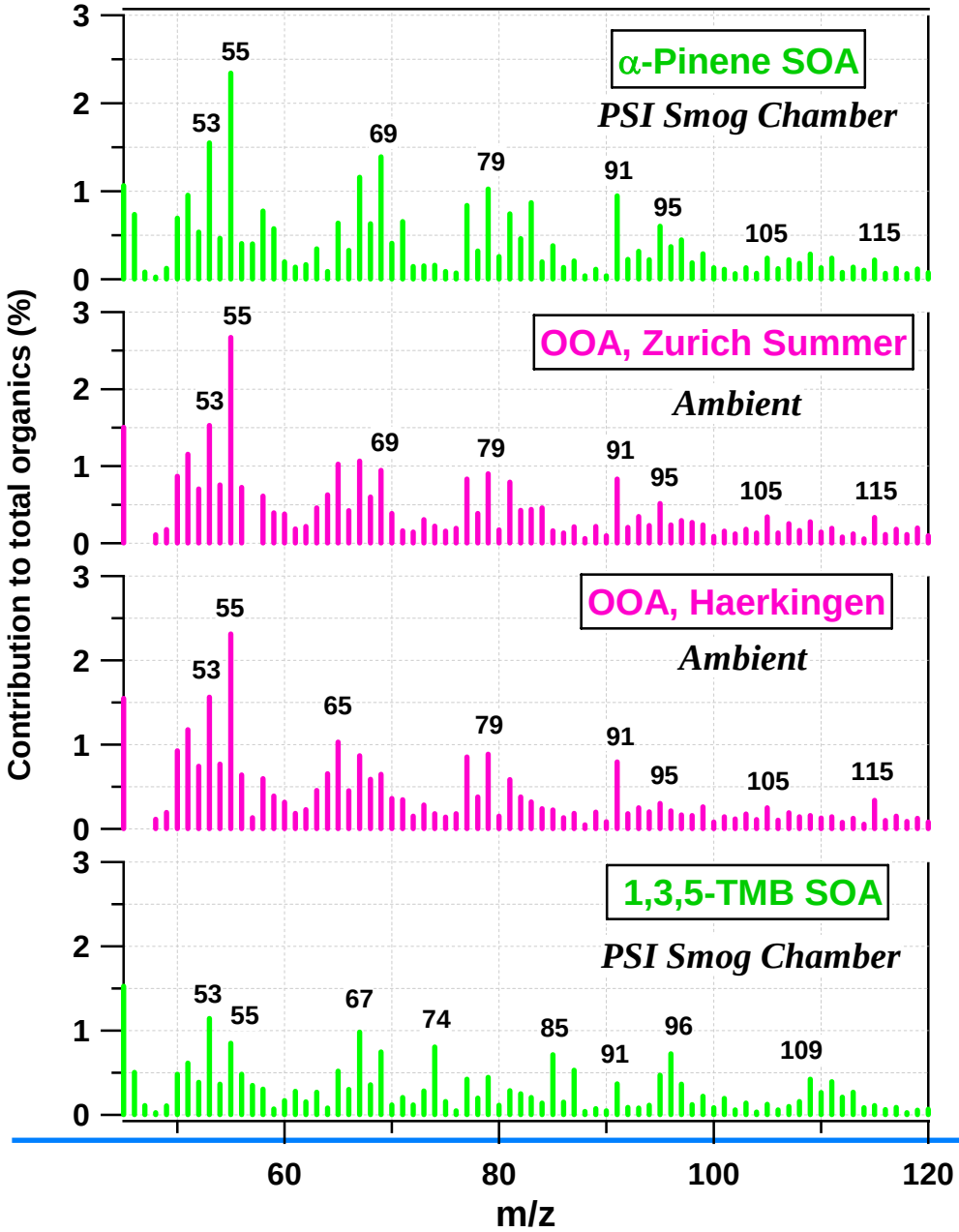
Ambient vs. smog chamber organic aerosols



R^2 Values

	α-Pinene SOA	TMB SOA
OOA, Zurich	0.83	0.64
OOA, Haerkingen	0.81	0.62

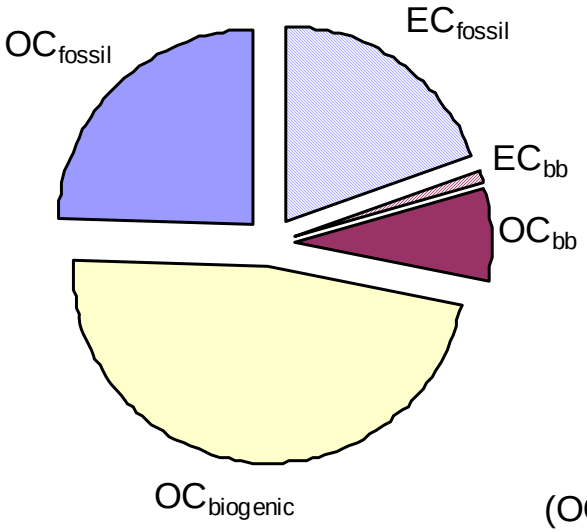


Ambient vs. smog chamber organic aerosols

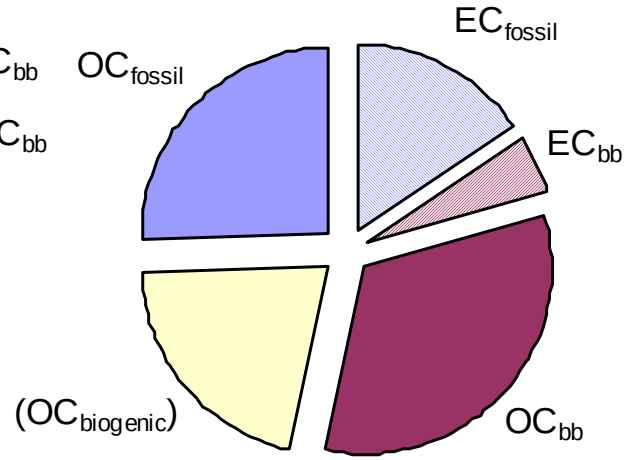
R^2 Values

	α-Pinene SOA	TMB SOA
OOA, Zurich	0.89 *(0.83)*	0.63 *(0.64)*
OOA, Haerkingen	0.87 *(0.81)*	0.63 *(0.62)*

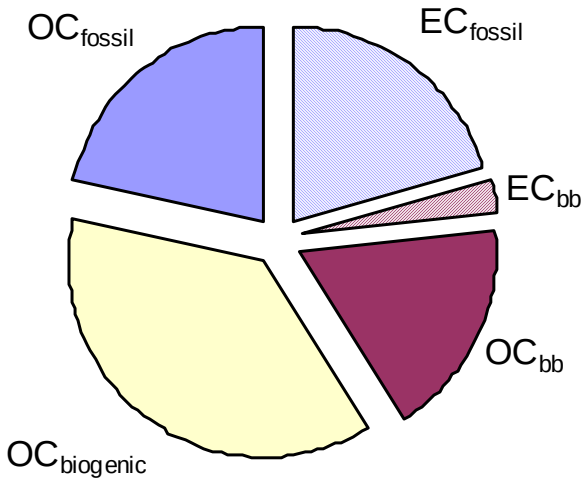
^{14}C source apportionment in Zürich



Summer 2002



Winter, February 2003



Spring like, March 2003

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Conclusions

- The Aerosol mass spectrometer and the ^{14}C radiocarbon method are very powerful tools to provide insight into the sources of the *organic* particles
- The combined use provides an even higher potential for highly time-resolved source apportionment that we only have started to explore
- Wood burning is a very important (sometimes dominant) source in Switzerland in Winter
- In summer, secondary organic aerosols are very important. Both mass spectra and the ^{14}C method identifies the biogenic secondary aerosols being more important than the fossil sources
- We would like to contribute to the Krakow study by analysing a couple of filters of Krakow, Katovice, and/or Zakopane to explore the importance of coal and wood burning in these places