Laboratory of Atmospheric Chemistry

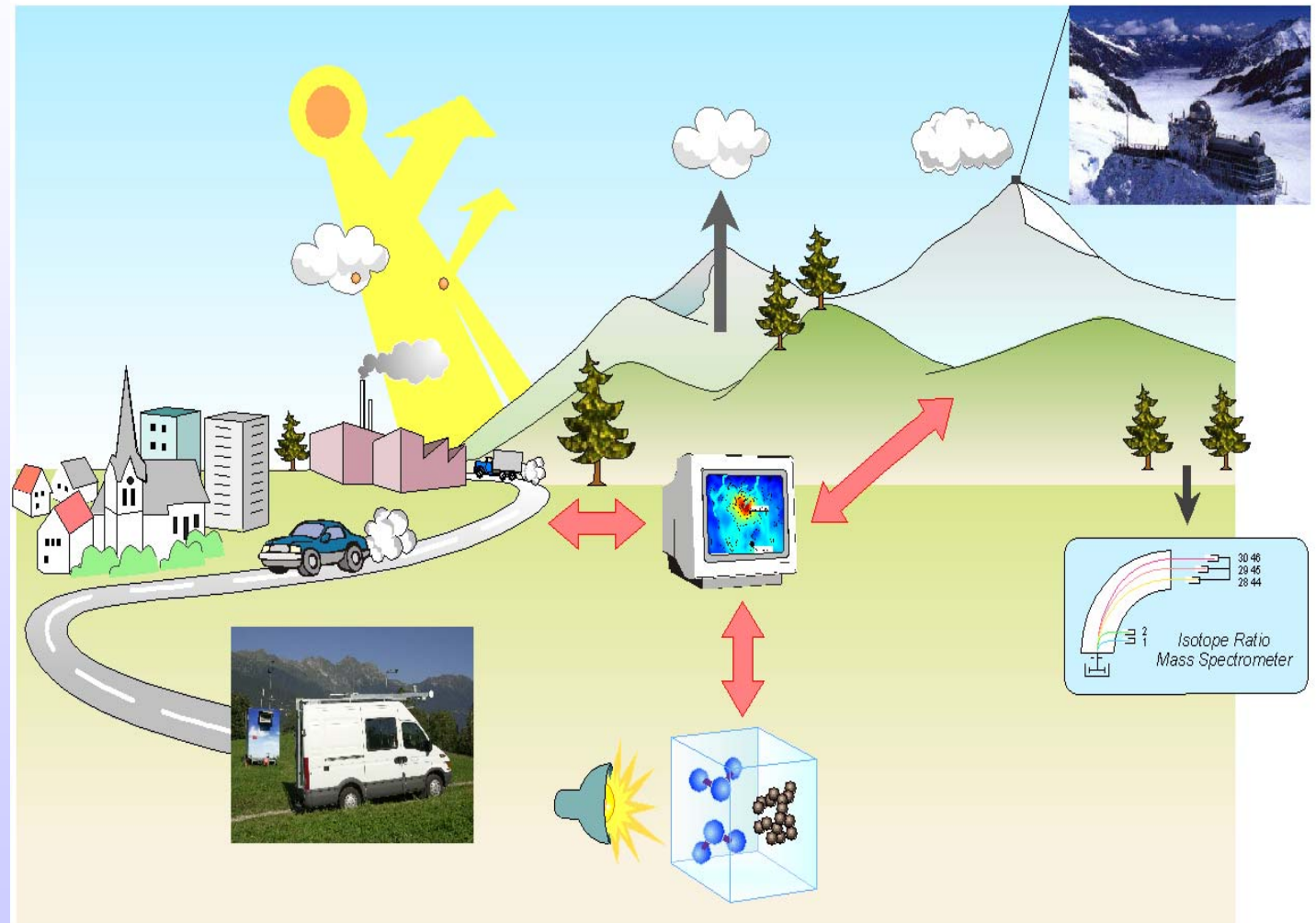**LAC :**

Head: Urs Baltensperger

15 Scientists/Postdocs

18 Phd students

3 Groups

- **Gasphase and Aerosol chemistry**

- **Aerosol physics**

- **Ecosystem fluxes**

Emission characterisation

EC, OM, inorganic aerosol, elements, acids, gases, aerosol size

AMS, SR-XRF, IC-MS, aethalometer

Transformation

Trace gas oxidation, SOA formation, gasphase-aerosol partitioning, aerosol processing

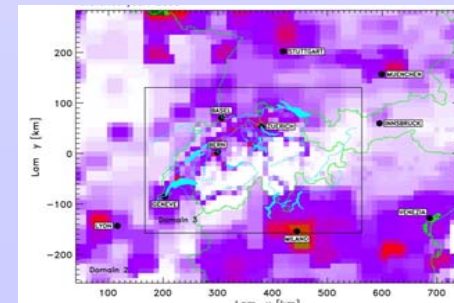*Smogchamber, PTR-MS, AMS, gasphase instruments; Master Chemical mechanism*

Ambient Measurements

EC, OM, inorganic aerosol, elements, acids, gases, aerosol size

Mobile van, AMS, ^{14}C, s-XRF, IC-MS, Aethalometer; statistical analyses
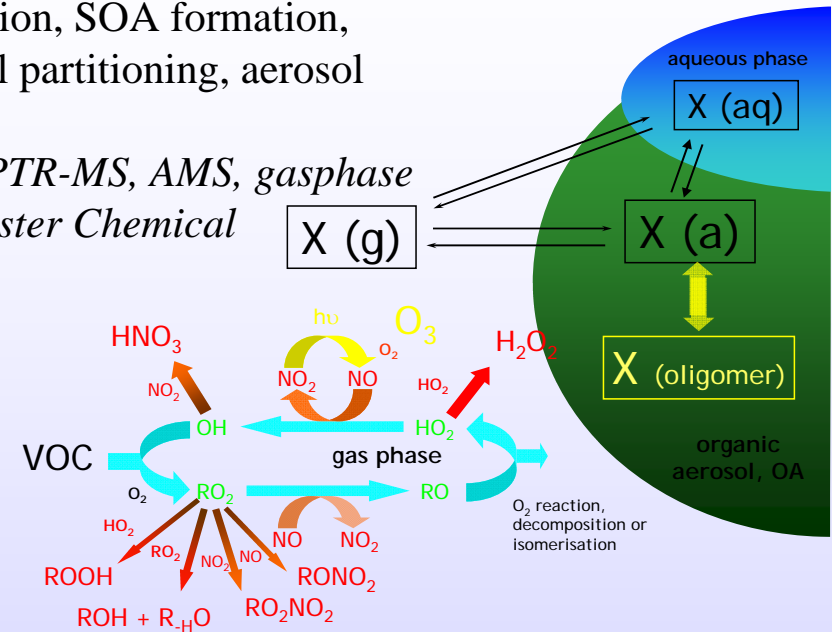
Chemical Transport Modelling

Particulate matter, ozone

CAM-x, MM5, COSMO

Field experiments

♦ Switzerland

♦ Europe

♦ Global

Locations with AMS Measurements

Härkingen (**May**)

Zürich (**July/August** and **January**)

Rhine valley
(**February**)

Reiden (**February**)

Payerne (**June**,
January)

JFJ (**Winter**, **Summer**)

Massongex
(**December**)

Riviera (**June**)

Roveredo (**March, December**)
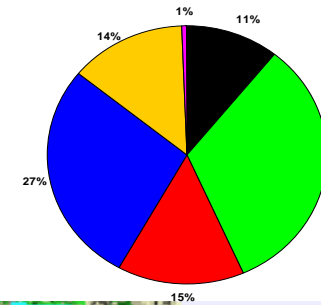
⭕ **Mobile measurements**

⭕ Milano (**June**)
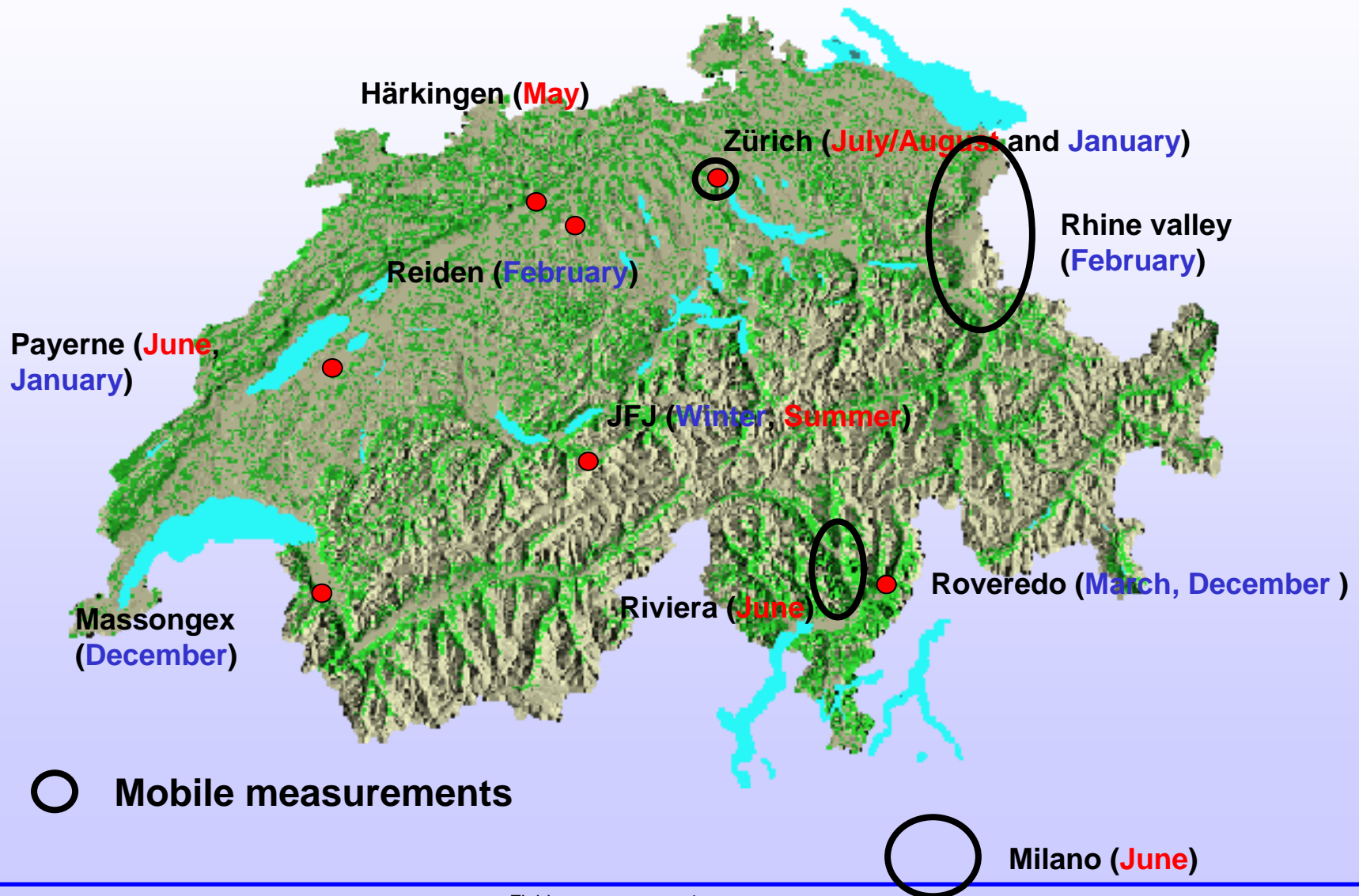
Average compositions in winter (

Reiden (**February**)
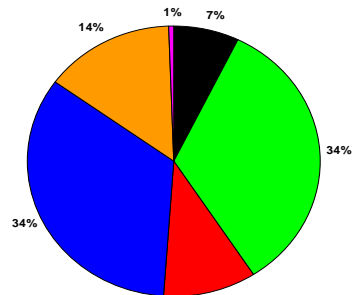
Zürich (**January**)

Payerne (**January**)
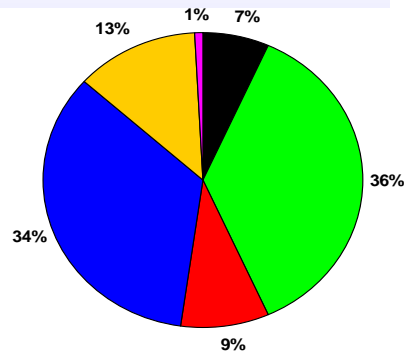
Massongex
(**December**)
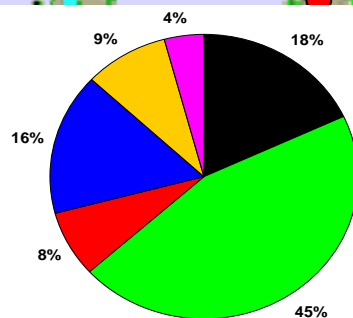
Roveredo (**December**)
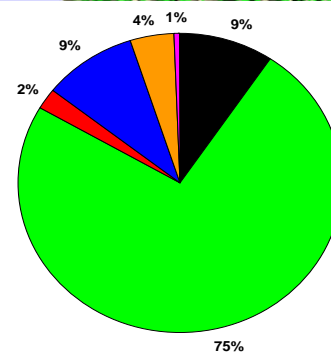
Black Carbon
Organic mass
Nitrate
Sulfate
Ammonium
Chloride

Overview over the winter ^{14}C analyses

Reiden, Winter

ECbiomass

ECfossil

OCnonfossil

OCfossil

Zürich, Winter

ECbiomass

ECfossil

OCnonfossil

OCfossil

Jungfraujoch, Winter

ECbiomass

ECfossil

OCnonfossil

OCfossil

Moleno, Winter

ECbiomass

ECfossil

OCnonfossil

OCfossil

Roveredo, Winter

ECbiomass

ECfossil

OCnonfossil

OCfoss
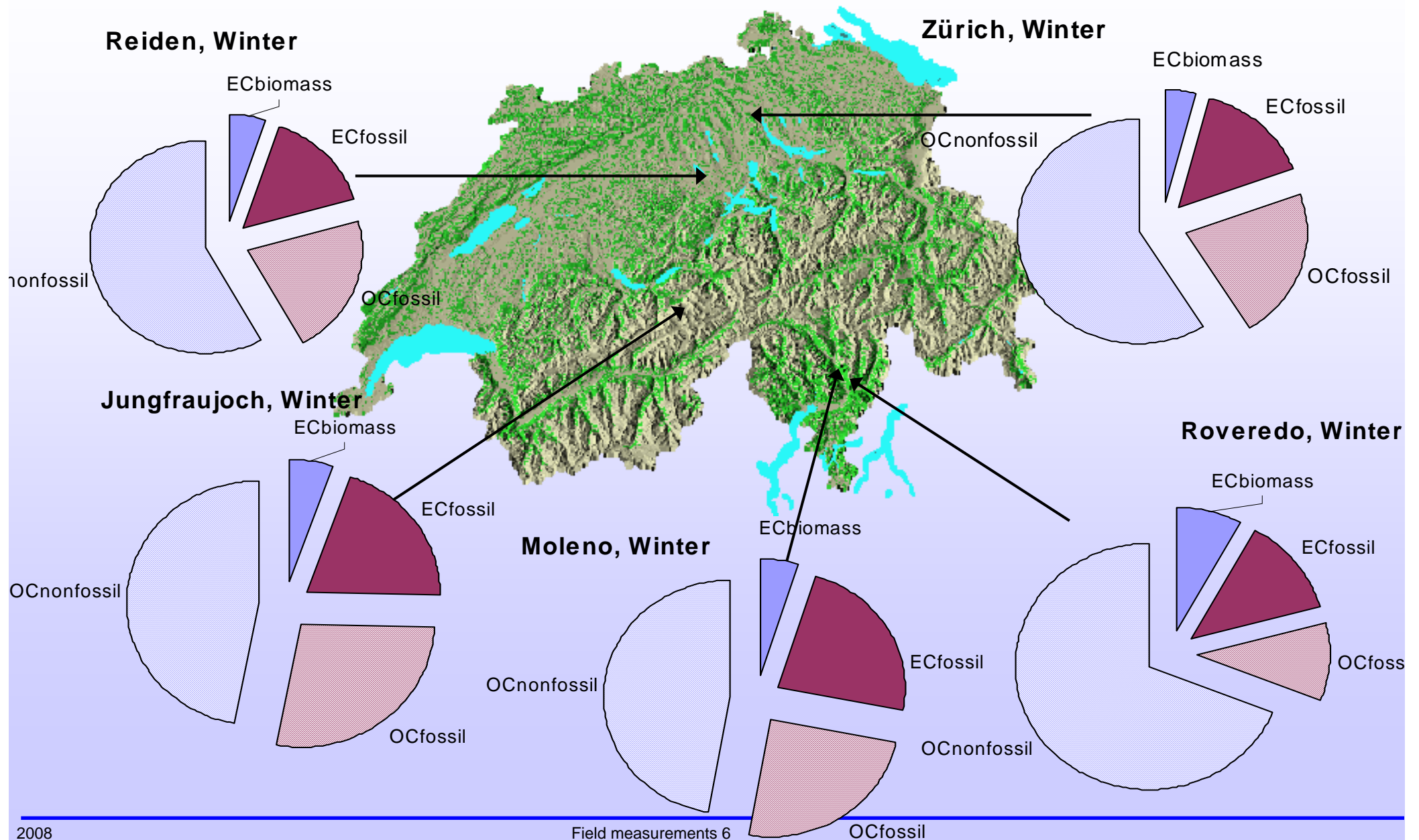
$EC_{biomass}/EC_{tot}$: Spatial distribution on 29.01.2006

Reiden
0.36

Sedel
0.33

Tänikon
0.40

Basel
0.38

Härkingen
0.34

Dübendorf
0.33

Zürich
0.33

Payerne
0.42

Lausanne
0.19

Bern
0.14
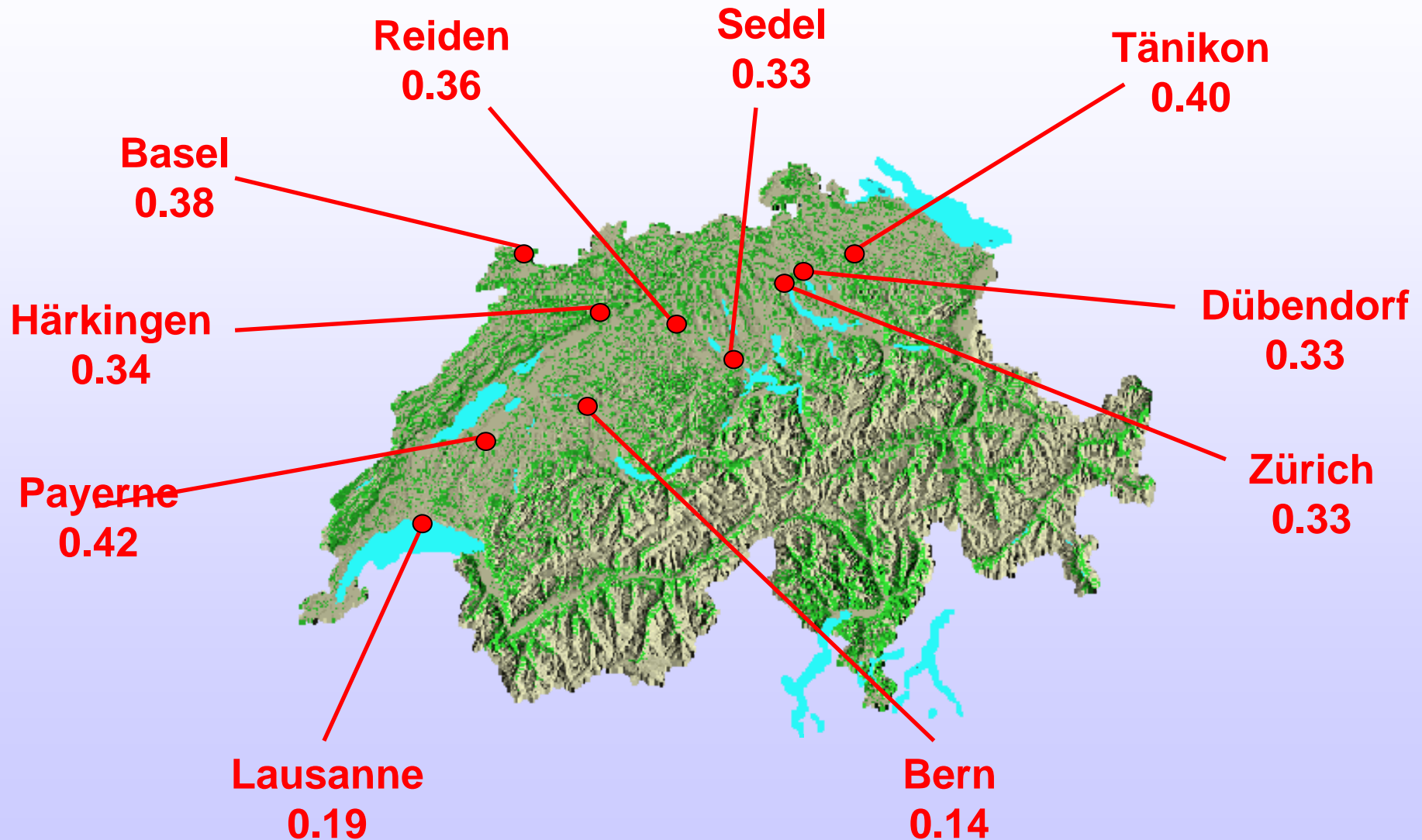
Holzverbrennung in Roveredo (GR), Januar 2005

06:00 – 14:00

ECbiomass 9%
ECfossil 13%
OCfossil 12%
OCnonfossil 66%

Roveredo (GR)

18:00 – 02:00

ECbiomass 11%
ECfossil 8%
OCnonfossil 81%
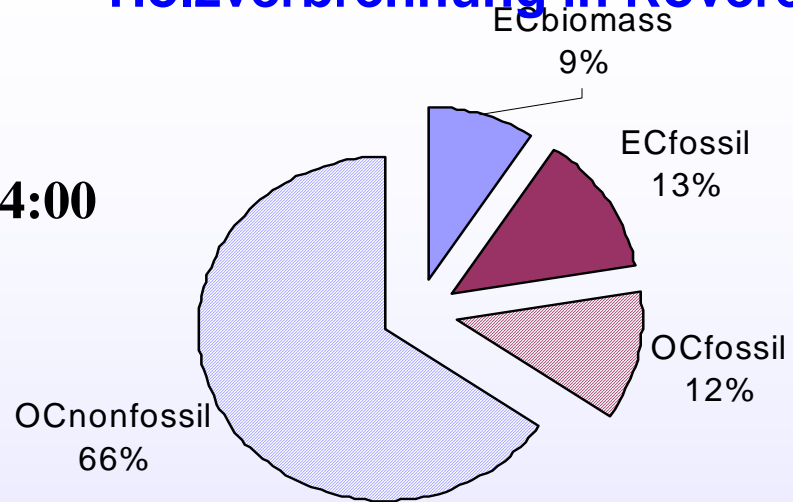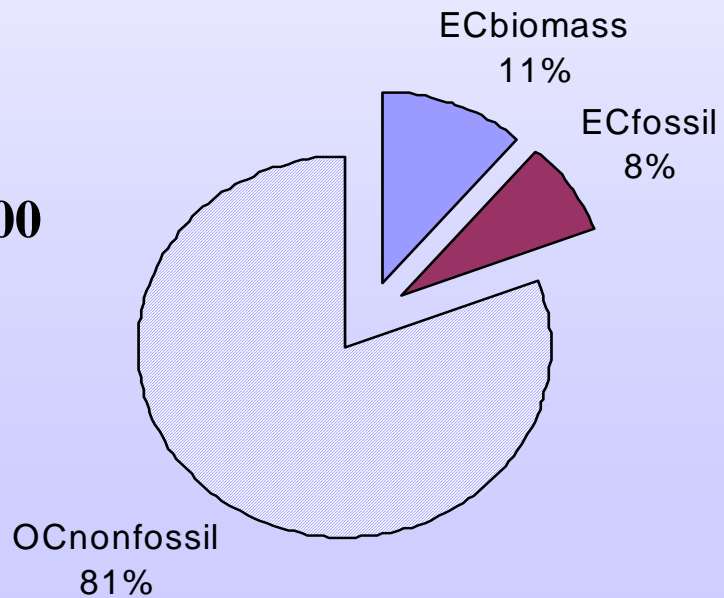
Szidat et al., GRL, 2007

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
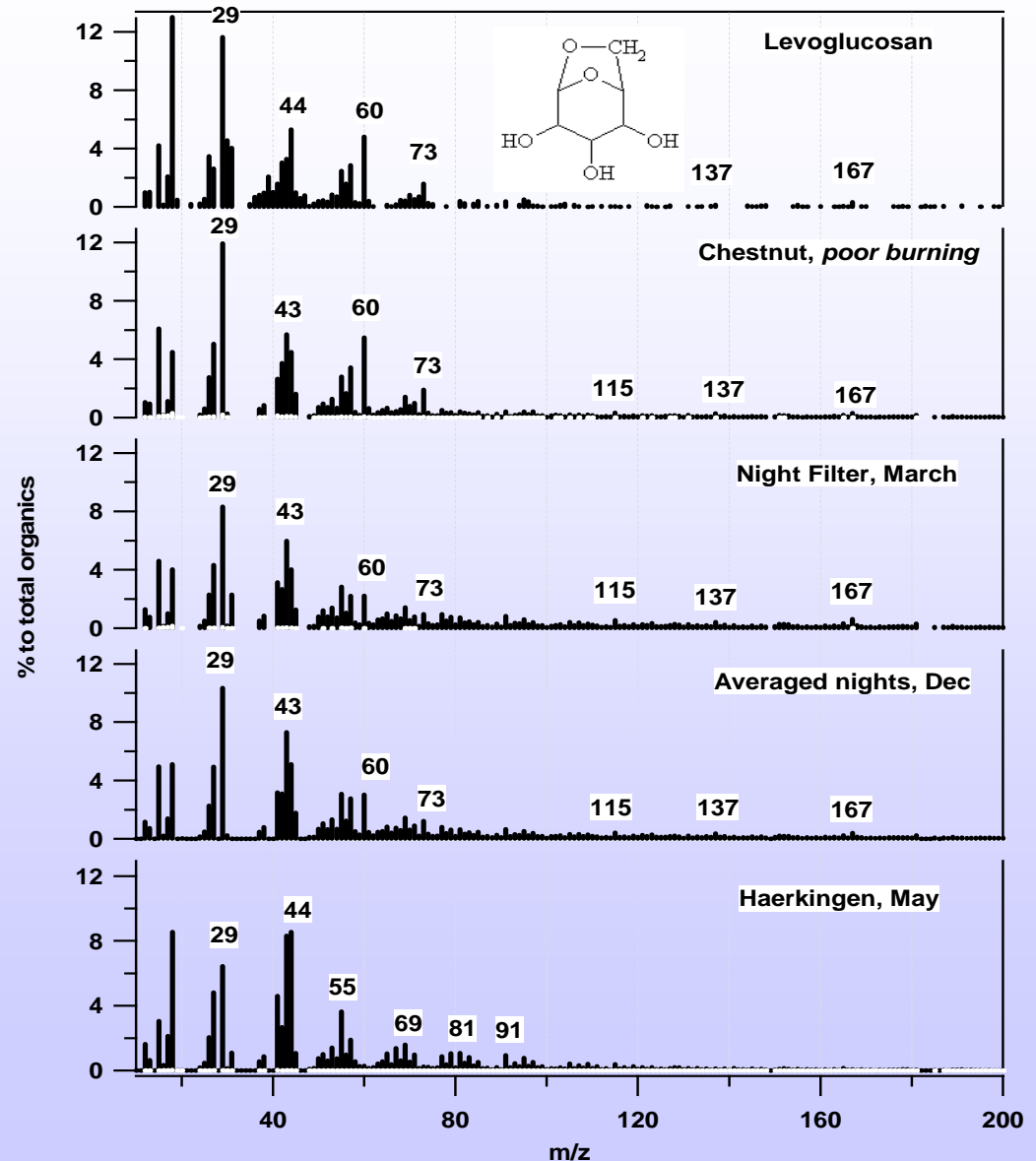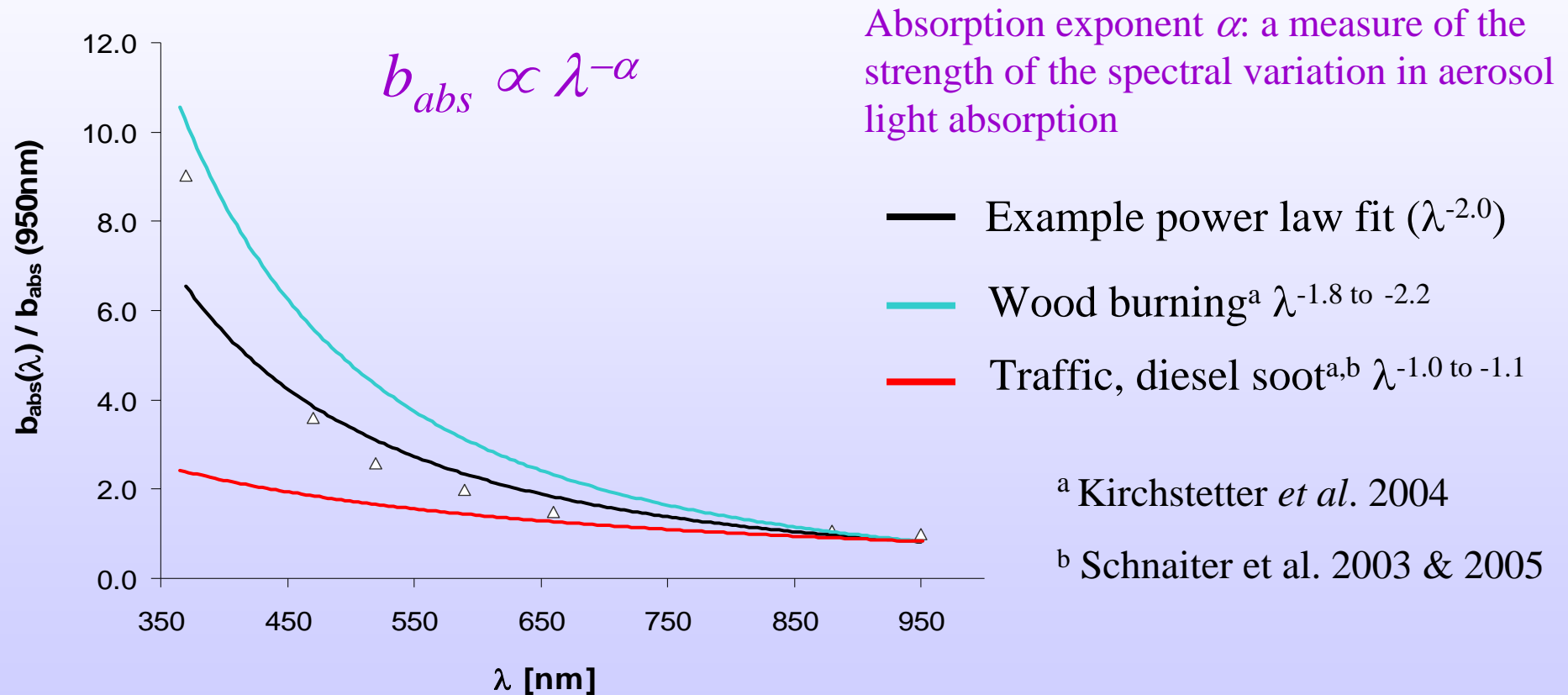
Mass spectra from a Motorway site in May

Alfarra et al. ES&T (2007)

Dependence of light absorption as a function of wavelength measured by an aethalometer

$$b_{abs} \propto \lambda^{-\alpha}$$

Absorption exponent α: a measure of the strength of the spectral variation in aerosol light absorption

—— Example power law fit ($\lambda^{-2.0}$)

—— Wood burning[a] $\lambda^{-1.8 \text{ to } -2.2}$

—— Traffic, diesel soot[a,b] $\lambda^{-1.0 \text{ to } -1.1}$

[a] Kirchstetter *et al*. 2004

[b] Schnaiter et al. 2003 & 2005

y-axis: $b_{abs}(\lambda) / b_{abs}$ (950nm)

x-axis: λ [nm]

Sandradewi et al., Atmos. Environ., 2008

Aethalometer model to derive the contribution of woodburning and traffic to PM1
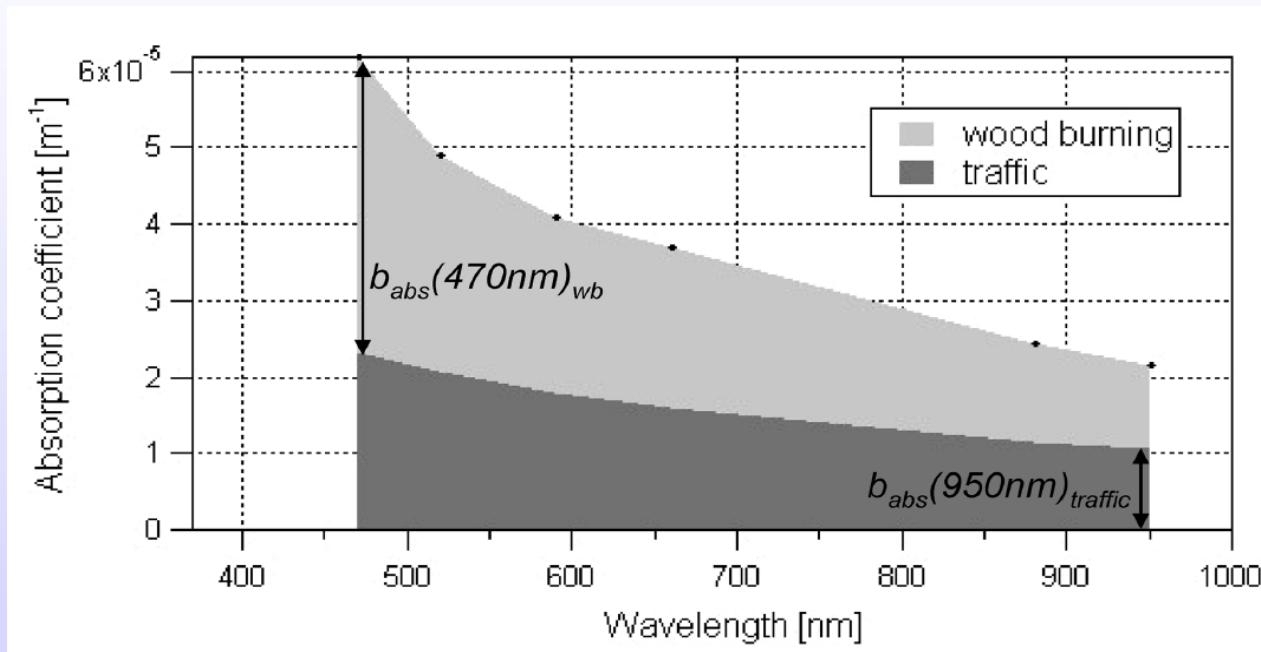
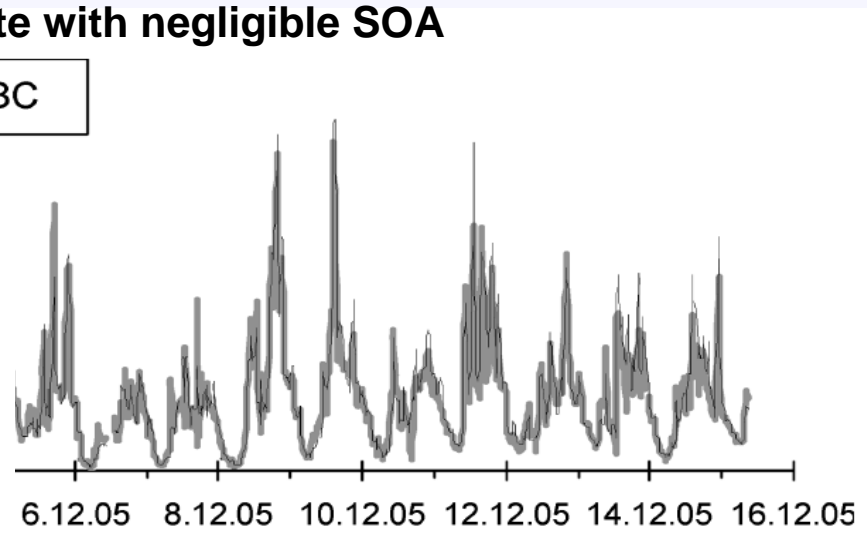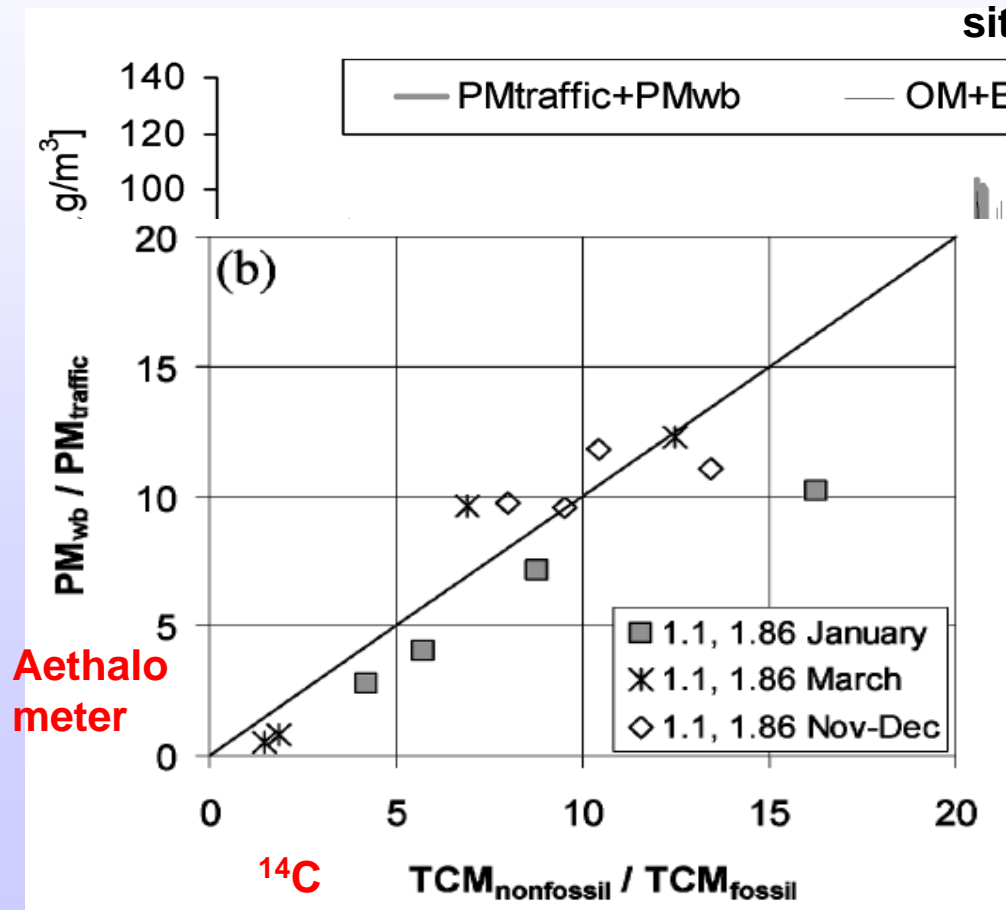**Carbonaceous material (CM)**

$$CM\ (PM1) = \underbrace{c1*b_{abs}(950nm)_{traffic}}_{PM_{traffic}} + \underbrace{c2*b_{abs}(470nm)_{wb}}_{PM_{wb}}$$

Sandradewi et al., ES&T, 2008
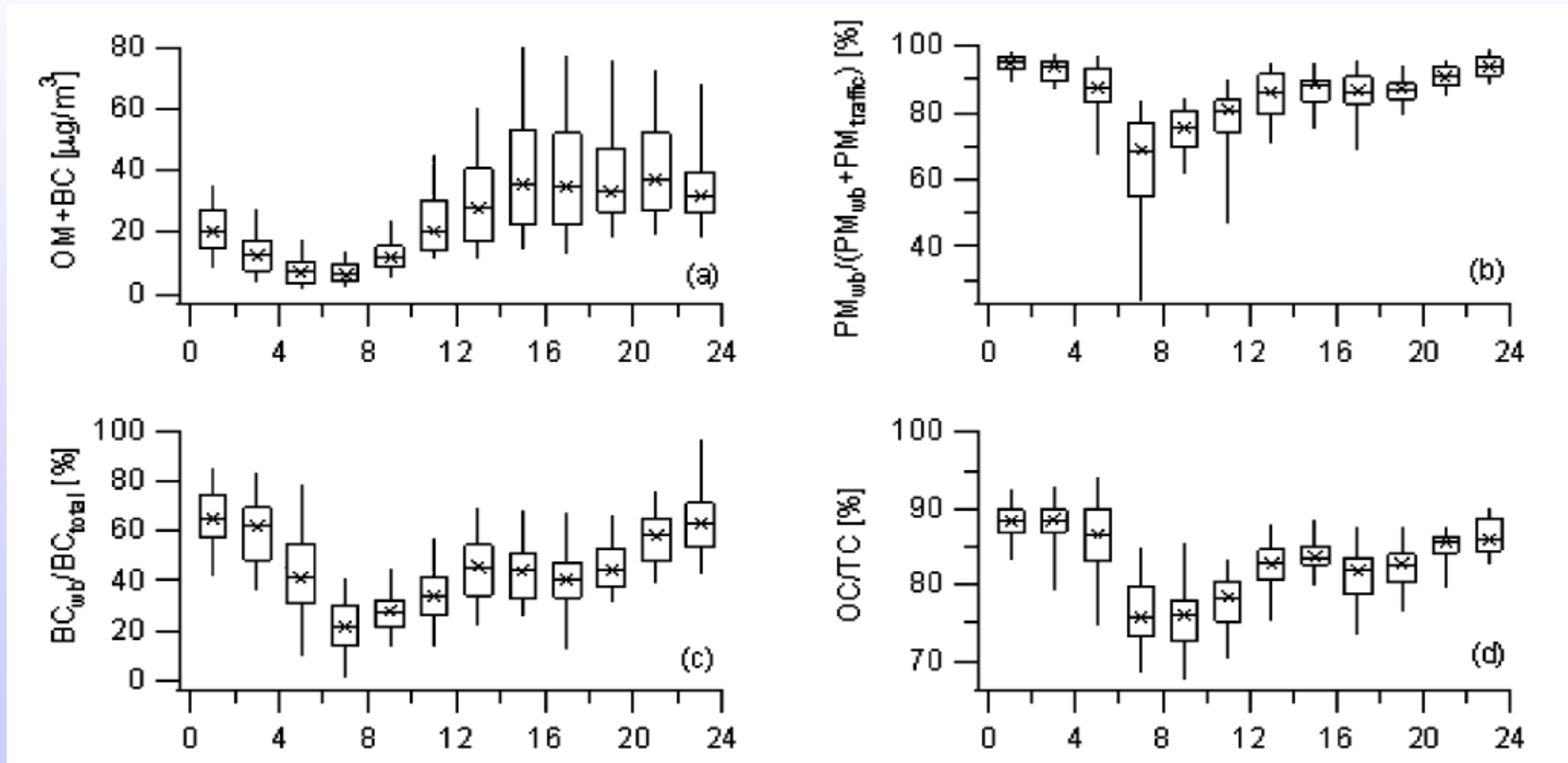
Validation of aethalometer model

The variability of OM+BC can be explained at a site with negligible SOA

Validation of aethalometer analysis with ^{14}C analysis

Aethalo meter

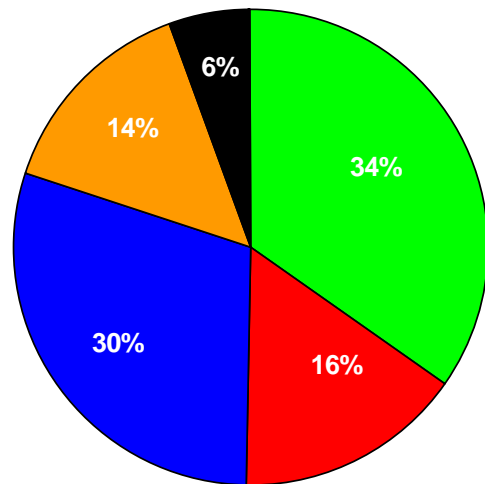**[14]C**

Sandradewi et al., ES&T, 2008

Average diurnal cycle of the carbonaceous material, OC/EC and wood burning versus traffic contributions

Sandradewi et al., ES&T, 2008

Fractions of BC, OM, NO_3, SO_4 and NH_4 and fossil and non-fossil contribution to EC and OC

Zürich

Reiden

Black Carbon
Organic mass
Nitrate
Sulfate
Ammonium

Zürich pie chart: 34%, 16%, 30%, 14%, 6%

Reiden pie chart: 33%, 11%, 34%, 15%, 7%

Zürich lower pie: ECbb 4%, ECfossil 17%, OCfossil 23%, OCnonfossil 56%

Reiden lower pie: ECbb 5%, ECfossil 17%, OCfossil 22%, OCnonfossil 56%
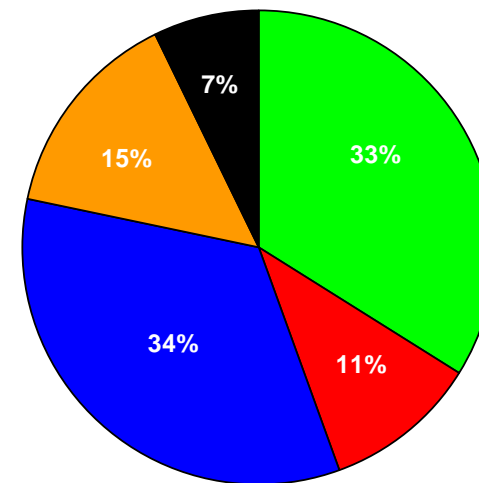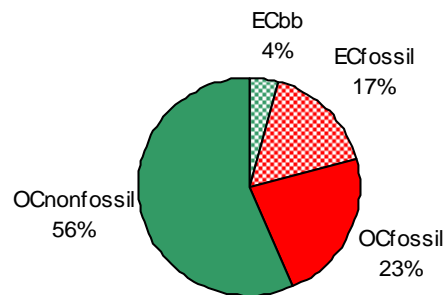
Urban background
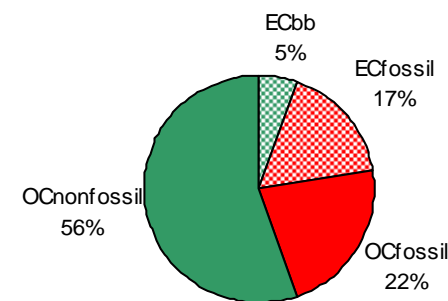
Highway/rural

Nearly identical composition

Chemical composition of PM1 with high time resolution in Zürich and Reiden (Kt. Luzern)
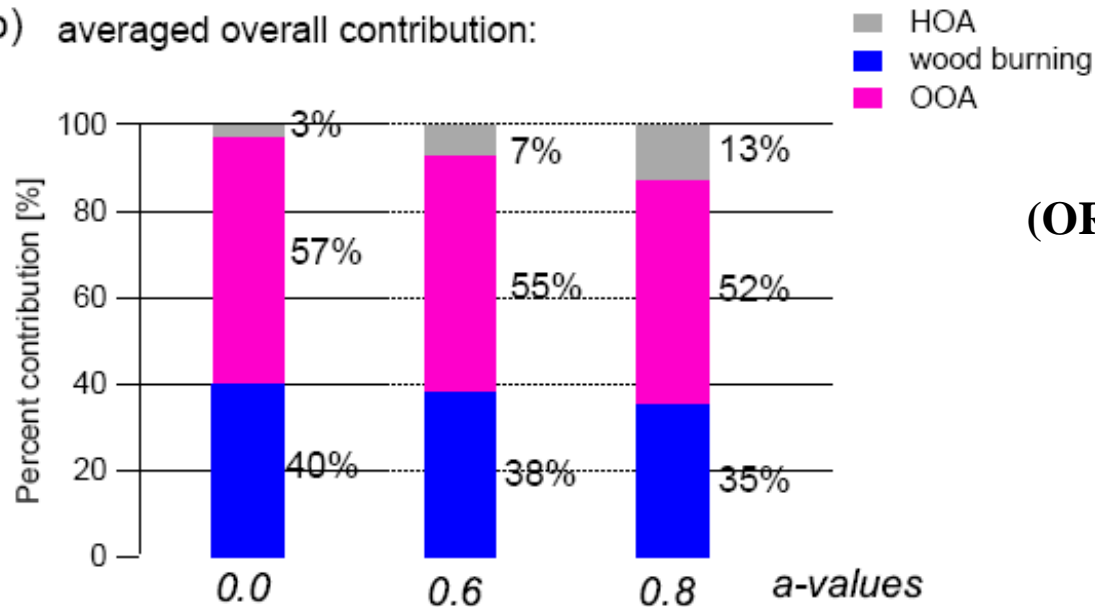
Organic aerosol sources in winter in Zurich

Statistical analysis of q-AMS data in Zürich (Lanz et al., ES&T, 2008)

$$(ORG)_{ij} = G_{i1}*F_{1j}+G_{i2}*F_{2j}+ G_{i3}*Traffic_j$$

Verification by comparing source strengths with tracers
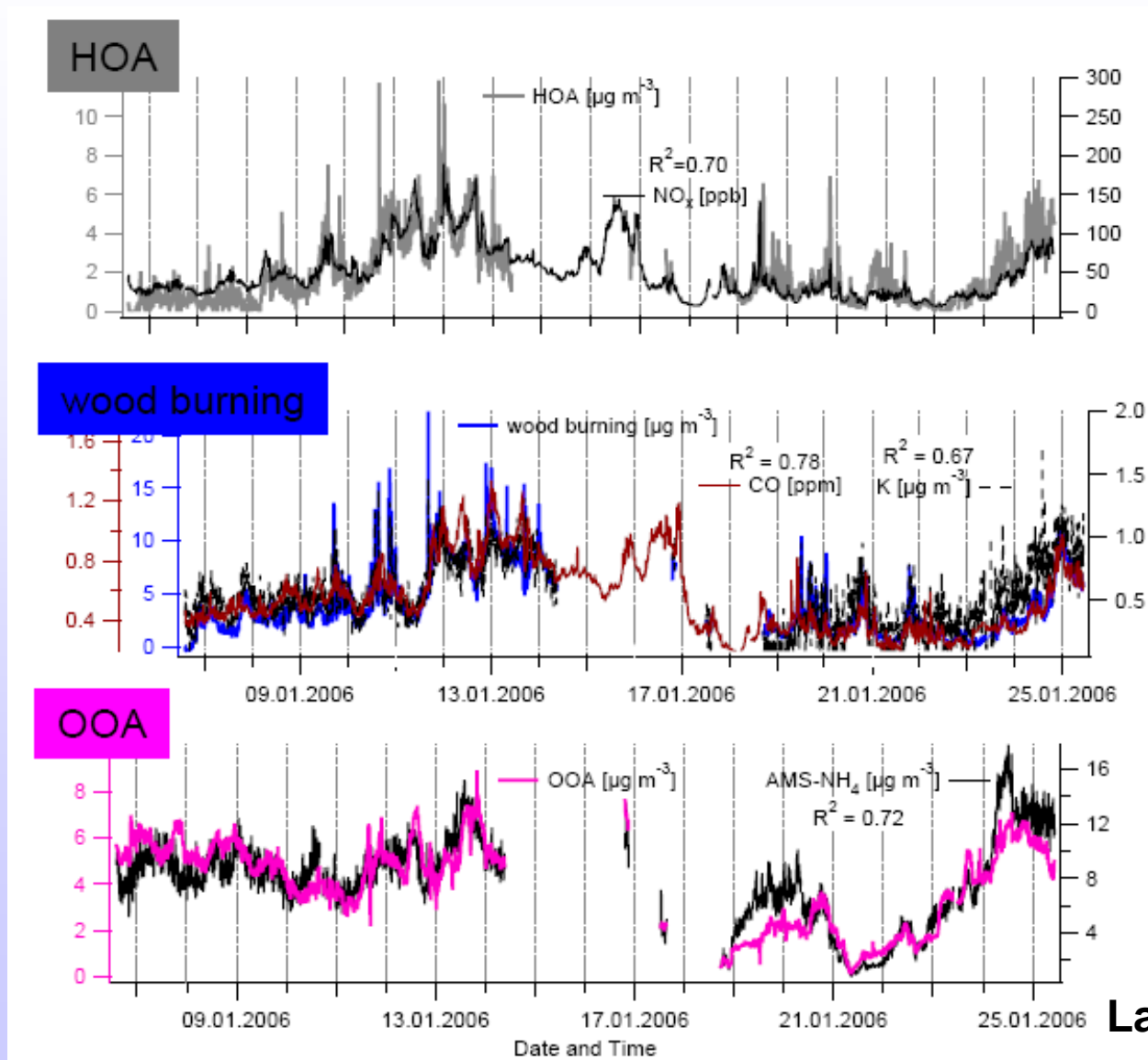
Lanz et al., ES&T, 2008

Carbon apportionment using ^{14}C analysis
Estimation of fossil and non-fossil SOA contribution

OM
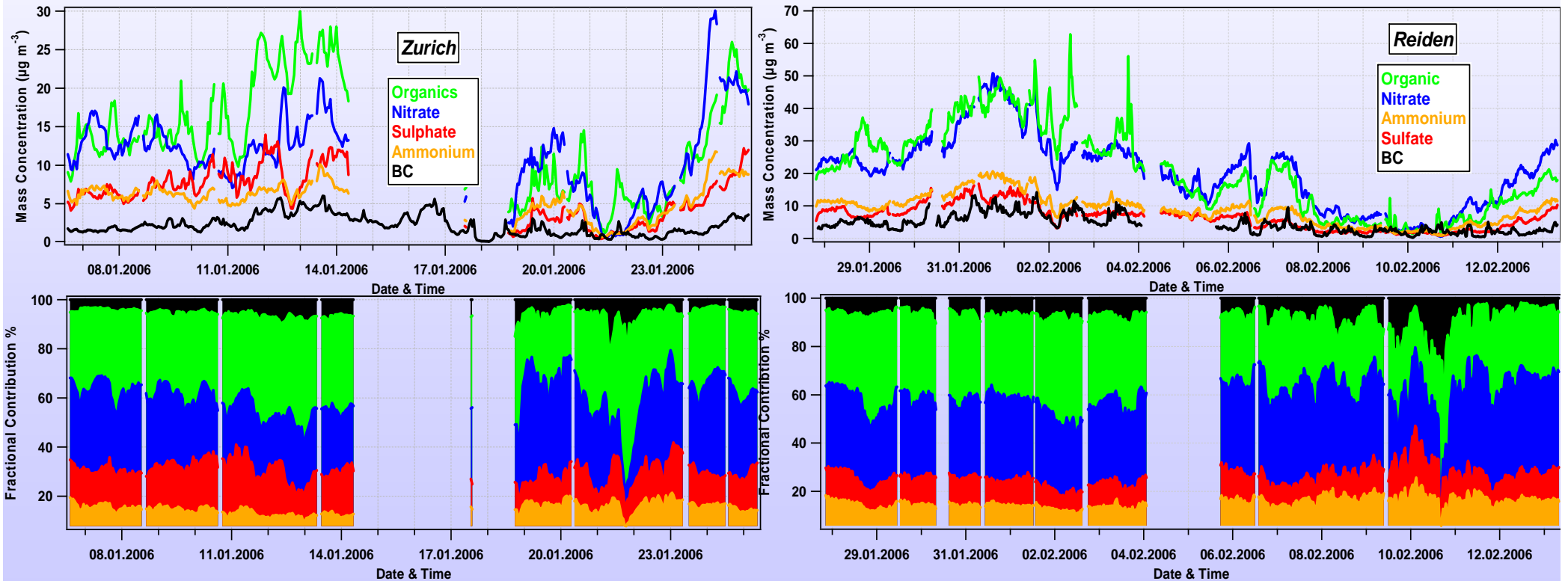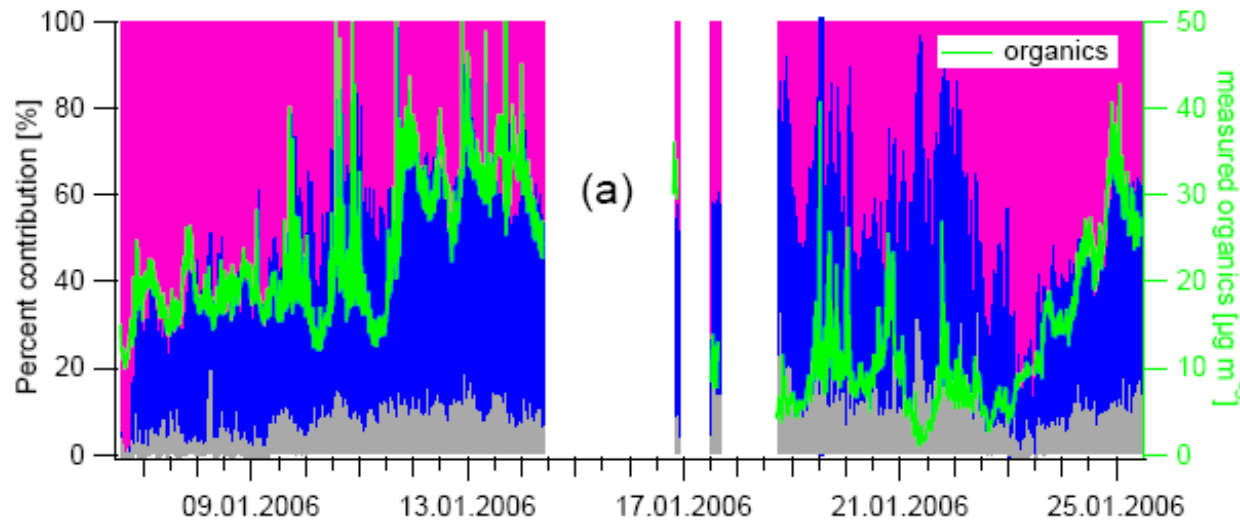
38%

38%

- Wood burning
- Traffic
- Secondary (fossil)
- Secondary (non-fossil)

17%   7%

EC

19%

- EC (fossil)
- EC (non-fossil)

81%
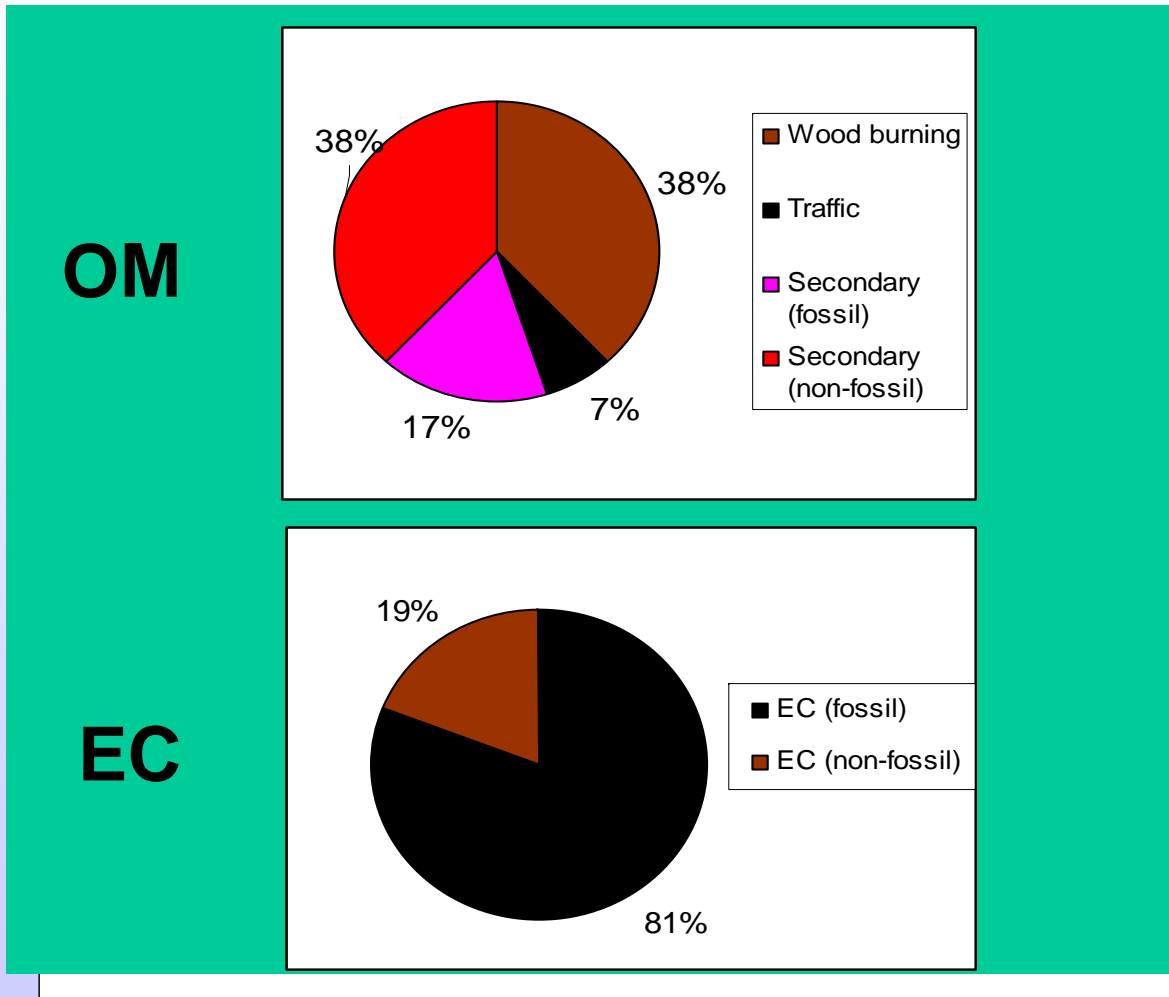
Use of AMS analysis :

- **wood burning 38%**

- **HOA 7%**

Assumptions :

- **only SOA, HOA and wood burning present**

- **OM/OC=2 for wood burning and SOA and OM/OC=1.2 for HOA**

- **RESULT : SOAnonfossil: 69% SOAfossil: 31%**

Lanz et al., ACP, 2007

Average composition in Zürich in summer and winter

Zürich (July)

Black Carbon	
Organic mass	
Nitrate	
Sulfate	
Ammonium	

Zürich (January)
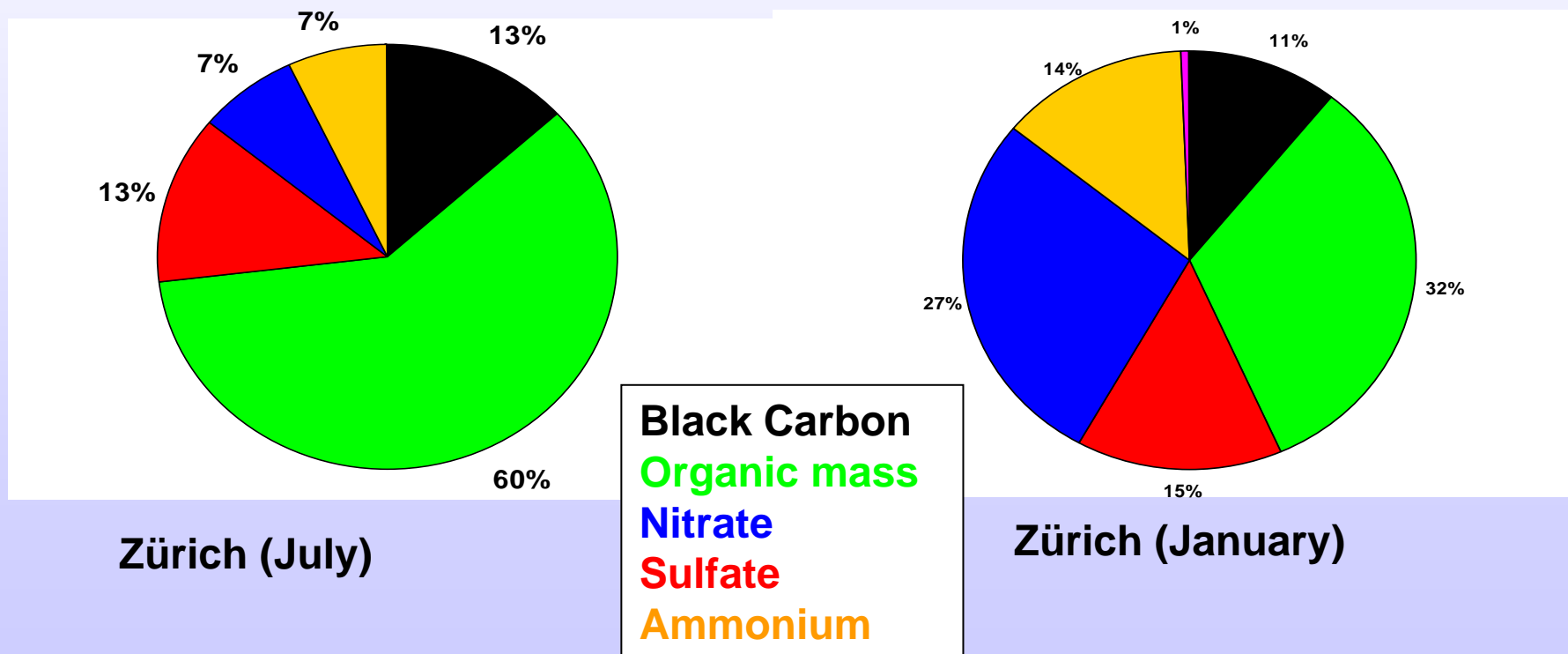
Chemical composition in Zürich summer and Positive Matrix Factorization of the organic matter

Organic mass

7% 7% 13%

13%

60%

Zürich (July)

Black Carbon
Organic mass
Nitrate
Sulfate
Ammonium

6%
10%
11%
7%
22%
44%

OOA, type I
OOA, type II
HOA
charbroiling
wood burning
minor (unknwon)
minor (food cooking)
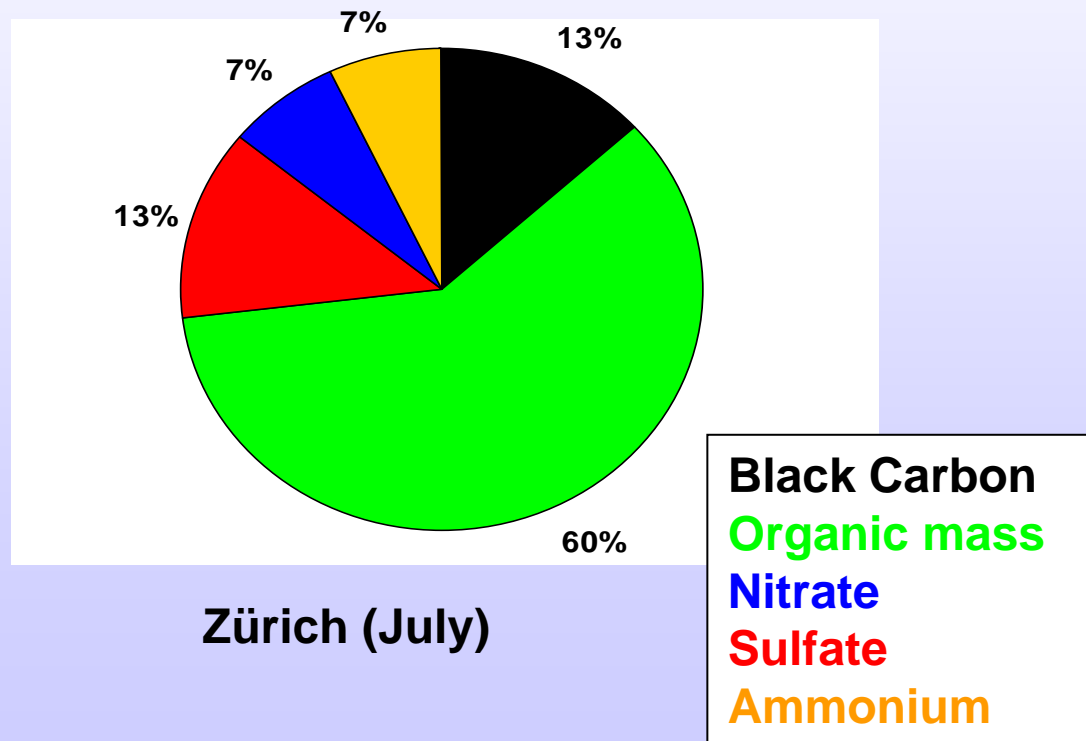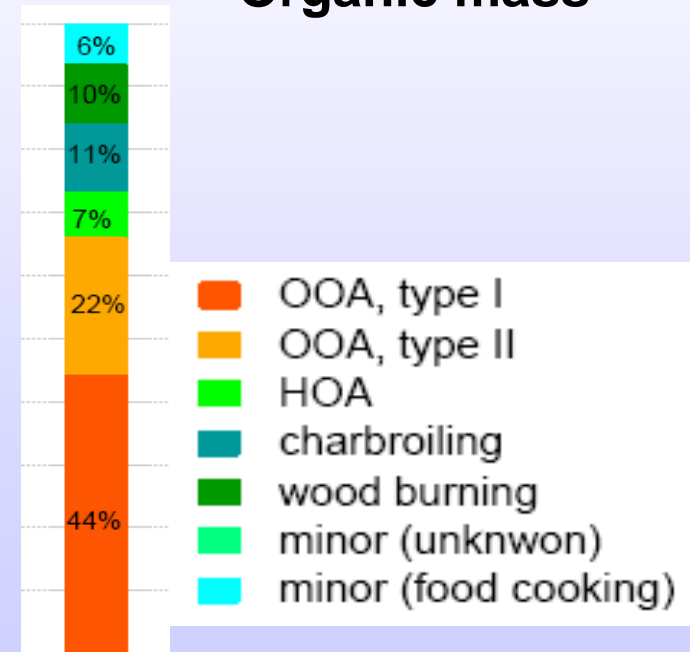
OOA: Secondary organic aerosol

HOA: mostly traffic

Lanz et al., ACP (2007)

Identification of two different oxidized organic aerosol components (volatile and non-volatile)
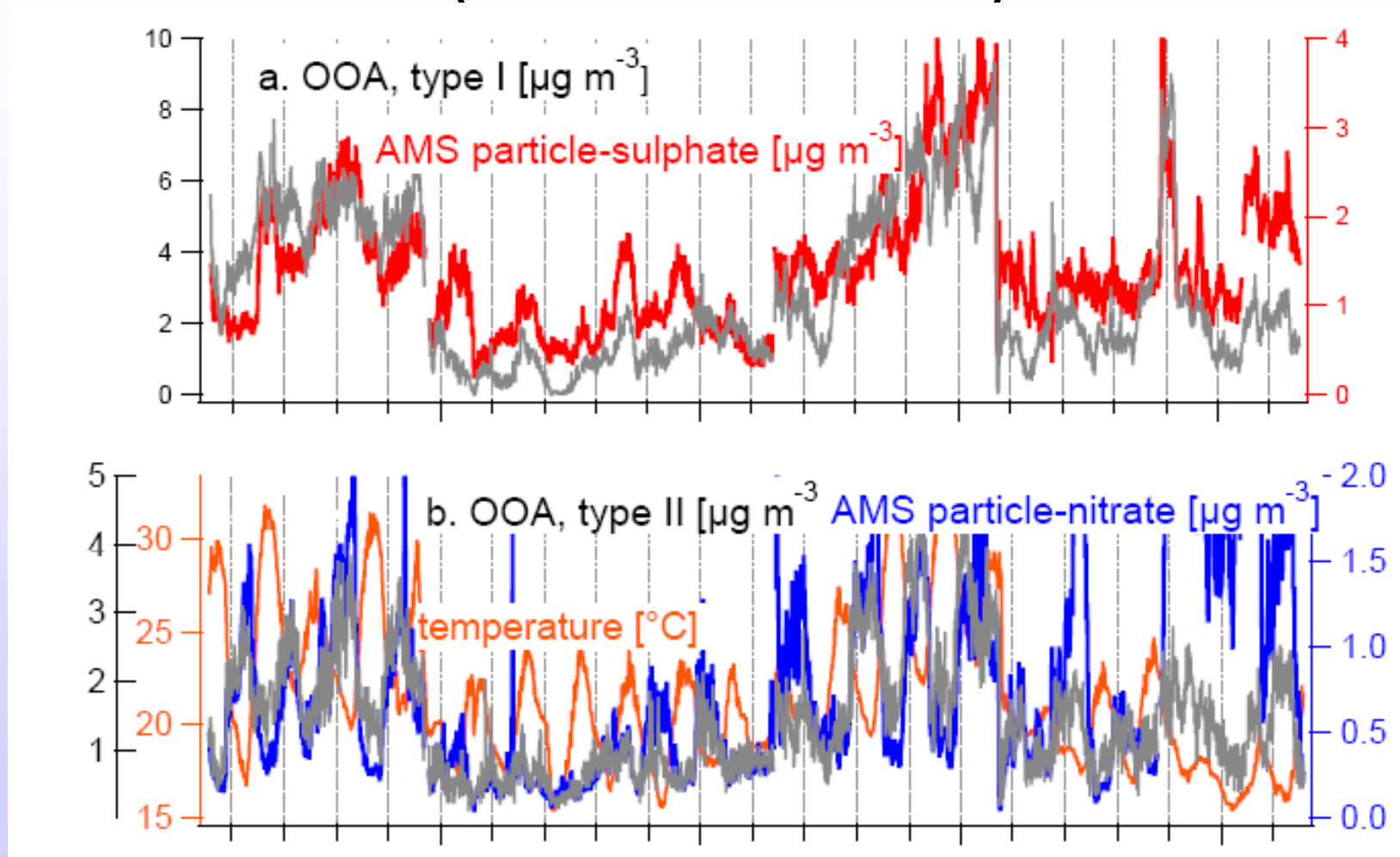
OOA probably corresponds mostly to SOA (secondary organic aerosol)

Lanz et al., ACP (2007)

Overview over the summer ^{14}C analyses

Jungfraujoch, Sommer

ECbiomass
ECfossil
OCfossil
OCnonfossil

Zürich, Sommer

ECbiomass
ECfossil
OCfossil
OCnonfossil
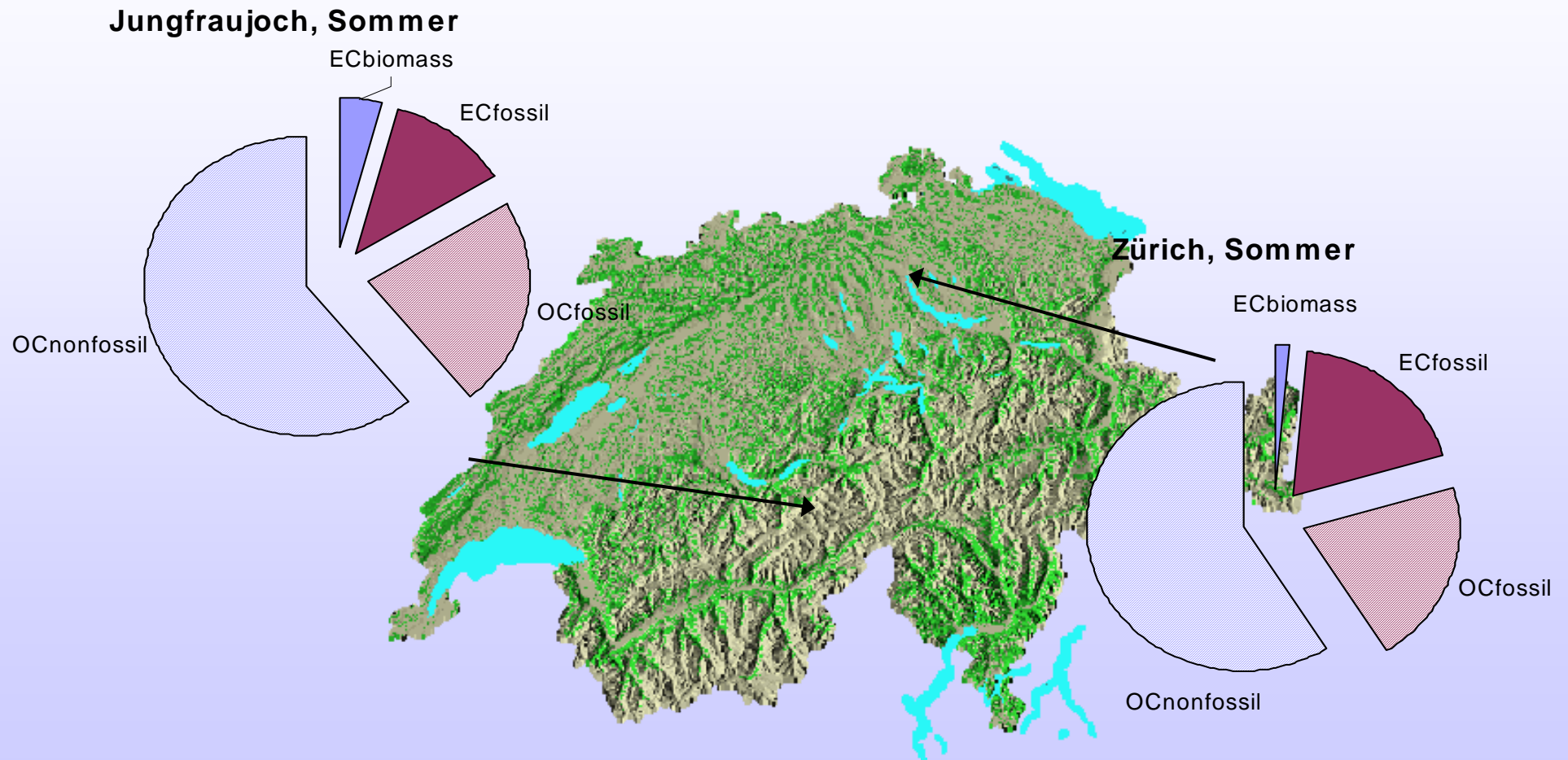
Observation of SOA oligomerization by Laser Desorption Ionization mass spectrometer

B) Time after lights on:
3.5 h

C) 4.5 h

D) 6.5 h
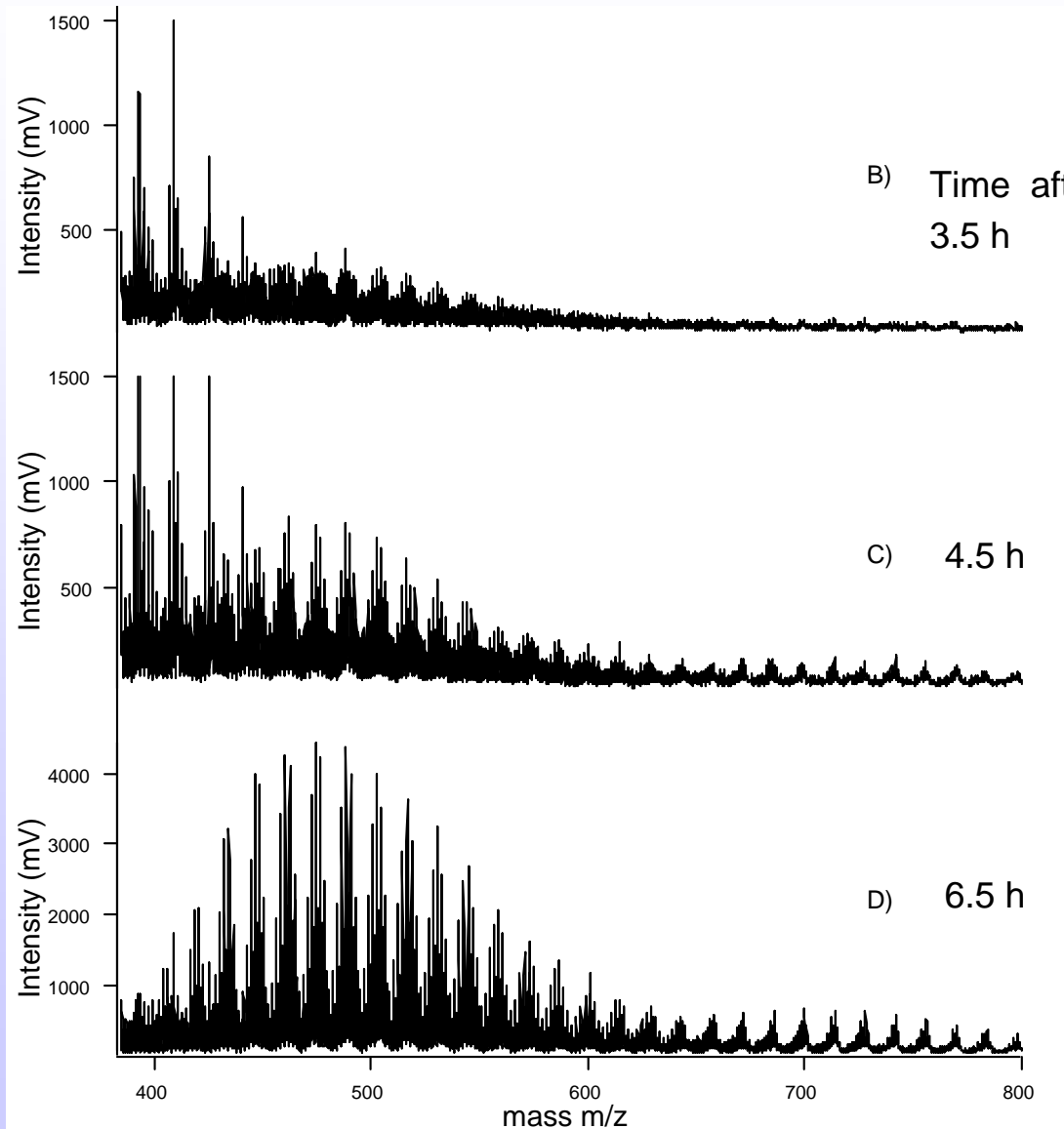
• High molecular masses are found that are not predicted by known gasphase oxidation chemistry

Kalberer et al., Science (2004)

Oligomers also found in the ambient air
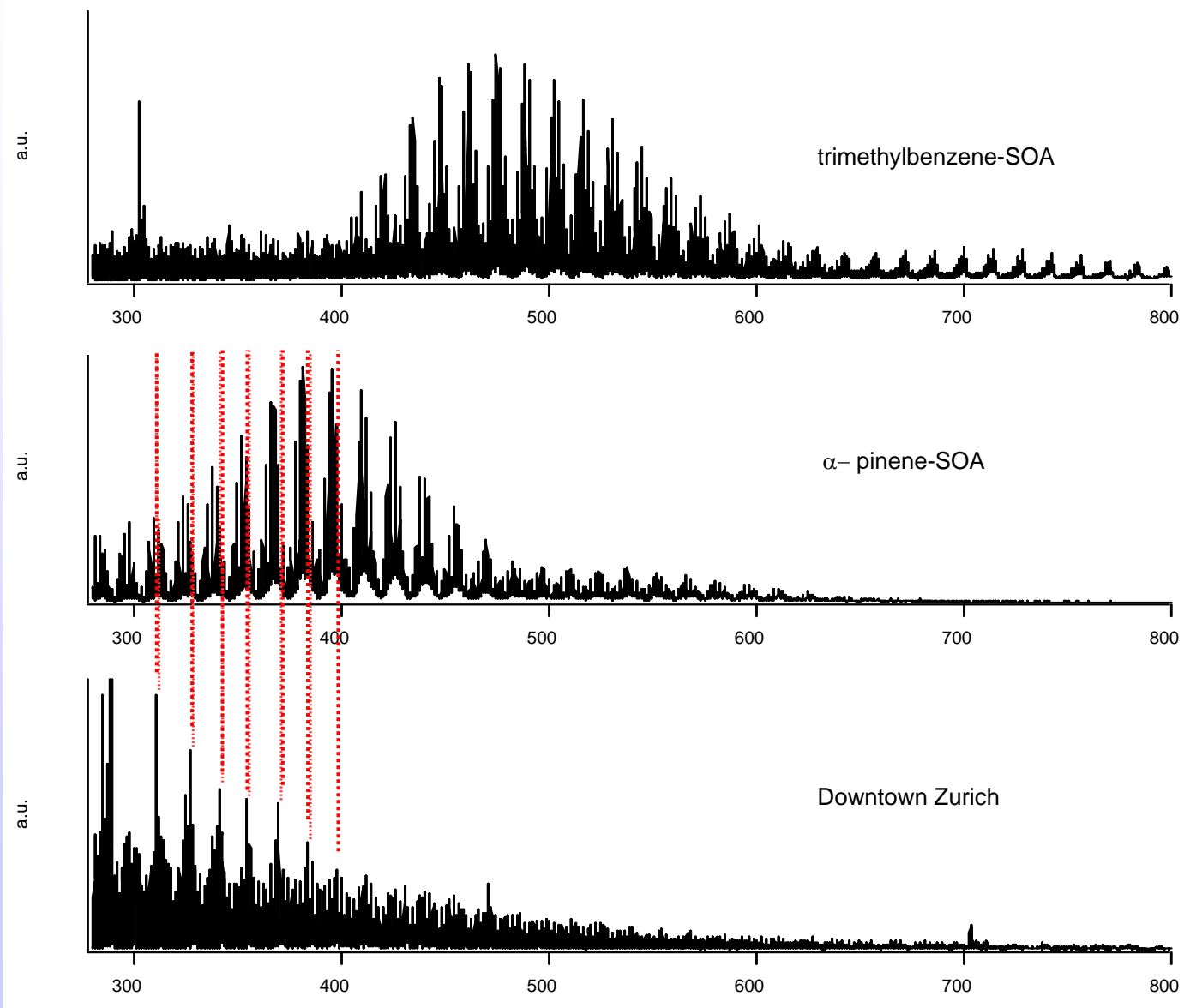
Pattern of Zurich points to α-pinene rather than TMB (or other anthrop. precursors)

Baltensperger et al. Faraday Disc. (2005)

Levoglucosan measurements versus ^{14}C and aethalometer analyses
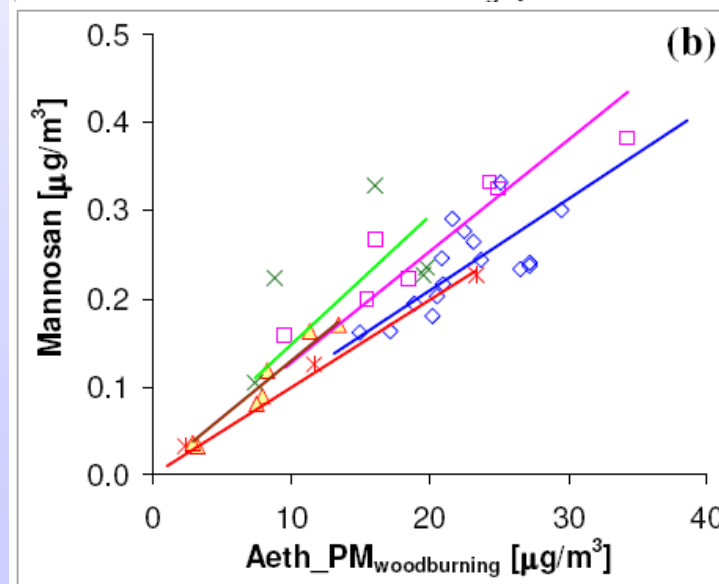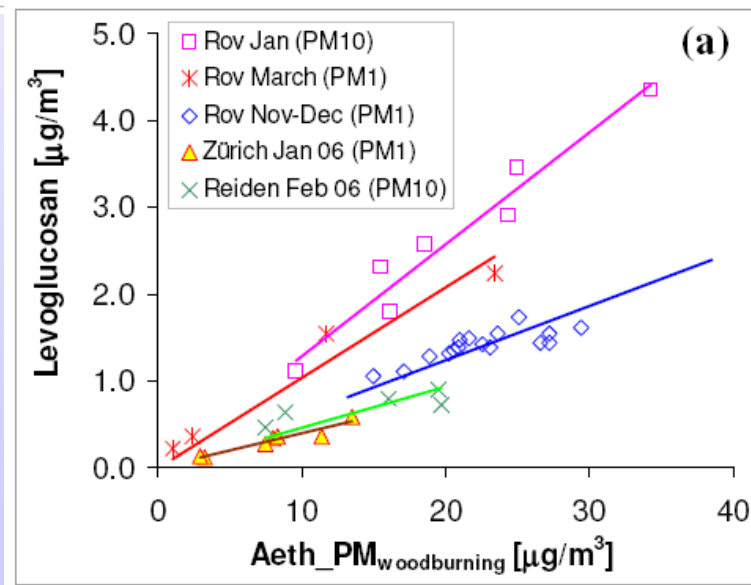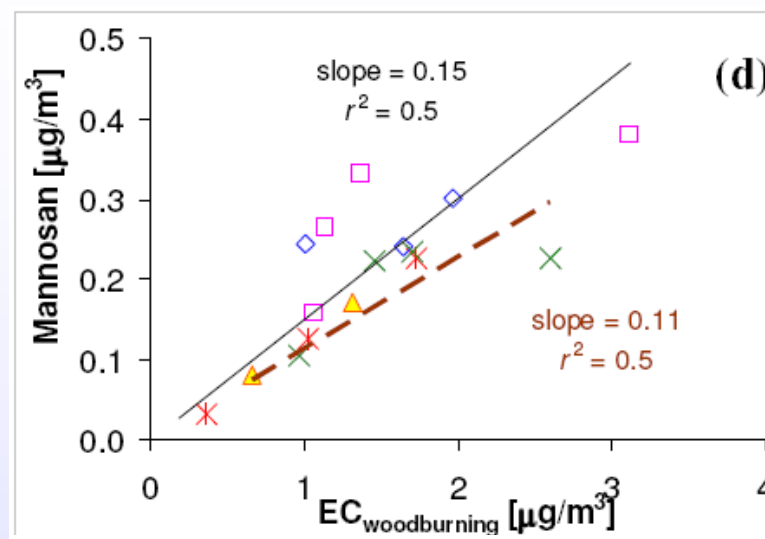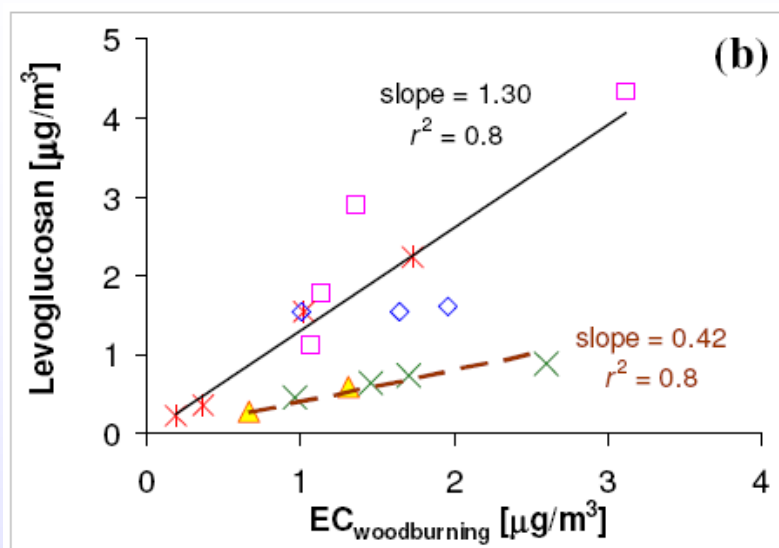
Sandradewi et al., ACPD (2008)

- Are different slopes caused by different emission properties or by atmospheric processing ??

EUROPEAN CARBOSOL project

$$SOA_{non\text{-}fossil} \, 1.15 = (\underline{EC} + \underline{OC}) \, \underline{f_M} - (OC_{bio}) \, 1.07$$
$$- (EC_{BB} + OC_{BB}) \, 1.15 - (EC_{FF} + OC_{FF} + SOA_{FF}) \, 0$$

$$SOA_{FF} = \underline{OC} - (OC_{BB} + OC_{FF} + OC_{bio}) - SOA_{non\text{-}fossil}$$
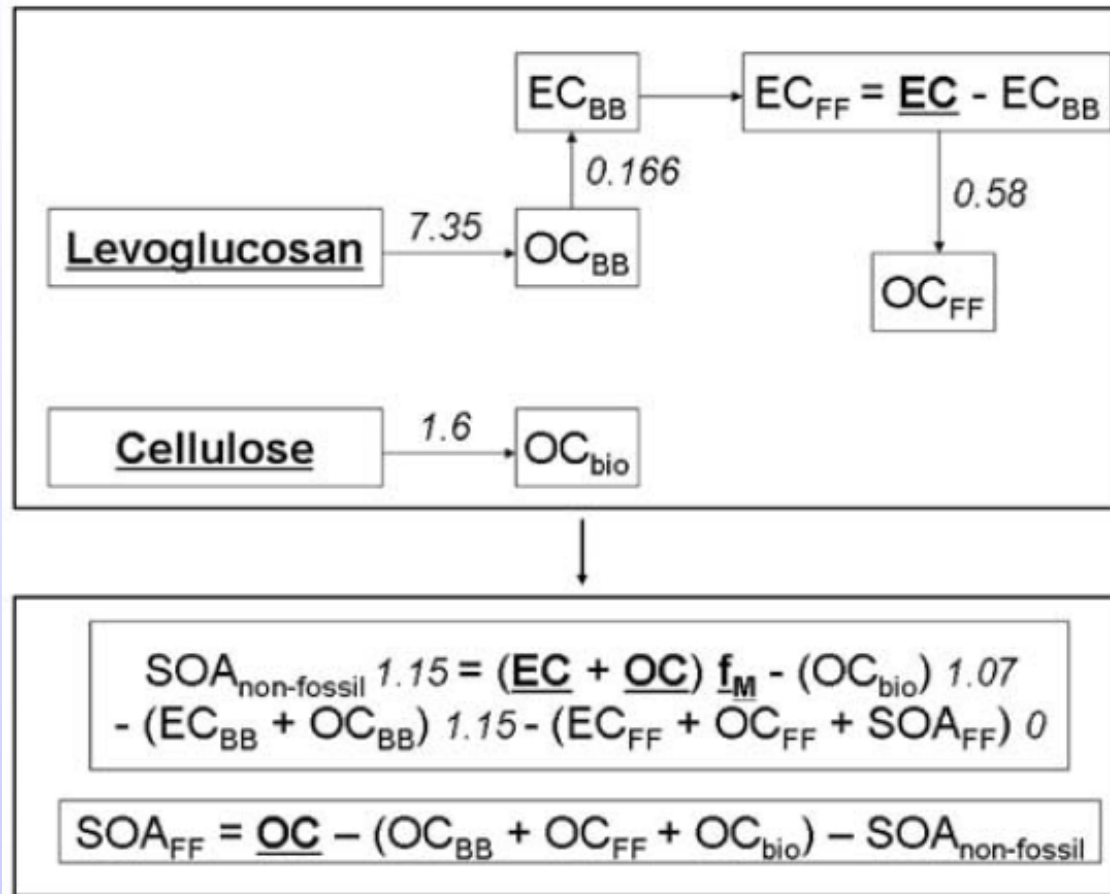
Gelencser et al., JGR, 2007

Levoglucosan yearly cycles at different sites in Europe
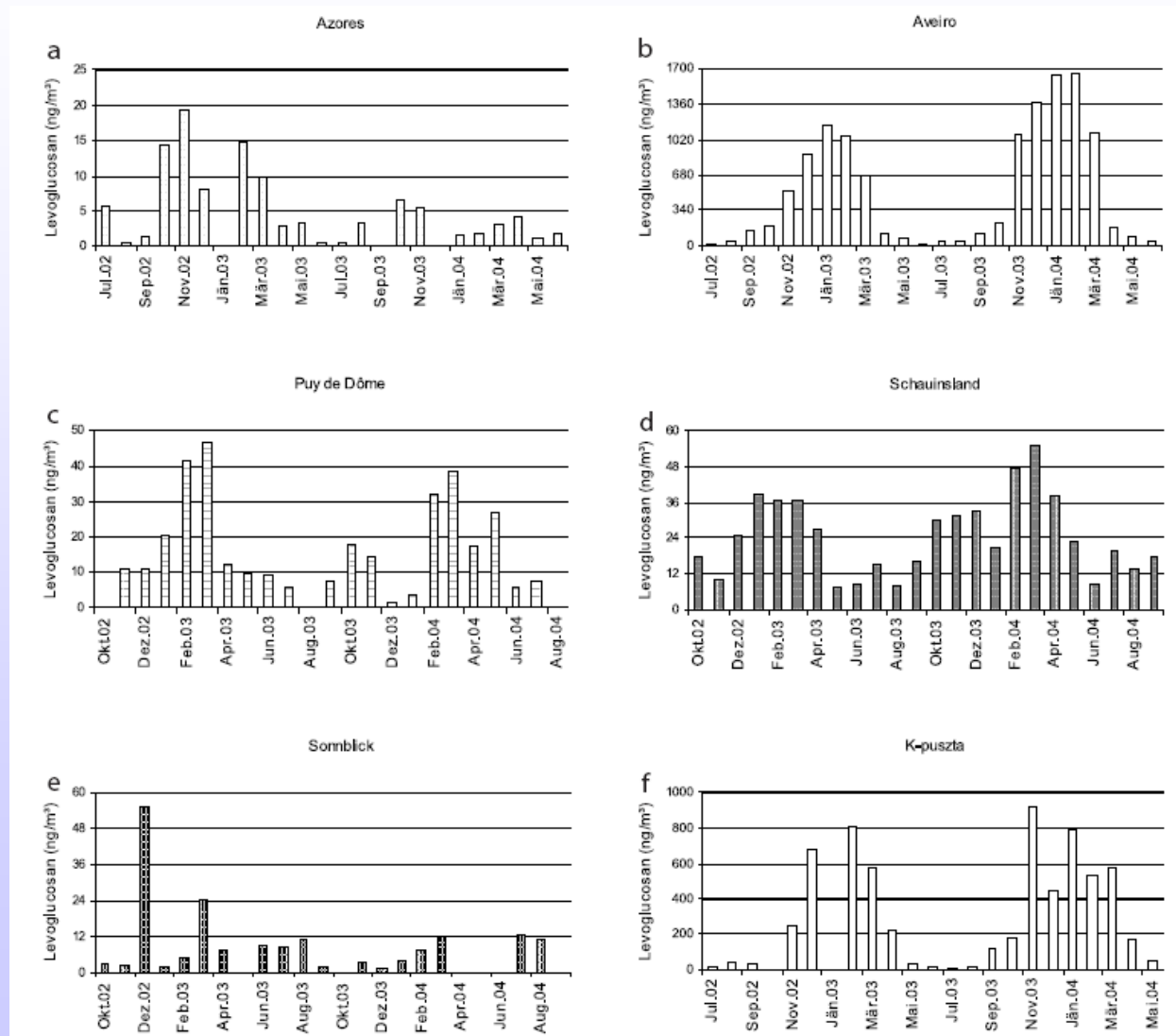
Results of source apportionment of OA (PM2.5) during the CARBOSOL project

Table 4. Relative Share of OC and EC Source Categories Within Total Carbon (TC)[a]

| Site	Season	OC_{BB}, %	EC_{BB}, %	OC_{FF}, %	EC_{FF}, %	OC_{bio}, %	$SOA_{nonfossil}$, %	SOA_{FF}, %
AVE	winter	64 (52–69)	11 (4.0–12)	1 (0.6–7.8)	2 (1.0–10)	1 (0.7–2.3)	5 (1.8–23)	16 (1.7–20)
AVE	summer	7 (5.7–11)	1 (0.5–5.0)	7 (4.6–14)	13 (7.9–16)	2 (0.8–2.9)	63 (52–65)	7 (1.8–19)
PDD	winter	9 (7.1–14)	2 (0.6–6.5)	13 (8.7–21)	23 (15.4–27)	3 (1.5–5.3)	44 (33–47)	7 (1.2–21)
PDD	summer	1 (0.9–1.7)	0 (0.1–0.7)	3 (2.3–6.7)	6 (4.2–6.9)	4 (2.2–7.7)	76 (66–78)	10 (6.3–19)
SIL	winter	14 (12–23)	2 (1.0–10)	8 (3.6–14)	15 (5.7–18)	2 (1.0–3.8)	54 (37–57)	4 (1.0–21)
SIL	summer	2 (1.5–2.9)	0 (0.1–1.3)	3 (2.3–7.0)	6 (4.2–7.3)	5 (2.9–10)	70 (60–73)	13 (8.8–21)
SBO	winter	11 (5.8–11)	2 (0.5–4.8)	5 (2.5–10)	8 (4.1–11)	8 (4.1–14)	46 (37–56)	22 (13–31)
SBO	summer	2 (1.5–3.0)	0 (0.1–1.3)	4 (2.9–8.7)	7 (5.4–9.0)	3 (1.7–5.8)	72 (61–77)	11 (3.5–22)
KPZ	winter	40 (33–56)	7 (2.7–13)	6 (1.6–13)	10 (2.6–16)	1 (0.7–2.6)	21 (4.1–31)	15 (3.2–28)
KPZ	summer	6 (5.3–10)	1 (0.4–4.7)	5 (3.0–9.8)	9 (5.0–11)	5 (2.7–9.2)	69 (57–71)	4 (1.0–15)

[a]Indices are the same as in Table 3. In parentheses the 5th and 95th percentiles are given as derived from the LHS statistical analysis.
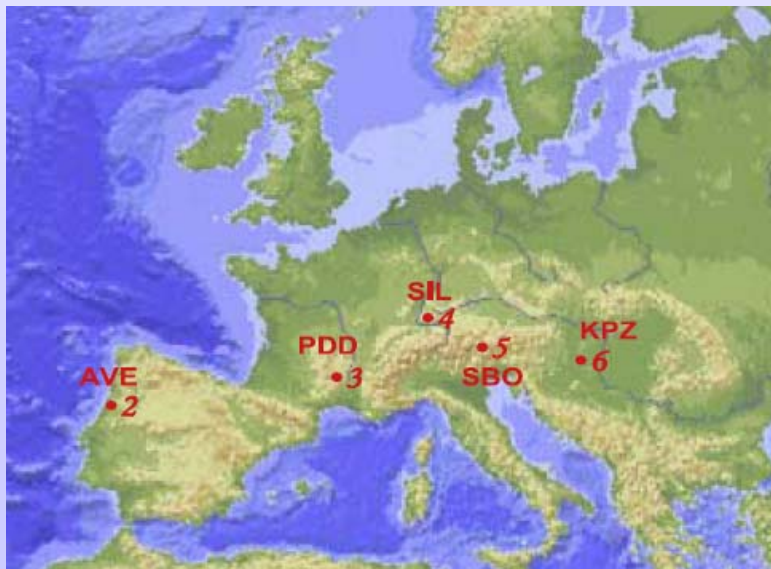
- SOA, especially non-fossil very important

- EC from fossil fuel mostly more important than EC from biomass burning

- OC from wood burning often more important than from traffic

- OC from primary biogenic sources less than 10%

Gelencser et al., JGR, 2007

TORCH campaign at Writtle, Essex July/August 2003

TORCH 2003 campaign site

Field measurements by:

Univ. York
Univ. Manchester
Univ. Leeds
Univ. East Anglia
Univ. Leicester
Univ. Aberystwyth

© Collins Bartholomew Ltd 2003   50 Miles
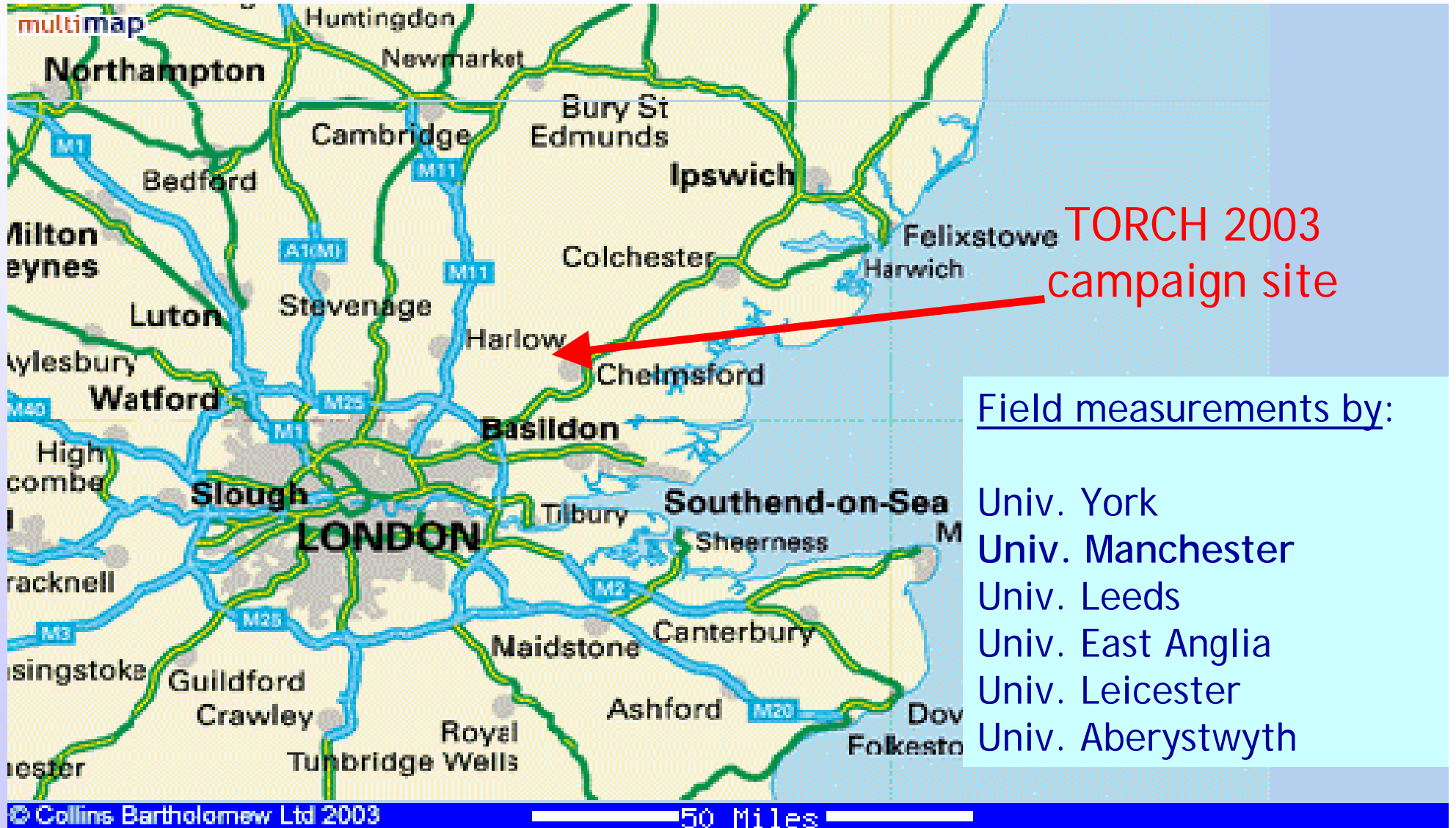
Observed and optimised simulated organic aerosol (MCM)
POA: estimated primary organic aerosol
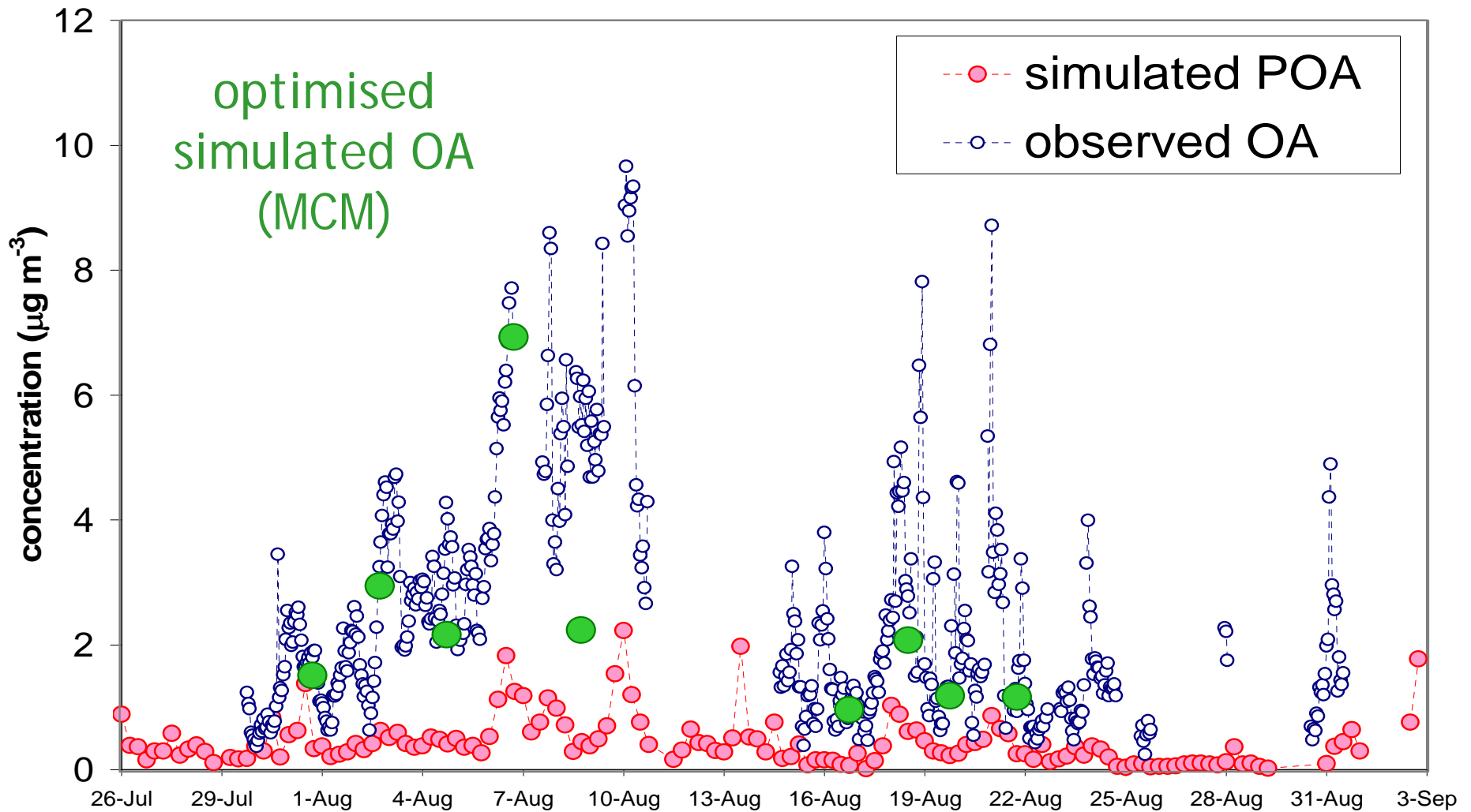
Johnson et al., ACP, 2006

Simulated OA for 9 case studies

Optimisation required:

- Assumption of a background concentration of a persistent (i.e. non-volatile) organic aerosol (model initialisation):

Background (hourly-mean) OA = 0.7 μg m^{-3}

- Scaling of partitioning coefficients for semi-volatile products of VOC oxidation:

Scaling factor = 500
(compared with ca. 10 –100 for chamber simulations)

Johnson et al., ACP, 2006
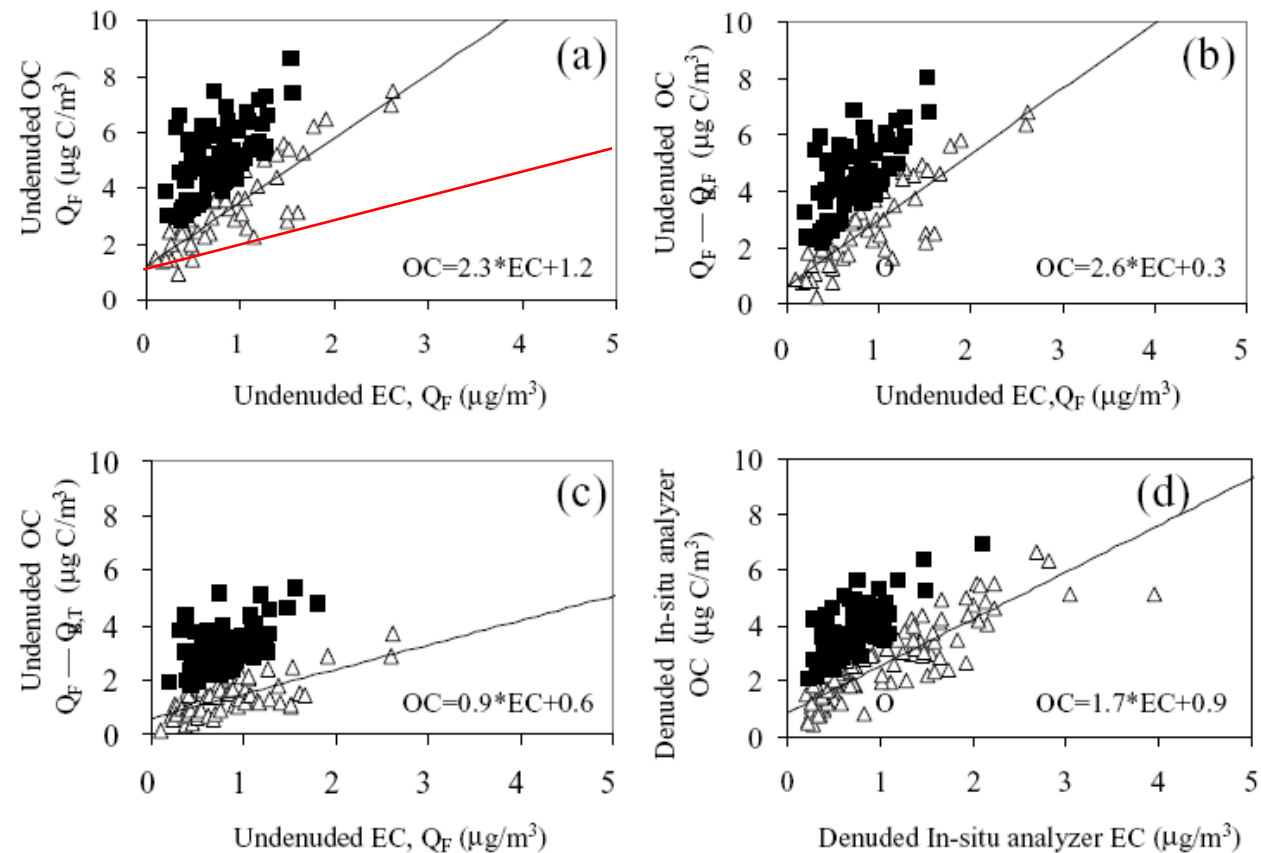
Figure 5. Estimated carbonaceous concentrations influenced by primary emissions and SOA production for high time resolution measurements (2–6 h samples) during the summer intensive at PAQS. Solid squares correspond to SOA-influenced concentrations and hollow triangles to primary-dominated concentrations. (a) Front quartz OC (Q_F) and EC concentrations. (b) Correcting the OC measurement with the backup quartz filter behind the front quartz ($Q_F - Q_{B,F}$). (c) Correcting the OC concentrations with the backup quartz filter behind the Teflon filter in the parallel undenuded line ($Q_F - Q_{B,T}$). (d) Denuded in situ analyzer.

Cabada et al., AS&T, 2004

Primary versus secondary OC in Pittsburgh from EC-OC method and AMS data
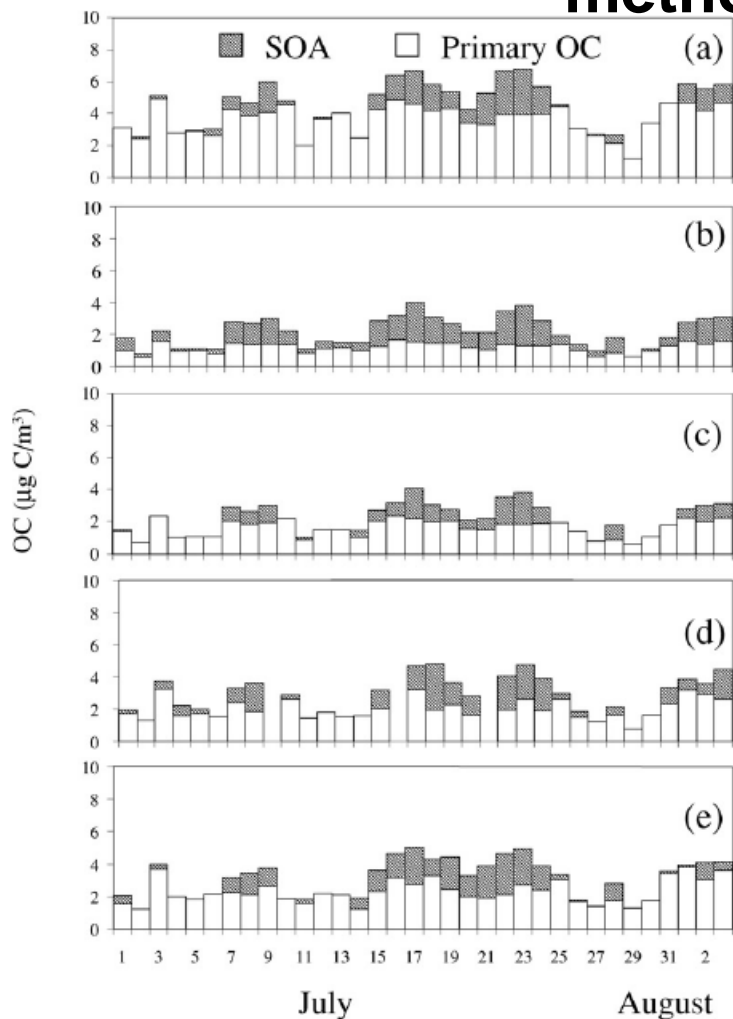
Figure 11. Daily-averaged SOA and primary OC concentrations during the summer intensive, estimated from the daily-averaged concentrations (24 h averages). (a) Undenuded sampler, Q_F. (b) Undenuded sampler, $Q_F - Q_{B,F}$. (c) Undenuded sampler, $Q_F - Q_{B,T}$. (d) Concentrations from the denuded in situ analyzer. (e) Concentrations from the denuder sampler.
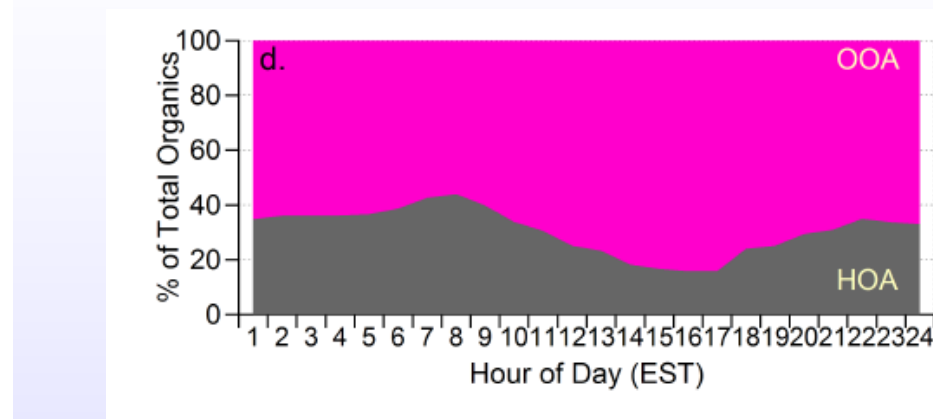
Fig. 12. Fractional distributions of (a) HOA and OOA estimated from the AMS data and POA and SOA estimated from OC/EC measurements assuming POC-to-EC ratio (b)=1.2, (c)=1 and (d)=2. POA and SOA are converted from POC and SOC assuming OM:OC ratios of $1.2\,\mu g\,m^{-3}/\mu g C\,m^{-3}$ and $2.2\,\mu g\,m^{-3}/\mu g C\,m^{-3}$, respectively.

Cabada et al., AS&T, 2004

Zhang et al., ACP, 2005

Measured tracers for different SOA precursors

Table 1
Tentative identification for organic compounds serving as tracer compounds

| Tracer ID	Organic compound name	Compound MW	Derivative MW	Major ions	Precursor HC
I-1	2-Methylglyceric acid	134	350	321, 203, 293, 219, 337	Isoprene
I-2	2-Methylthreitol	136	424	409, 219, 319, 293, 203	Isoprene
I-3	2-Methylerythritol	136	424	409, 219, 319, 293, 203	Isoprene
A-1	3-Isopropylpentanedioic acid	174	318	229, 239, 111, 275, 303	α-Pinene
A-2	3-Acetylpentanedioic acid	174	318	229, 239, 111, 257, 303	α-Pinene
A-3	2-Hydroxy-4-isopropyladipic acid	204	420	243, 153, 125, 317, 333	α-Pinene
A-4	3-Acetyl hexanedioic acid	188	332	331, 405, 449, 213, 235	α-Pinene
A-5	3-Hydroxyglutaric acid	148	364	349, 275, 303, 185, 365	α-Pinene
A-6	2-Hydroxy-4,4-dimethylglutaric acid	176	392	377, 303, 393, 343, 213	α-Pinene
A-7	3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid	172	244	227, 317, 199, 301, 345	α-Pinene
PA	Pinic acid	186	330	241, 315, 151, 197, 331	α-Pinene
PNA	Pinonic acid	184	256	257, 121, 139, 167, 187	α-Pinene
T-3	2,3-Dihydroxy-4-oxopentanoic acid	148	364	349, 247, 259, 275, 303	Toluene
C-1	β-Caryophyllinic acid	254	398	309, 383, 399, 427, 439	β-Caryophyllene

Ketopinic acid (TMS derivative) ions consist of 165, 239, 255, 283 and 295.

Kleindienst et al., Atmos. Environ., 2007

Different SOA, biomass burning and other OC
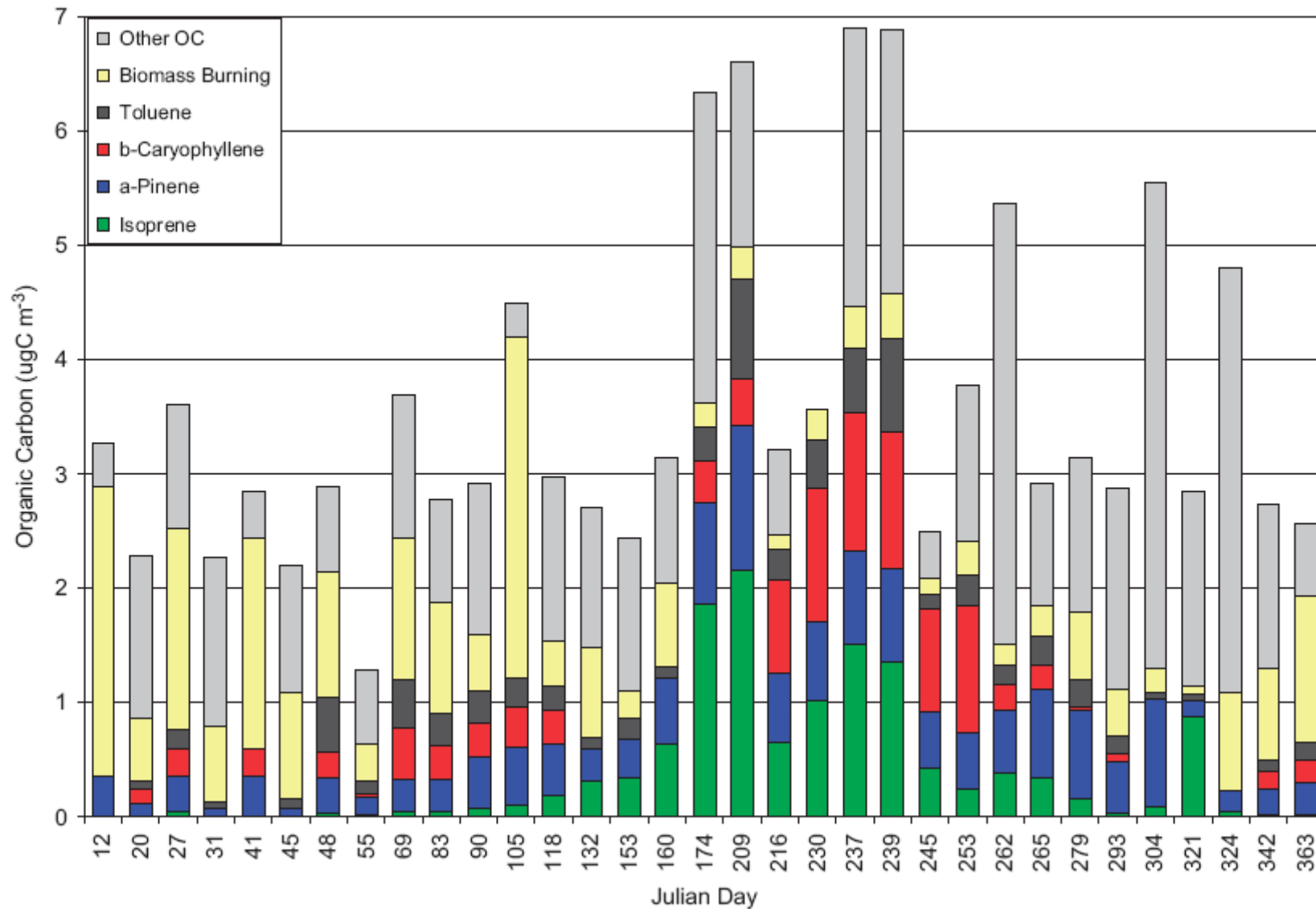
Kleindienst et al., Atmos. Environ., 2007

Estimated primary and secondary organic carbon from tracer measurements
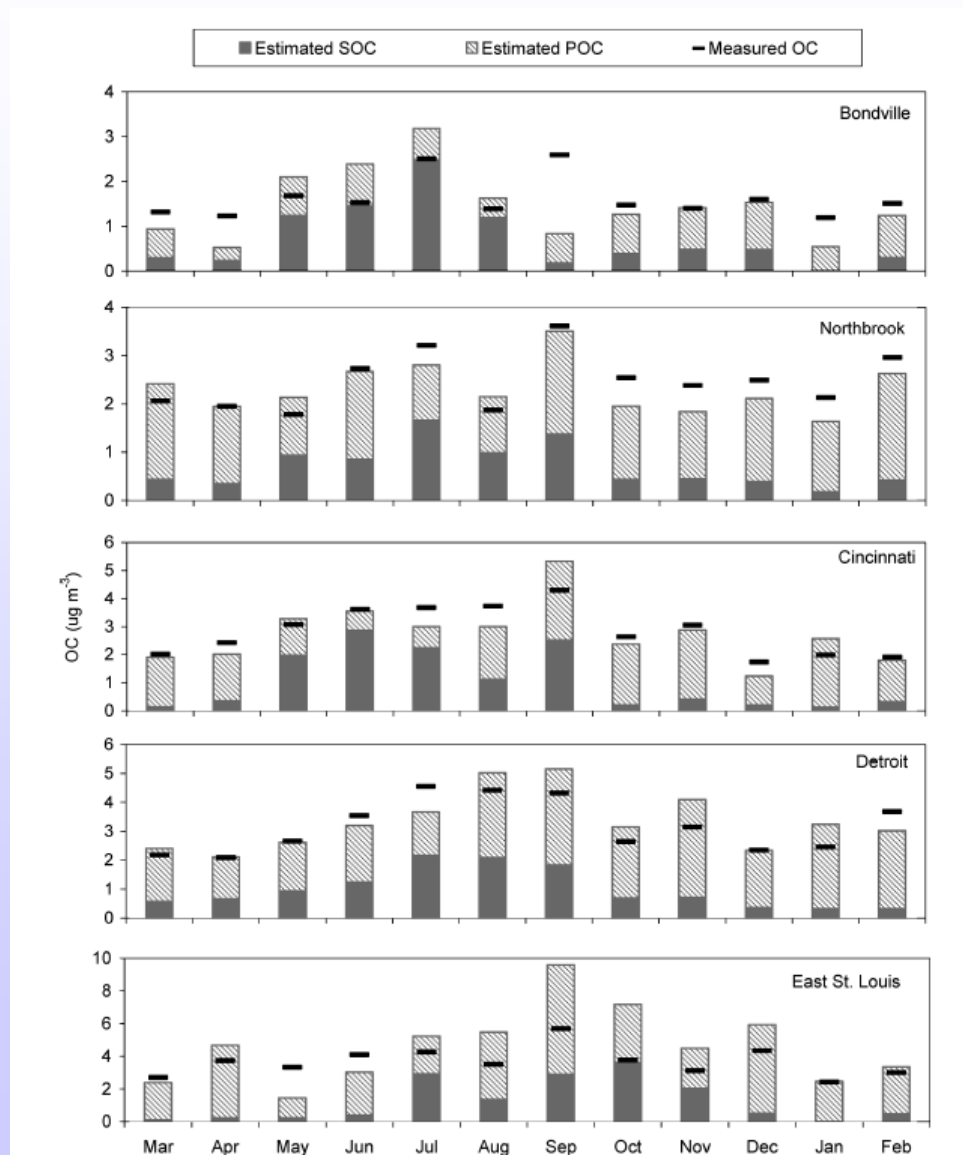
Lewandowski et al., ES&T, 2008

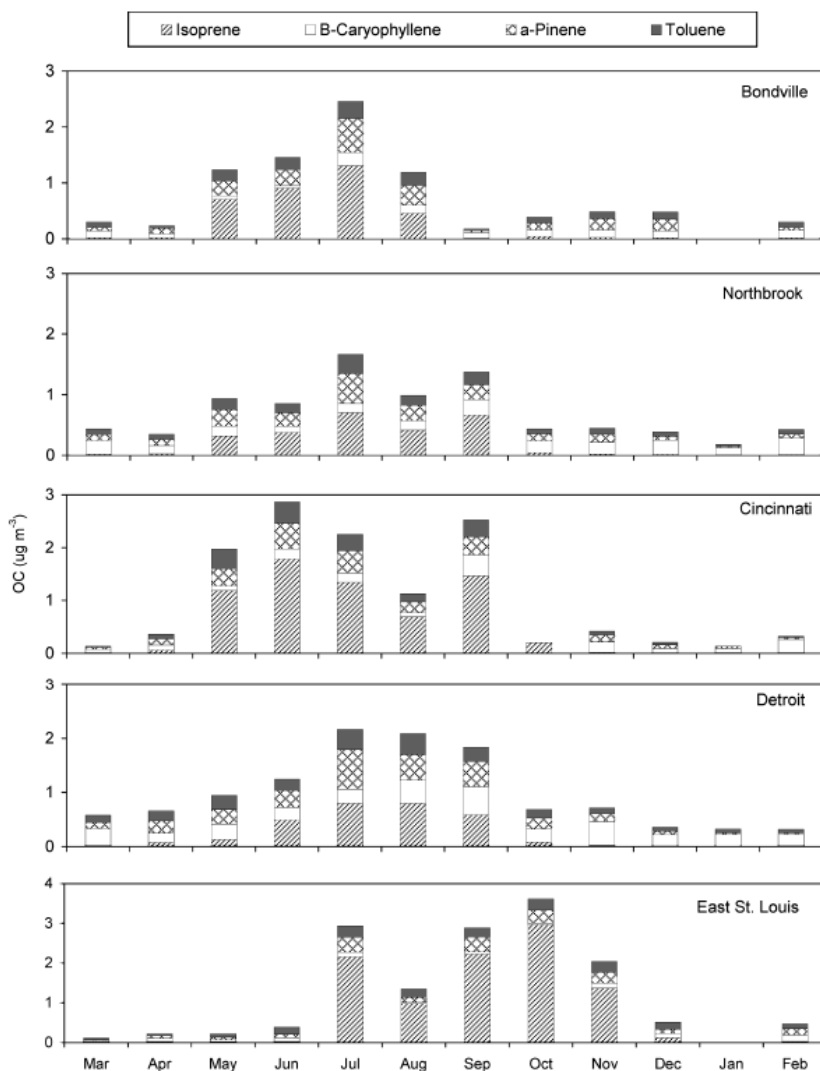# Contribution of different precursors to SOA and SOC

FIGURE 2. Detailed secondary contributions to ambient $PM_{2.5}$ in Bondville, Northbrook, Cincinnati, Detroit, and East St. Louis for March 2004 through February 2005.

TABLE 1. Seasonal and Annual SOC Averages in $\mu g\ m^{-3}$

	Mar−May	Jun−Aug	Sep−Nov	Dec−Feb	annual
Bondville					
isoprene	0.25	0.89	0.03	0.02	0.32
β-caryophyllene	0.09	0.14	0.12	0.13	0.12
α-pinene	0.14	0.42	0.12	0.13	0.21
toluene	0.12	0.25	0.09	0.12	0.15
Northbrook					
isoprene	0.12	0.50	0.24	0.01	0.22
β-caryophyllene	0.18	0.14	0.22	0.21	0.18
α-pinene	0.16	0.32	0.16	0.05	0.17
toluene	0.12	0.21	0.13	0.06	0.13
Cincinnati					
isoprene	0.42	1.27	0.56	0.01	0.56
β-caryophyllene	0.09	0.15	0.20	0.14	0.14
α-pinene	0.16	0.37	0.16	0.05	0.18
toluene	0.16	0.29	0.13	0.02	0.15
Detroit					
isoprene	0.07	0.69	0.23	0.00	0.25
β-caryophyllene	0.26	0.31	0.41	0.22	0.30
α-pinene	0.20	0.51	0.27	0.04	0.25
toluene	0.19	0.33	0.18	0.07	0.19
East St. Louis					
isoprene	0.02	1.05	2.18	0.07	0.90
β-caryophyllene	0.06	0.08	0.07	0.14	0.09
α-pinene	0.04	0.20	0.32	0.13	0.18
toluene	0.06	0.22	0.26	0.15	0.18

Lewandowski et al., ES&T, 2008

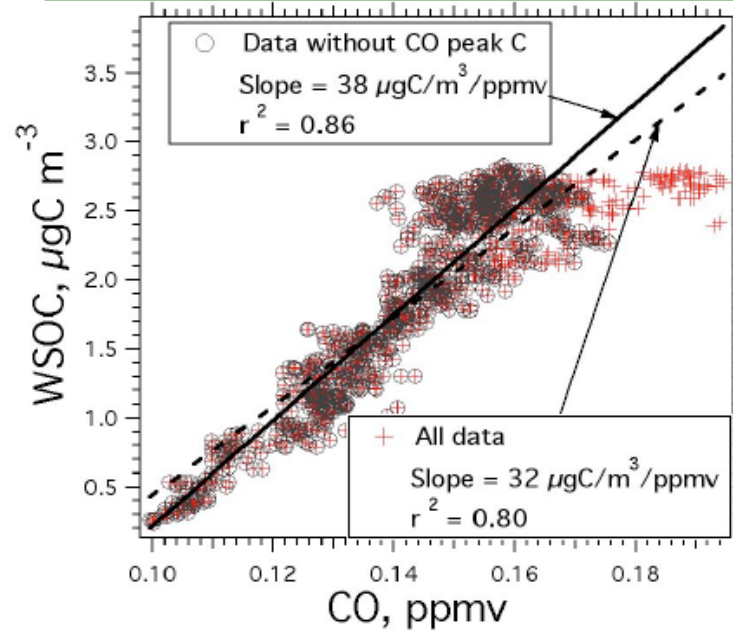Isopropyl Nitrate and WSOC Atlanta/NYC:
Correlated and Similar Proportions

Slope = 0.20 ± 0.04 µgC/m3/pptv
Intercept = 0.29 ± 0.41 µgC/m3
r^2 = 0.74
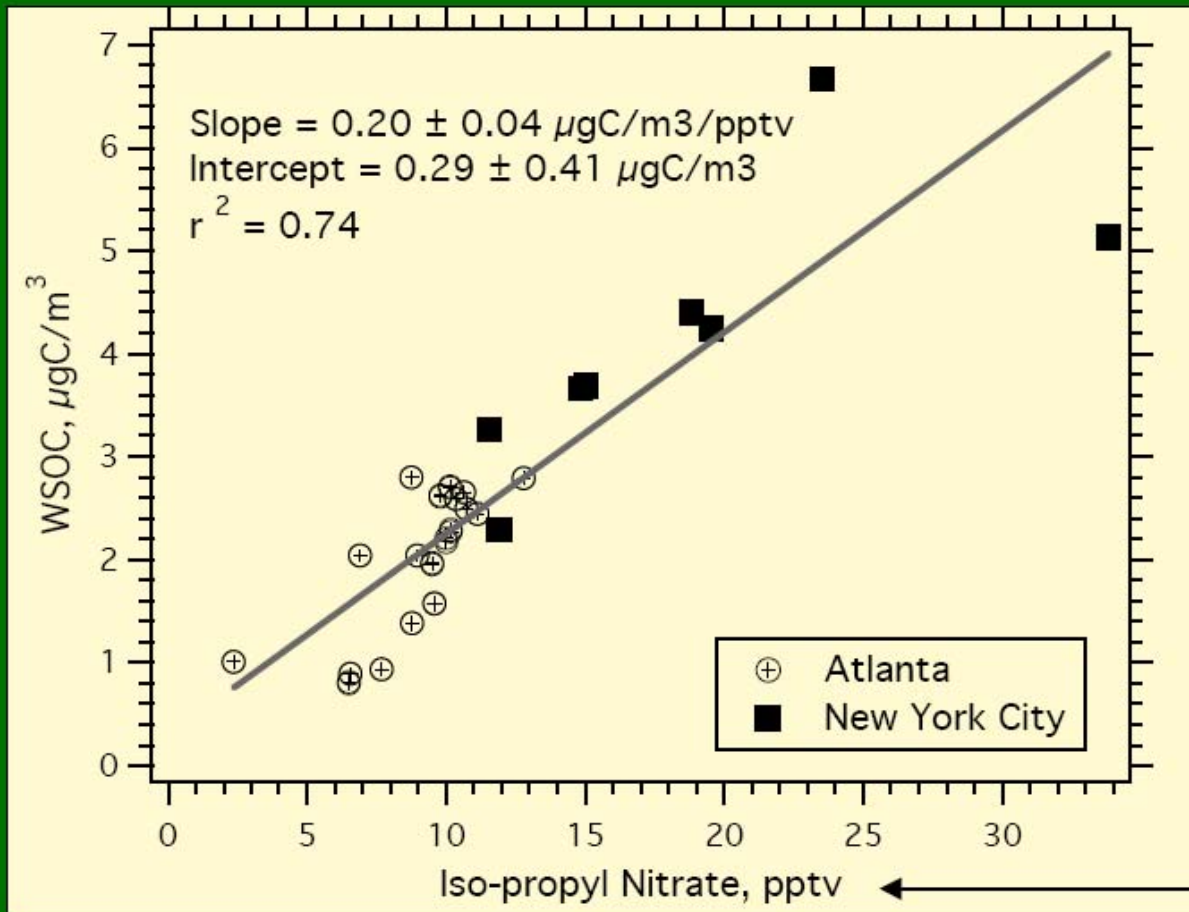
NYC plumes over 1-day old

Secondary anthropogenic VOC

Weber R. et al., JGR, 2007

Comparison: Atlanta / NYC

ΔWSOC/ΔCO: Atlanta = NYC

Slope = ΔWSOC/ΔCO
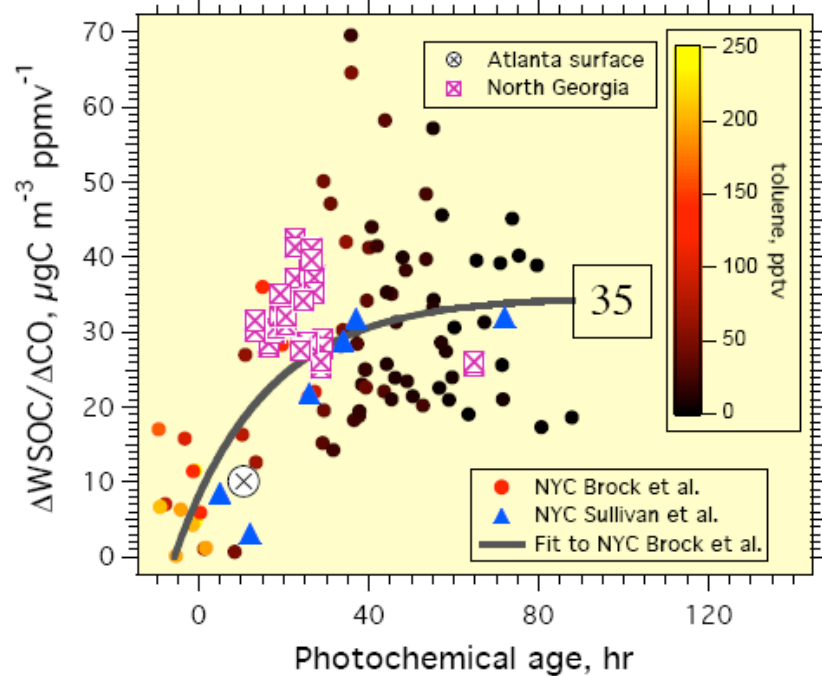
• Slope of WSOC vs CO plot = 38, similar to aged NYC plumes
OVERALL: Atlanta SOA formation seems similar to NYC

Weber R. et al., JGR, 2007

Radiocarbon on Atlanta WSOC & Levoglucosan
Expt 1: SEARCH Network Filters

^{14}C analysis on WSOC from PM2.5 Hi Volume Filters in Atlanta

Sample Date	Levoglucosan $\mu gC\ m^{-3}$	Modern Fraction
6/14/04	0.036	0.81
6/17/04	0.053	0.70
6/23/04	0.030	0.76
6/29/04	0.056	0.67

WSOC 70 to 80% Modern

Minimal biomass burning influence

Weber R. et al., JGR, 2007

Atlanta/NYC Comparison and Radiocarbon

• Atlanta: strong link between SOA formation and anthropogenic emissions.
• Atl. SOA produced per CO is similar to regions with less biogenic VOCs (i.e., NYC).
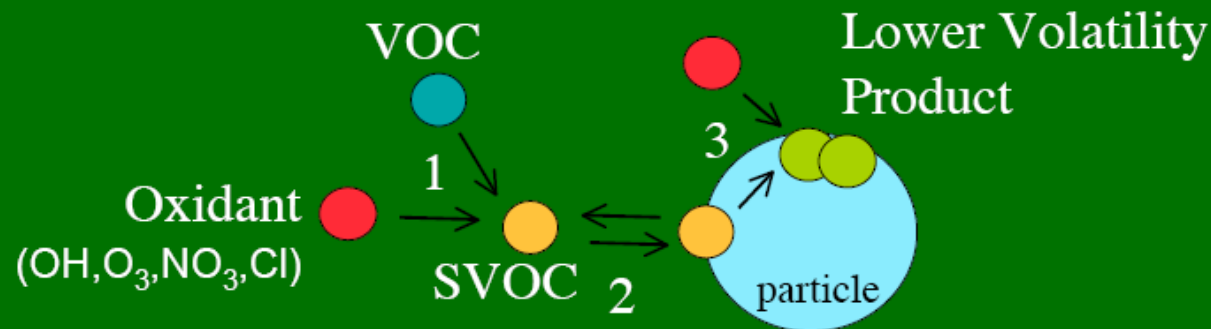
v.s.

Radiocarbon analysis suggest SOA carbon in Atlanta is largely modern.

Atlanta SOA largely involves biogenic VOCs, but the mass of SOA formed is "*controlled*" by anthropogenic component(s)

Weber R. et al., JGR, 2007

How can we explain this?

VOC

Lower Volatility Product

3

1

Oxidant
(OH,O$_3$,NO$_3$,Cl)

SVOC   2

particle

Mass of SOA formed controlled by:
1) VOC oxidation step (oxidant or other component, e.g. NO)
   • Results analogous to NOx limited O$_3$ production
2) Partitioning step (function of preexisting particulate OC)
3) Heterogeneous reactions forming low volatility products
   (e.g., anthropogenic component leads to oligomers)

Kanakidou, M., K. Tsigaridis, F.J. Dentener, and P.J. Crutzen (2000), Human-activity-enhanced formation of organic aerosols by biogenic hydrocabon oxidation, *J. Geophys. Res.*, *105* (D7), 9243-9254.
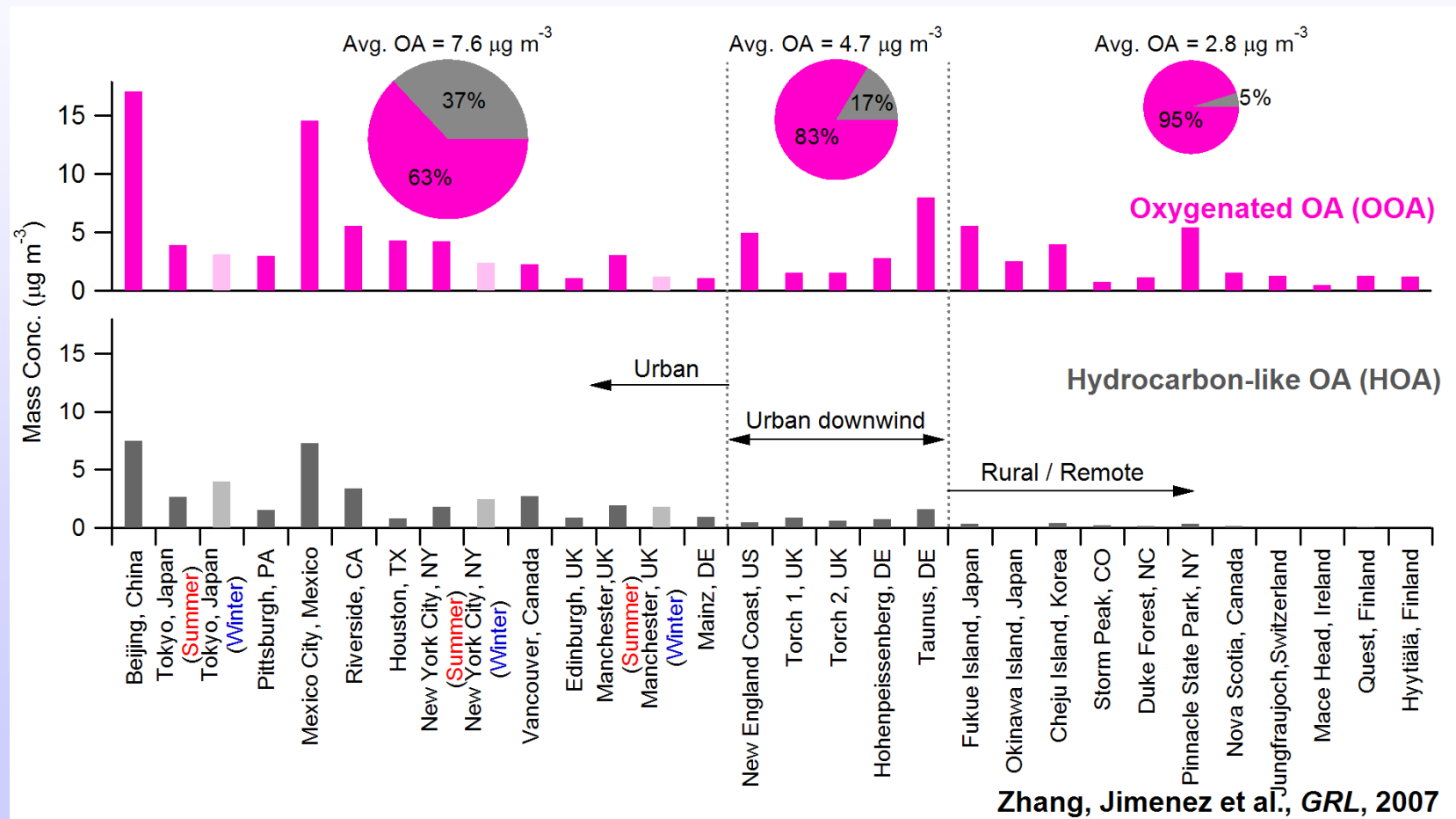
Weber R. et al., JGR, 2007

Relative composition of organics, sulfate, ammonium, nitrate
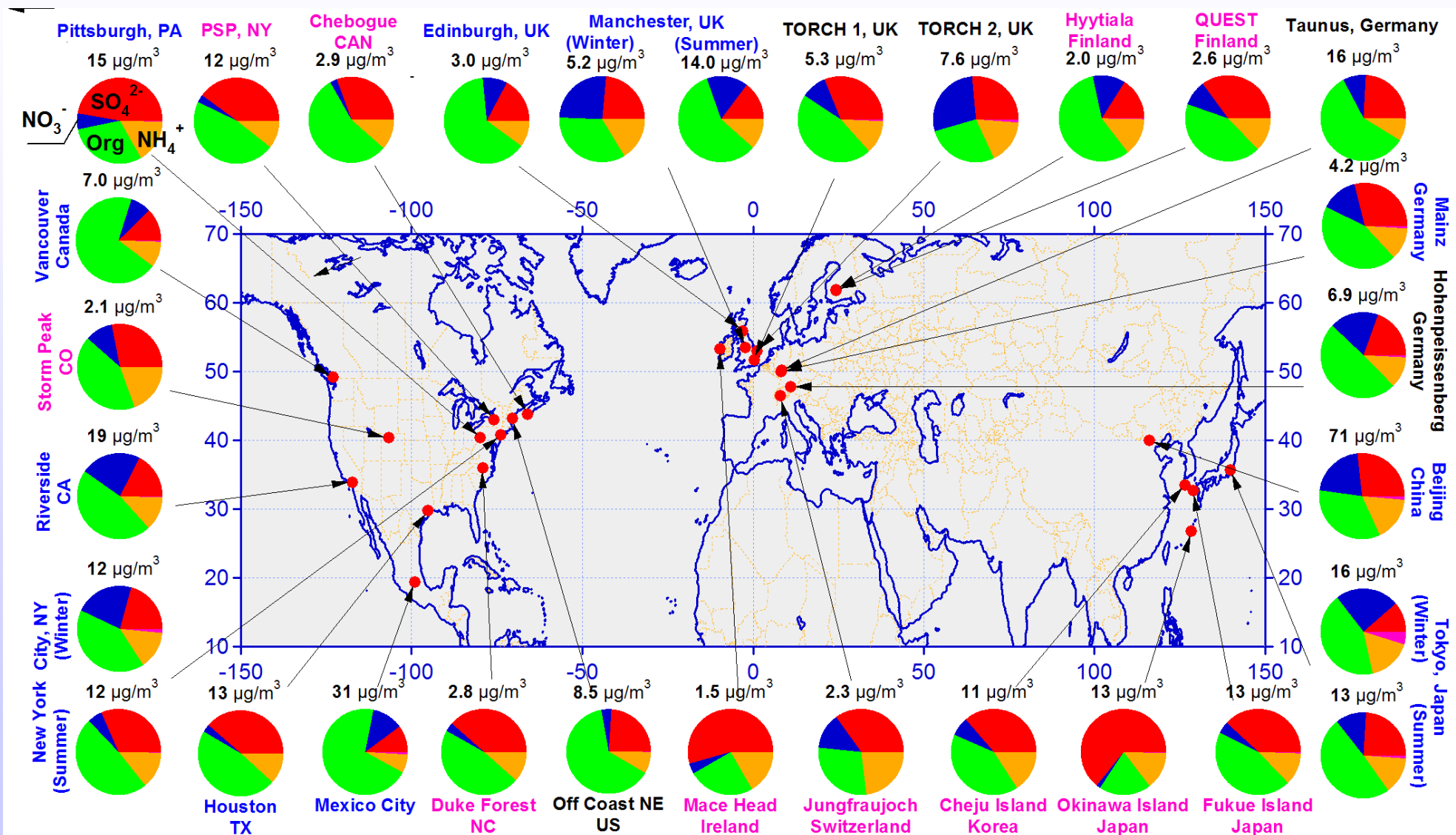
Zhang, Jimenez et al., *GRL*, **2007**

Field Measurements of organic aerosols

Relative composition of hydrocarbon-like and oxygenated organic aerosol in different parts of the world

Summary

♦ Black/elemental carbon in Switzerland mostly due to fossil sources (diesel)

♦ Organic mass is in Switzerland dominated by OOA (probably mostly SOA), in both winter and summer dominated by non-fossil contributions (SOA from biogenic precursors and OA/SOA from wood burning)

♦ In Europe, at many places wood burning is considered to be more important than previously thought. In winter it is and will be more important than traffic because of the emission reductions due to particulate filters of diesel vehicles

♦ Also in the United States, non-fossil OA is dominating over fossil OA. However SOA still seems to be connected to anthropogenic activity.. Explanation not clear..

♦ At many places of the world, the most important fraction of PM1 is the organic aerosol. At most places, the oxygenated aerosol is much more important than the hydrocarbon-like aerosol

♦ Measurements show often more OA (especially OOA or SOA) than expected by models

FUTURE

- ◆ More combined off-line and on-line analyses at the same location

- ◆ More advanced long-term monitoring

- ◆ Combination of various stations and aircraft data like in Mexico City

- ◆ More smogchamber/flow tube versus field comparisons for process studies

- ◆ More combination of chemical and physical characterization of the aerosol

- ◆ Further improvement of models with inclusion of new processes necessary