An overview of recent OC/EC and organics aerosol particle measurements of TROPOS ACD

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Field studies

- **Aerosol measurements**
  in the polluted regime (East middle Europe, China)
  under marine conditions (Baltic, northern tropical atlantic), the SML, concerted measurements (MARPARCLOUD; MARSU)
- Field aerosol-cloud studies (such as FEBUKO or HCCT-2010)
- Biomass burning (such as SEIFFEN)
- Dust-related studies (CVAO, SALTRACE)
- **Dedicated case studies (often on regional air quality, with agencies)**

Lab studies

- ‚New' gas phase chemistry (Criegees, HOMs, terpenes, isoprene)
- Chamber studies (SOA)
- Aqueous phase chemistry (aqSOA, radicals, kinetics and photochemistry)

Multiphase Modelling

- Different flavours of CAPRAM

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Outline

- **(1) Leipzig Aerosol 2013-2015 project**

  PM Sources & Changes

  Emphasis on primary emission species

- **(2) BB studies in Germany**

  Seiffen study 2008

  Melpitz study 2012 - 2014

- **Summary**

Part 1: LfULG Aerosol Project (2013 - 2015)

Tasks and goals ‘Leipzig Aerosol 2013-2015’ project

- **Scientific measurements to characterize air quality at 4 sites in/around Leipzig**

- Continuous number size distributions + BC (cf. Alfred)

- **Size-resolved chemical particle characterization during selected days**
  → Assess local/regional air quality beyond legislative parameters

- **Source apportionment of PM**
  → Identify main sources and analyze impact of biomass burning and long-range transport

- **Compare with data from similar project in 1999/2000**
  → Assess changes in air quality

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Experimental approach

- 2 Campaigns (summer+winter 2013-2015)
- 4 Sampling sites in parallel
- 24h samples with 5-stage Berner impactor during 21 sampling days per season
- Comprehensive chemical characterisation
  → inorganic ions
  →OC/EC, WSOC
  → organics: oxalate, mono-saccharides, alkanes, PAHs, hopanes
  → metals

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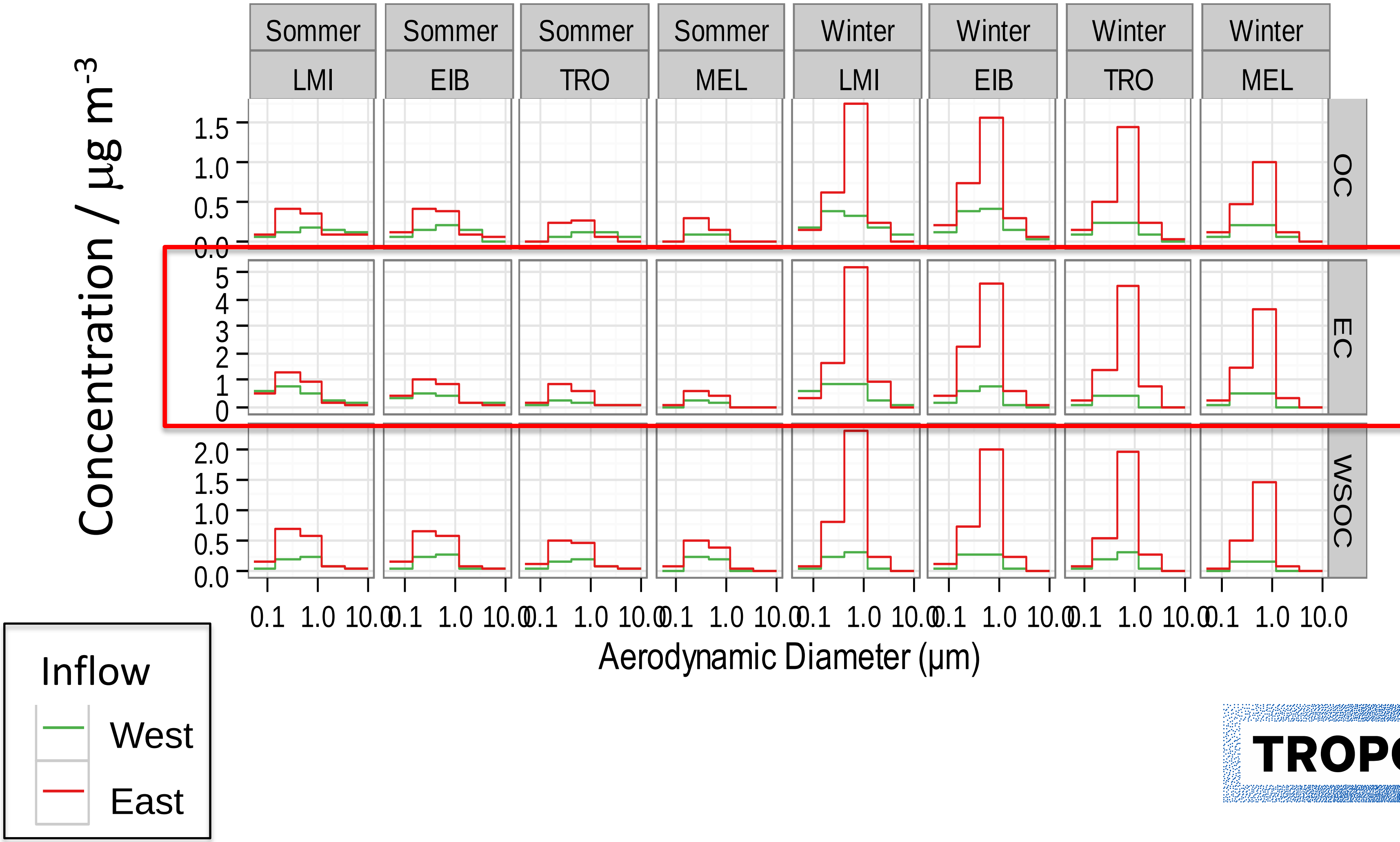
Results:
Composition and Sources

Multidimensional dataset: Season/Site/Species/Size/Sector

Mean size distributions of main PM constituents per season, site, species, and inflow sector - here OC, EC, WSOC:



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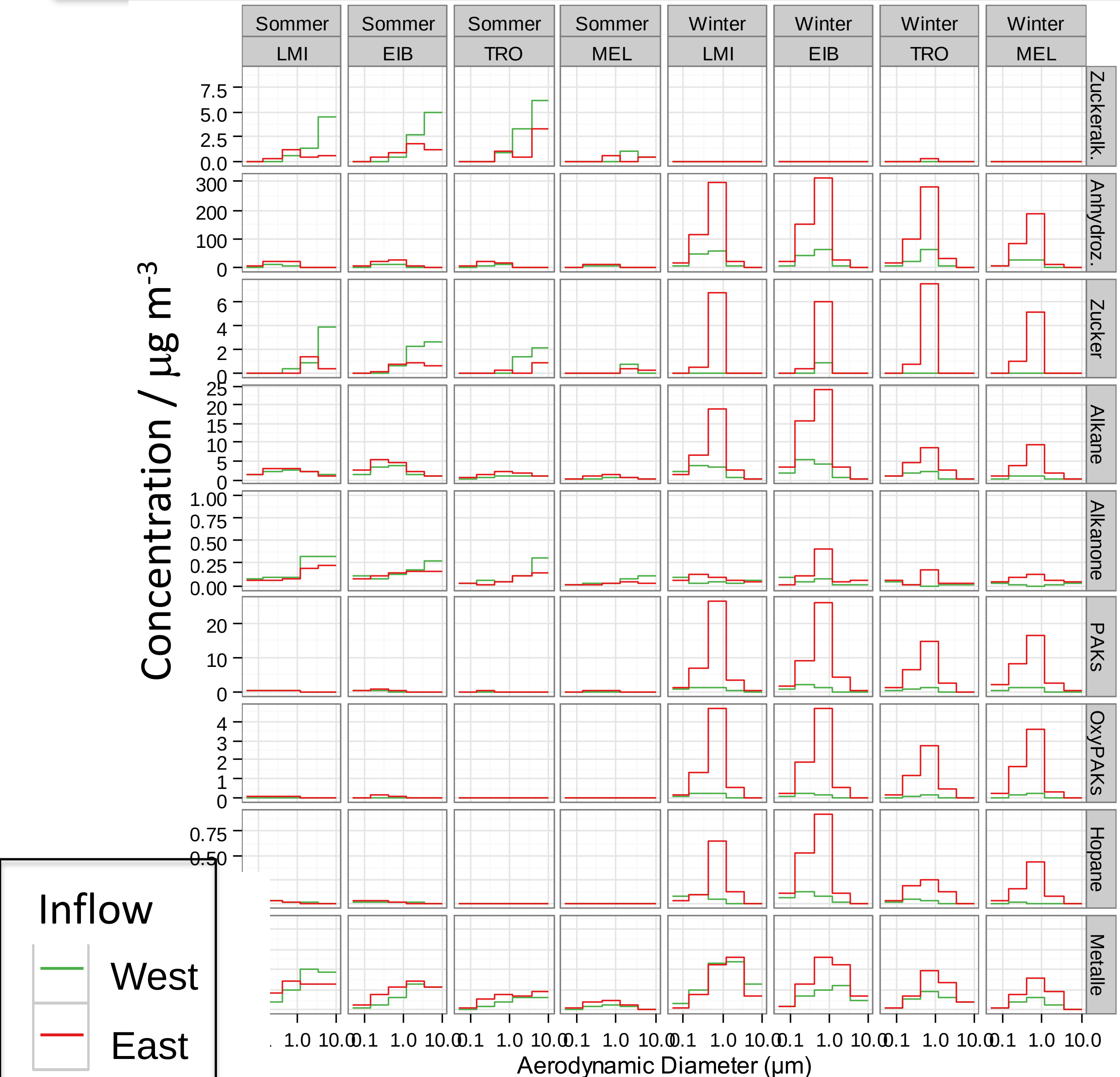
Multicategorial dataset: Season/Site/Species/Size/Sector



Sugaralcohols (arabitol)

Anhydrosugars (levo)

Sugars

Alkanes

Alkanones

PAHs

Oxy-PAHs

Hopanes (traffic/coal burning)

Metals

Source apportionment approaches I: Lenschow

Lenschow et al., 2001:

PM as superposition of sources in different regions

traffic increment = c(LMI, EIB) - c(TRO)

urban background increment = c(TRO) - c(MEL)

regional background = c(MEL)

Macrotracer

Use established ratios of characteristic constituents to derive source conc.

$PM_{BiomassBurning}$ = c(Levoglucosan) x 11 (Schmidl et al., 2008)
$PM_{FungalSpores}$ = c(Arabitol) x 28 (Bauer et al., 2008)

Positive Matrix Factorization (PMF)

Factor analysis method to extract underlying sources in multidimensional datasets

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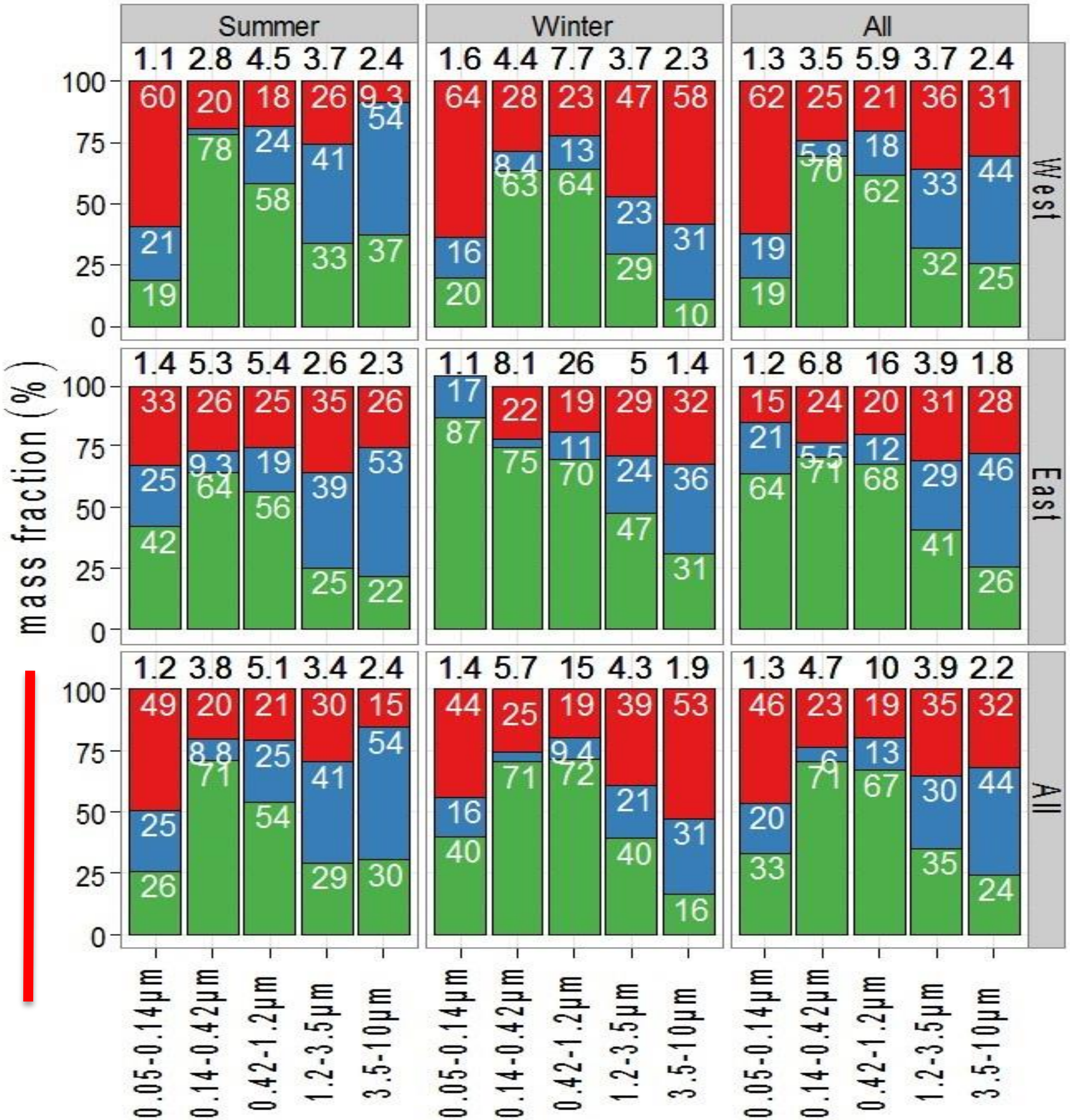
Lenschow: Local vs. regional PM mass contributions at LMI



Typical regional (transported) contributions:

- 20-30% for ultrafines
- 60-70% for accumulation mode particles
- 20-30% for coarse particles

PM10:

50 – 60% regional contribution

PM1.2:

60 – 70% regional contribution

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Comparison of source apportionment approaches

Project mean concentrations and mass fractions

PM_{10} Traffic Source

Lenschow:	6.5 µg m^{-3} (23 %)
PMF:	5.3 µg m^{-3} (30 %)

PM_{10} SIA

Macrotracer:	6.6 µg m^{-3} (27 %)
PMF:	8.2 µg m^{-3} (37 %)

PM_{10} Biomass Combustion

Macrotracer:	1.3 µg m^{-3} (5 %)
PMF:	1.4 µg m^{-3} (6 %)

PM_{10} Fungal Spores

Macrotracer:	0.08 µg m^{-3} (0.5 %)
PMF:	0.18 µg m^{-3} (1.2 %)

→ Generally good agreement between approaches

→ Confidence in PMF solution (more sources than other approaches)

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Positive Matrix factorisation (PMF)

Variant of factor analysis (Paatero und Taper, 1994)

$$X = G \cdot F + E \qquad F_{ij}, G_{ij} \geq 0$$

with
X: matrix of samples (n observations x m species)
G: matrix of source contributions (n observations x p sources) → „weights"
F: matrix of source profiles (p sources x m species) → factors, emission profiles
E: matrix of residuals (difference between measured data X and modelled data Y (=GF))

PMF in this project

- EPA PMF 5.0
- „unconstrained" solutions
- all sites pooled into 1 dataset
- Five separate PMF solutions for 5 particle size intervals
- 7 – 9 factors used per size interval, based on
  - mathematical parameters (Q/Qexp, distribution of normalised residuals)
  - correlation of modelled vs. measured mass concentrations,
  - plausible chemical source profiles,
  - plausible time series of source contributions at different sites

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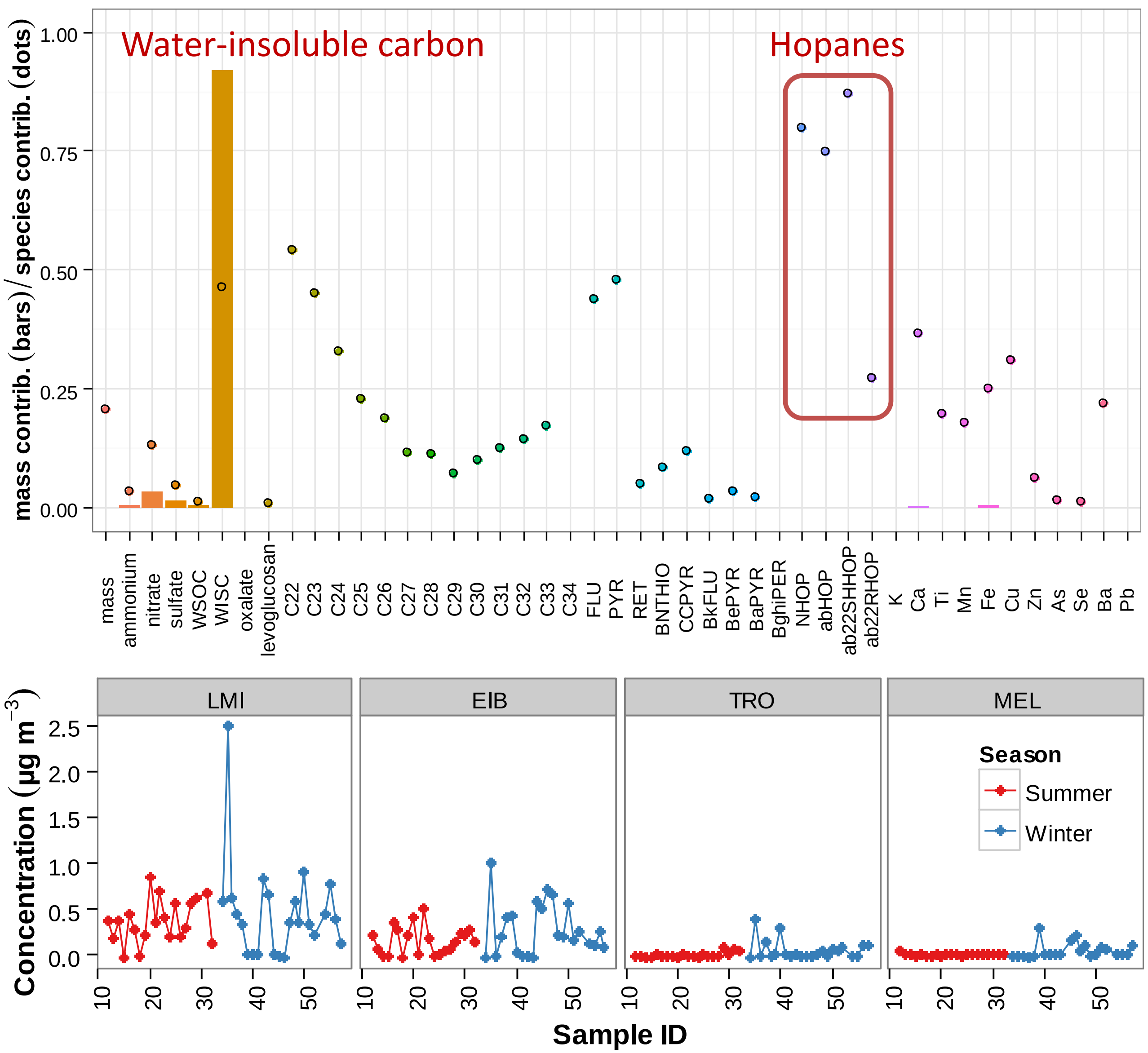
PMF: Example of source attribution



Factor profile

Mass contribution (bars): ΣSpecies = 1

Species contribution (dots): ΣFactors = 1

→ 90% of source mass is water-insoluble carbon

→ 80 % of hopane conc. in this source

→ traffic exhaust or coal?

Factor concentrations

„Time series“ during seasons

→ Concentrations high only at traffic sites

→ no seasonal trend

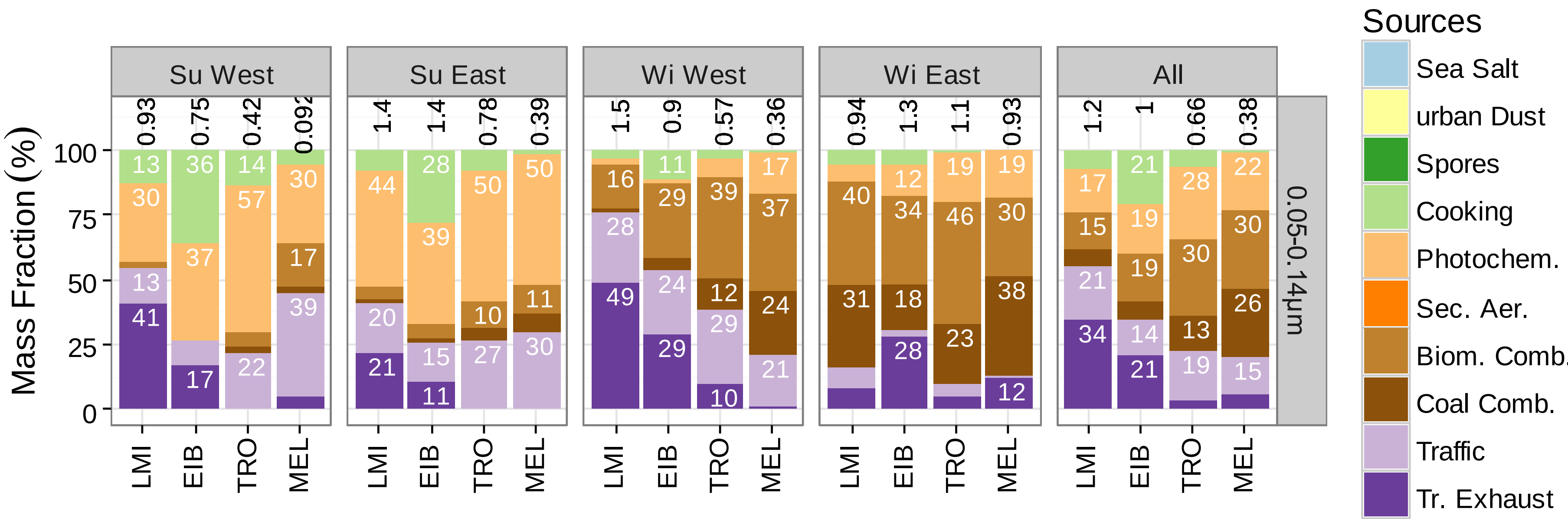
→ **Traffic exhaust**

PMF: Identified sources

Source	Size range	Main constituents	Marker compounds
Traffic exhaust	ultrafine coarse	WISC	Hopanes, <C25 n-Alkanes
Traffic	ultrafine fine coarse	WISC, (Fe)	Copper, Barium
Coal Combustion	ultrafine fine (coarse)	WISC, Sulfate	PAHs, Arsenic, (Hopanes)
Biomass Combustion	ultrafine fine coarse	WISC,WSOC	Levoglucosan, Potassium
Photochemistry	ultrafine fine	Sulfate, WSOC	Oxalate
Secondary (inorganic) aerosol	fine (coarse)	Nitrate, Ammonium, Sulfate	WSOC
Cooking	ultrafine fine	WISC	odd n-Alkanes
Crust material (urban)	coarse	Nitrate, WSOC	odd n-Alkanes, Magnesium, Calcium, Oxalate
Fungal spores	coarse	WISC, WSOC	Arabitol
Fresh sea salt and road salt	coarse	Chloride, Sodium	Magnesium
Aged sea salt	coarse	Nitrate	Sodium, Magnesium

Sources in ultrafine particles (0.05 – 0.14 µm)

Impactor Stage 1



→ Traffic at traffic sites: ca. 0.2 – 1 µg m^{-3}, 20 – 70 % of stage 1 mass (means)

→ Photochem. at urban sites in summer: ca. 0.2 – 0.6 µg m^{-3}, 20 – 50 %

→ Solid fuel combustion in winter: ca. 0.2 – 0.9 µg m^{-3}, 20 – 70 %

Detailed chemical UFP composition and source apportionment can be done this way !

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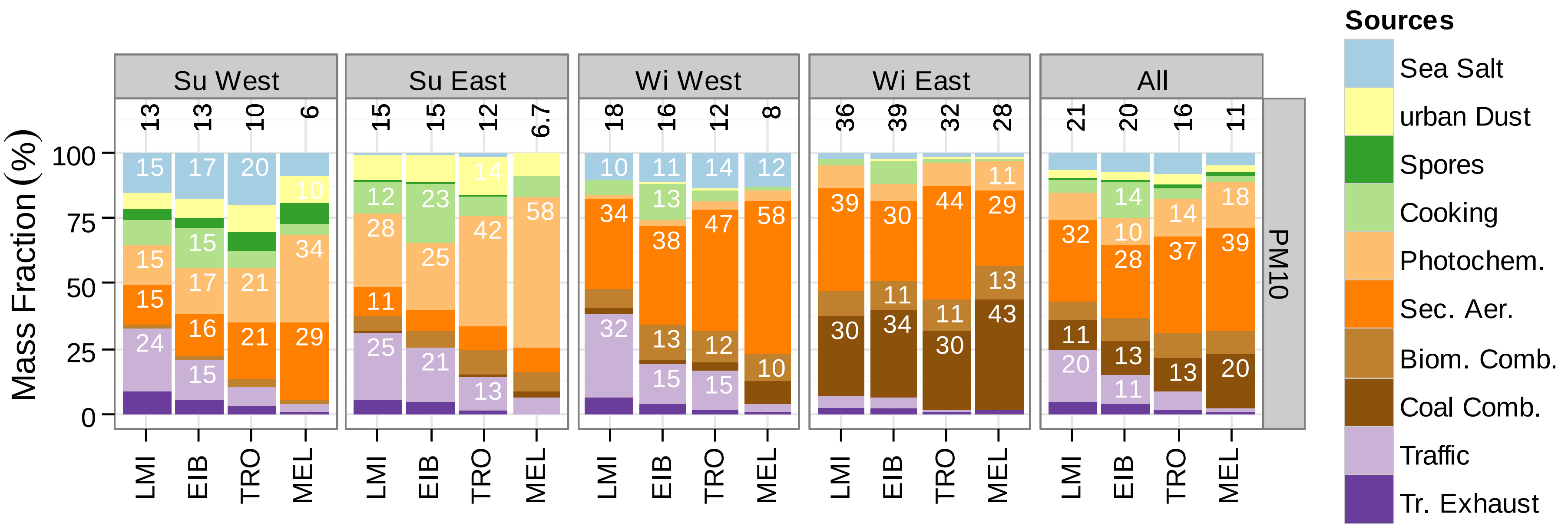
Summary: Total source contributions for PM_{10}



<u>Main sources at most polluted sites:</u>

→ Traffic: ca. 2 – 7 µg m^{-3}, 20 – 40 % of PM_{10} mass (8 % Wi East)

→ Combustion particles: 0.4 – 1.3 µg m^{-3}, 3 – 12 % (summer), 2- 18 µg m^{-3}, 10 – 45 % (winter)

→ Sec. material: ca. 4 – 18 µg m^{-3}, 30 – 45 %

<u>Exceedings days at traffic sites:</u>

Traffic: 15 %,

Regional combustion aerosol: 40 %,

Sec. aerosol: 30 %

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Implications for air pollution abatement strategies

Traffic

- Further development of low emission zone, e.g. include construction machines
- Further promotion of public transportation systems
- Further improvements in bicycle roads
- Optimize car traffic flow through city

Secondary aerosol

- Larger scale reductions of SO_2 and NO_x
- Reduction of Diesel NO_x
- Reduction of agricultural NH_3 emissions
- Promotion of alternative energy systems
- Promotion of energy efficiency (e.g. heat insulation, modern heating systems)

Combustion aerosol

- Limitîng values for small scale heating stoves (1. BImSchV 2010): Filters ?
- Further emission reductions in Eastern Europe, esp. solid fuel burning for heating

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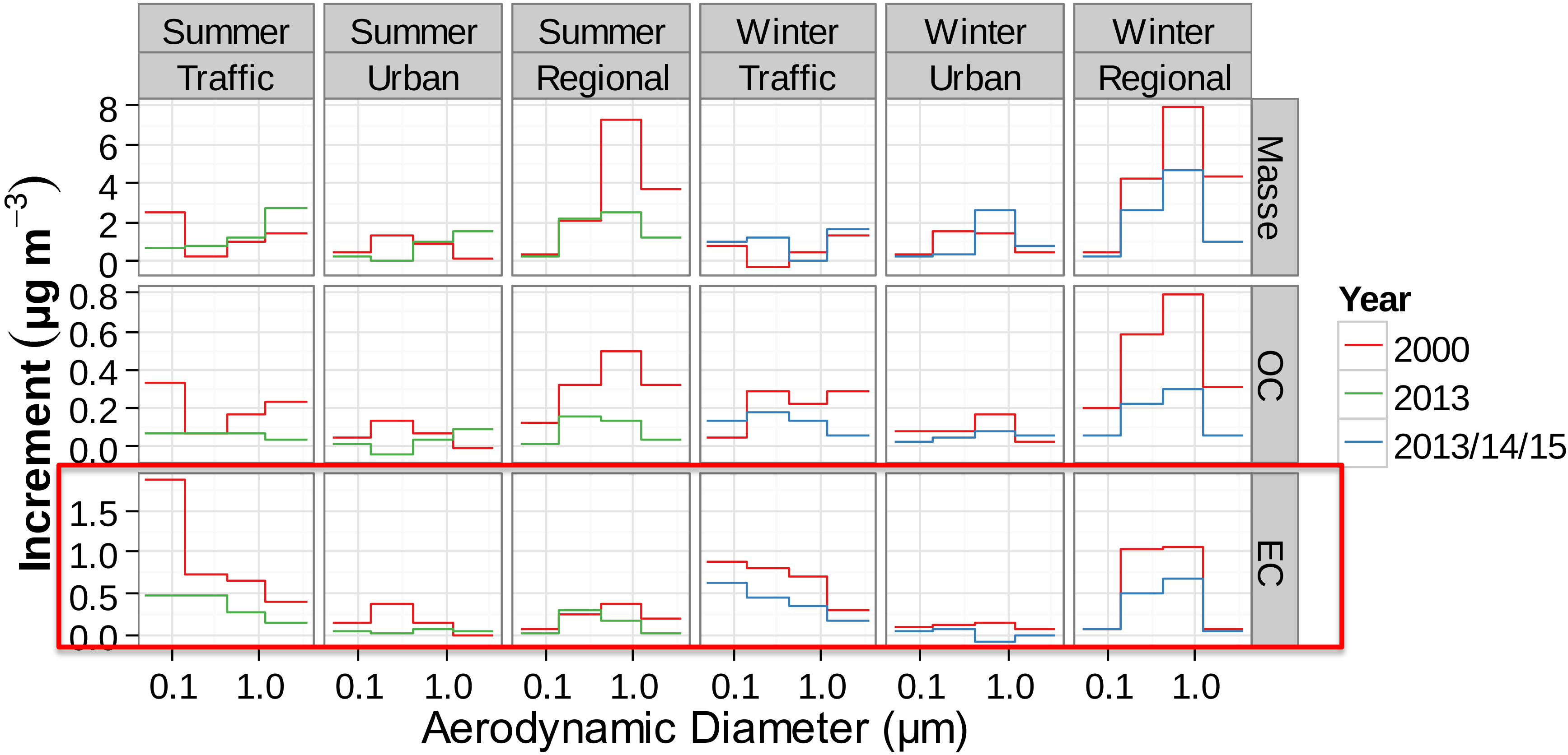
Comparison with year 2000

Project in 2000:

- 3 sites (LMI, TRO, MEL)
- 8 samples per season
- only West sector sampled
- only 4 stages analysed ($PM_{3.5}$)

→ Compare only „West“ days
→ Conc. at all sites decreased
→ Calculate Lenschow increments



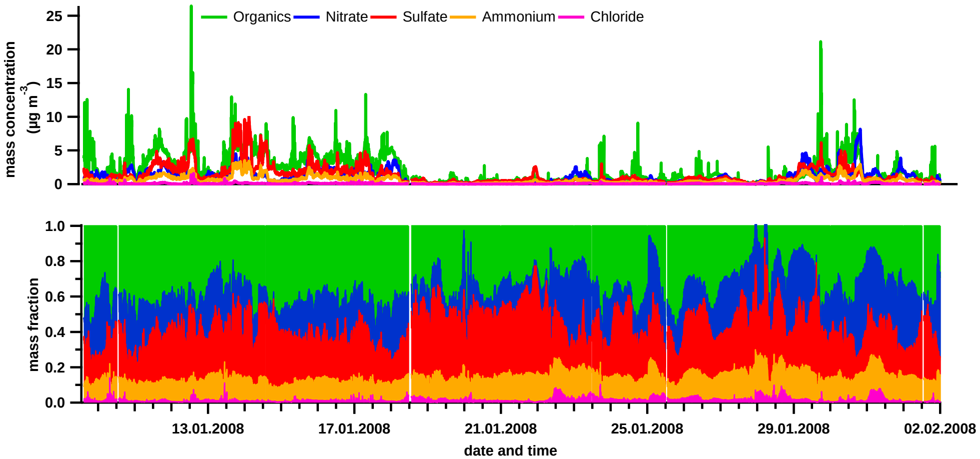
Part 2: (A) LfULG
Seiffen Biomass burning study
(2008)

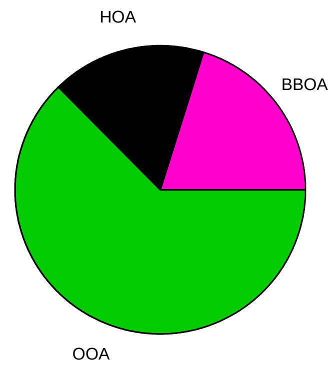
Seiffen (Erzgebirge)

Seiffen – population 2,600

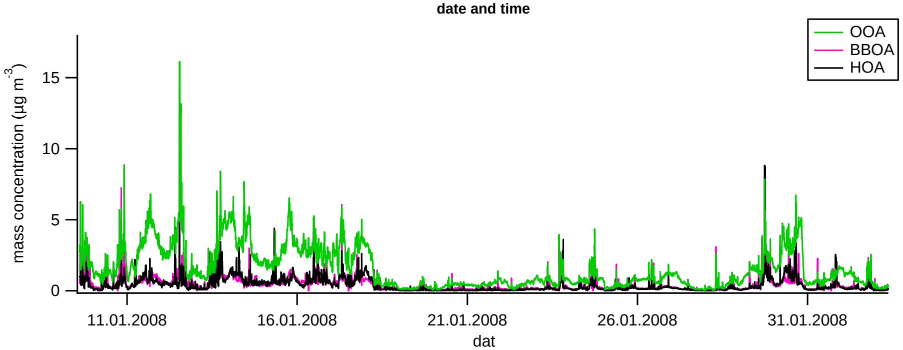
Production of wood decoration

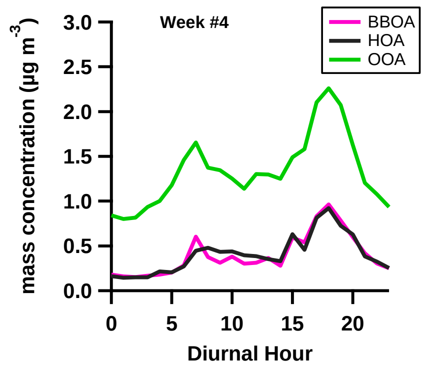
Overview of the Seiffen 2008 measurements

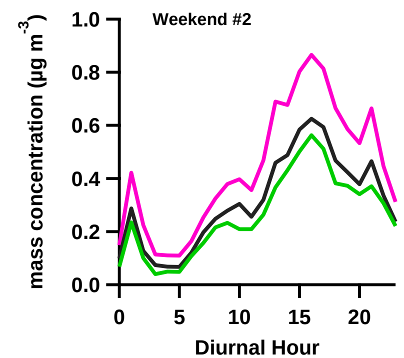


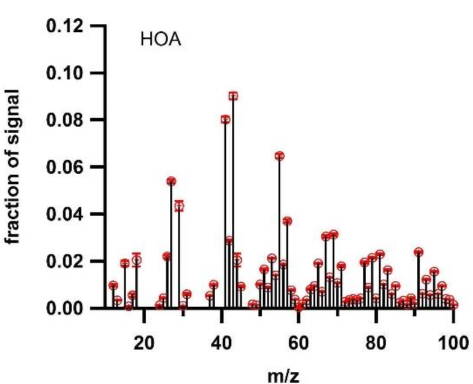


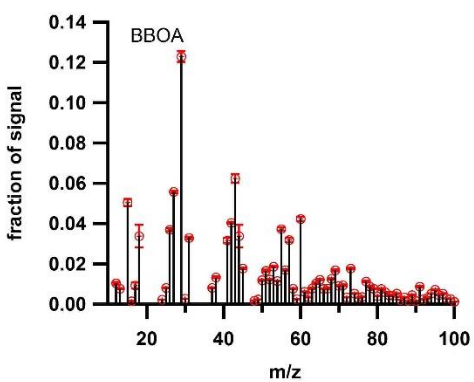
HOA = liquid fuel (car exhaust and house heating)
BBOA = solid fuel (biomass burning)
OOA = oxygenated Organic (aged, transported OA)

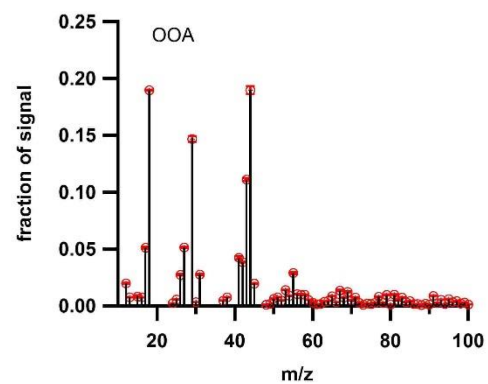






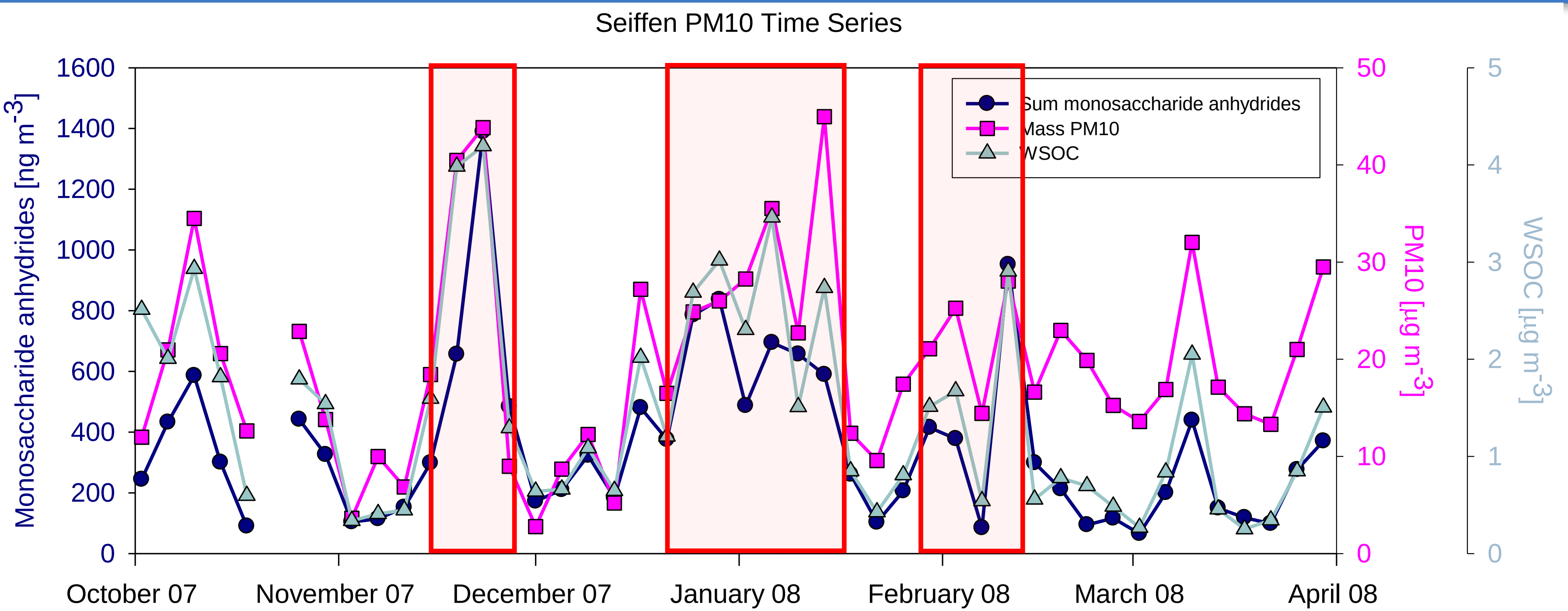






Poulain et al., 2011

Relative Contribution of Wood smoke to PM10 and WSOC at Seiffen



- Based on the meteorological data, back trajectories, and tracer concentrations, these three periods are identified as 'wood smoke' episodes.
- These periods are characterised by at least eight times higher average concentrations of levoglucosan than the background periods.

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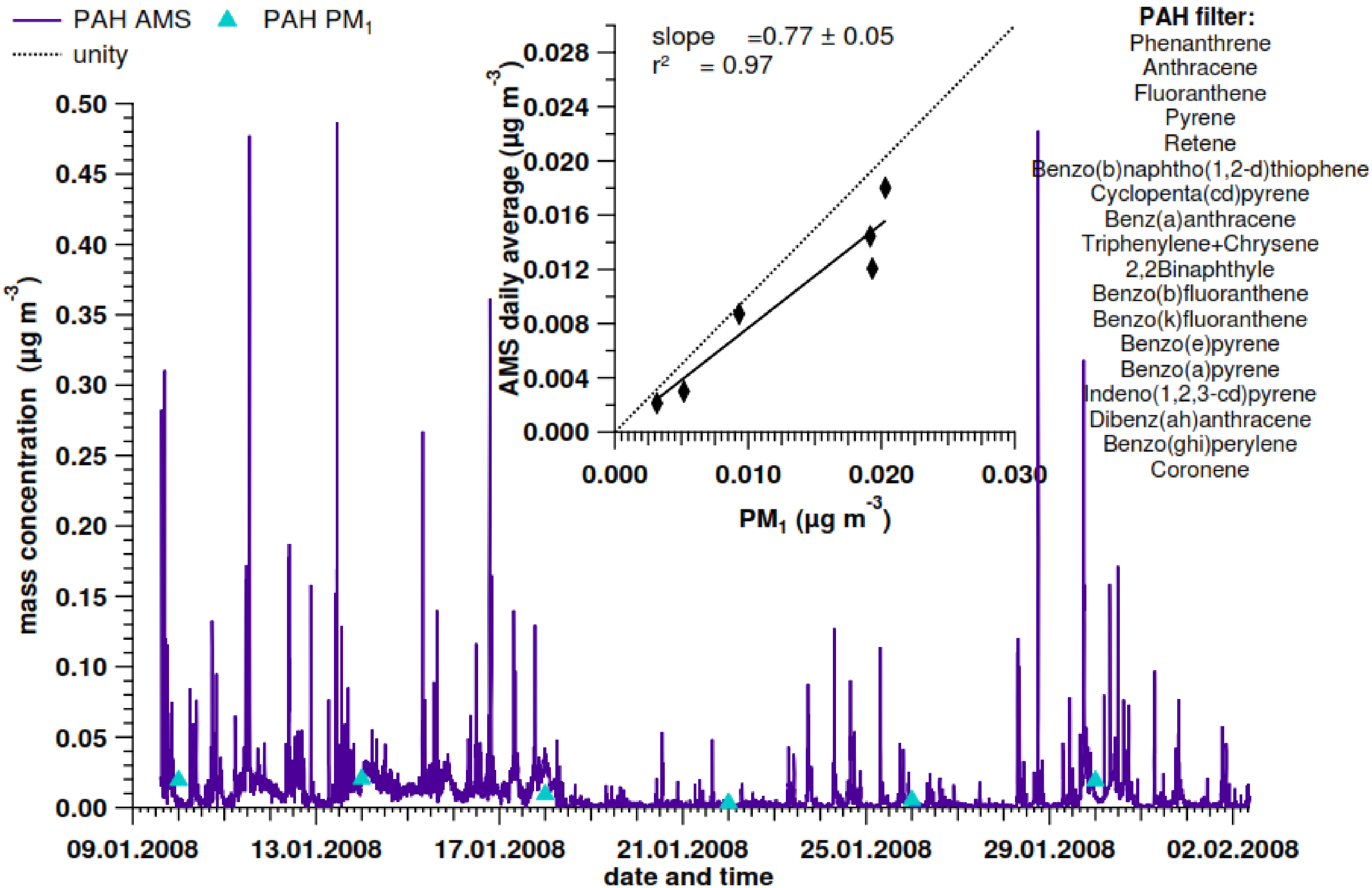
BBOA and PAHs



AMS PAHs mass concentration estimated using Dzepina et al. (2007) agrees quite well with the total PAHs identified on PM_1 filters.

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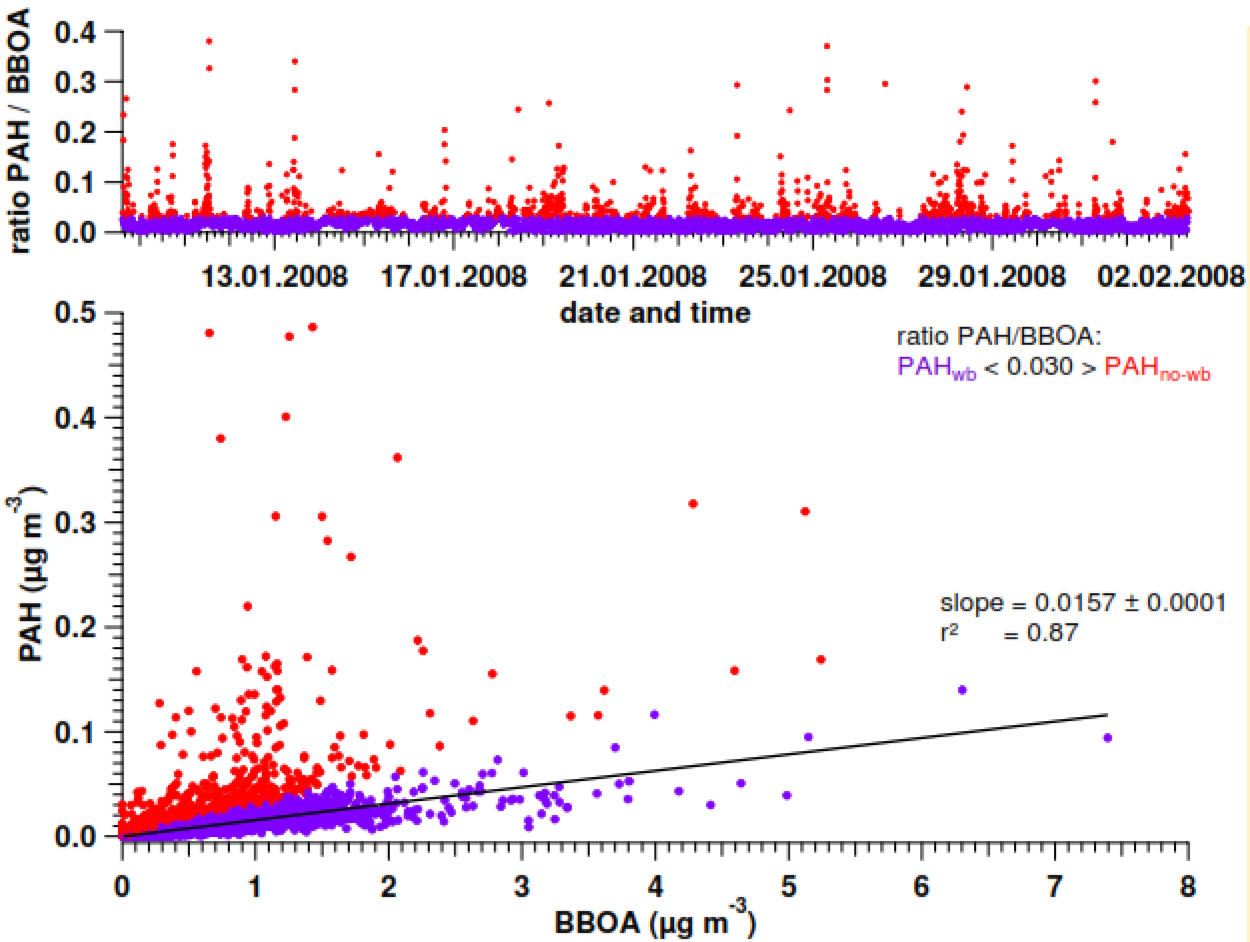
Influence of wood burning to total PAHs



Using the off-line measurements, ratio PAHs/MA = 0.03 in agreement with literature

A similar ratio was considered for the online PAH/BBOA

< 0.03 PAH wood burning (PAH_{wb} in blue)

>0.03 other PAHs sources (traffic, house heating…) (PAH_{no-wb} in red)

⇒ PAH_{wb} = 1.5% of the emitted mass of BBOA

⇒ **PAH_{wb} = 62% of total PAH mass conc.**

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MA = monosaccharides anhydrides

More info here

Atmos. Chem. Phys., 11, 12697–12713, 2011
www.atmos-chem-phys.net/11/12697/2011/
doi:10.5194/acp-11-12697-2011

Atmospheric Chemistry and Physics

Diurnal variations of ambient particulate wood burning emissions and their contribution to the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in Seiffen, Germany

L. Poulain[1], Y. Iinuma[1], K. Müller[1], W. Birmili[1], K. Weinhold[1], E. Brüggemann[1], T. Gnauk[1], A. Hausmann[2], G. Löschau[2], A. Wiedensohler[1], and H. Herrmann[1]

[1]Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig, Germany
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Received: 5 April 2011 – Published in Atmos. Chem. Phys. Discuss.: 13 April 2011
Revised: 26 October 2011 – Accepted: 29 November 2011 – Published: 16 December 2011

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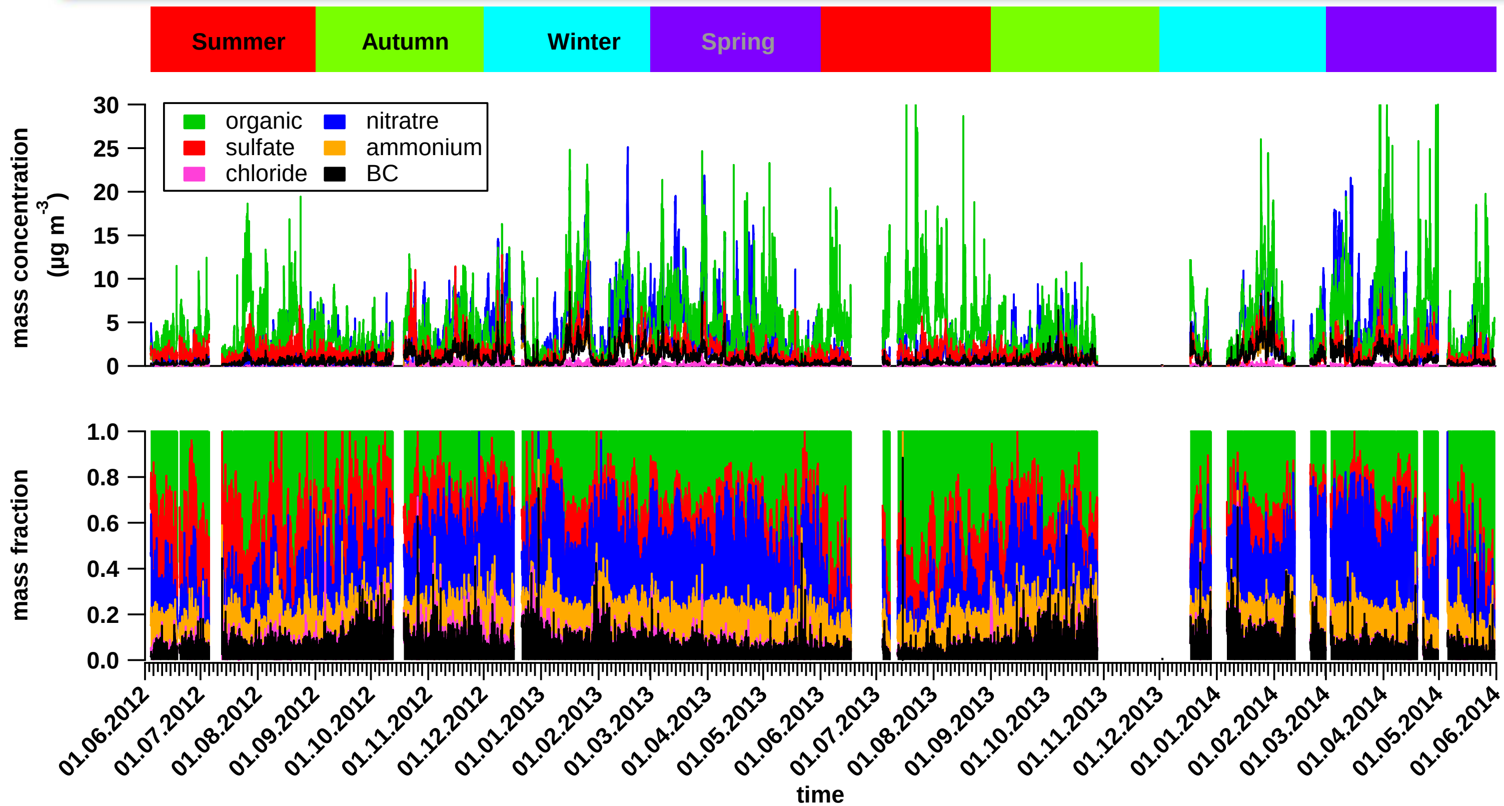
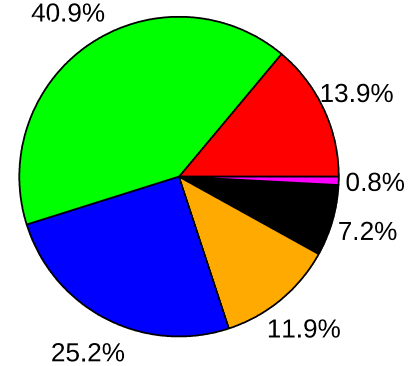
Part 2: (B) Melpitz POA AMS study (2012 - 2014)

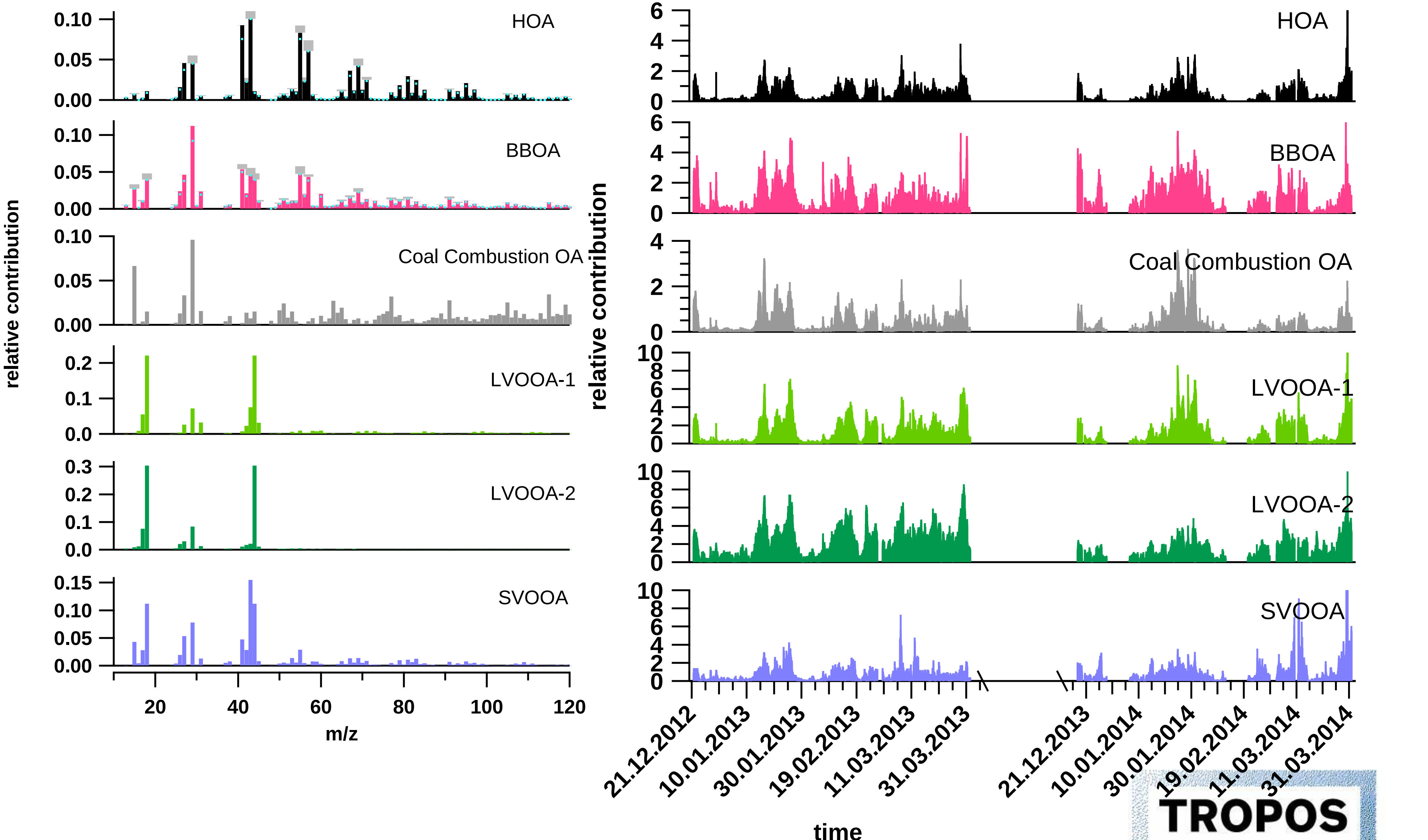
Overview of the aerosol composition





Average mass concentration of 10.7 µg m^{-3}

Organic aerosol source apportionments



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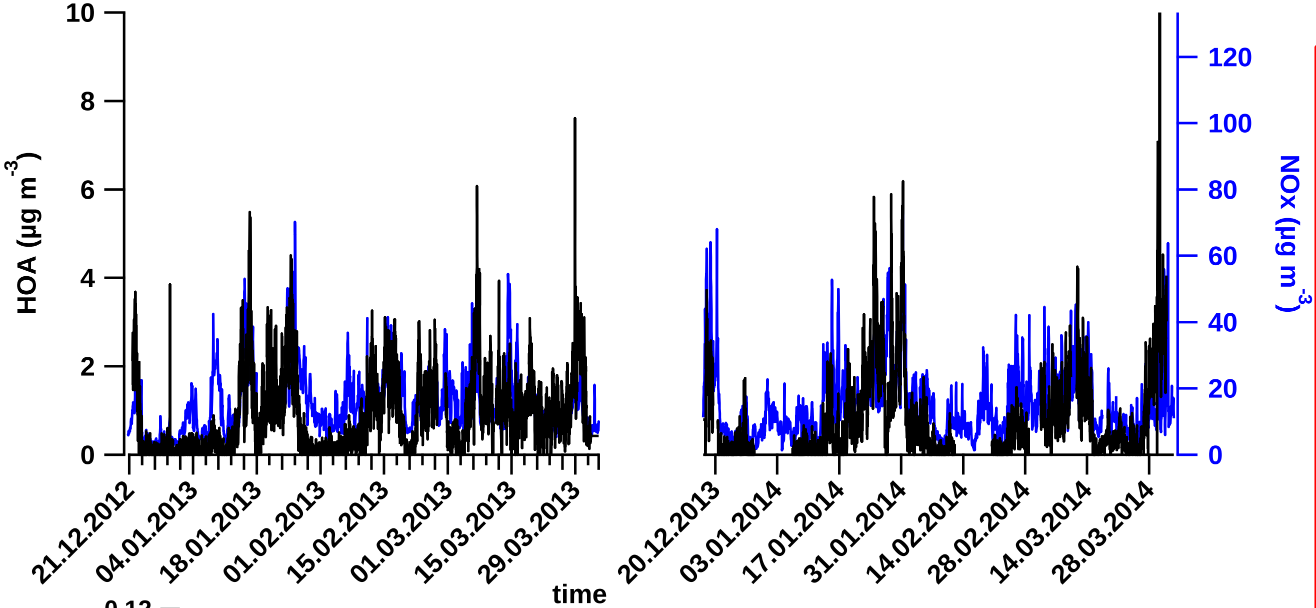
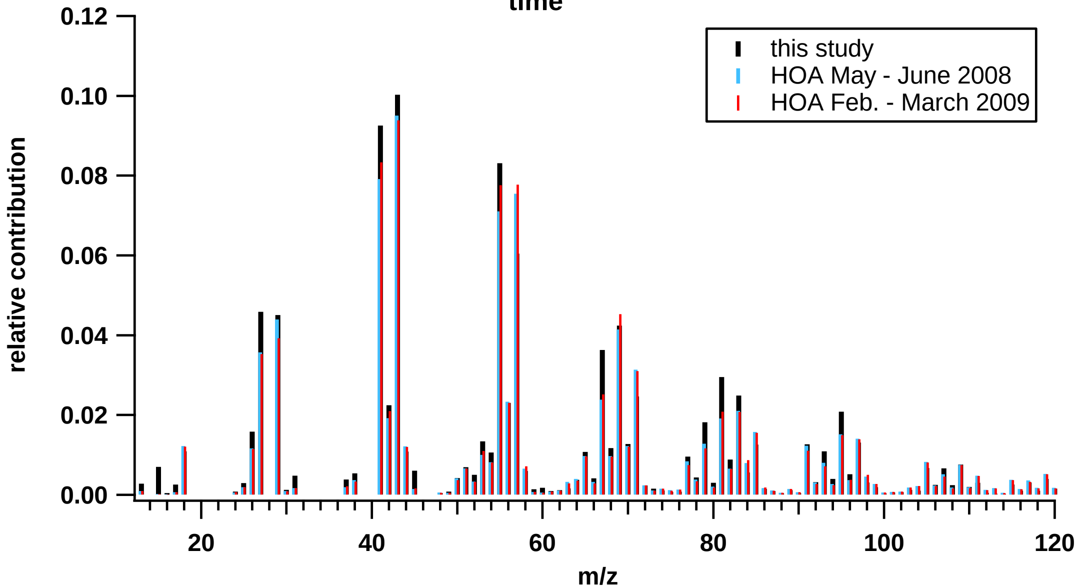
Hydrocarbon-like OA (HOA)





- HOA has quite similar time variation as NOx
- Although HOA-MS was constrained by reference HOA from fall 2008, the resulting HOA-MS agrees also well to the other HOA-MS from Melpitz

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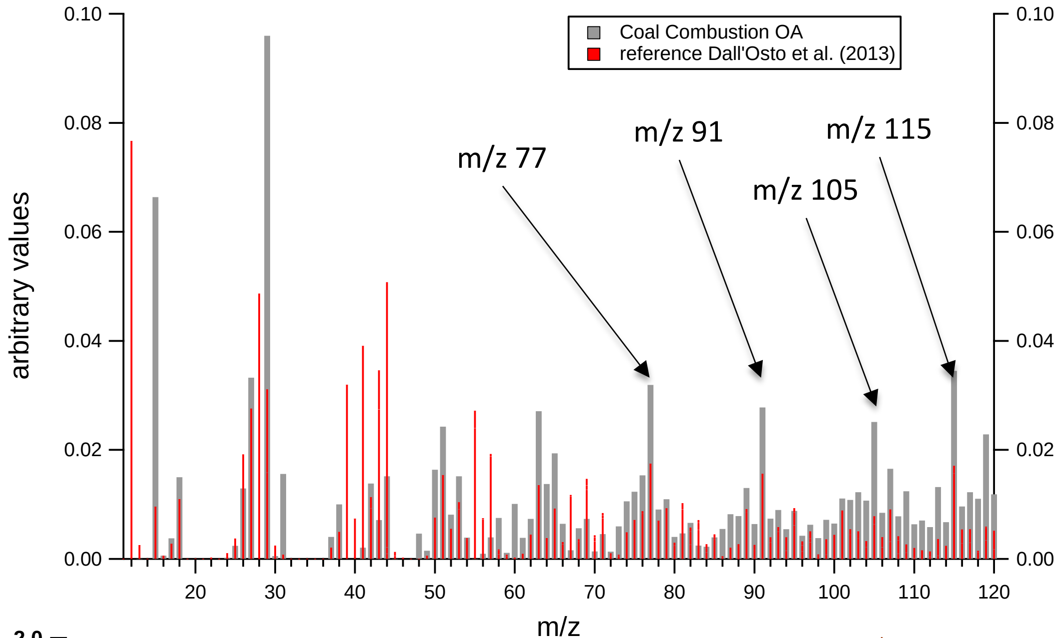
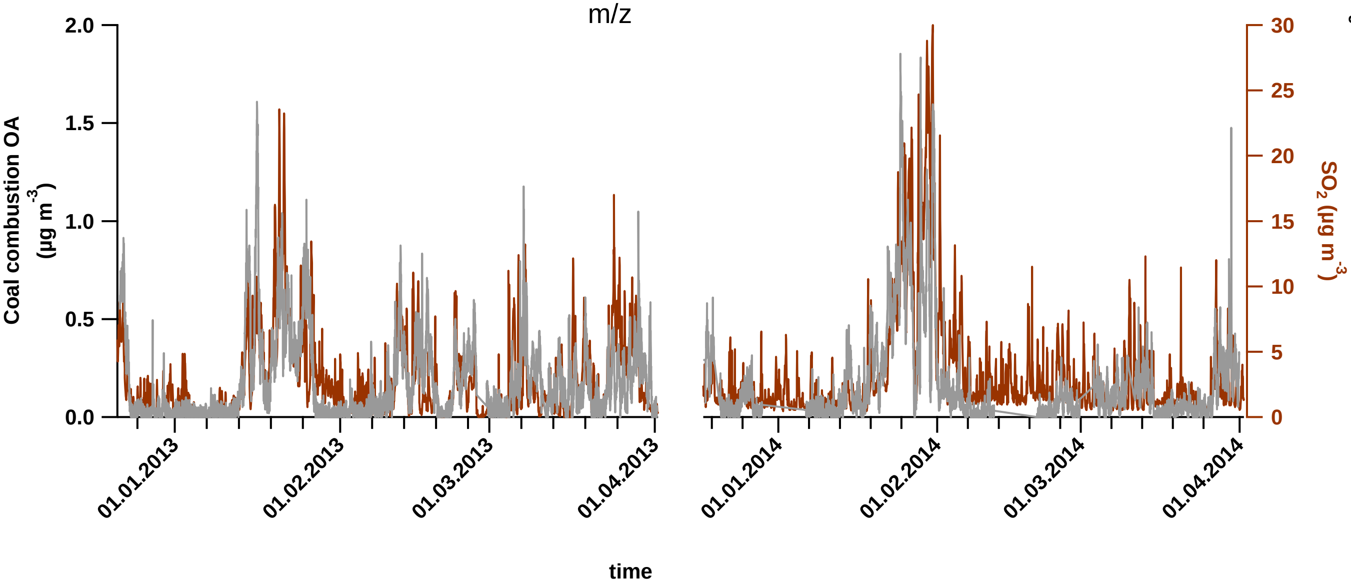
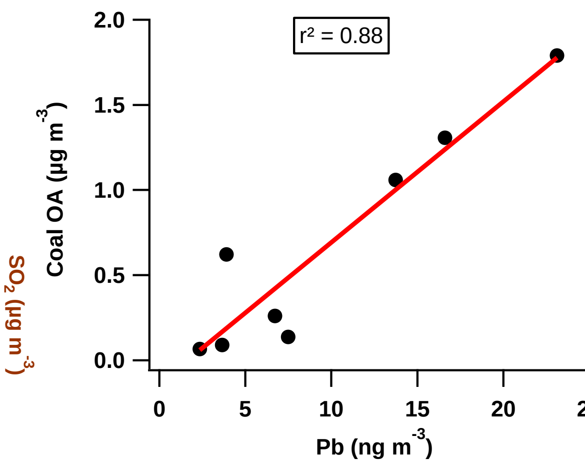
Coal Combustion OA





- MS agrees well with previously reported Coal Combustion OA (Dall'Osto et al. 2013, Cork, Ireland)
- Good correlation with SO_2 and Pb



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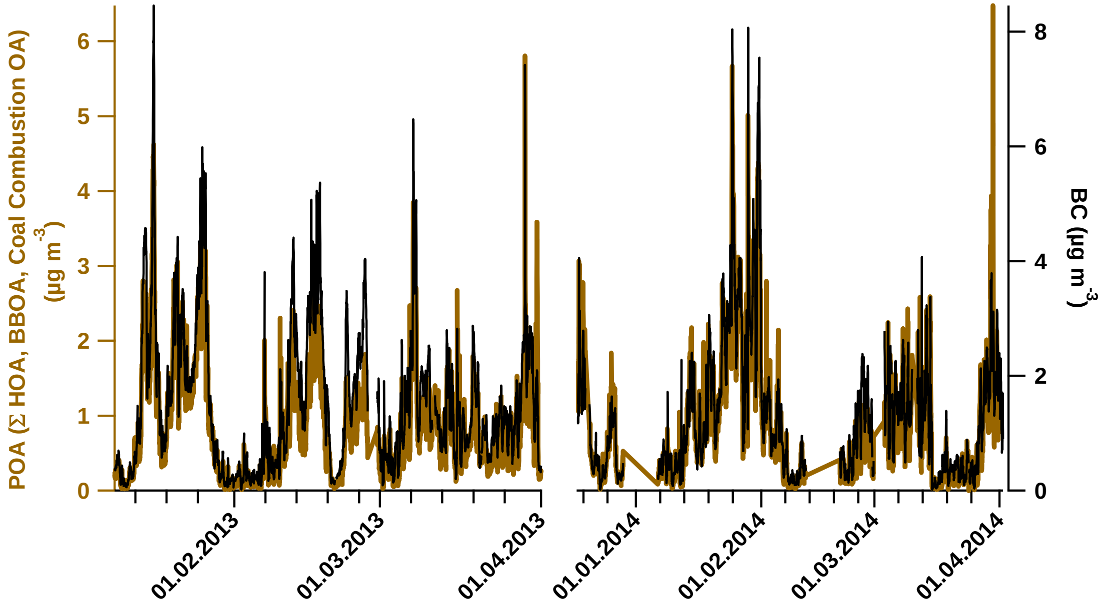
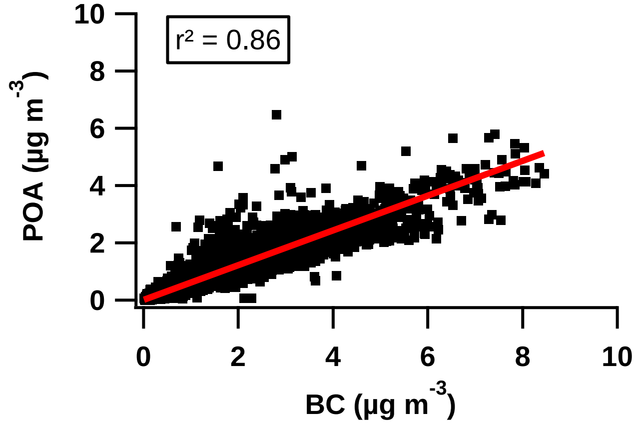
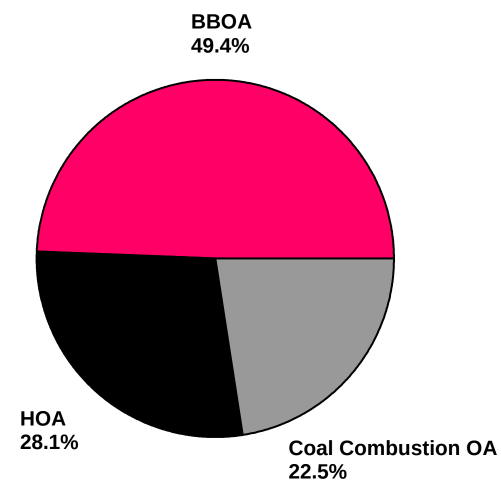
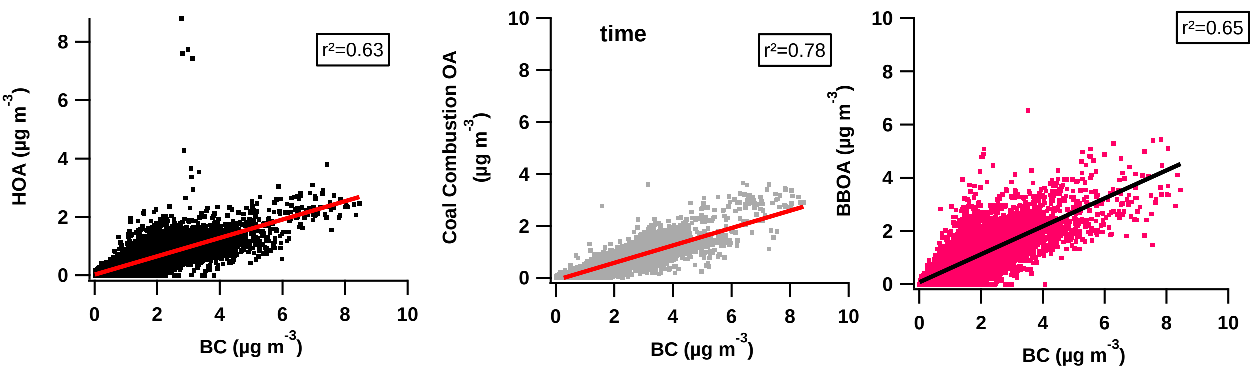
Summary primary OA (POA)









POA (sum HOA + BBOA + Coal Combustion OA) correlates well with BC

POA contribution: BBOA > HOA > Coal Combustion OA

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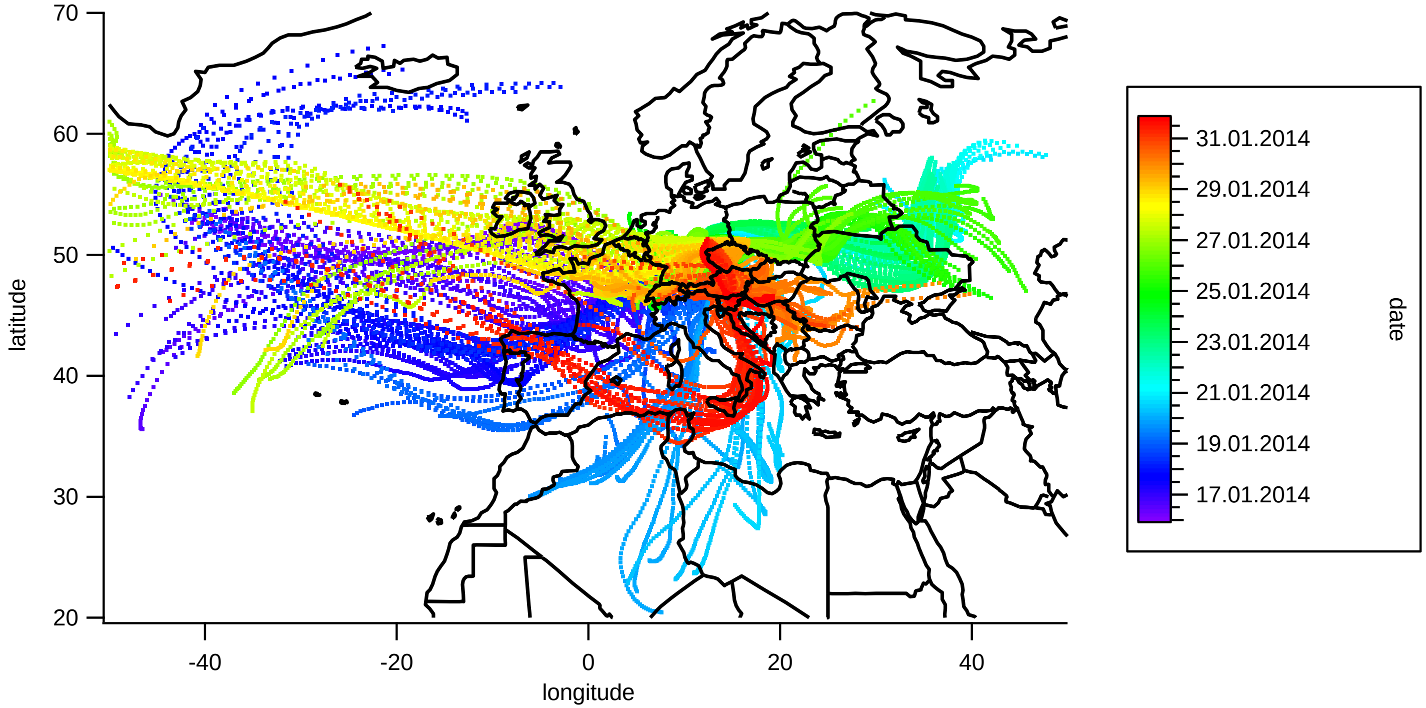
Identification of the potential locations of POA sources

Potential Source Contribution Function (PSCF) Malm et al. (1985), Pekney et al. (2006)

=> estimate the most probable emission area of the pollutant

Available in „openair“ R package (Carslaw and Ropkins (2012))
HYSPLIT: hourly backward trajectories (96h)



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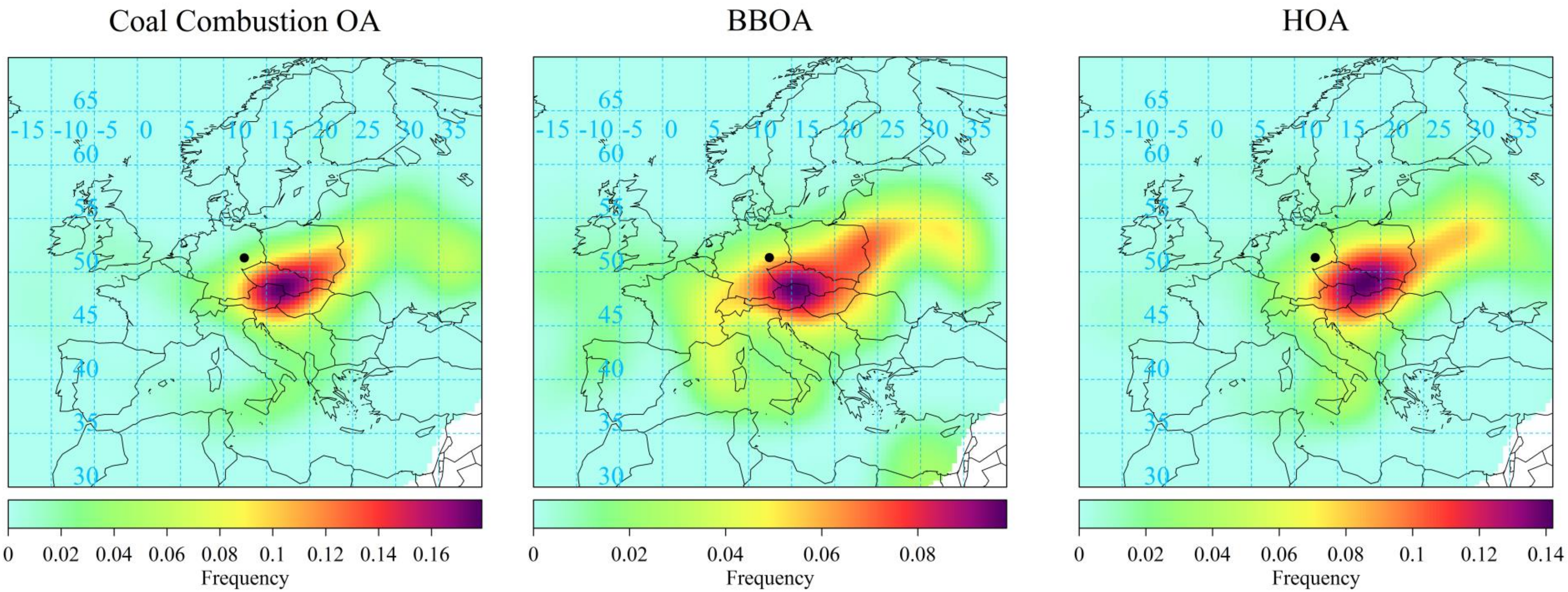
POA potential sources



- Coal Combustion OA sources mostly locate in Eastern European countries
- In agreement with recent measurements made in 2 cities located at both sites of the German-Czech Republic border where domestic brown coal combustion can represent 30-40% of PM_1 OC in winter (Schladitz et al. Atm Env, 2015)
- BBOA covers a larger area

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Summary of winter OA source apportionment

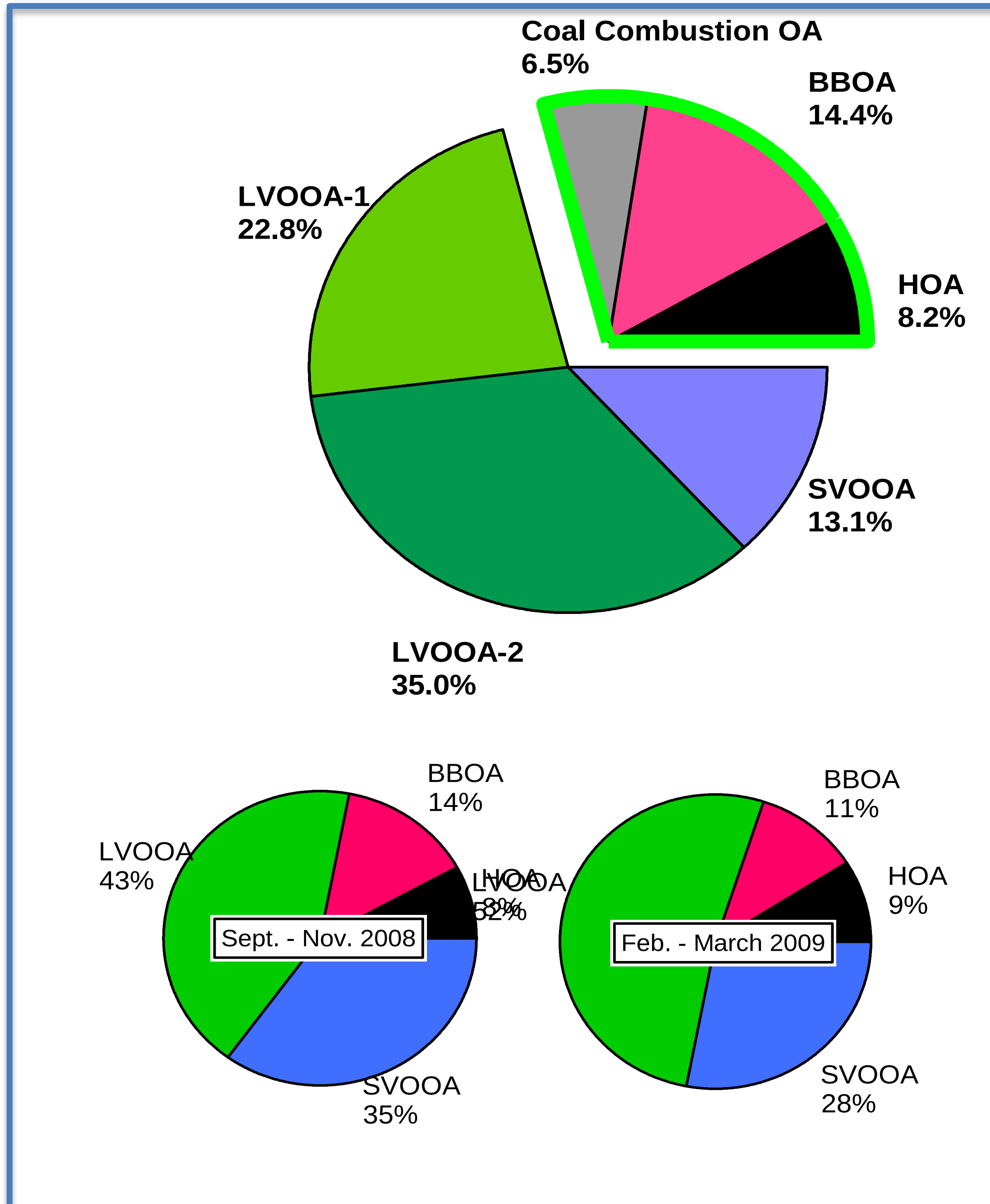
-2 years of measurements provides deep details on seasonal change of aerosol composition (especially Organics)

- in winter, 3 different POA were identified (HOA; BBOA, Coal Combustion OA)

- POA represents near 30% of total

- Potential Source Contribution Function (PSCF) was applied to provide a statistical location of POA sources

-**Long term measurements are a unique opportunity to follow change in aerosol composition and impacts of mitigation strategies on anthropogenic emissions**

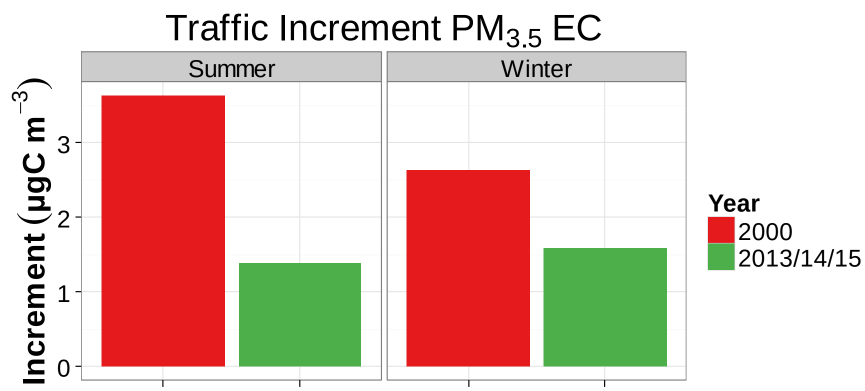


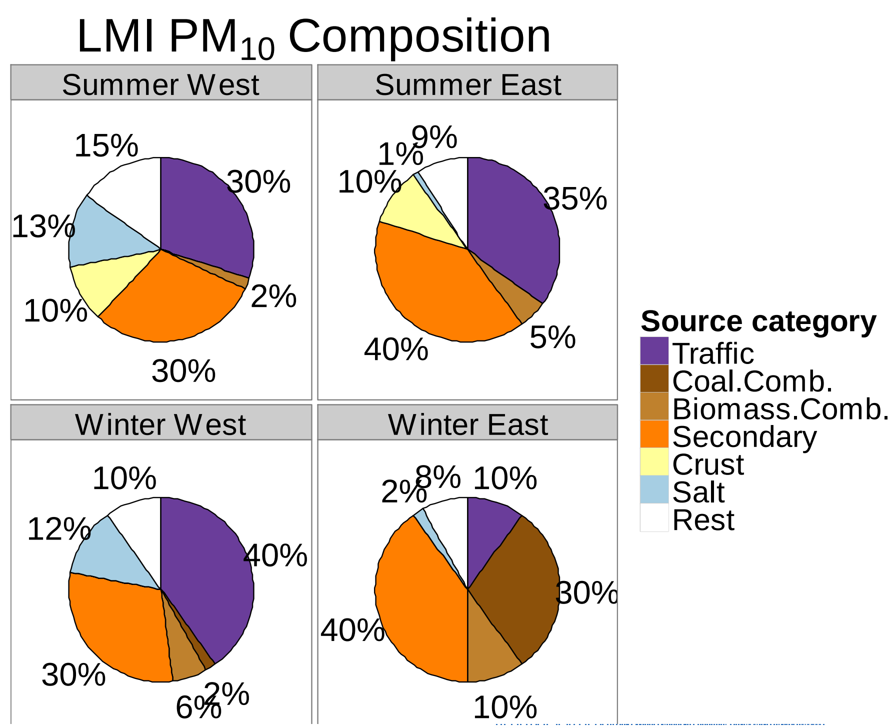
Summary

Specific Summary LfULG Leipzig Aerosol

- Air quality in Leipzig has improved
- EC traffic increment approx. 50 % of year 2000
- Traffic at LMI 30 – 40 % of PM_{10} mass concentration
- Only 10 % in „Winter East"
- „Winter East": 40 % of PM_{10} mass is trans-boundary combustion pollution
- Continued emission reductions in Eastern Europe necessary

van Pinxteren et al., Faraday Discussions, 2016





Seiffen (near source)

Fractions of wood smoke to local PM10 loadings during the “wood smoke” periods are estimated based on the available levoglucosan to PM ratios.

- PM10: approx. 18%, max 27%
- PM1: approx. 28%, max 61%

These numbers are only for primary wood smoke contributions. Actual domestic contributions may be higher due to the SOA formation from the oxidation of biomass burning VOCs.

Melpitz (regional background)

POA represents near 30% of total OC, one third BBOA (PM 1)

Thank you for your kind attention

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Surplus

Summary - Primary air pollutants

- Soot is a problem in urban environments, especially when traffic-dominated
- Soot and the associated individual organics have adverse health effects
- The Diesel engine is thermodynamically great but causes Diesel soot. Its abatement causes a NO_2 problem in cities
- Wood burning is important in Germany in wintertime and is a desaster for air hygiene - it overcompensates PM reduction from the traffic sources
- POA constitutes 1/3 of particle OC, half of this fm BB

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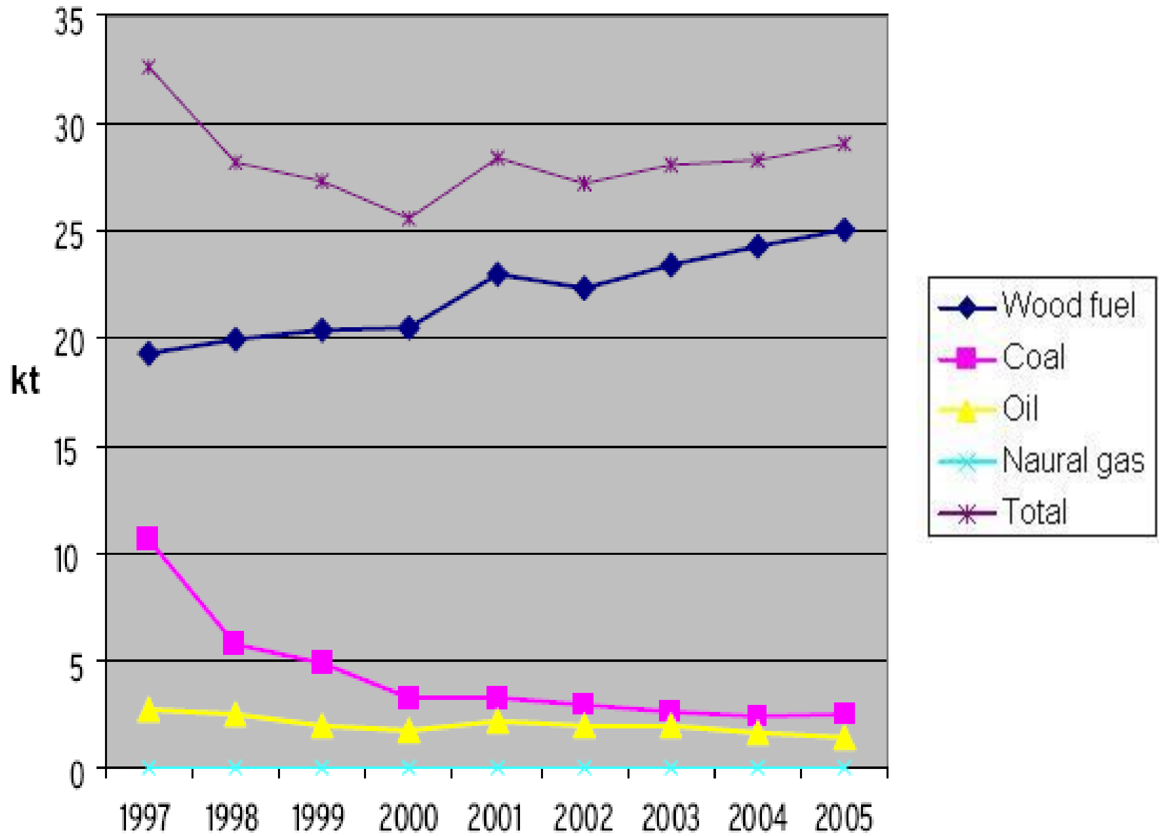
PM10 Emissions from Various Combustion Sources in Germany



- A constant increase in PM10 emissions from wood fuel combustion. This trend is expected to continue.
- In contrast, the emissions from road traffic exhaust are expected to go down dramatically (e.g. 25.4 kt/year in 2002 → 22.7 kt/year in 2003).

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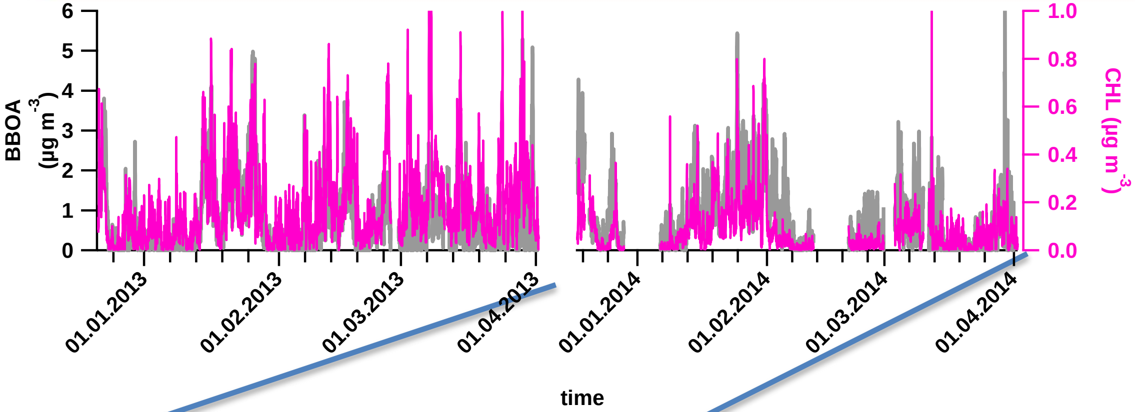
Source: DIE NEBENWIRKUNGEN DER BEHAGLICKEIT: FEINSTAUB AUS KAMIN UND HOLZOFEN, Umweltbundesamt, 200

Biomass Burning OA (BBOA)



- Pretty good correlation between BBOA and non-sea-salt chloride (ACSM) as well as levoglucosan ($PM_{1.2}$ from Berner impactor)
- BBOA mass spectra agrees also well with other BBOA-MS reported at Melpitz