Modelling OC in Europe: Status

David Simpson

Norwegian Meteorological Institute and Chalmers Radio & Space Science

Approaches in EMEP

1. α-K approach (Pankow, Odum)
2. Gas-Particle chemical schemes
3. Search for correlations .....

The EMEP BC/OC model

- Primary:
  - FFUEL: Coal + oil
  - WOOD: Domestic burning
- Secondary:
  - ASOA: Anthropogenic SOA (from aromatics)
  - BSOA: Biogenic SOA (from terpenes)
- BGND: Background OC (mix of oil/wood/BSOA)

Emissions

- Revised BC/OC inventory for 2000, IIASA, Feb 2005-Mar 2006 (Kupiainen, and Klimont, 2006)
- Focus on PM_1
- In consultation with national experts

Emissions

SNAP Code	Sources	Emissions (Gg/yr) BC	OM	TCM	Fraction of total TCM (%)
1	Combustion in energy and transformation industries	3.50	3.57	7.07	(0.4)
2a	Non-industrial combustion plants	89.78	140.13	229.91	(12.5)
2b	Residential/comm. woodburning	165.13	456.36	621.49	(33.7)
3	Combustion in manufacturing industry	3.79	10.32	14.11	(0.8)
4	Production processes	34.77	23.58	58.35	(3.2)
5	Extraction and distribution of fossil fuels and geothermal energy	13.33	2.67	16.00	(0.9)
7	Road transport	212.76	147.15	359.91	(19.5)
8	Other mobile sources and machinery	205.57	148.31	353.88	(19.2)
9	Waste treatment and disposal	14.85	41.56	56.41	(3.1)
10	Agriculture	30.06	94.90	124.96	(6.8)
Sum		773.55	1068.56	1842.11	(100)

SOA: α-K approaches

Smog-chamber data could be explained with:

VOC + Ox $\Rightarrow$ α_1 $SVOC_1$ + α_2 $SVOC_2$

SOA: Partitioning

$$\frac{A_i}{G_i} = K_i.M_0 = \frac{RT}{m_w \zeta_i p^0_{L,i}}.M_0$$

where
A_i, G_i are aerosol and gas-phase concs. of i
K_i is partitioning coefficient
M_0 is mass of existing aerosol
m_w is average MW of absorbing OM
ζ_i is activity coefficient
$p^0_{L,i}$ is vapour pressure

ASOA

Four anthropogenic species:

- AROM + Ox $\Rightarrow$
  - $\alpha_{1,1}$ XYLAIR1 + $\alpha_{1,2}$ XYLAIR2 (50%)
  - $\alpha_{2,1}$ TOLAIR1 + $\alpha_{2,2}$ TOLAIR2 (50%)

following Odum/Griffin, Pun. α-KT approach

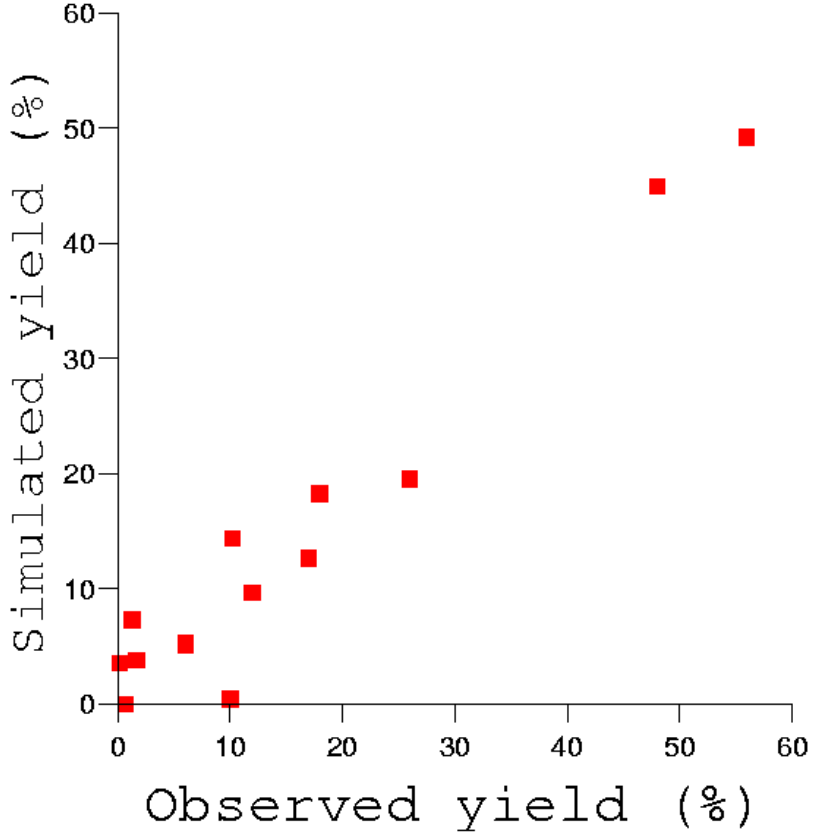
BSOA; Method 1

Kam-2: Explicit α-pinene gas-particle chemistry, with dimer formation (Kamens et. al, 1999, Andersson-Sköld and Simpson, 2001).

- VOC + Ox $\Rightarrow$ SVOC, and degredation of products
- 21 Reactions
- 15 product species
  - representing e.g. pinonaldehyde, pinic acid, pinonic acid, etc.

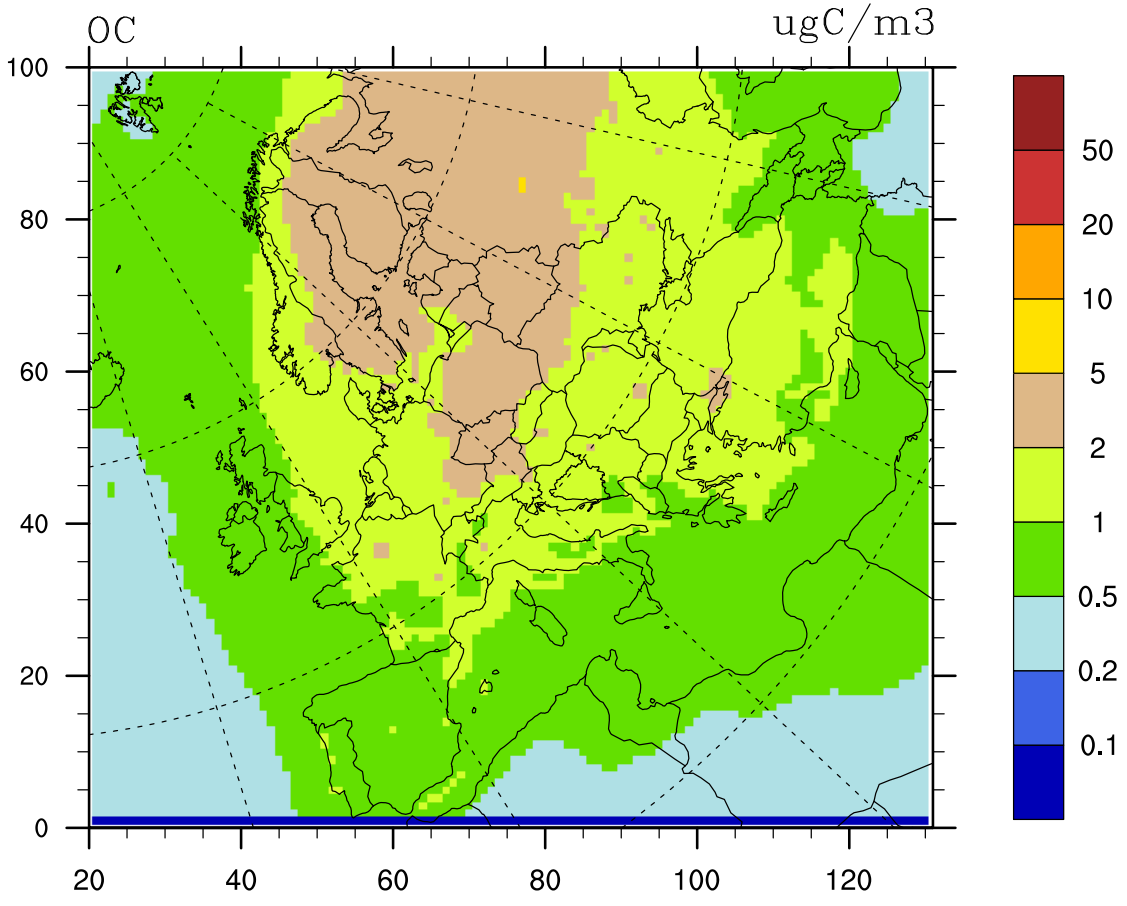
BSOA; Method 1

9-820 ppb α-pinene
0-240 ppb NOx



Results

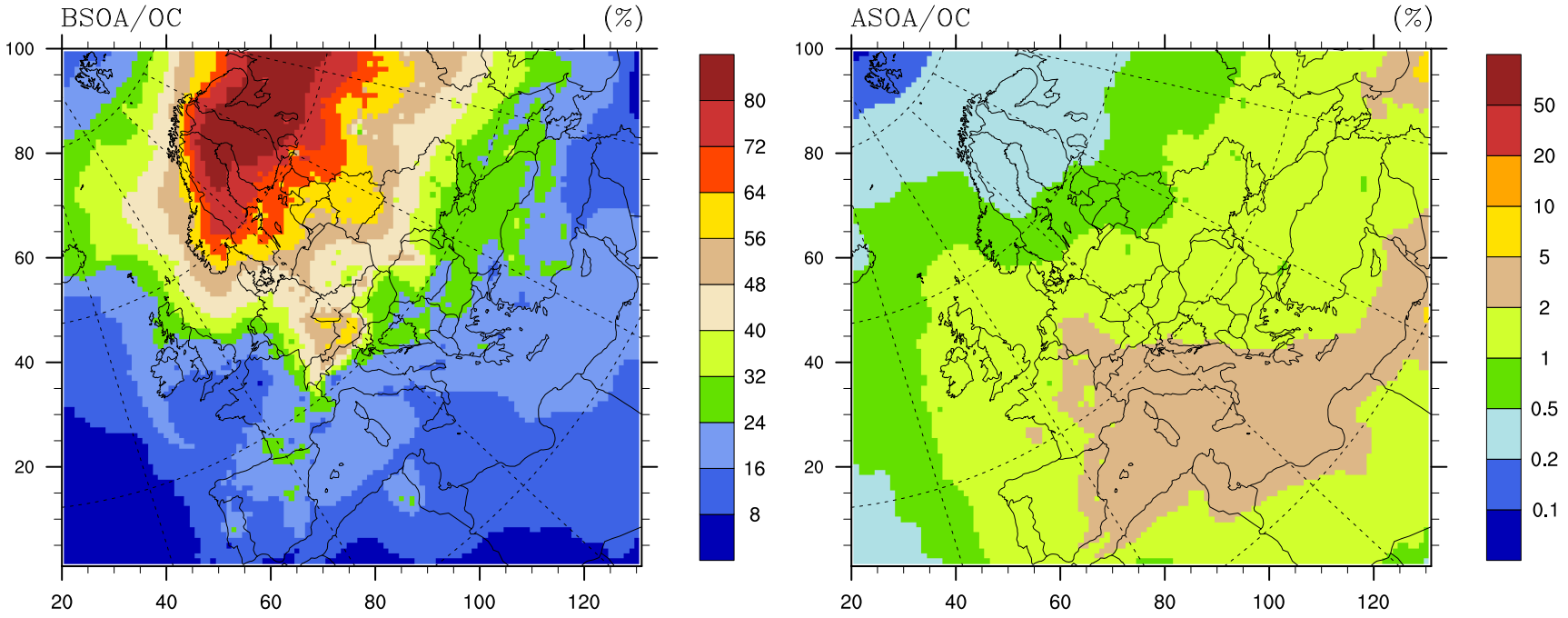
Results: Annual Average OC, year 2002 (ugC/m3)



BSOA contribution

BSOA/OC (%)

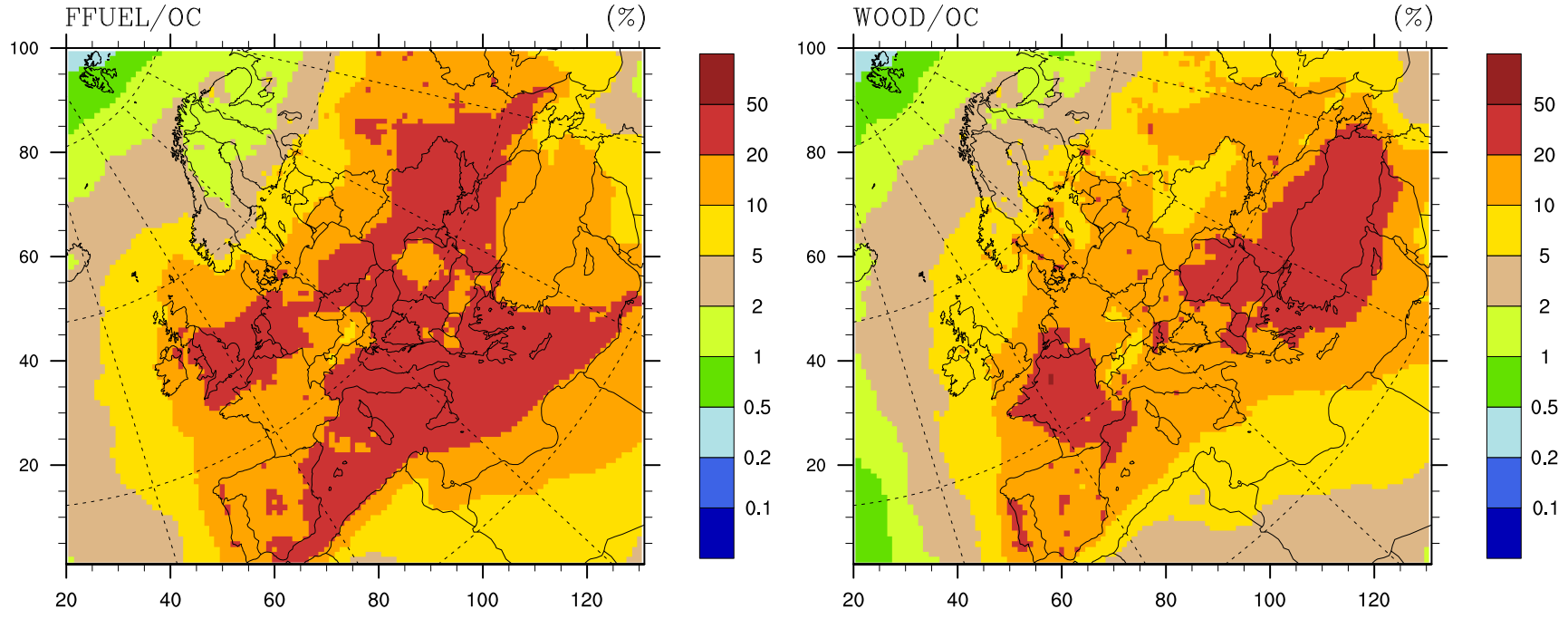
ASOA/OC (%)



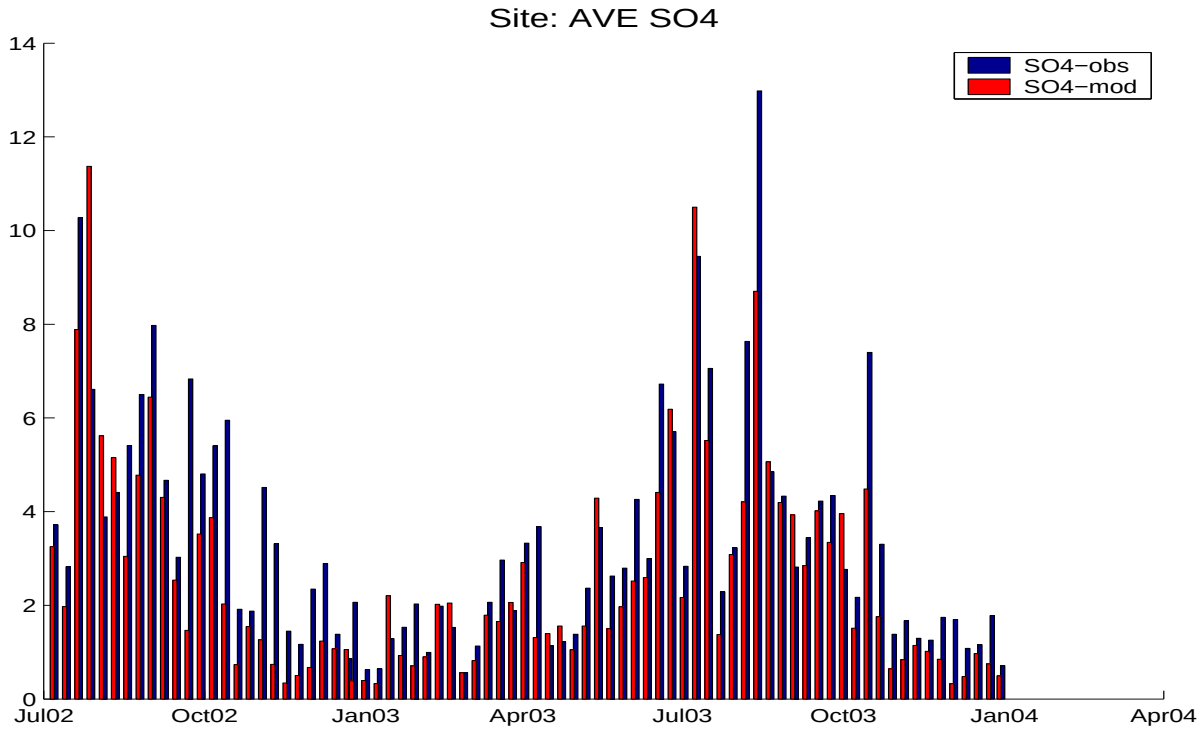
Primary OC

FFUEL

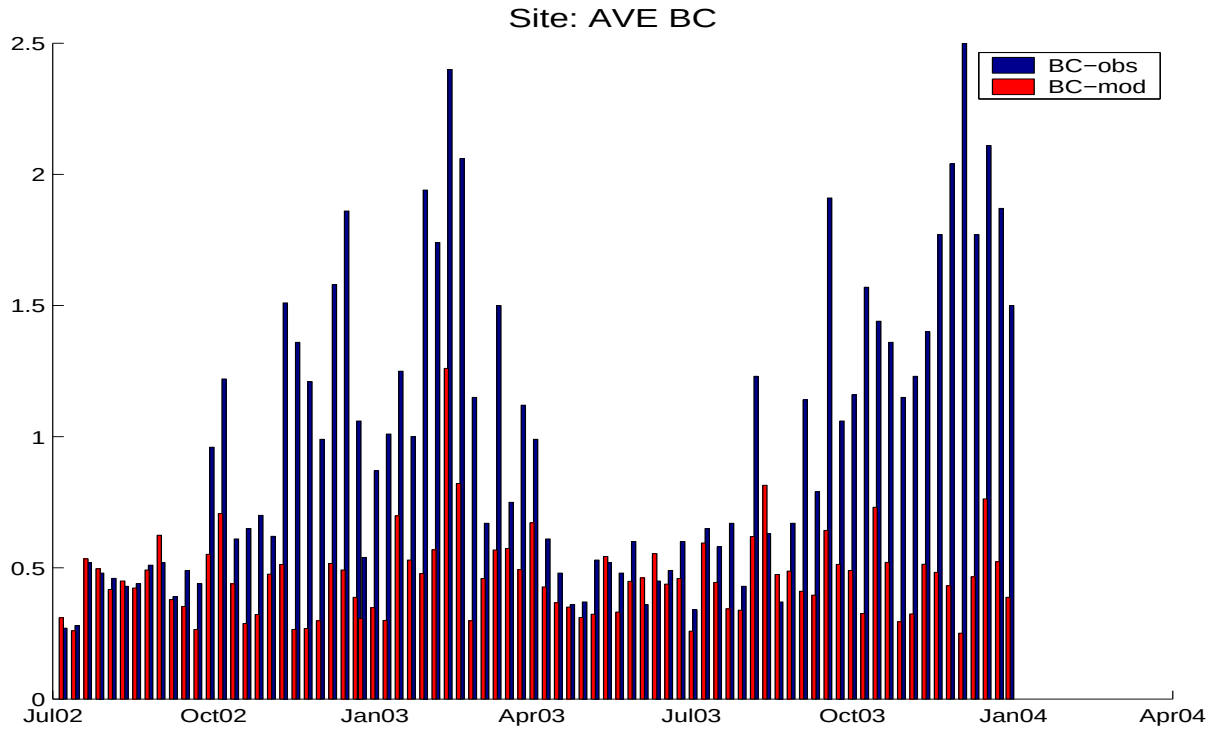
WOOD



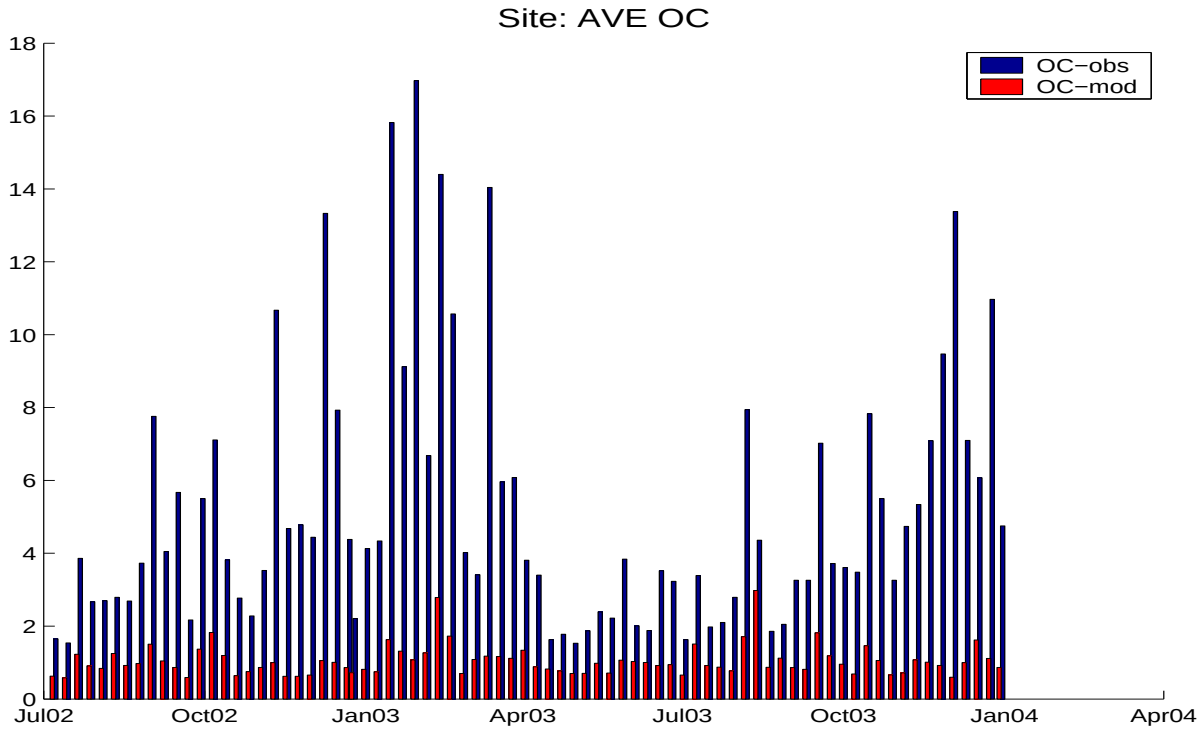
CARBOSOL Comparisons



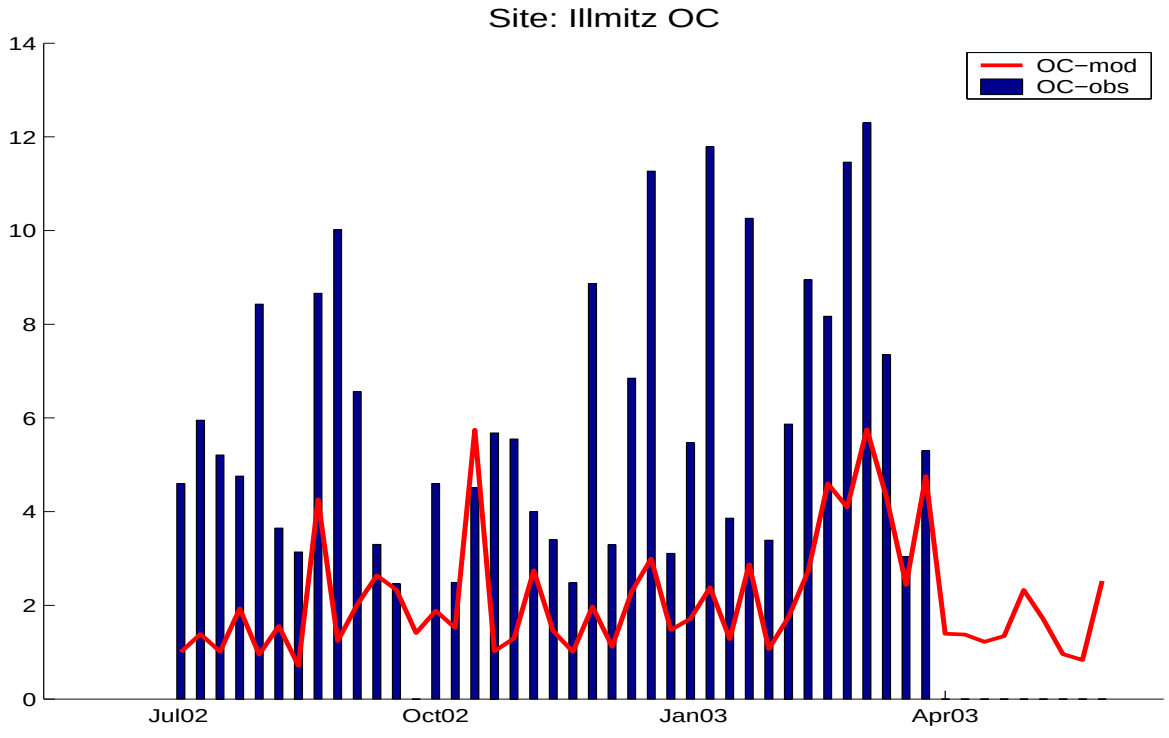
CARBOSOL Comparisons



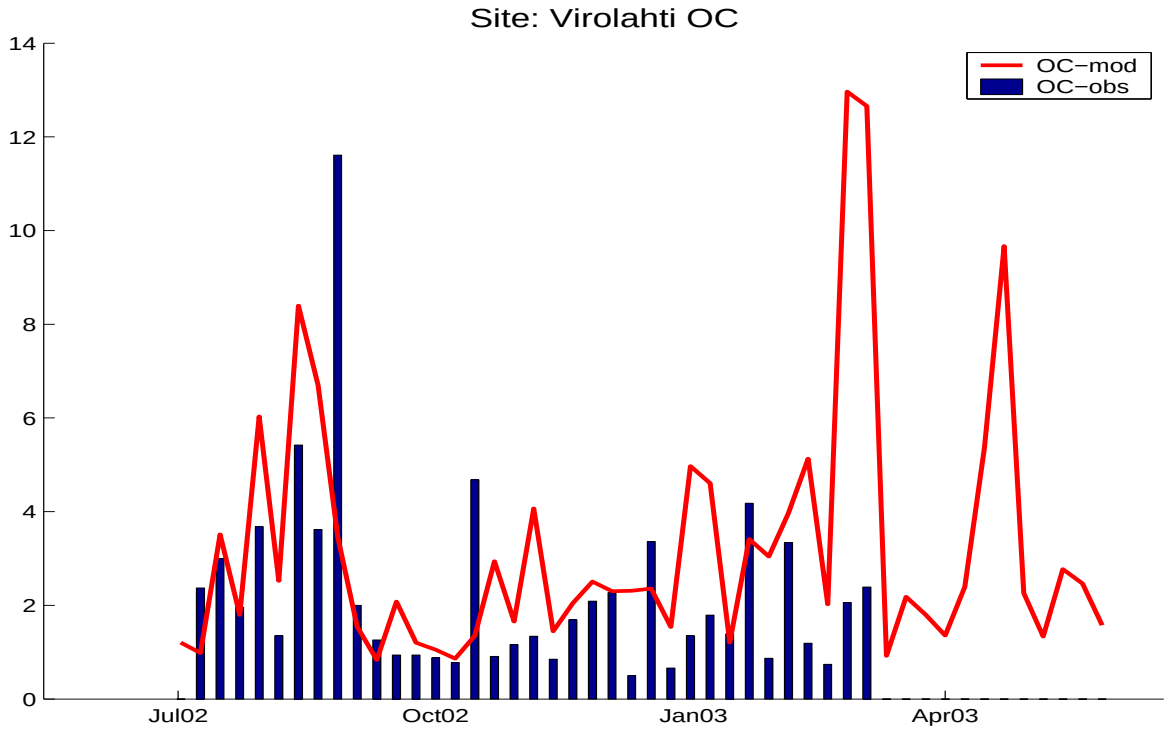
CARBOSOL Comparisons



EMEP Comparisons

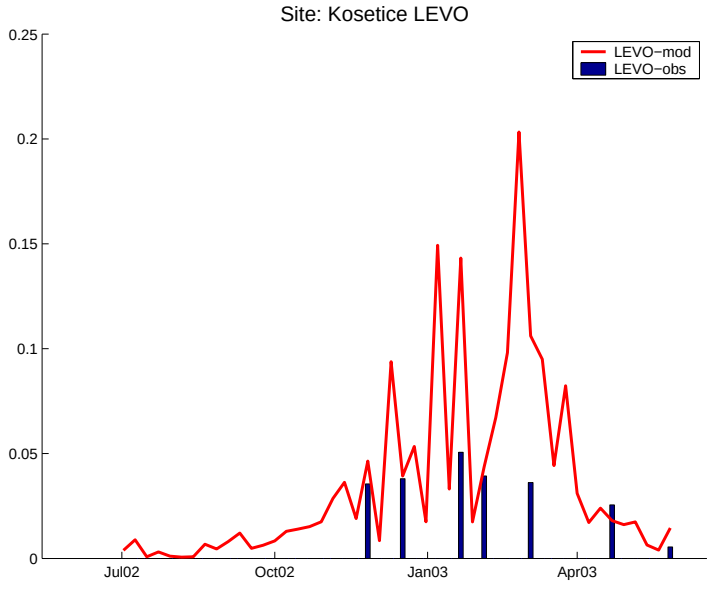


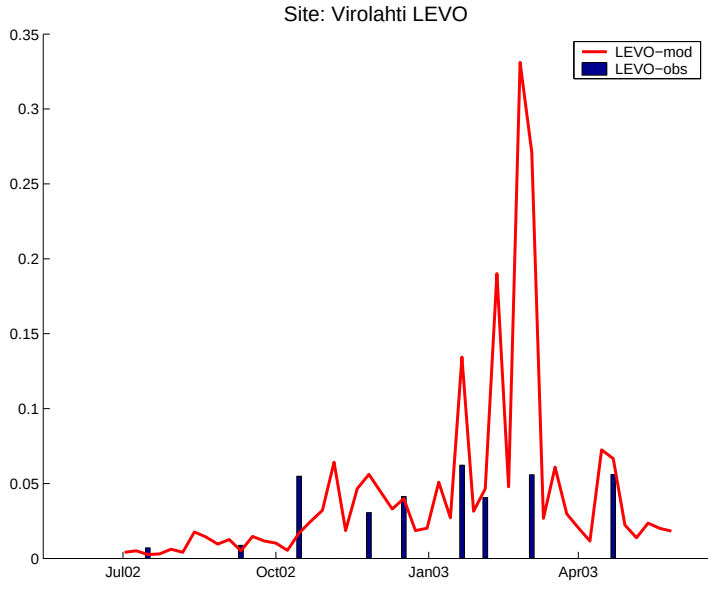
EMEP Comparisons



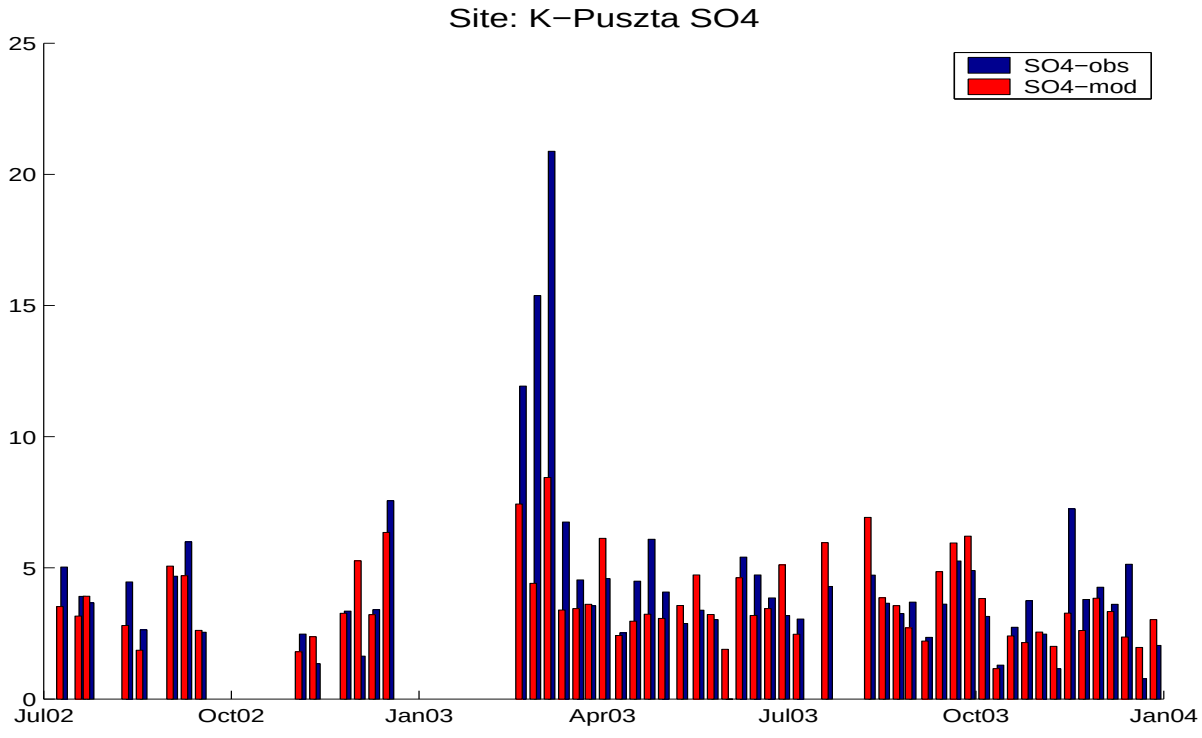
Levoglucosan

Tracer of wood-burning ($\sim$ 10% of emission)

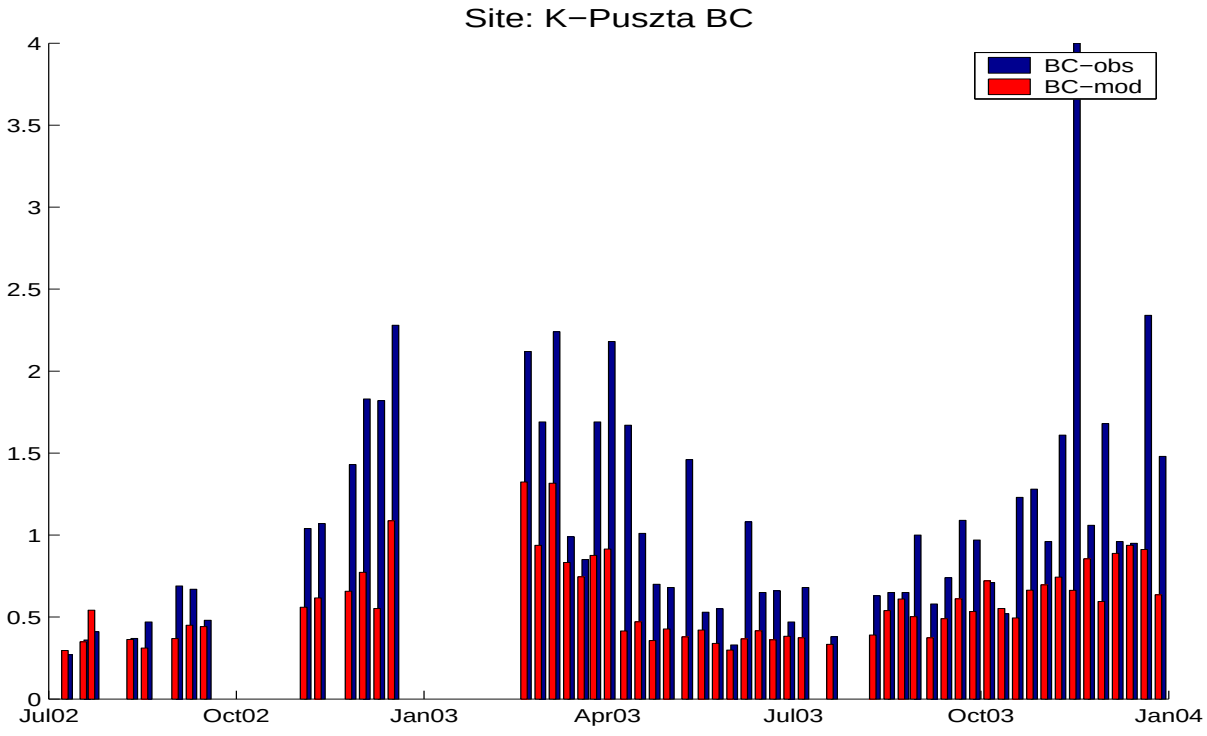




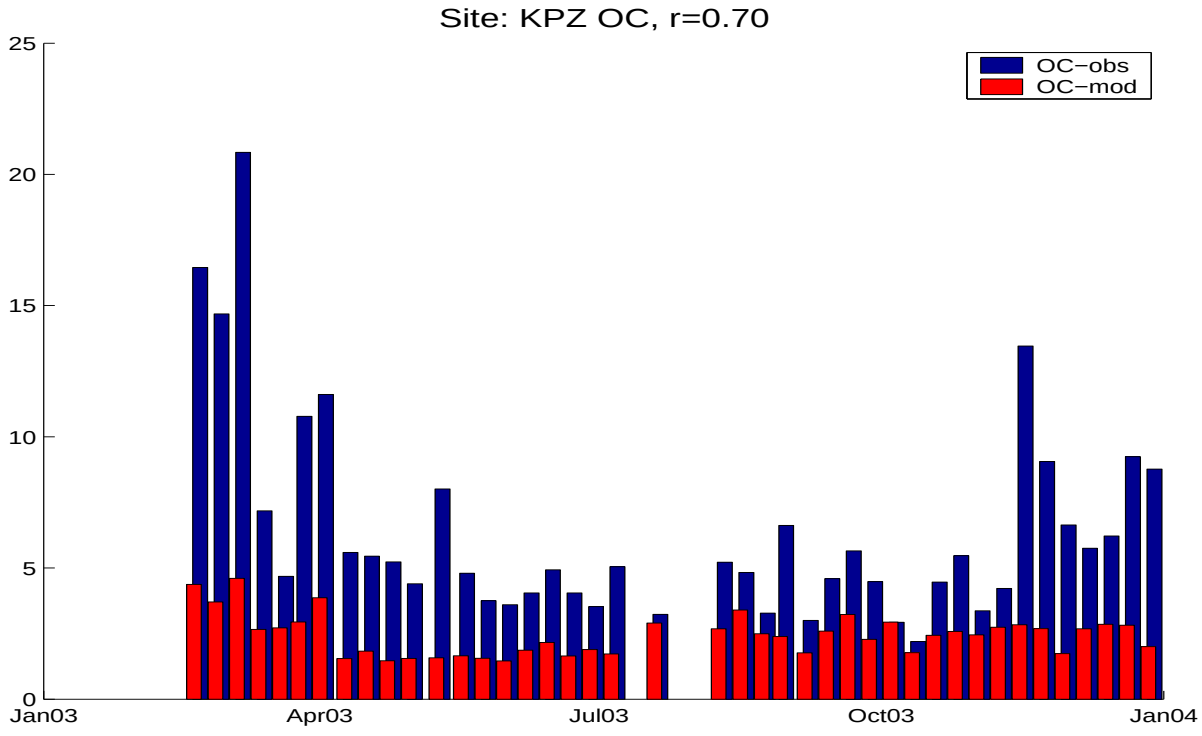
SO4


Site: K−Puszta SO4
SO4−obs
SO4−mod
25
20
15
10
5
0
Jul02
Oct02
Jan03
Apr03
Jul03
Oct03
Jan04

BC


Site: K−Puszta BC
BC−obs
BC−mod
4
3.5
3
2.5
2
1.5
1
0.5
0
Jul02
Oct02
Jan03
Apr03
Jul03
Oct03
Jan04

OC - base


Site: KPZ OC, r=0.70
OC−obs
OC−mod
25
20
15
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Jan03
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Jul03
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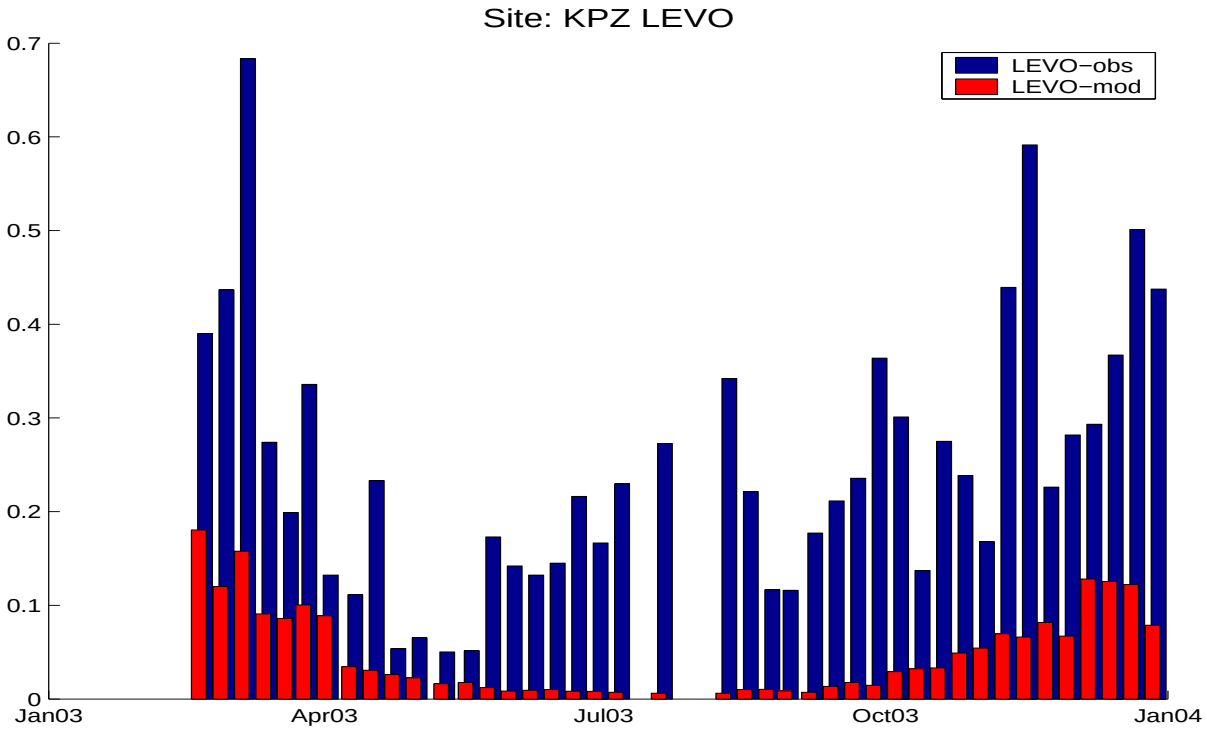
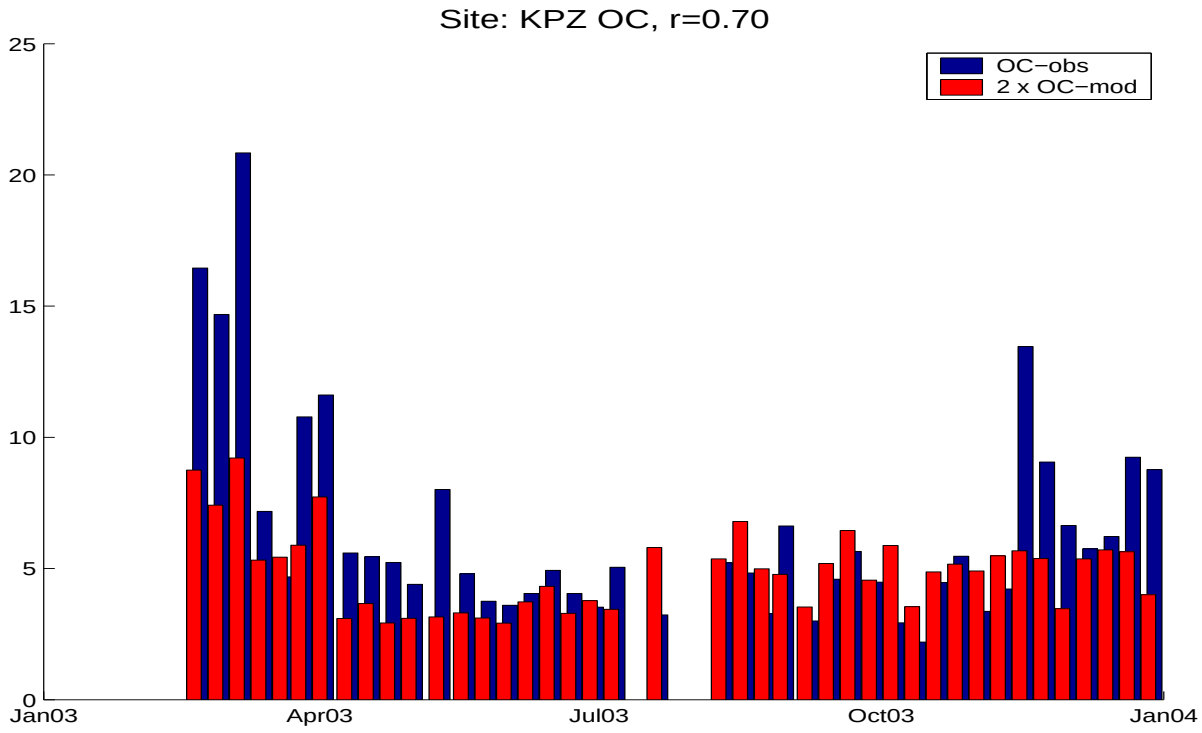
Levoglucosan



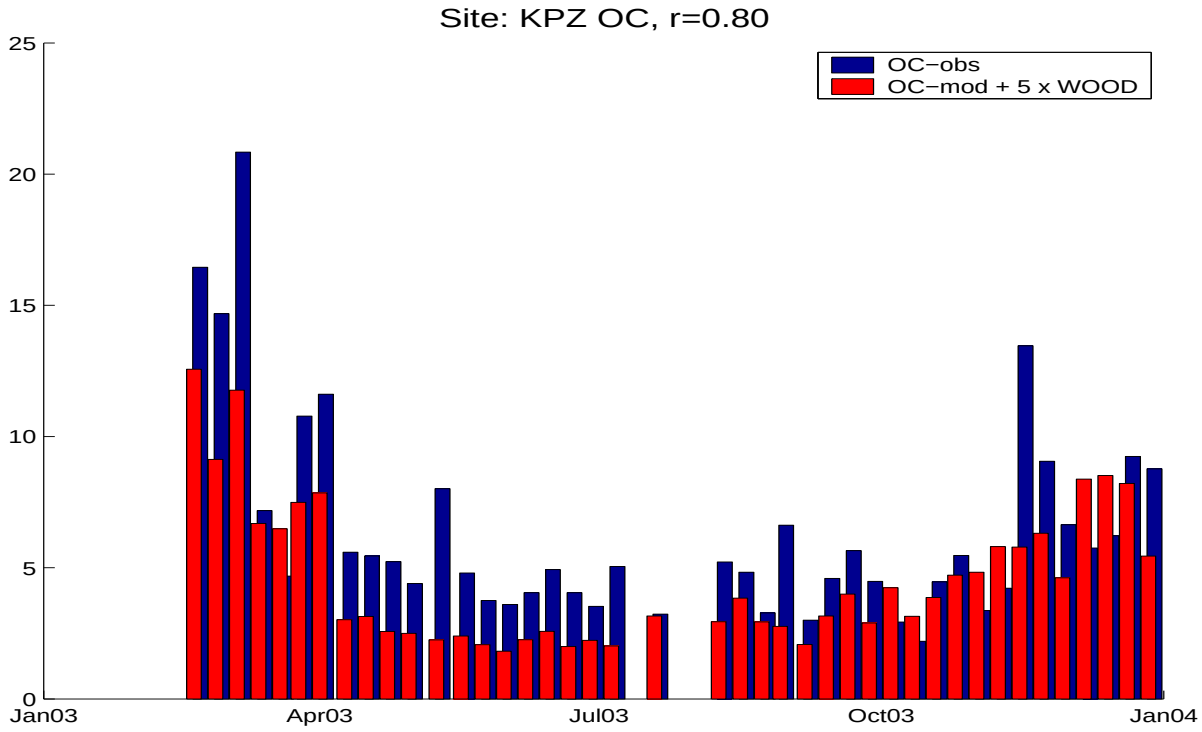
Test 1

Use of 2× FFUEL



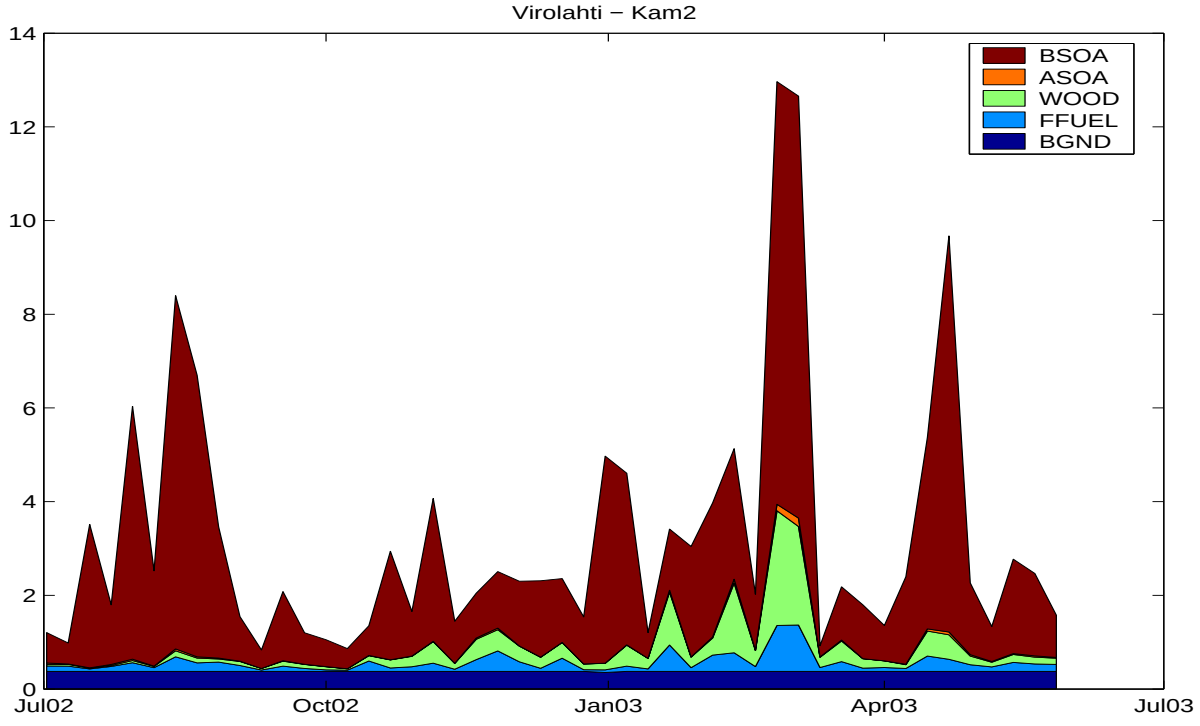
Test 2

Use levoglucosan to ‘correct’ WOOD

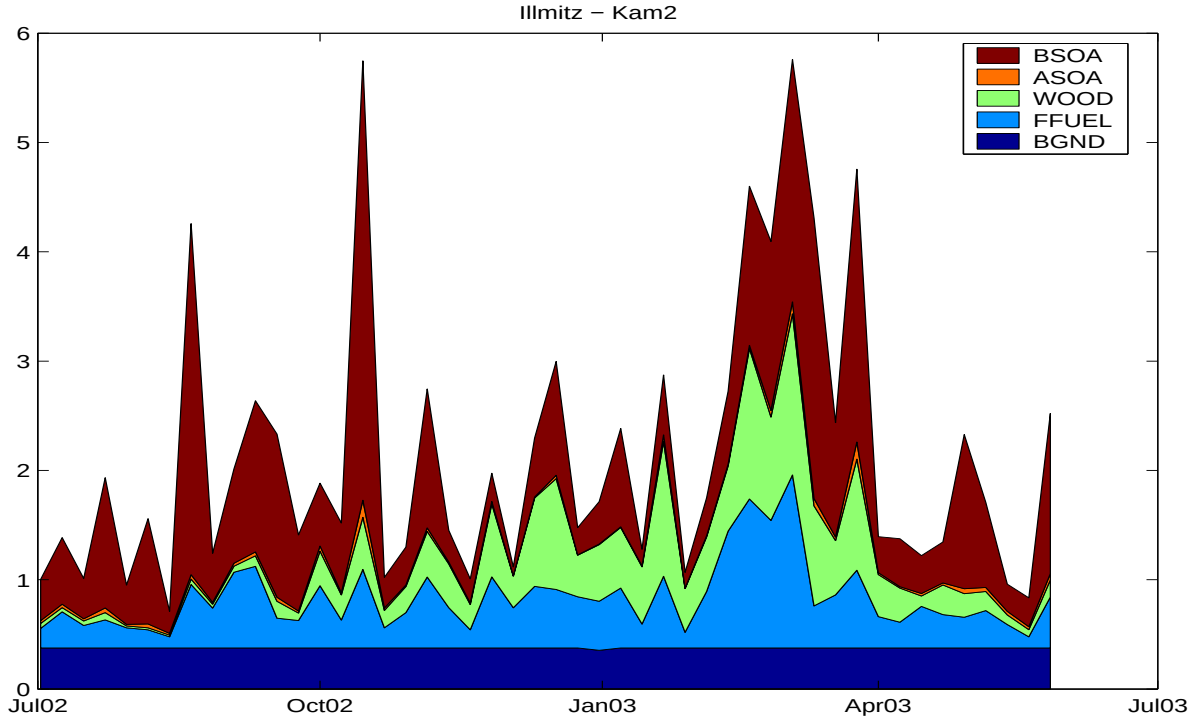


Promising :-)

Origin of OM: Virolahti

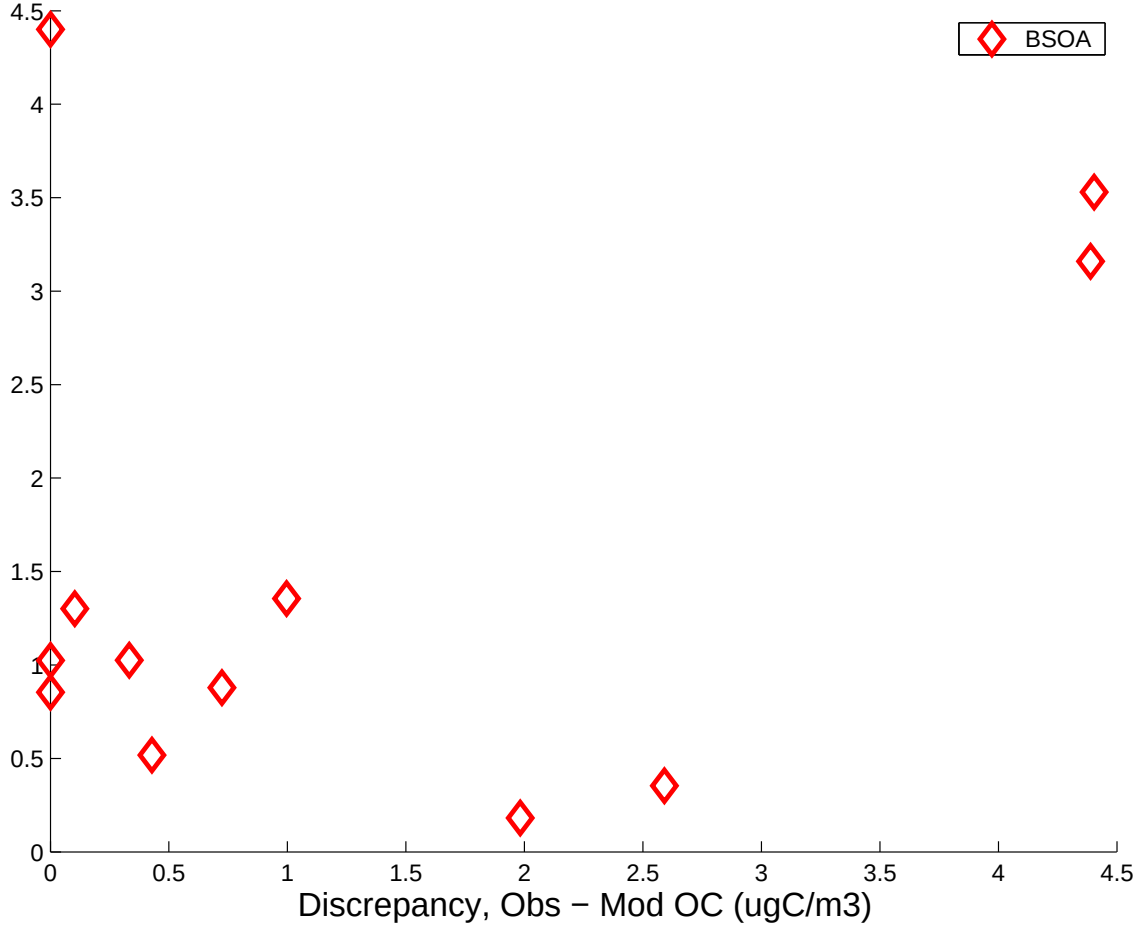


Origin of OM: Illmitz

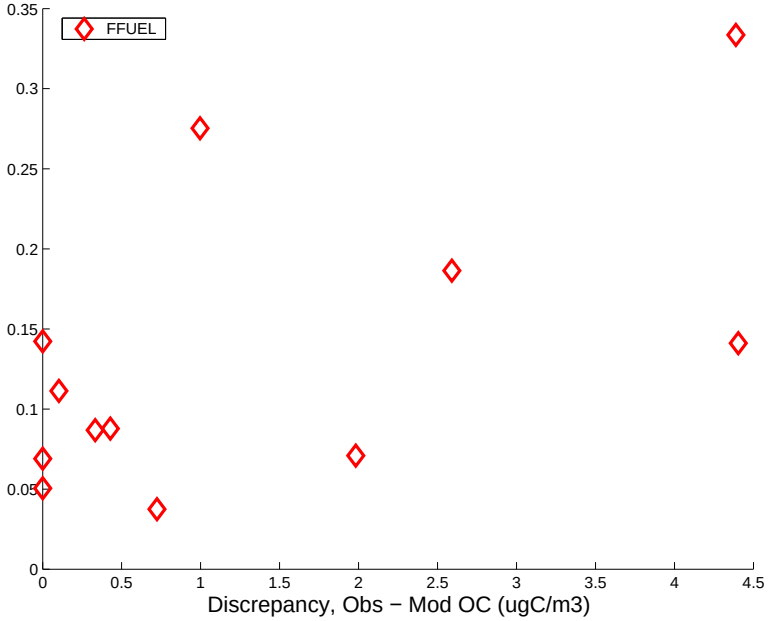


Correlations?

Correlate Obs-Modelled discrepancy against model BSOA (Aspvreten, Sweden):



Correlations?

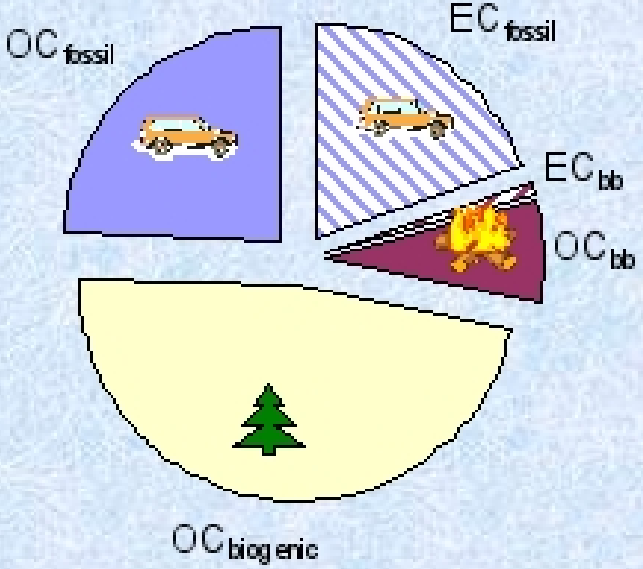


Fossil-fuel?:
Overall - results vary very much from site to site. No obvious ‘easy’ answers.

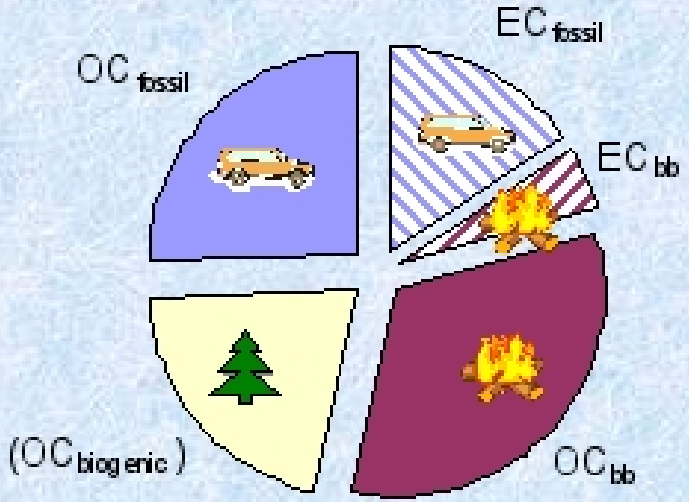
What do we know

- Much new OC/EC (EMEP, CARBOSOL, national)
  - $\Rightarrow$ seasonal variations
- Levoglucosan - linked to wood-burning
- $^{14}C \Rightarrow$ modern versus fossil sources

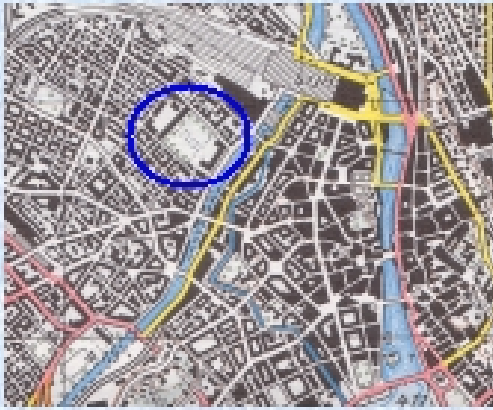
Average contributions of different sources to EC and OC in Zurich, Switzerland

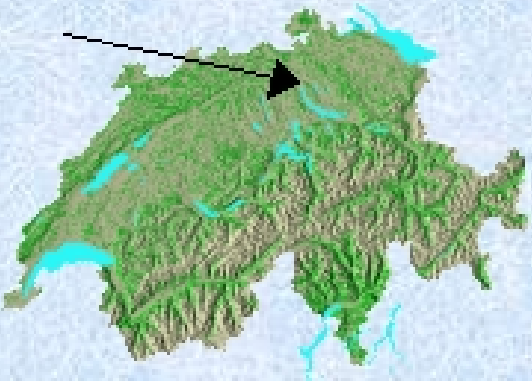


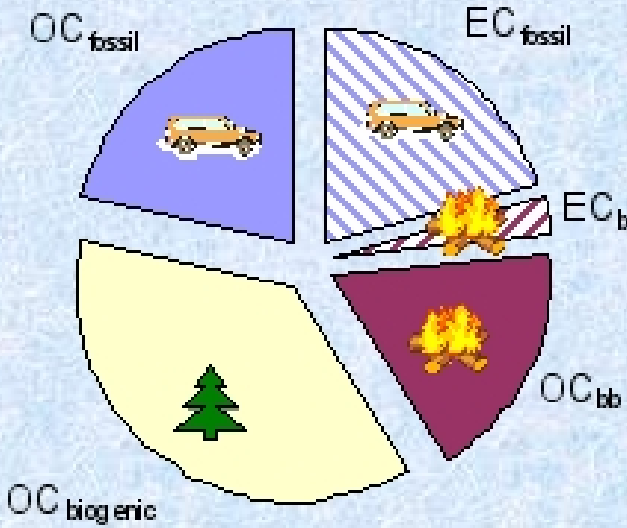
Summer



Winter







Spring

Szidat et al., J. Geophys. Res., submitted

CARBOSOL

- 6 sites across south-central Europe
- 1-week filters (PM_2), analysed for:

  cellulose $\Rightarrow$ biological particles

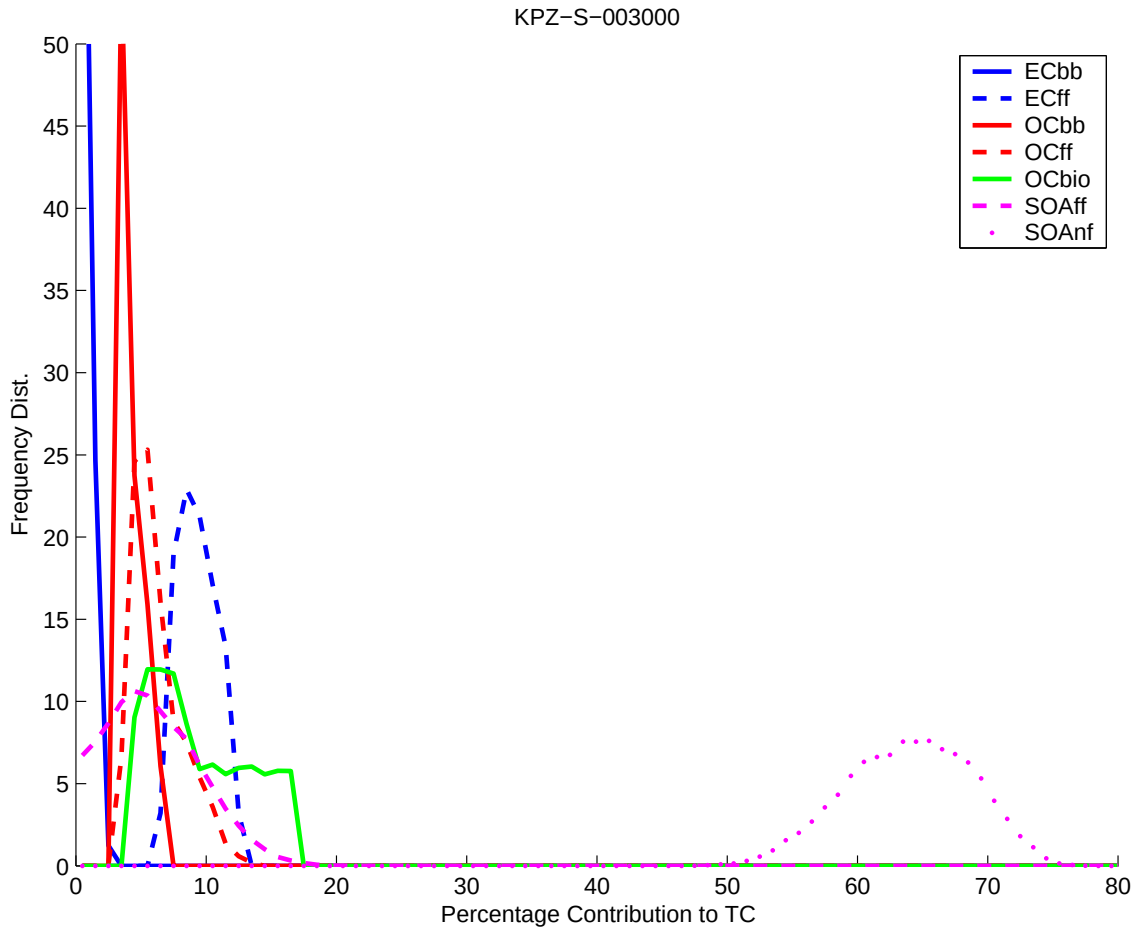
  levoglucosan $\Rightarrow$ biomass-burning

  OC/EC $\Rightarrow$ primary emissions

  ^{14}C $\Rightarrow$ modern/fossil

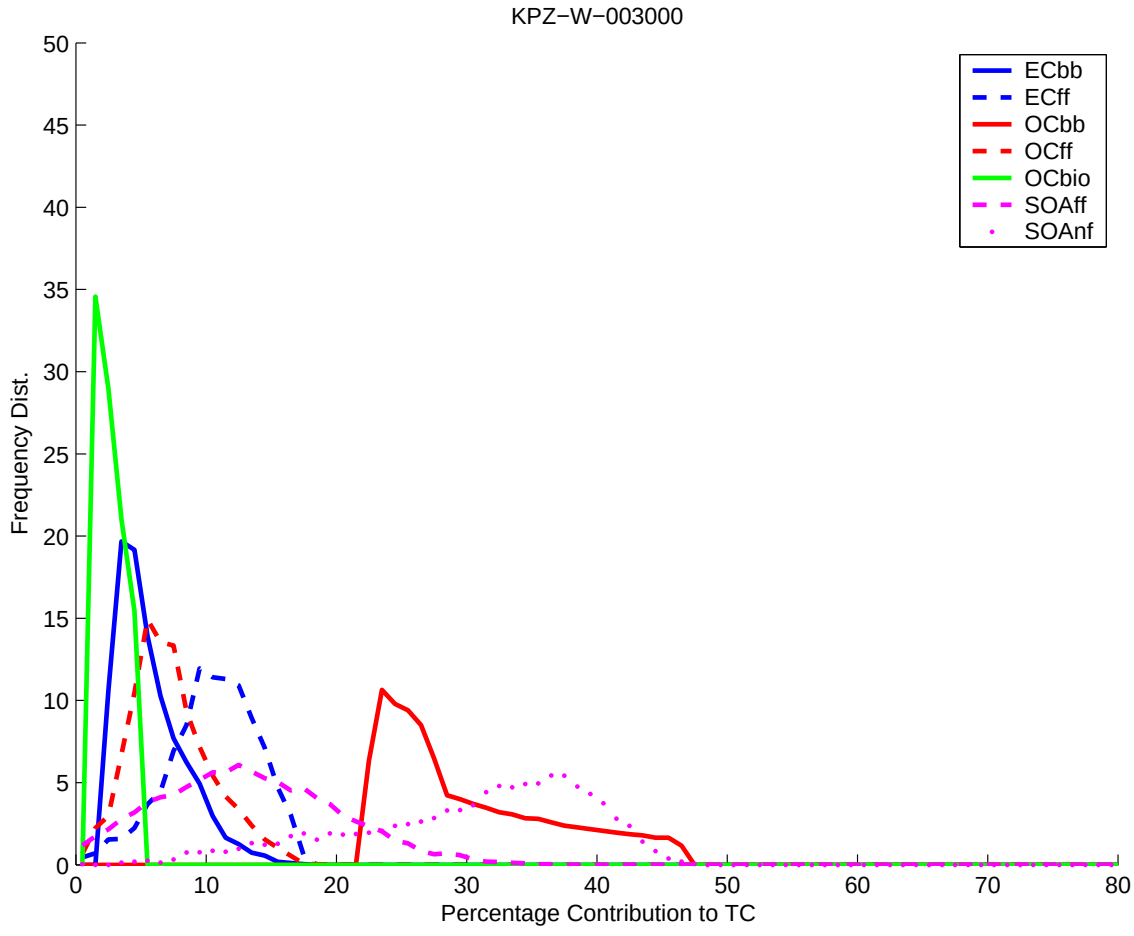
- - all factors approximate

OM: K-Puszta, Summer



(Gelencsér et al., 2006, PROVISIONAL)

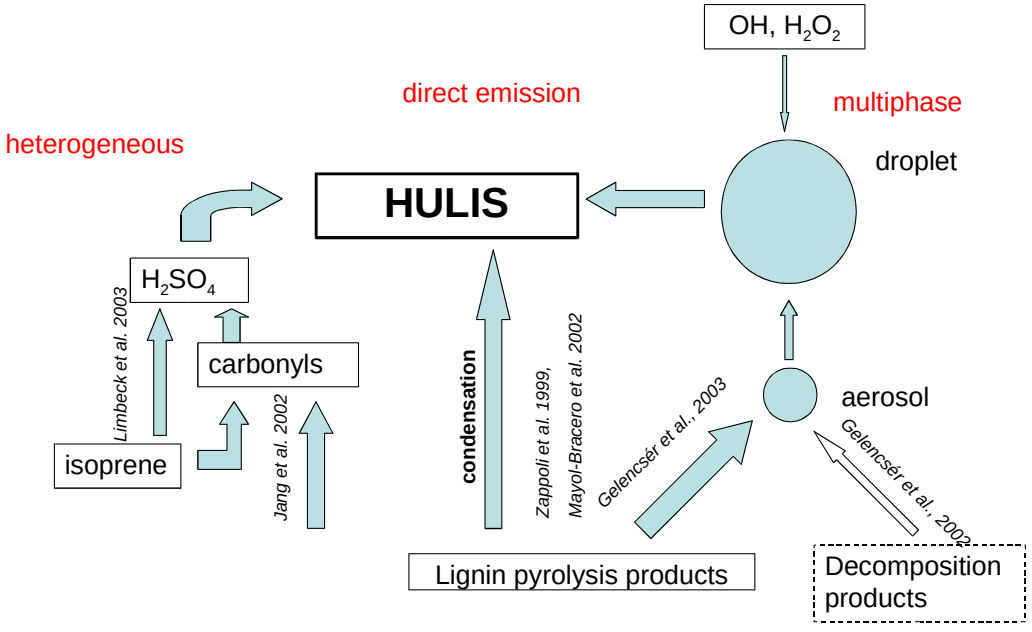
OM: K-Puszta, Winter



(Gelencser et al., 2006, PROVISIONAL)

Alternatives

Working hypotheses for HULIS formation



- Still changing - e.g. Warneck, Ervens suggested aqueous pathways with oxalic acid as source of SOA

Conclusions

- A model with current emissions underpredicts OC across Europe
- Levoglucosan suggests strong under-prediction of POC from wood-burning at some sites (- local sources?), but overprediction at others (emissions inventory)
- Correction for this might help explain a significant fraction of missing OC in wintertime at some sites, not all, and not for summer
- Summer problems probably partly due to lack of polymer formation and/or aqueous pathways?
- Correlation analysis suggests that the missing OC results from both SOA and missing POC.

Conclusions

- State of OC science ‘in infancy’ (Donahue et al., 2005)
- Modellers have no "mechanism" for in-aerosol reactions
- Model results are extremely sensitive to assumptions!
- But, model’s can serve to test theories and emissions
- Measurements are required to constrain models and validate emissions
- Needs chemical speciation, tracers, many locations
- Long-term field data + campaigns+supersites ideal
- Emissions? Primary OC/BC emissions need verification (near-source measurements?)

Acknowledgements

- IIASA & FEI (SYKE) - Z. klimont and K. Kupiainen - emissions
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- CARBOSOL - A. Gelencsér, H.Puxbaum, A.Kasper-Geibl, Pio, M. Legrand