Modelling Organic Aerosol

David Simpson

EMEP, MET.NO & Chalmers

Overview

- Introduction
- Approaches to modelling
- SOA models
- Examples of model usage + evaluation
- Conclusions

What is EMEP?

Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

(European Monitoring and Evaluation Programme)

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Aims: To provide sound scientific support for the Convention, in particular in the areas of:

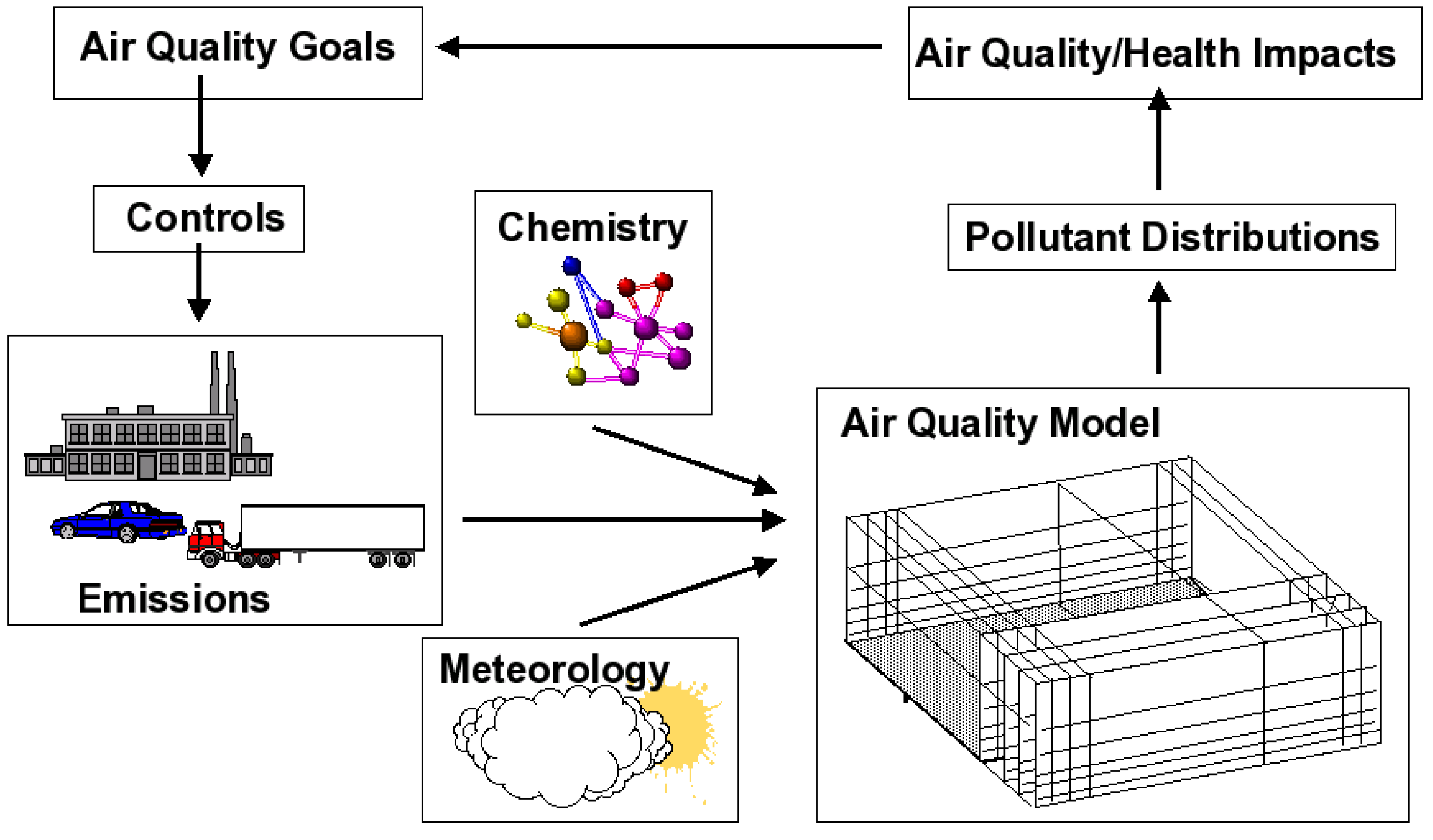
- Atmospheric monitoring and modelling
- Emission inventories and emissions projections
- Integrated assessment

EMEP . . .

CLRTAP: Convention on Long Range Transboundary Air Pollution

- Adopted 1979
- 51 Parties
- Eight Protocols
  - EMEP, 1984
  - Last one: Göteborg, 1999
- Contribution to EU NEC Directives + CAFE

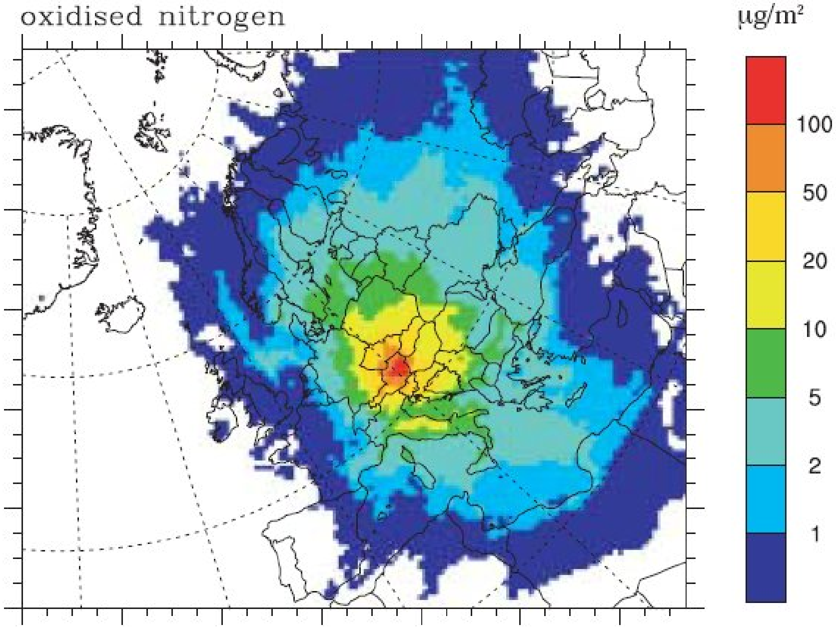
Air Pollution Modelling



Purpose of Modelling

1. Policy - emission control
2. Scientific research
3. Both!

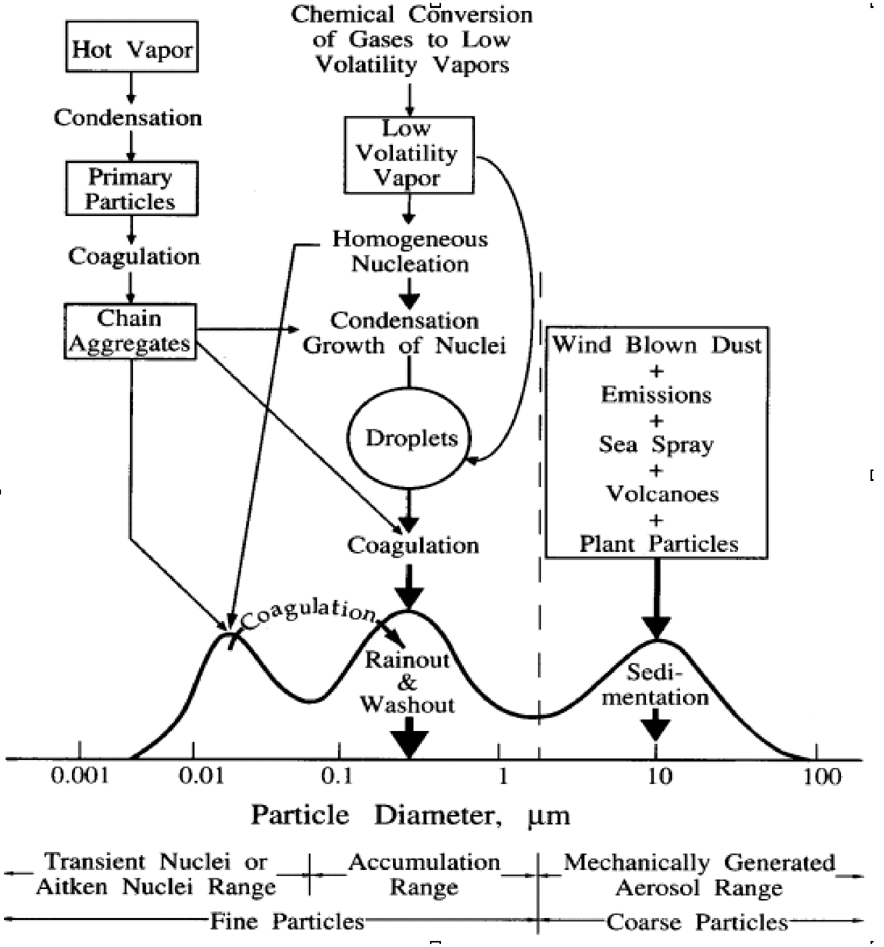
Example: d(Dep(N))/d(E_{NOx}), Austria



Complete approach

Detailed understanding might require:

- size distributions
- complex chemical processes

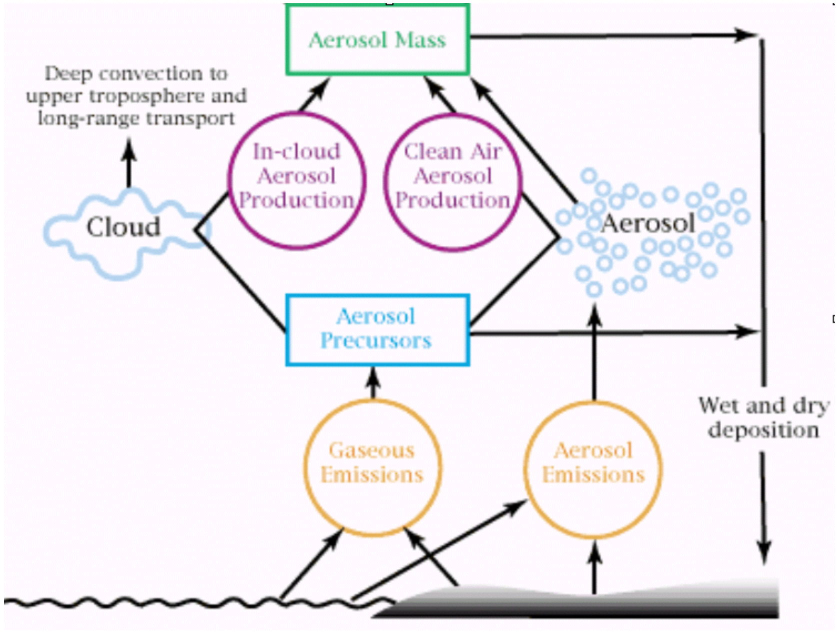


Policy/Global Models

Typically require:

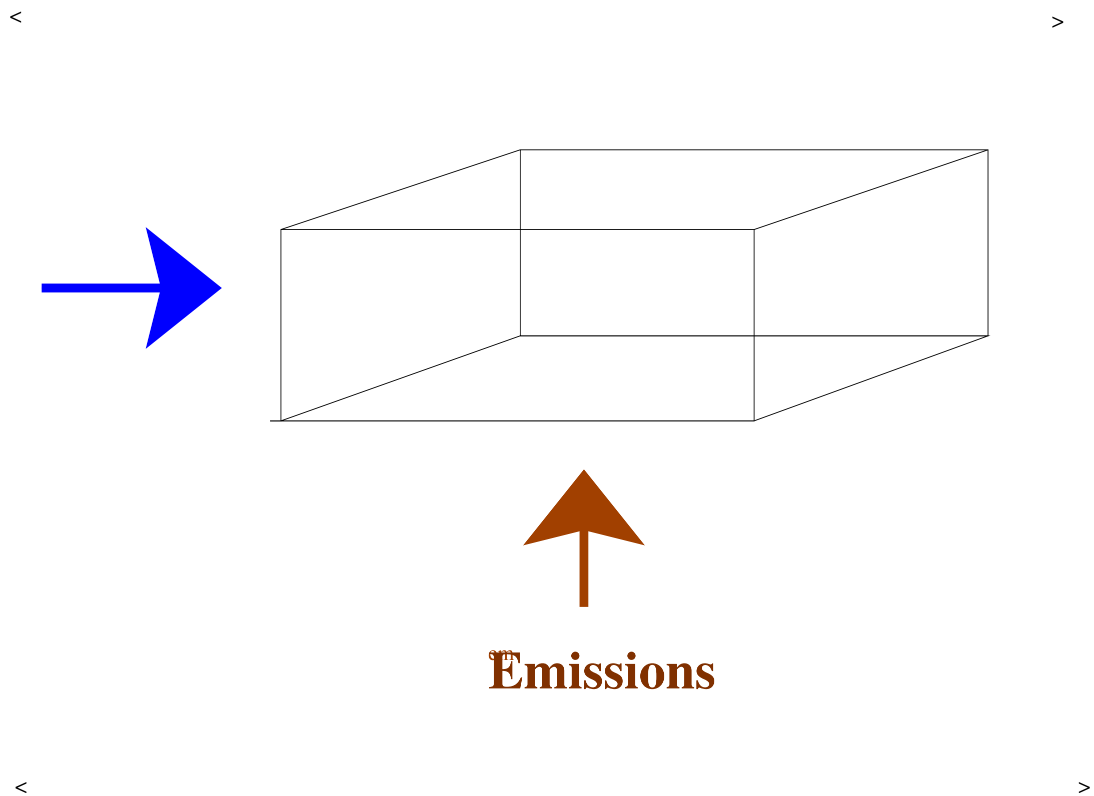
- simpler - only masses ($PM_{2.5}$, PM_{10})
- Well evaluated (trustworthy) models

Concentrate on main processes:



Box model

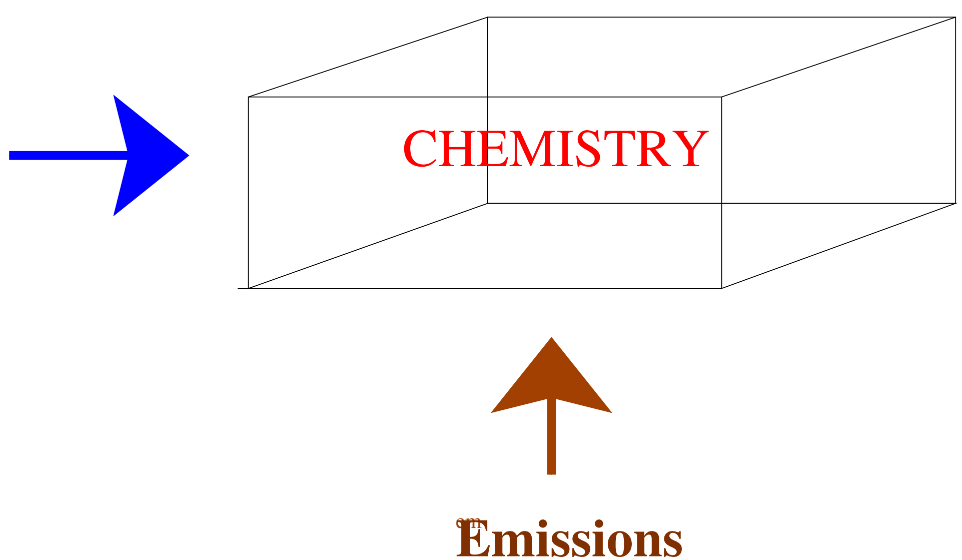
The simplest model:



$$\frac{dC}{dt} = \frac{E}{h} - u.(C - C_0)$$

Box model

Adding Chemistry:



$$\frac{dC}{dt} = \frac{E}{h} - u.(C - C_0) + P - L.C$$

Box model, cont.

... and more terms

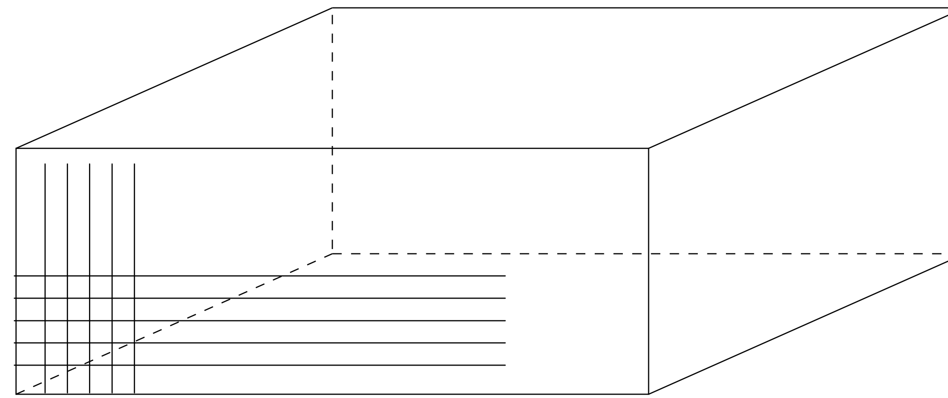
- -Vg. C : dry deposition
- -L . C : wet deposition
- entrainment
- ...

Allow the box to move?

$\Rightarrow$ Lagrangian

The Eulerian 3D model

- Represents all main physical and chemical processes
- Numerical integration



Scientifically most sound method of calculating air pollution

Eulerian model, cont.

3D models are CPU-expensive:

$170 \times 130 \times 20$ = 440 000 gridcells
$\times 100$ species
$\Rightarrow$ 44 million concentrations

Typically requires supercomputer for long simulations.

Eulerian model, cont.

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$\Rightarrow$ 44 million concentrations

Typically requires supercomputer for long simulations.

(But, the times they are a changing.....)

Aerosol Extras

- $\Rightarrow$ Many other ‘effective’ species

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Aerosol Extras

- $\Rightarrow$ Many other ‘effective’ species
- Nucleation
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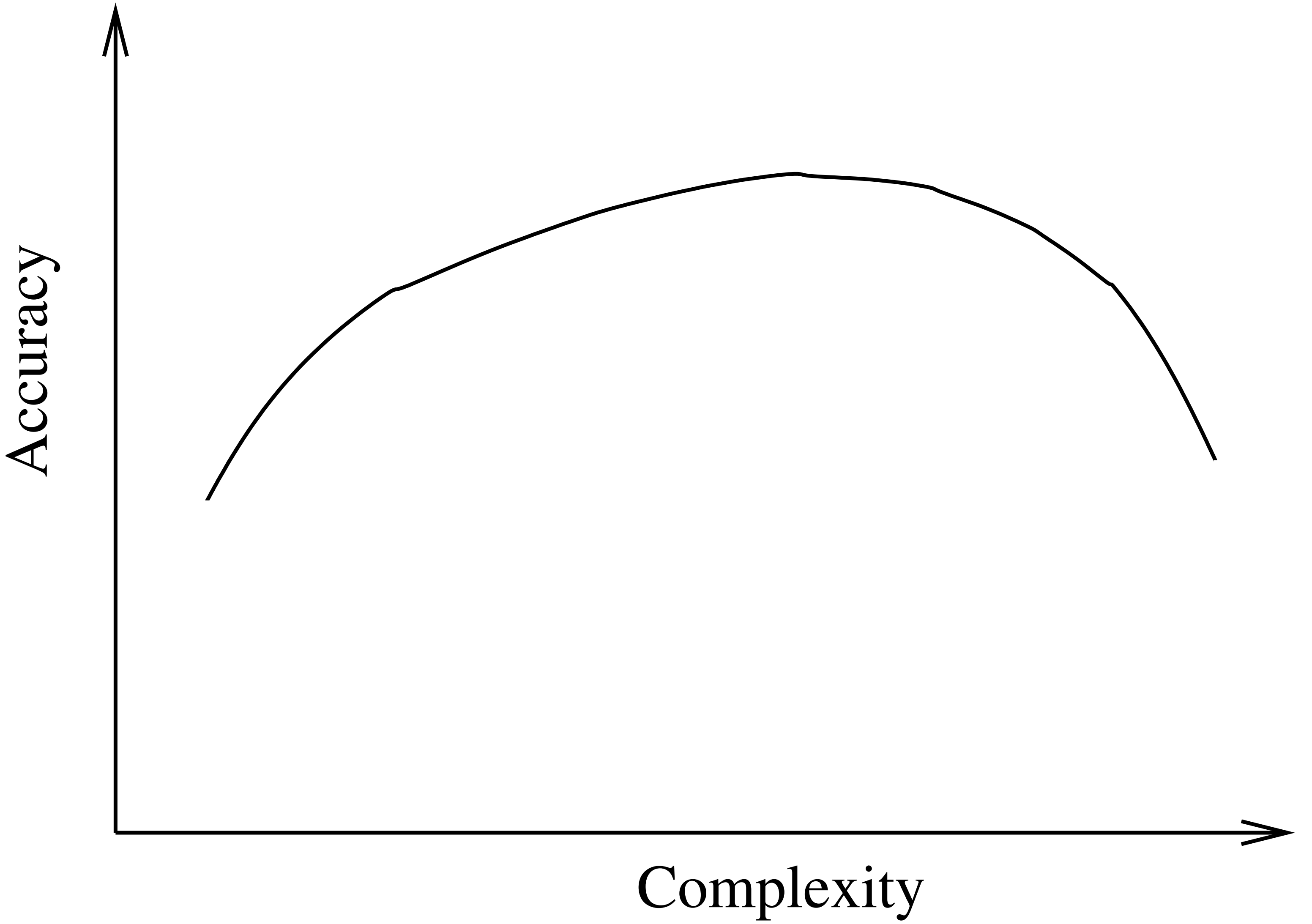
- Condensation
- Cloud-processes
- Size-resolved emissions

Aside: Is complexity good?



Aerosol modelling

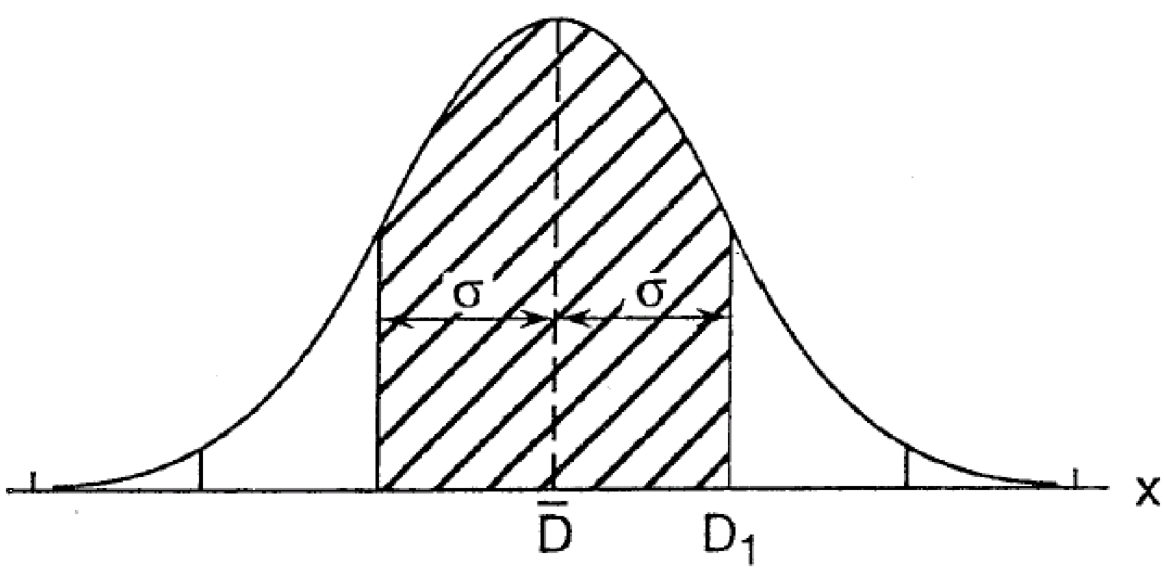
Two main approaches:

1. Modal models
2. Sectional models

Modal models

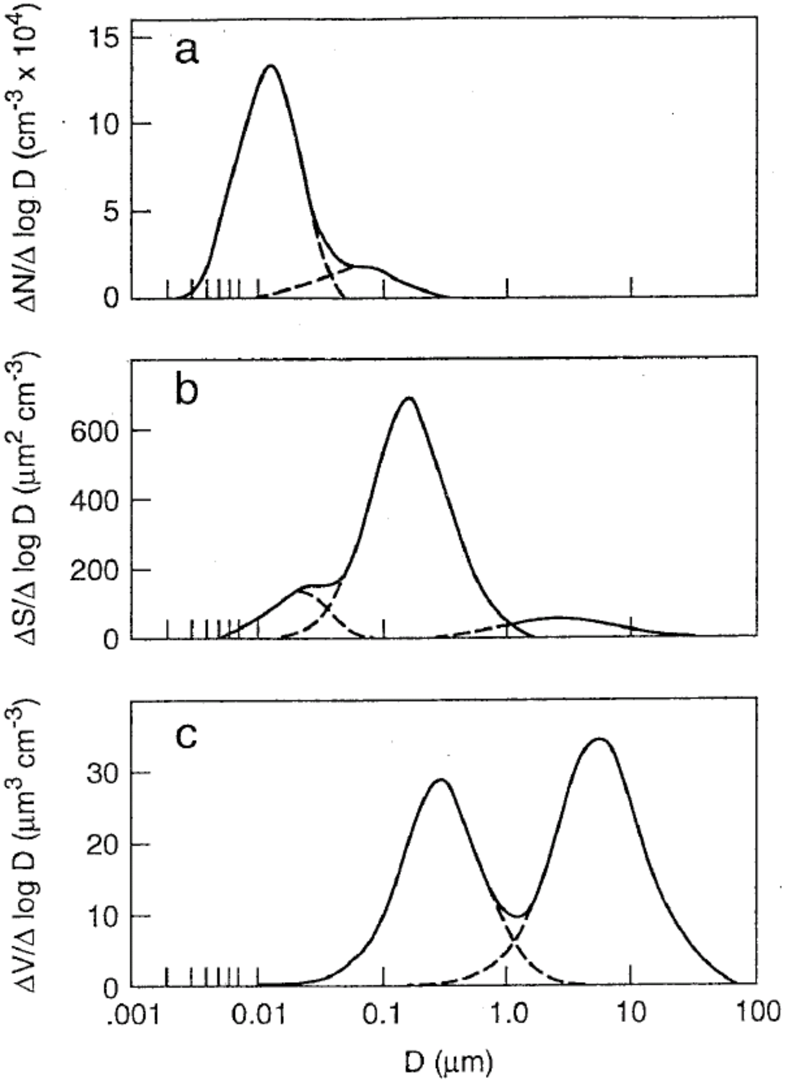
Make use of log-normal distribution

$$n(\ln D_p) = \frac{N}{\sqrt{2\pi}\,\ln\sigma_g}\exp\left[-\frac{1}{2}\frac{(\ln D - \ln D_{p_g})^2}{\ln^2\sigma_g}\right]$$



Modal models, cont.

Break-down atmospheric distribution in 2-3 modes



Modal models, cont.

The kth moment is defined as:

$$M_k = \int_{-\infty}^{+\infty} D_p^k n(\ln D_p) d(\ln D_p)$$

with solution

$$M_k = N.D_{p_g}^k \exp\left[\frac{k^2}{2}\ln^2\sigma_g\right]$$

M_0	=	total particle number concentration
M_2	$\propto$	surface area
M_3	$\propto$	volume, mass

Modal models, cont.

Advantages

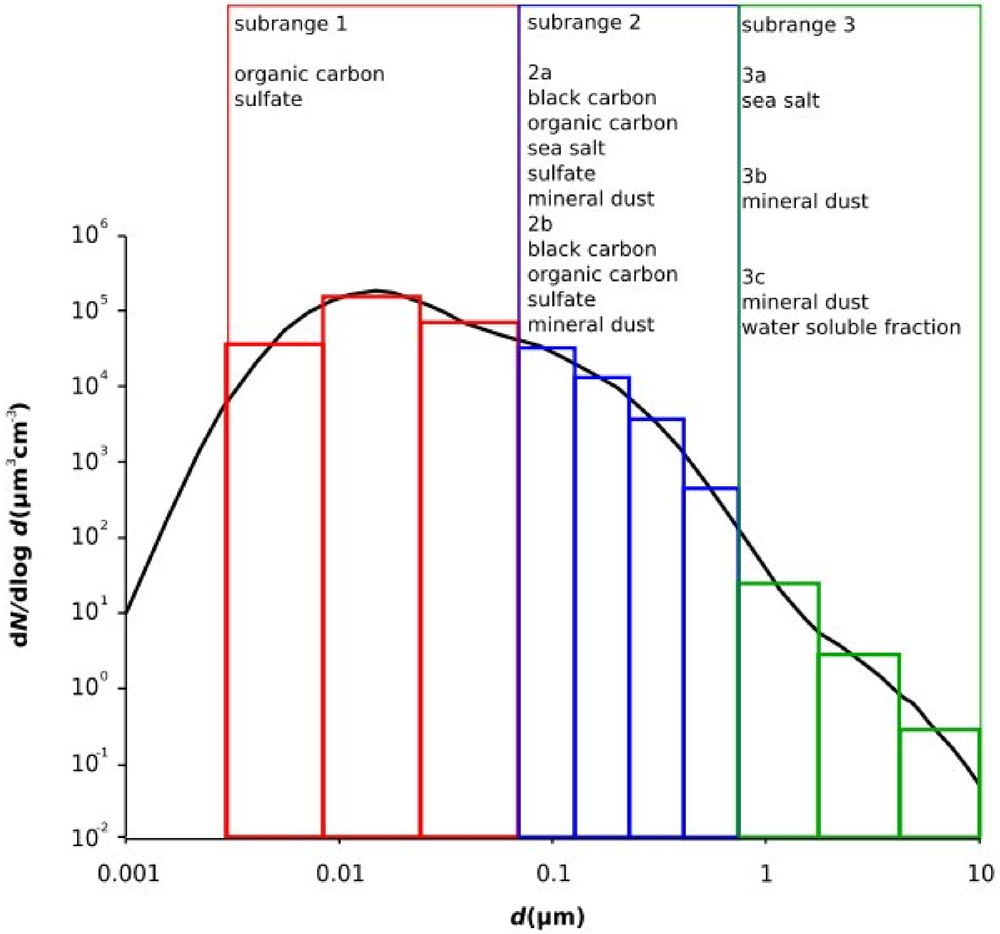
- Requires very few parameters (σ, D_{p_g})
- Computationally inexpensive

Dis-Advantages

- Has no explicit size-distribution, therefore conditions assumed uniform within a mode

Sectional models

Divide aerosol distribution into ‘bins’ or ‘sections’. Typically 4-100, e.g.



Sectional models, cont.

Advantages

- State-of-the-art description (with many sections)
- Allows different chemical mixtures at different sizes
- Flexible

Dis-Advantages

- Computationally expensive
- Physics/chemical basis not always known

Belief in models?

The basic rule:

Belief in models?

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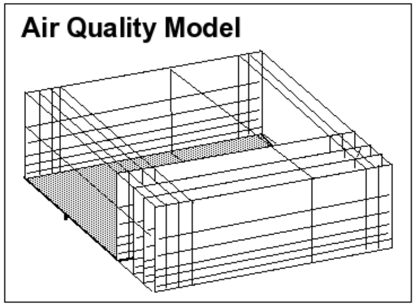
Garbage in ⇒ 

⇒ Garbage out:

Belief in models?

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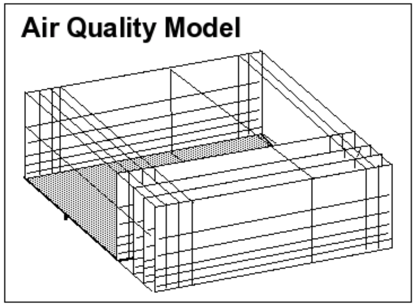
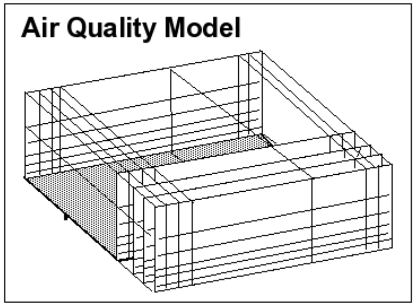
Garbage in ⇒ 

⇒ Garbage out:

SOA twist:

Belief in models?

The basic rule:

Garbage in ⇒ 

⇒ Garbage out:

SOA twist:

Garbage in the middle! 

Sources of OC

OC_{bb} OC from residential wood burning

EC_{bb} EC from residential wood burning

OC_{ff} OC from combustion of fossil fuel

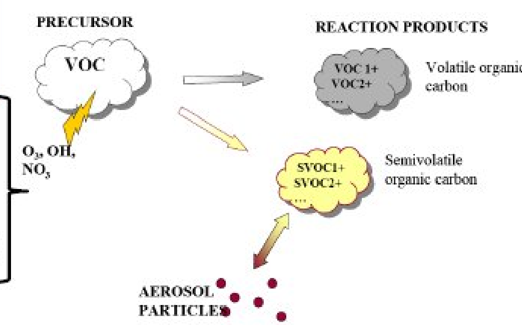
EC_{ff} EC from combustion of fossil fuel

OC_{pbs} OC from fungal spores

OC_{pbc} OC from plant debris

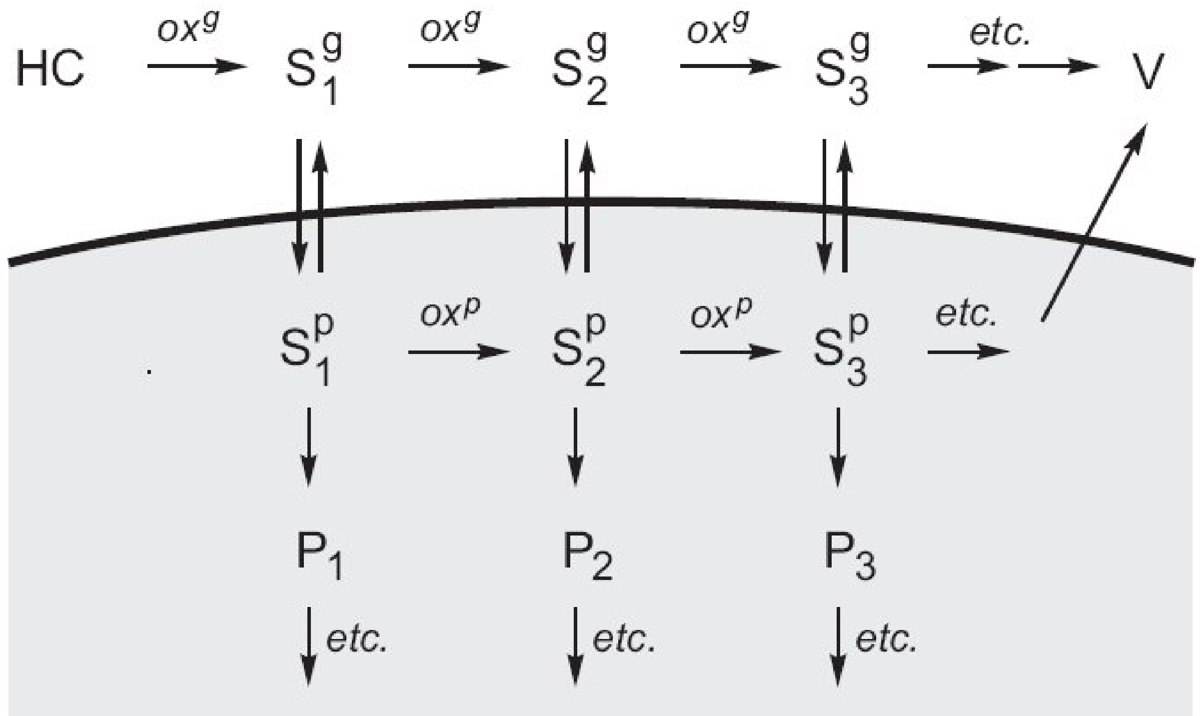
OC_{bsoa} OC from biogenic sec. org. aerosols

OC_{asoa} OC from anthropogenic sec. org. aerosols



Organic Aerosol

OA: Subject=Horrendous!! 1000s of compounds, mainly unknown. Formation mechanisms complex and unkown!



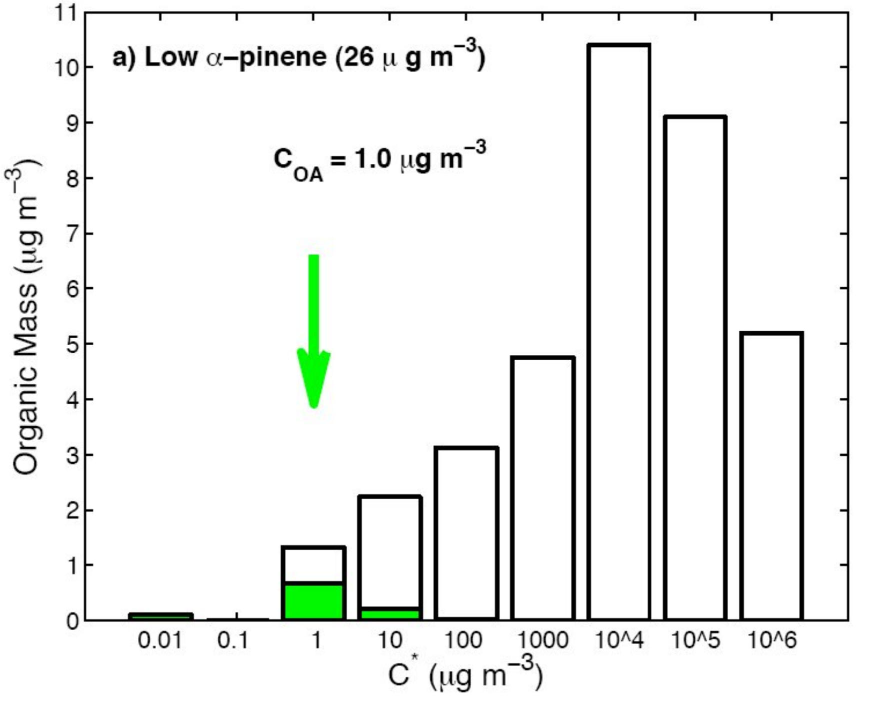
Partitioning

- Gas-Particle partitioning:

$$\frac{A_i}{G_i} = \frac{C_{OA}}{C_i^*}$$

where

- C_i^* is saturation concentration, $= f$(Vapour pressure)



G/P cont.

A multitude of eqns found, e.g.

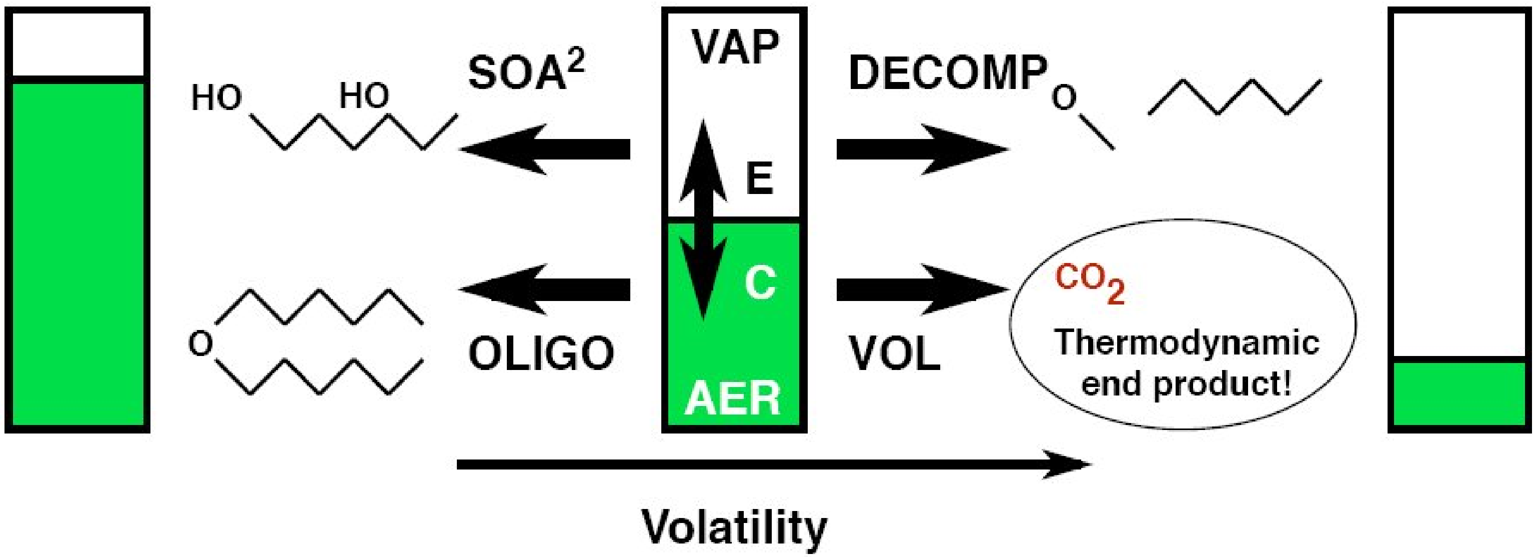
$$\frac{A_i}{G_i} = K_i.\mathsf{C}_{OA} = \frac{RT}{\overline{MW}\zeta_i p^0_{L,i}}.\mathsf{C}_{OA}$$

$$\frac{A_i}{G_i} = \frac{\mathsf{C}_{OA}}{C^*_i} = \frac{RT}{MW_i \zeta'_i p^0_{L,i}}.\mathsf{C}_{OA}$$

Smog-chambers:

$$Y = \mathsf{C}_{OA} \sum \frac{\alpha_i K_i}{1 + \alpha_i K_i \mathsf{C}_{OA}}$$

Chemistry < − > SOA?



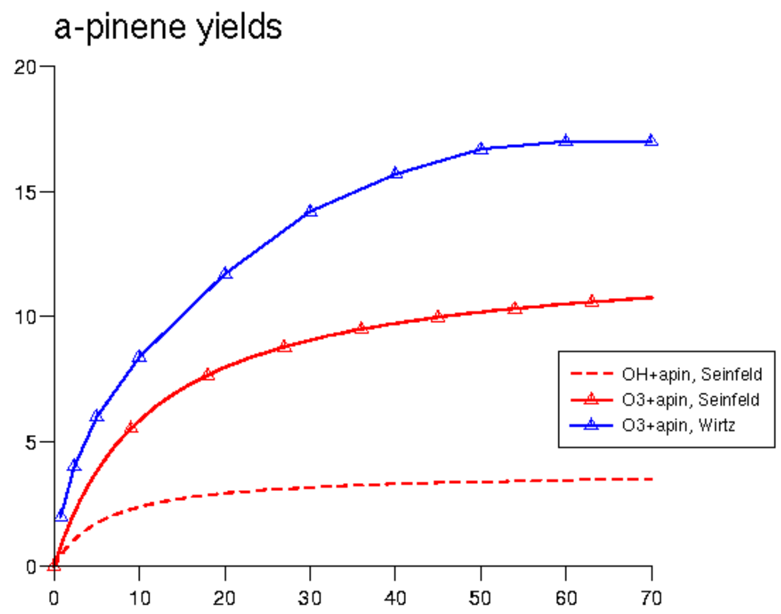
Stolen from Neil...

SOA: α-K approaches

Smog-chamber data could be explained with:

VOC + Ox $\Rightarrow \alpha_1$ P_1 + α_2 P_2

G/P approaches



$\mathsf{C}_{OA}(\mu\mathsf{g/m}^3) \Rightarrow$

$$P_i = A_i + G_i$$

$$\frac{A_i}{G_i} = K_i.\mathsf{C}_{OA}$$

$$\frac{A_i}{G_i} = \frac{\mathsf{C}_{OA}}{C_i^*}$$

α-K approaches, cont.

Pros:

- Easy-to-use
- Available for many compounds

α-K approaches, cont.

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- Easy-to-use
- Available for many compounds

Cons:

- Derived from smog-chambers, often 40°C, 100s ppb, v.low RH
- Not flexible/mechanistic

α-K approaches, cont.

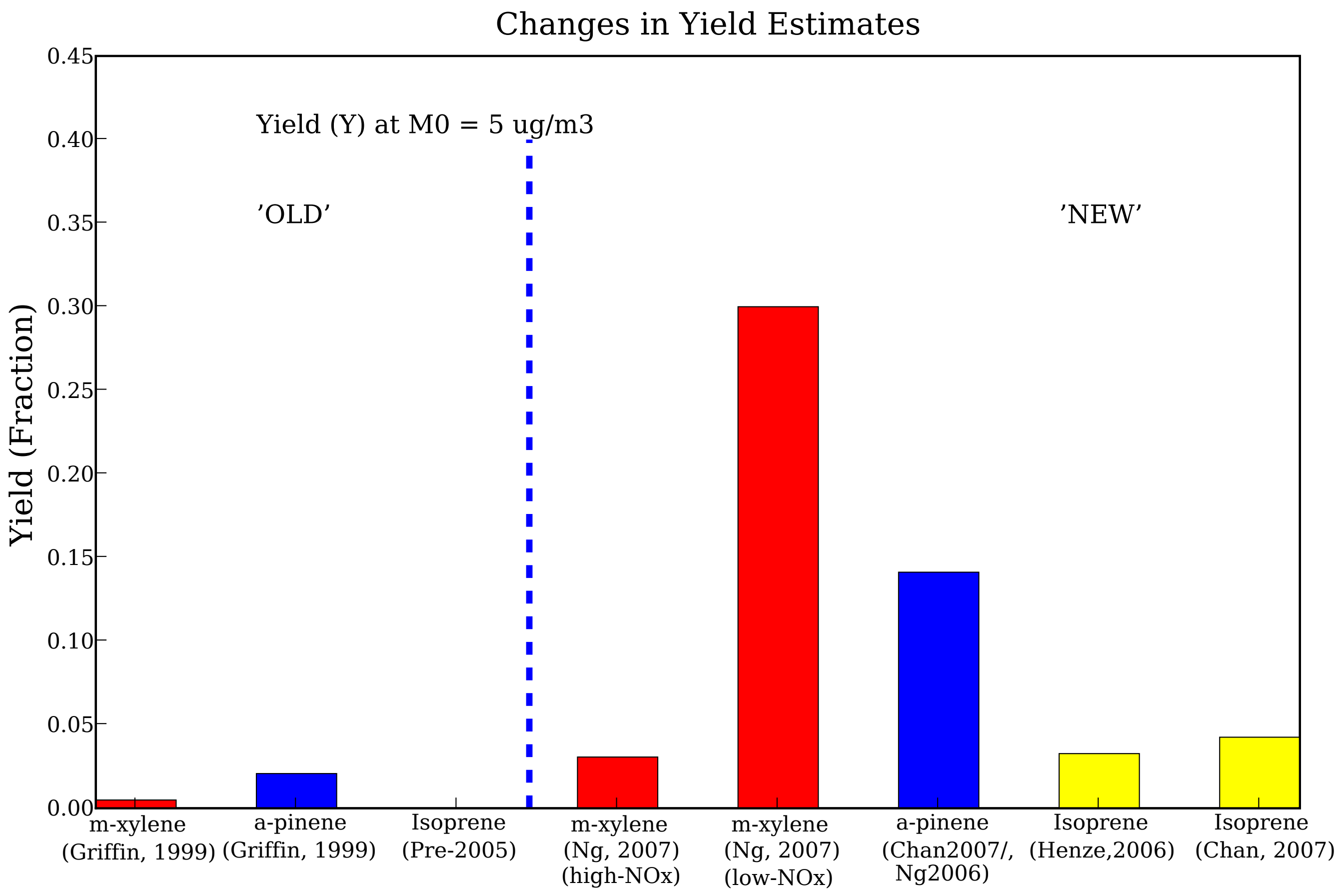
Pros:

- Easy-to-use
- Available for many compounds

Cons:

- Derived from smog-chambers, often 40°C, 100s ppb, v.low RH
- Not flexible/mechanistic
- Coefficients used so far, wrong?

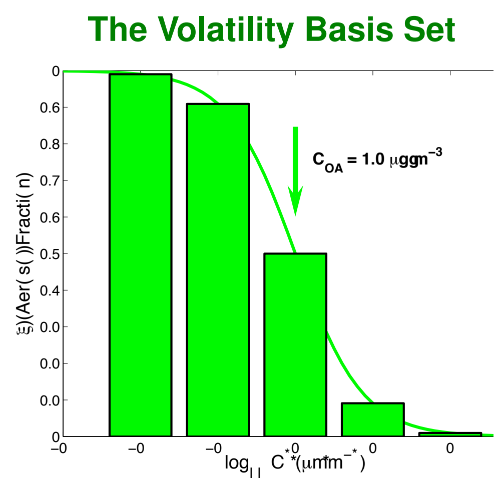
New Evaluations



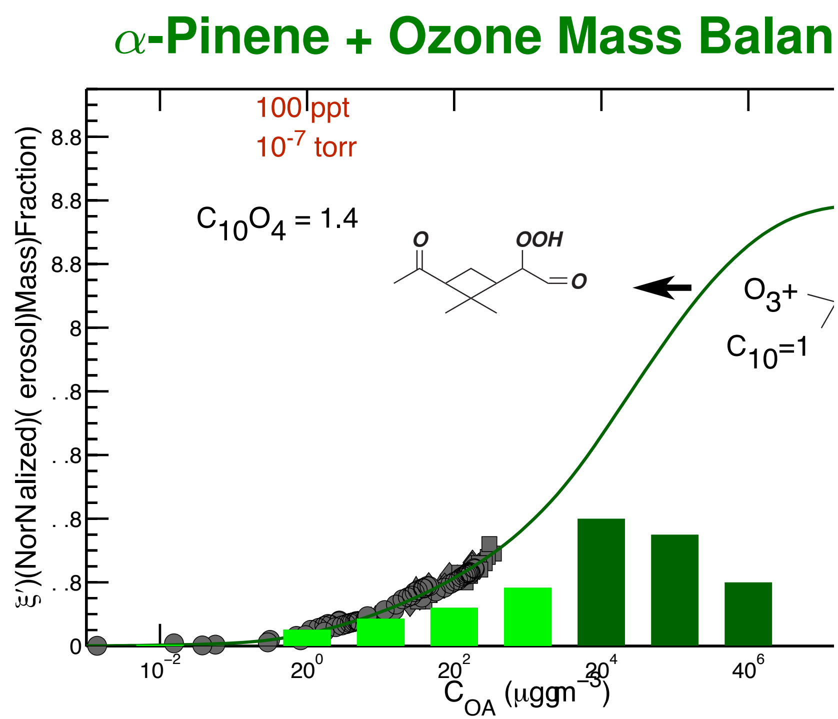
e.g. Ng et al. (2006, 2007), Chan et al. (2007)

Volatilty Approach

Donahue, Robinson....



$C_i^* = \{0.01, 0.1, 1, 10, 100, 1000, 10^4, 10^5, 10^6\}$ μg



- Mass yields $\alpha_i' = \{.004, 0, .05, .09, .12, .18, ...\}$
- Only around 0.055 SOA formation from α-pinene in the LVOC rar
- Mass balance for 'nominal product' demands $\xi_{\max} = \sum_i \alpha_i \simeq 1.$

Volatility methods?

Pros:

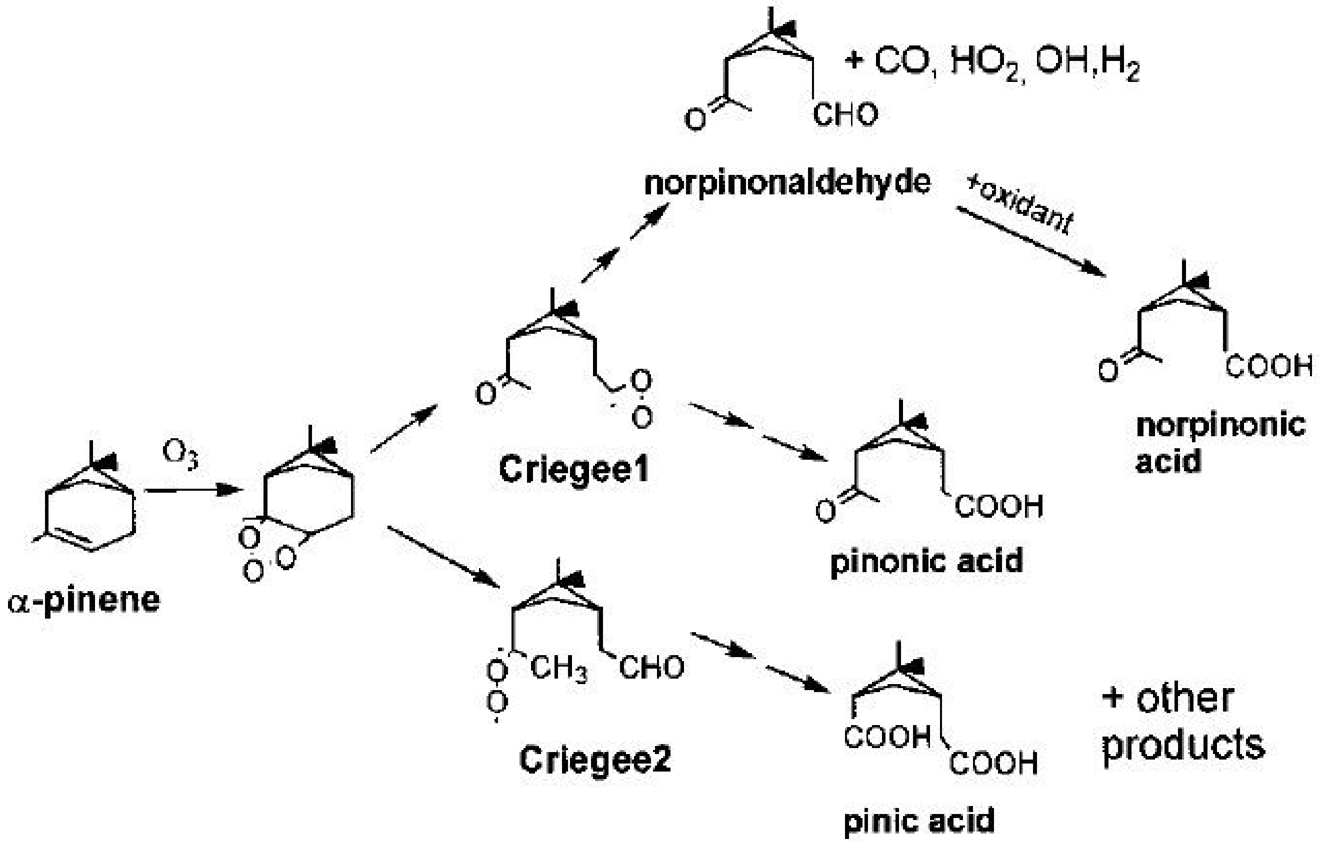
- Flexible framework
- Maps more of parameter space
- Easier to link new data/experiments
- Efficient for global models

Cons:

- Still not mechanistic

EMEP approach

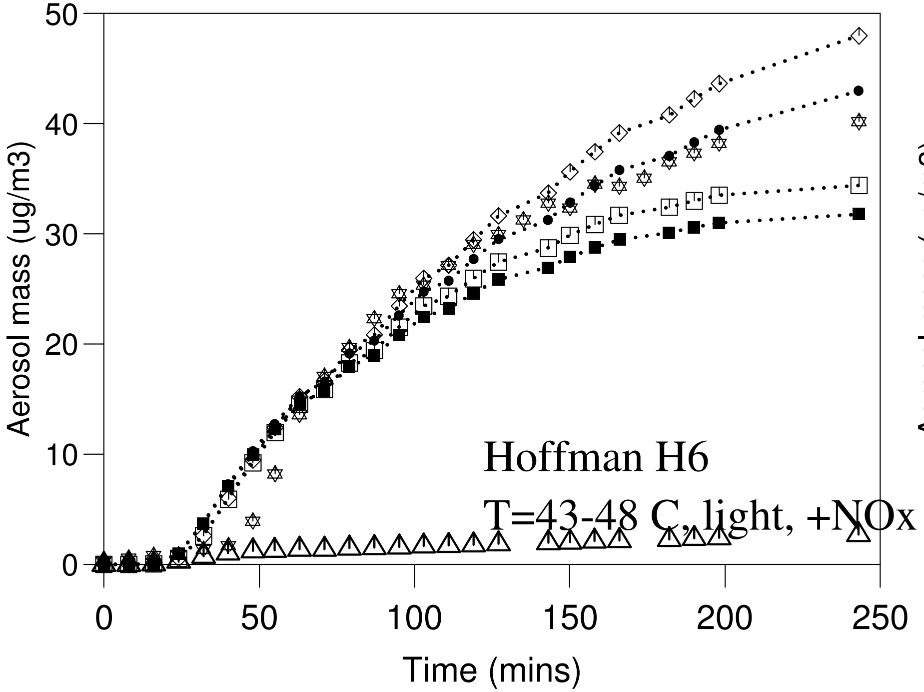
EMEP Kam-2 Method: ‘Explicit’, extended from Kamens et al.:

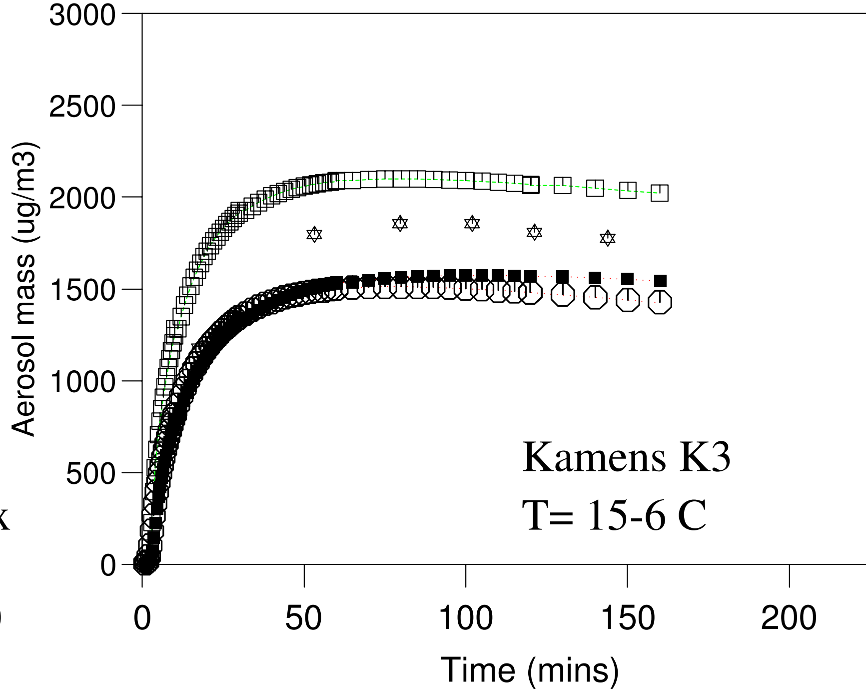


21 reactions, 15 products, dimer, ... Andersson-Sköld and Simpson, JGR, 2001

EMEP BSOA, Kam-2

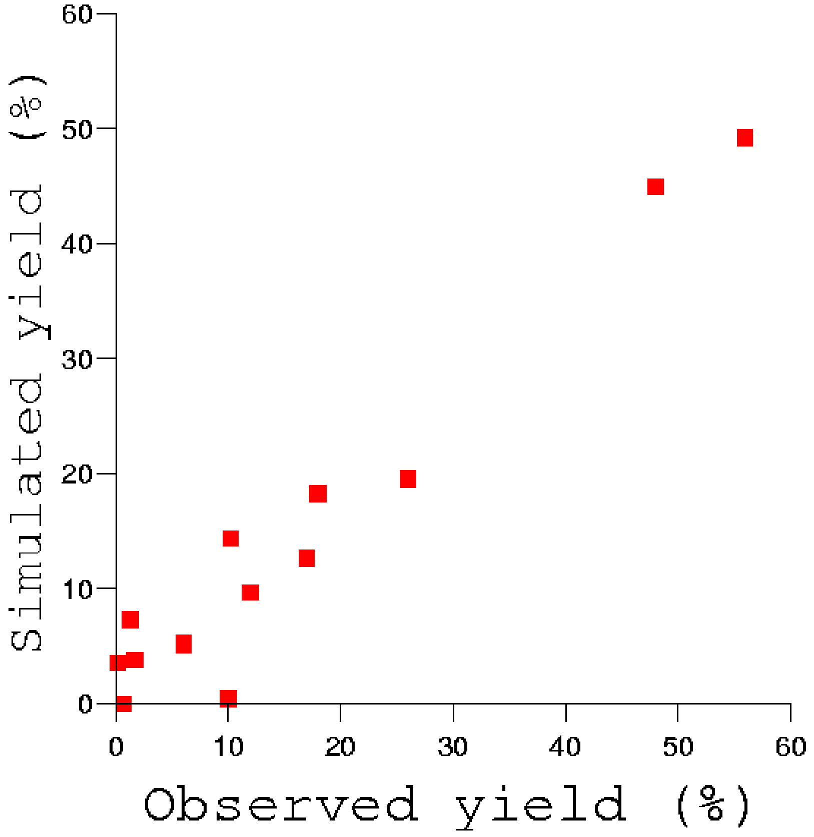
Evaluated against smog-chamber:





BSOA; Kam-2 Method

Comparison with Smog-Chambers good (Andersson-Sköld and Simpson, 2001): 9-820 ppb α-pinene, 0-240 ppb NOx



EMEP Kam-2(X)

Pros:

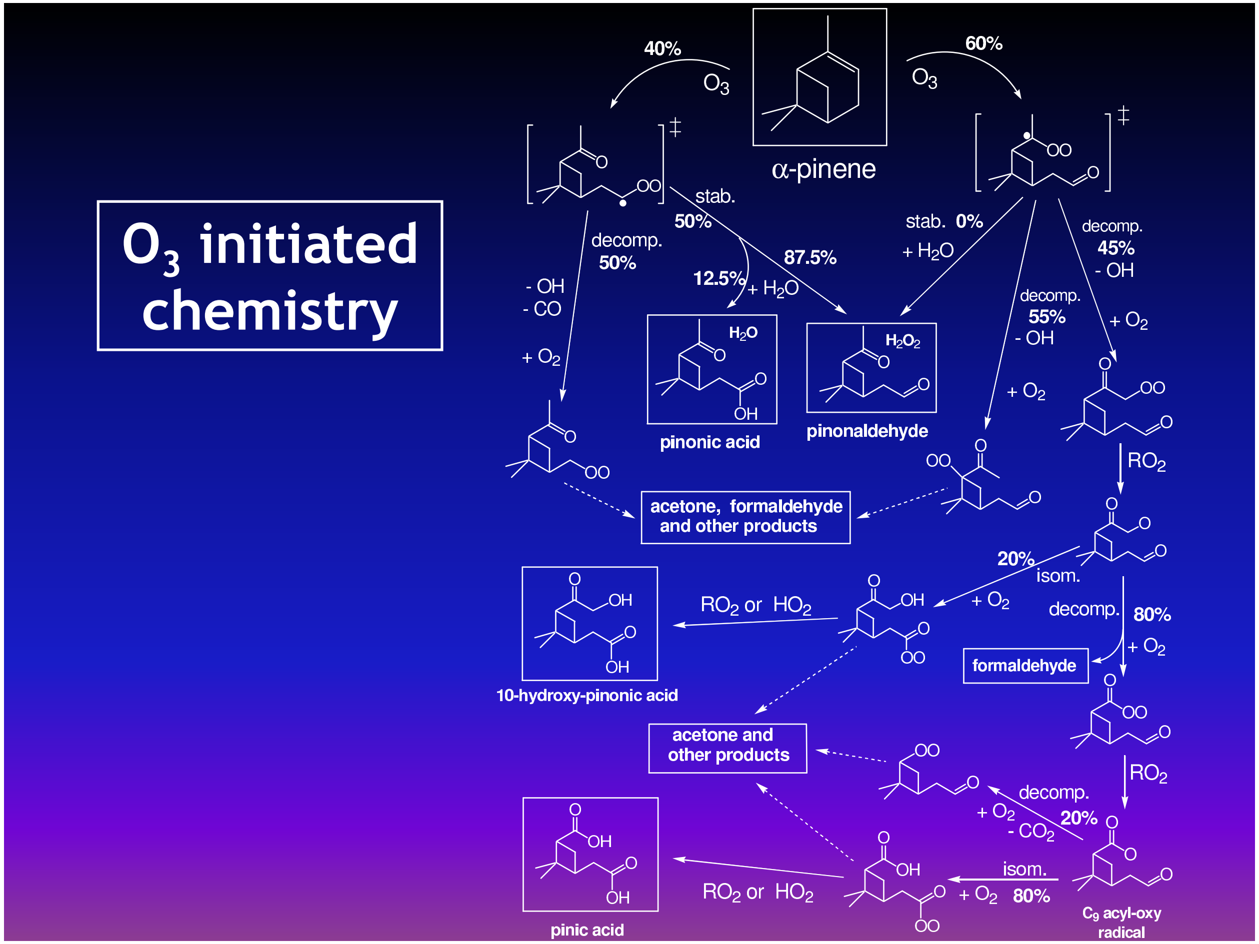
- Flexible framework
- ‘Real’ species (surrogates anyway)
- Linked with gas-phase chemistry
- Evaluated against several smog-chamber exps.

Cons:

- No aqueous/heterogenous chemistry
- One (α-pinene!) species
- Old

The Big Stuff

MCM, 1000s reactions, 200 SVOC species (Jenkin et al., JGR, 2004)



(or CACM, Griffin et al.)

MCM-type

Pros:

- Explicit framework
- ‘Real’ species
- 1000s of reactions - as realistic as possible

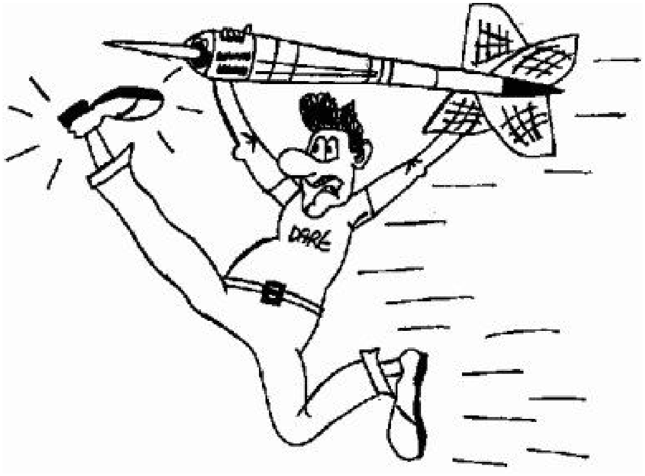
Cons:

- No aqueous/heterogenous chemistry
- Two (α, β-pinene) species
- Needs very large (100-500) correction factors for volatility

MCM-type, cont.

Cons:

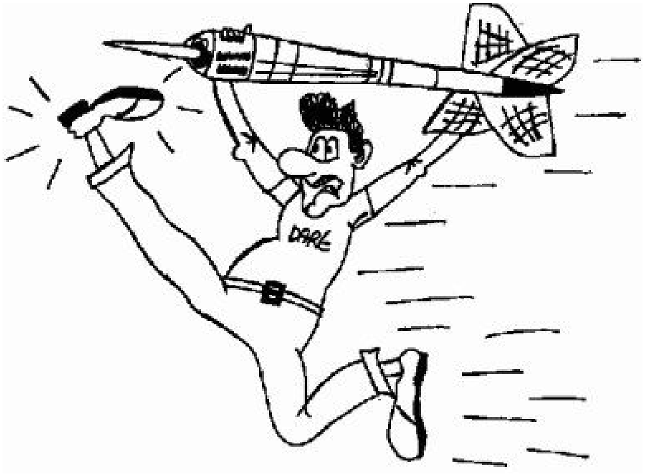
- Heavy!



MCM-type, cont.

Cons:

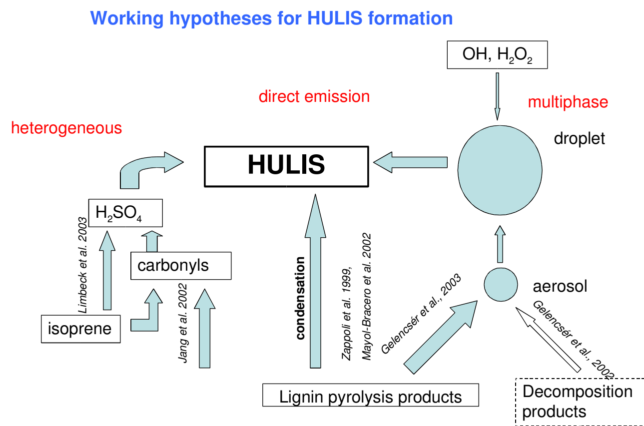
- Heavy!



Pro:

- Attempt to incorporate be
understanding

New issues....



- Still changing - e.g. Warneck, Ervens, Jang, Griffin, suggest aqueous/heterogenous pathways as source of SOA. Isoprene, glyoxal, oxalic acid, ...
- Do we know which pathway to follow?

Sensitivity

All models sensitive to:

- Vapour pressure
- ΔH assumptions
- Activity coefficients
- Deposition assumptions
- Emissions

Sensitivty: ΔH

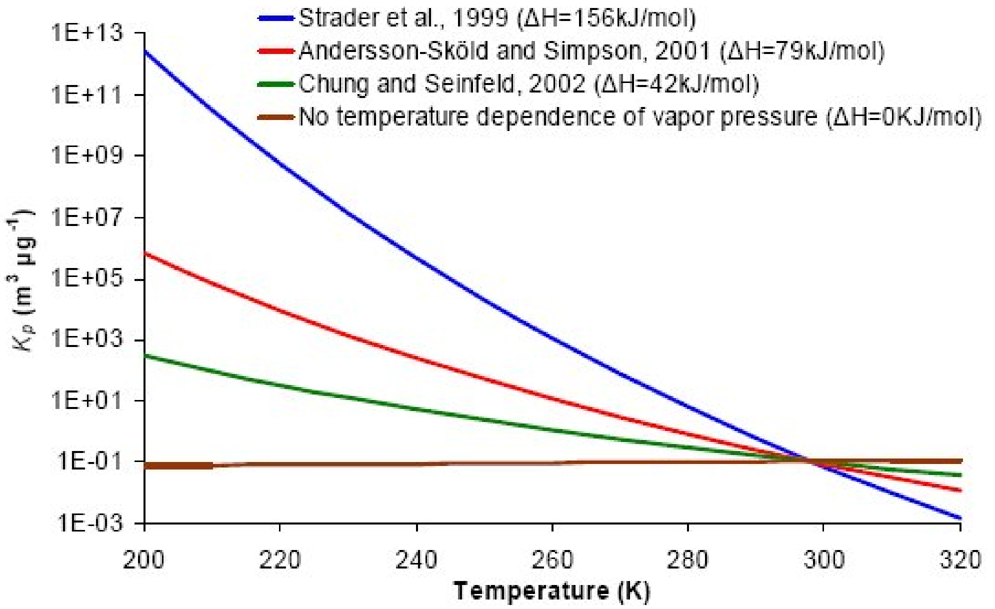
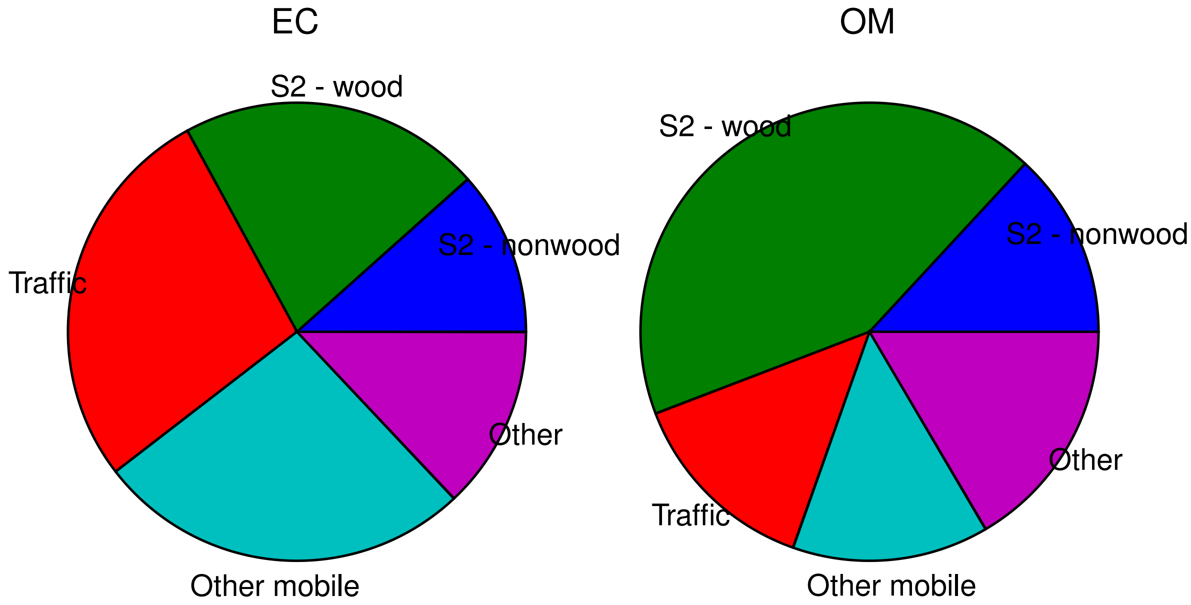


Fig. 1. Variation of K_p with temperature, for the case K_p=0.11 at 298 K.

Tsigaridis+Kanakidou, ACP, 2003

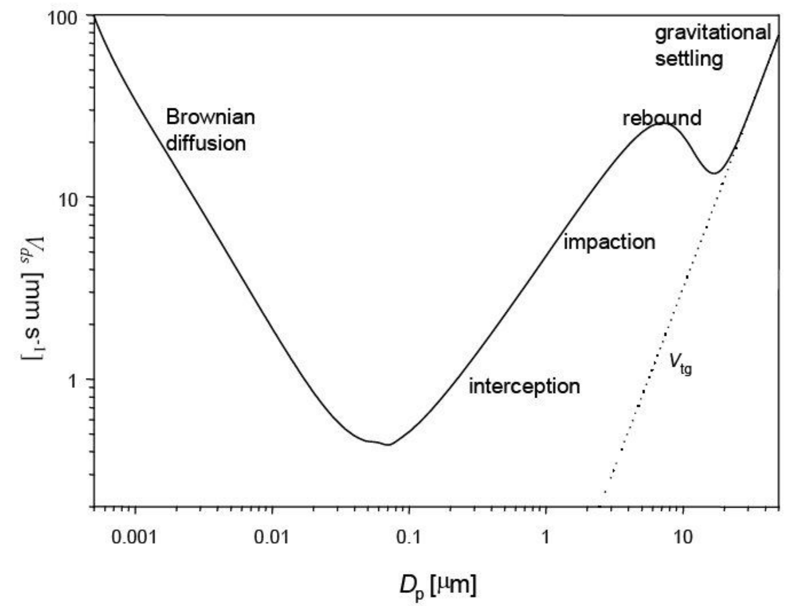
Emissions – IIASA

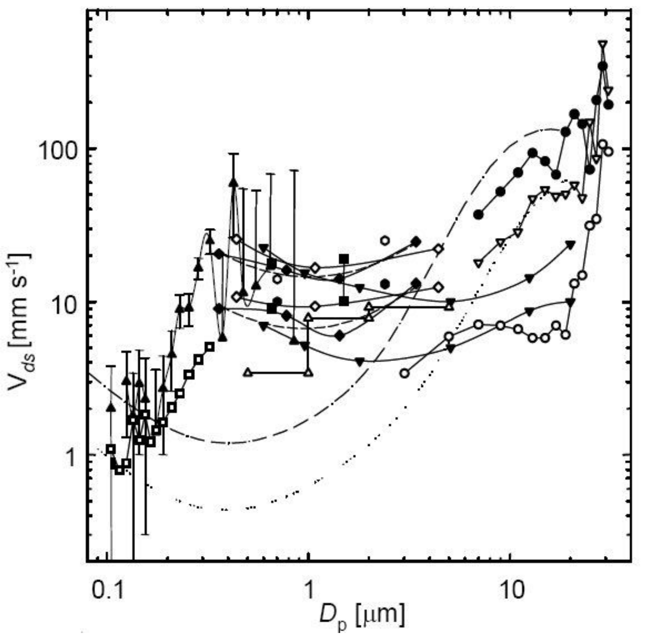


Fine-particle emissions - Kupiainen, and Klimont, 2007

Dry Deposition

Problems of Theory vs. Measurements:





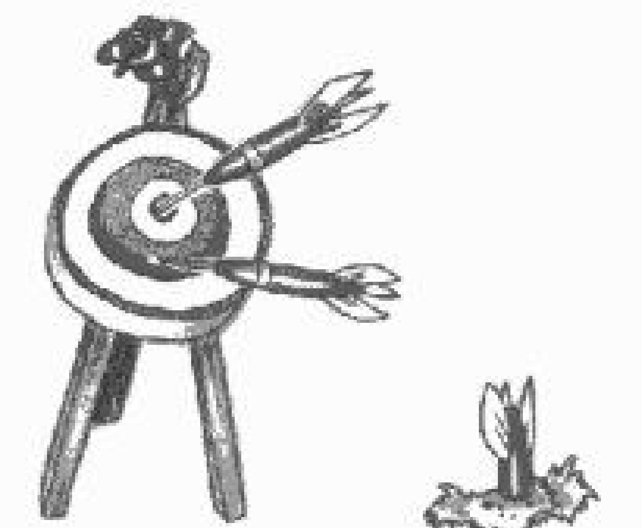
From PhD Thesis, Rick Thomas

Summary of Models

Many models

Little basis for choosing!

Little basis for evaluation!



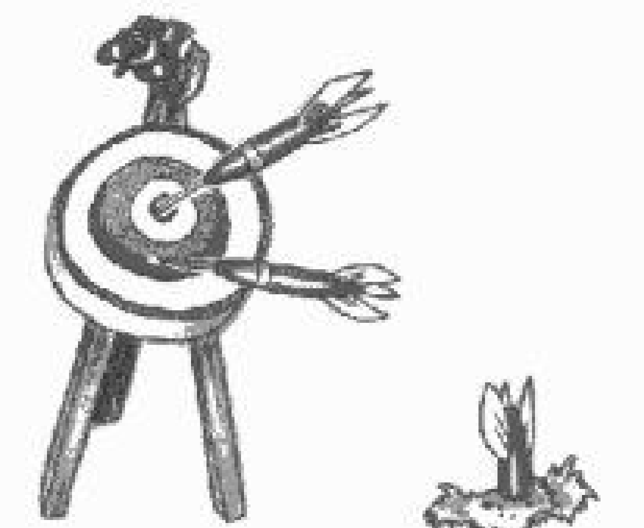
Summary of Models

Many models

Little basis for choosing!

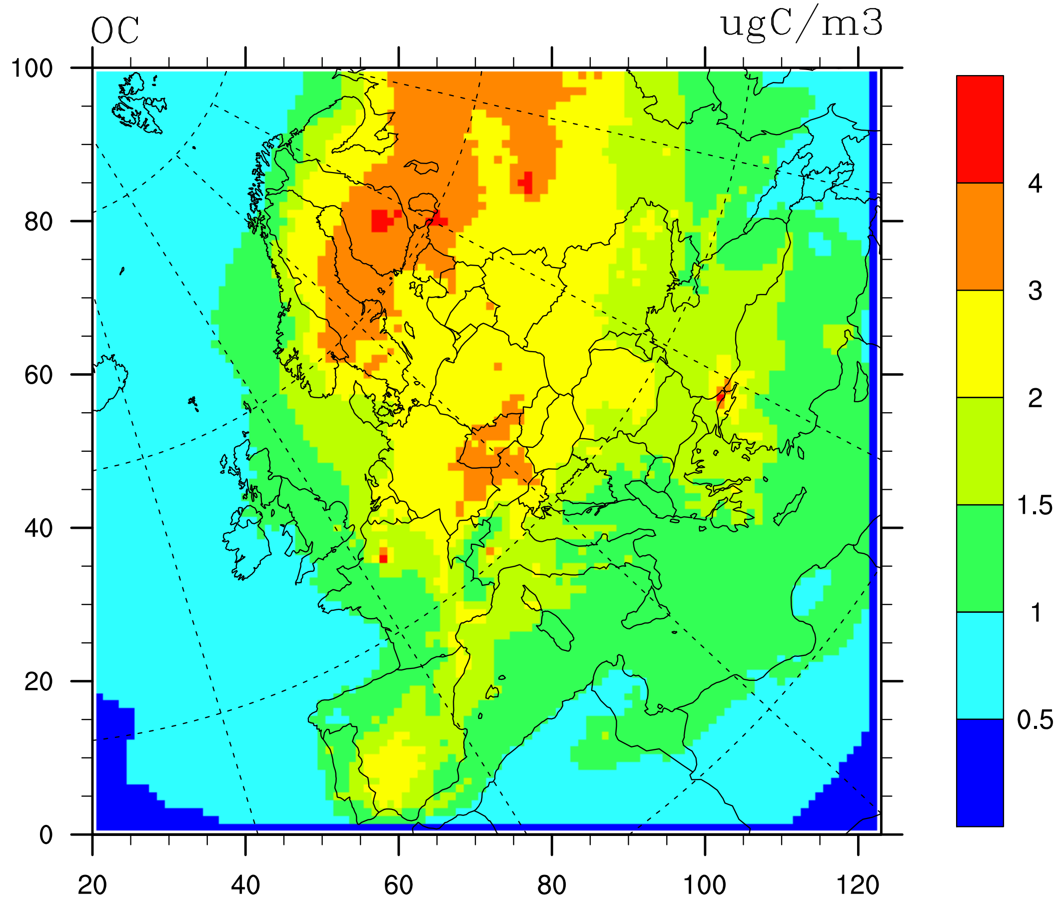
Little basis for evaluation!

Unconstrained!
Need Observations!



Results

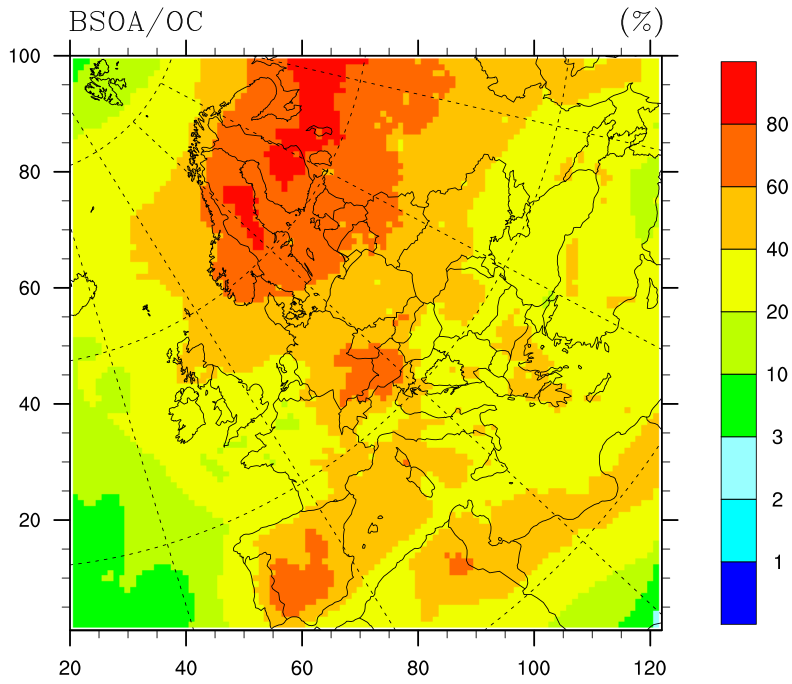
Results: Annual Average OC, year 2002 (ugC/m3)

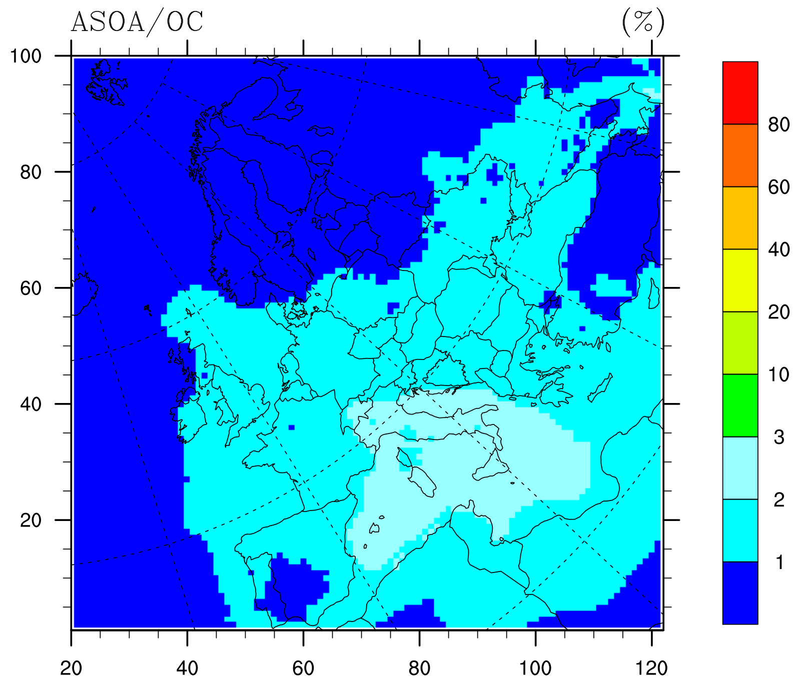


BSOA contribution

BSOA/OC (%)

ASOA/OC (%)





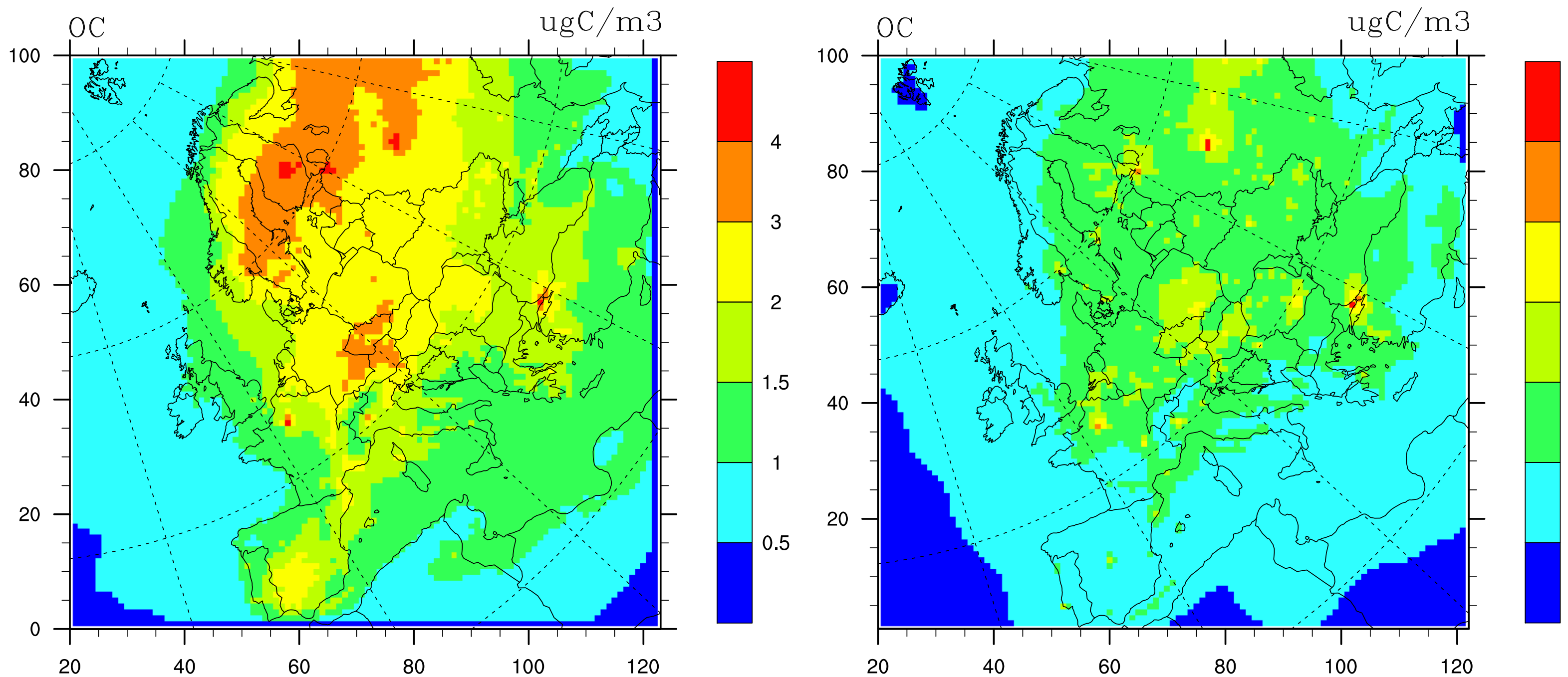
Kam2X

OC, take 2

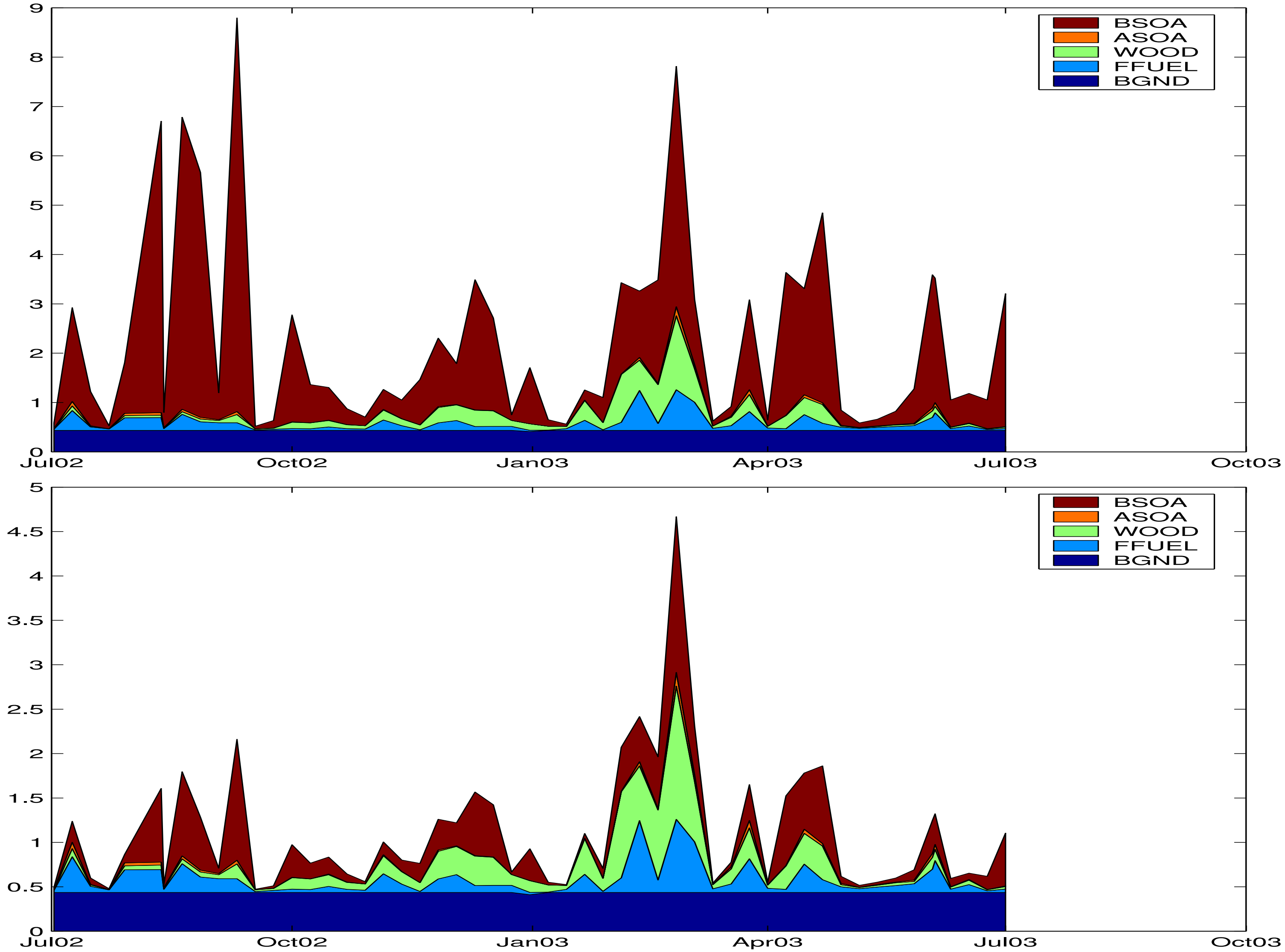
OC with alternative vapour pressures

Kam-2X

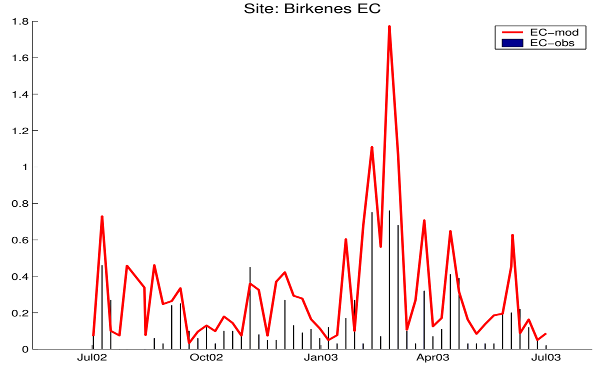
Kam-2

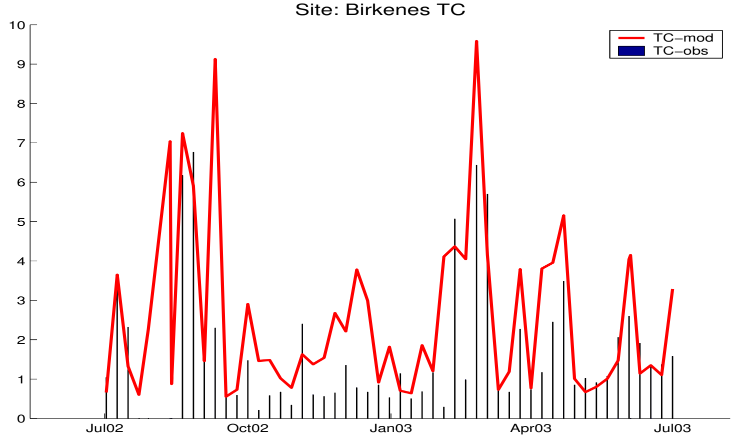


Sensitivity of OC: Birkenes



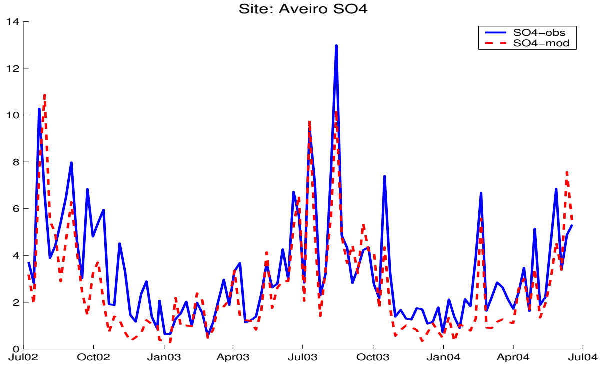
Birkenes EC, TC

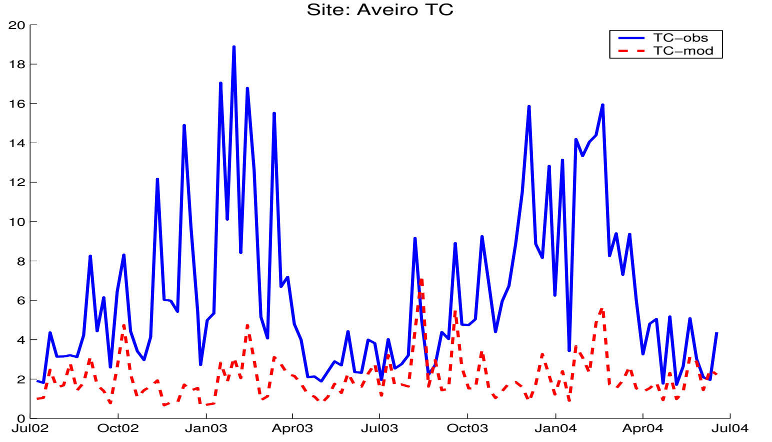




Model performance - quite good at all Northern European sites

Aveiro SO_4^{-2-}, TC

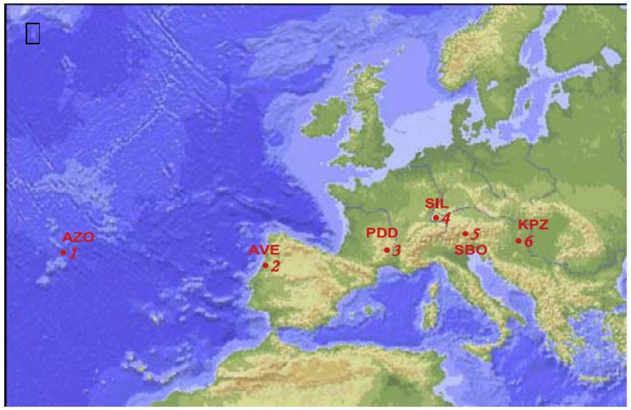




Model performance - quite bad for TC at all southern European sites

CARBOSOL Project

1-week filters (PM_2), analysed for:

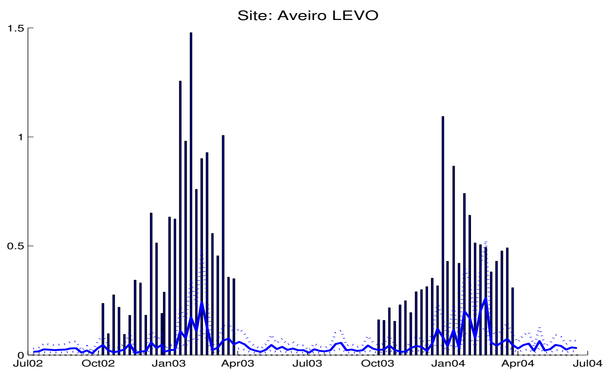


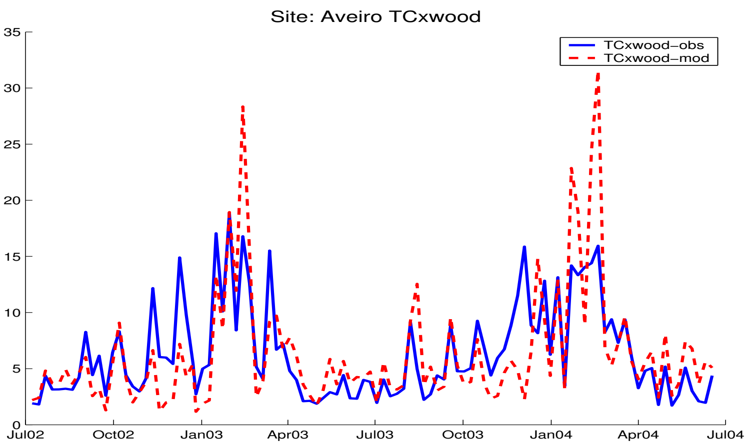
cellulose	$\Rightarrow$	biological particles
levo-glucosan	$\Rightarrow$	biomass-burning
OC/EC	$\Rightarrow$	primary emissions
^{14}C	$\Rightarrow$	modern/fossil

16 papers: Present and Retrospective State of Organic Aerosol Over Europe, J. Geophysical Research, VOL. 112, D23, 2007

Aveiro revisited...

Use levoglucosan to 'correct' WOOD





Promising :-)

cf CARBOSOL

K-Puszta (Hungary), Summer

	Obs.-Derived (5–95th %ile)	EMEP Model (Kam2 - Kam2X)
TC	5.2	1.6 – 2.7
WOOD	0.3 – 0.5	0.05
EC	0.4 – 0.7	0.4
FFUEL	0.2 – 0.5	0.4
BSOA	2.9 – 3.6	0.2 - 1.4
ASOA	0.05 – 0.7	0.03 - 0.04

Units: μg C m^{-3}

Simpson et al., JGR, 2007

Use of tracers, cont.

SORGA: Norwegian project

- Tove Svendby, Karl-Espen Yttri, ...
- David Simpson, MET.NO
- Hans Puxbaum + co. (TUV)
- Kristina Stenström, Lund Univ.

SORGA

Measurement campaigns

Summer period: 19 June - 5 July 2006
Winter period: 1 - 8 Mars 2007

Oslo (Urban background)

Hurdal (rural background)

Source-Apportionment, cont

- Other tracers:

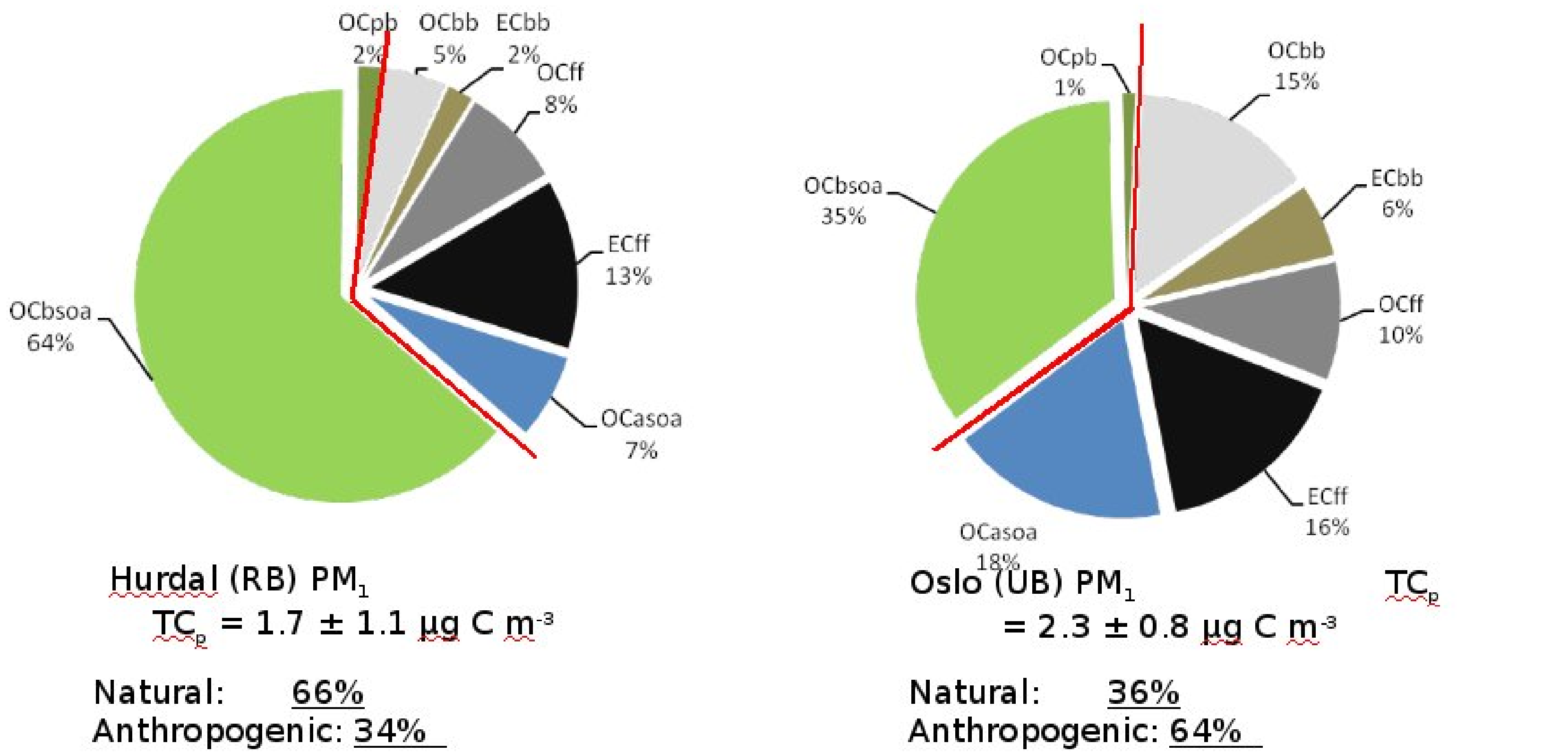
^{14}C	⇒	modern/fossil
cellulose	⇒	plant matter, ...
sugars/alcohols	⇒	fungi, ...
OC/EC	⇒	primary emissions
levoglucosan	⇒	biomass-burning

- - all factors approximate.
- - some ‘traps’, e.g. some modern ^{14}C could be from cooking oils, tyres, etc.

(e.g. Gelencsér et al., JGR, 2007)

SORGA

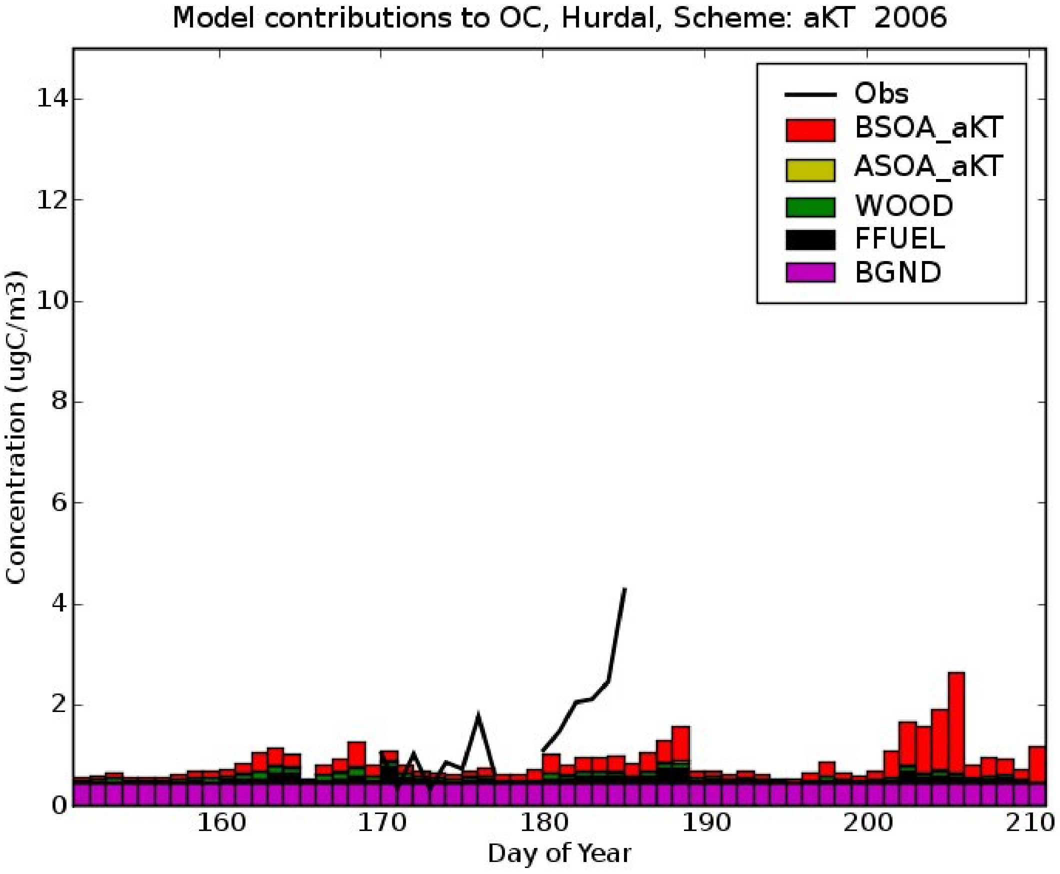
Sources of PM_1, Summer:



(K.E. Yttri et al., 2008, Prelim)

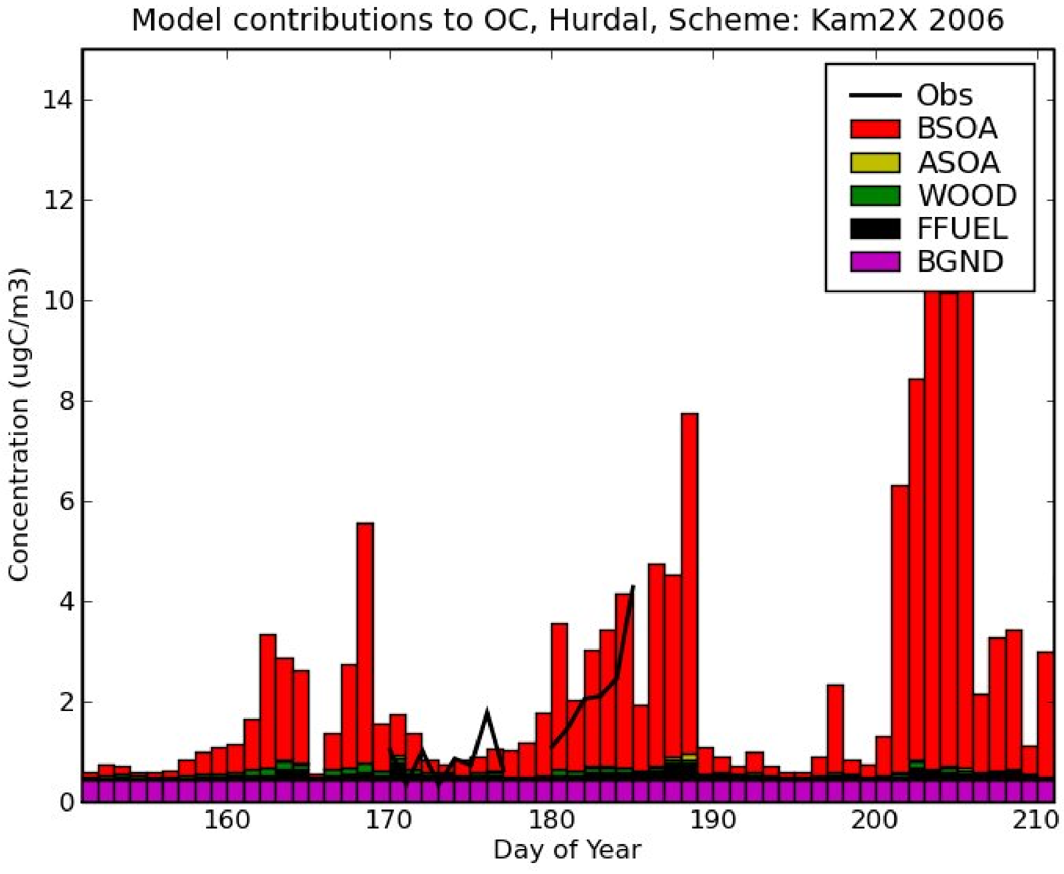
SORGA

aKT-EMEP model, Hurdal:



SORGA

Kam-2X-EMEP Model, Hurdal:



The Target

Do we know how much OC we want?

Key words:
Artifacts (EC/OC, -ve, +ve, ...)
– can be of order 50% ?

Representativity - what does e.g. [OC] mean?

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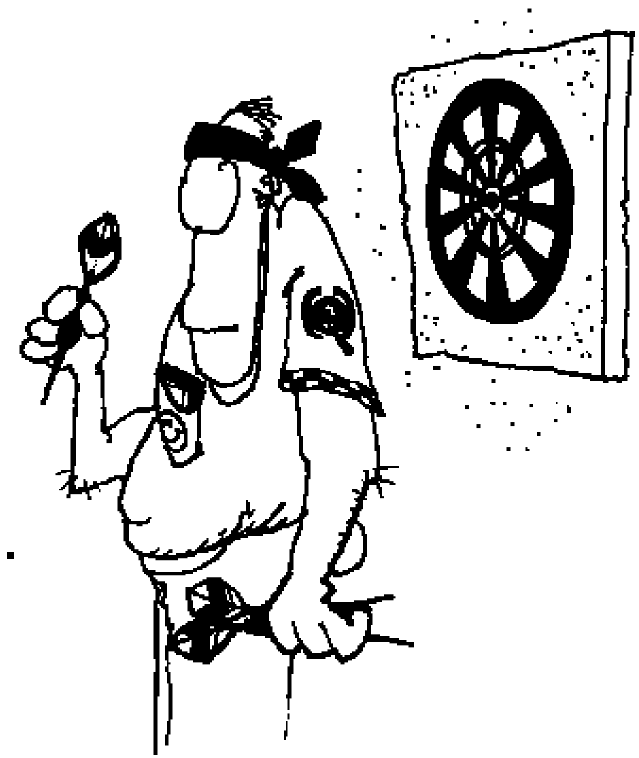


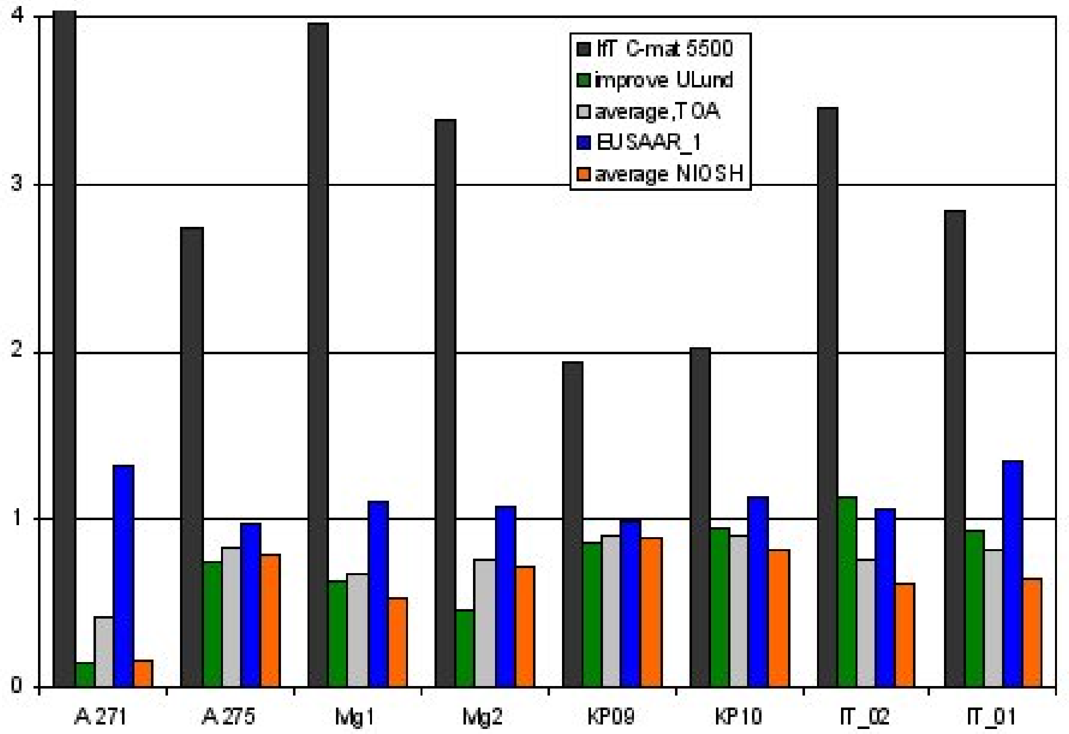
Representativity - what does e.g. [OC] mean?

Artifacts

EUSAAR result:

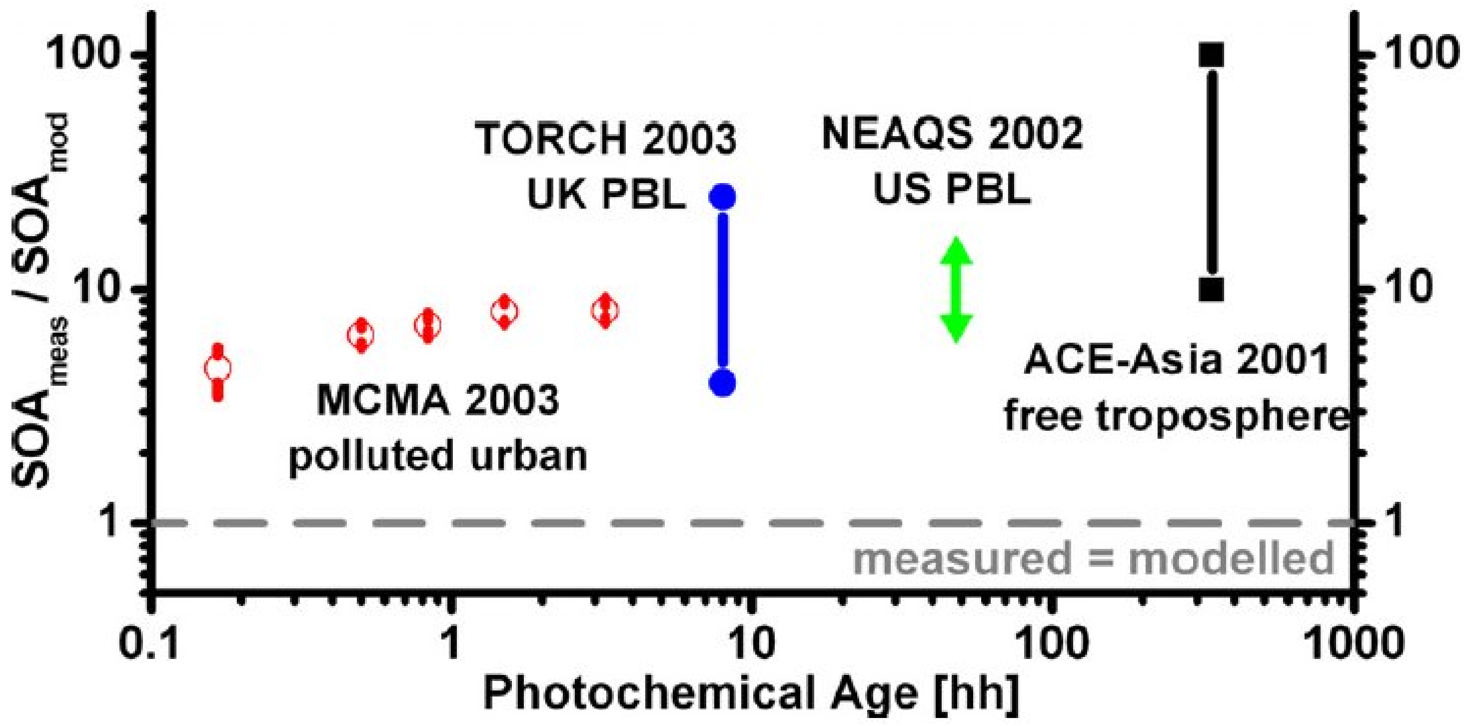
Standard deviation among EUSAAR Partners

- using NIOSH: 48%
- using EUSAAR: 13%



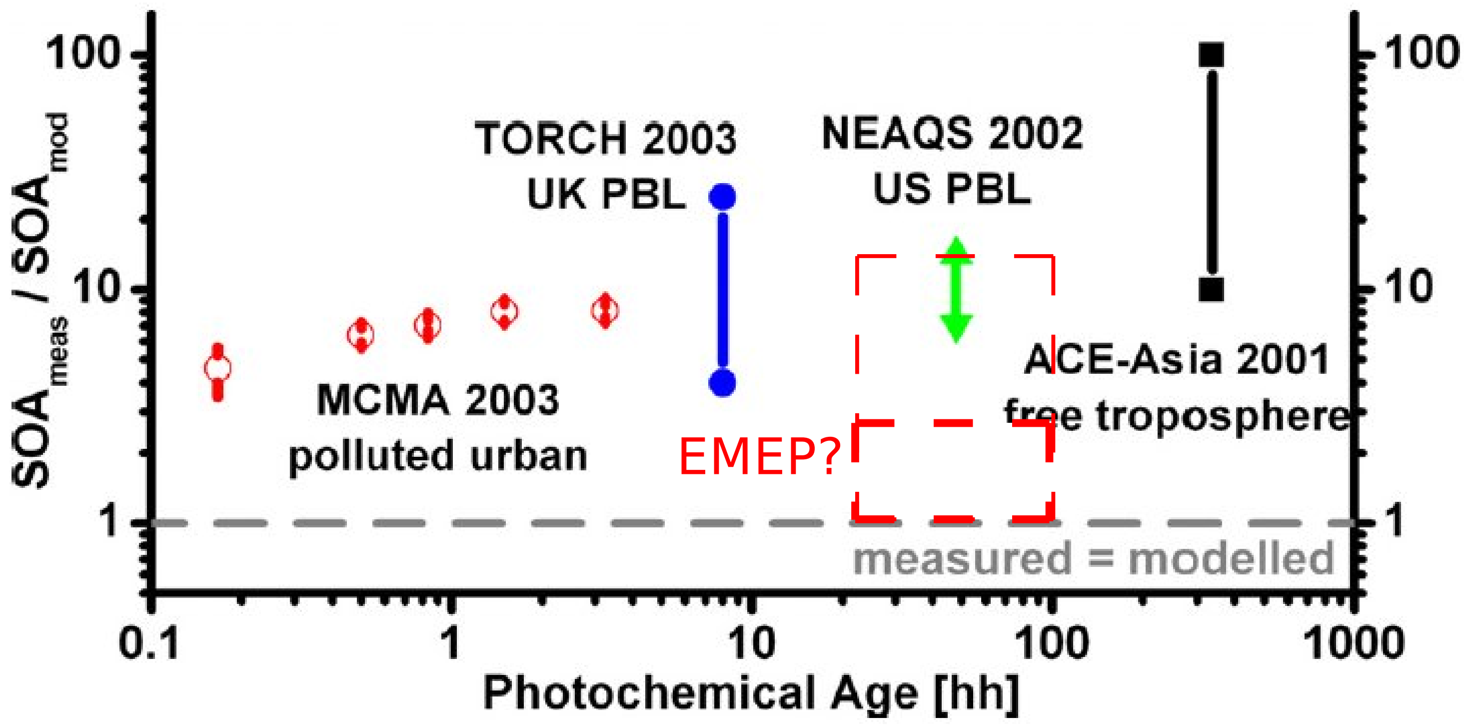
: Fig. from Jean-Philippe Putaud

Other studies



Volkamer et al., GRL, 2006

Other studies



Volkamer et al., GRL, 2006

Conclusions

- State of OC science ‘in infancy’ (Donahue et al., 2005)

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- . . . because as we know, there are known knowns; there are things we know we know. We also know there are known unknowns; that is to say we know there are some things we do not know. But there are also unknown unknowns - the ones we don’t know we don’t know.

  \- (Donald Rumsfeld, 2005)

Conclusions

- Modellers have no way to ‘solve’ SOA modelling until chemists have understood the basics.
- But, model’s can serve to test theories and emissions
- Emissions? Primary OC/BC + precursor (terpenes!) emissions need verification (near-source measurements?)

Conclusions 2

Measurements are required to develop and constrain models and validate emissions

- Needs chemical speciation, tracers, many locations
- Long-term field data + campaigns+supersites ideal
- AMS, C14, ...

Wishes...

Would be good to specify:

- Emissions (AVOC, BVOC, volatility)
  - Volatile E(PM)? Or Condensible E(VOC)?
- Source of Atmos. Aerosol:
  - How much is modern/fossil
  - How much is biomass/BSOA
  - How much is through aqueous pathway
  - Acidity/S ?
  - Mixing polar/nonpolar/liquid/other??
- Which smog-chamber data are relevent?
- Link smog/flow-chambers – atmosphere

Garbage Avoidance

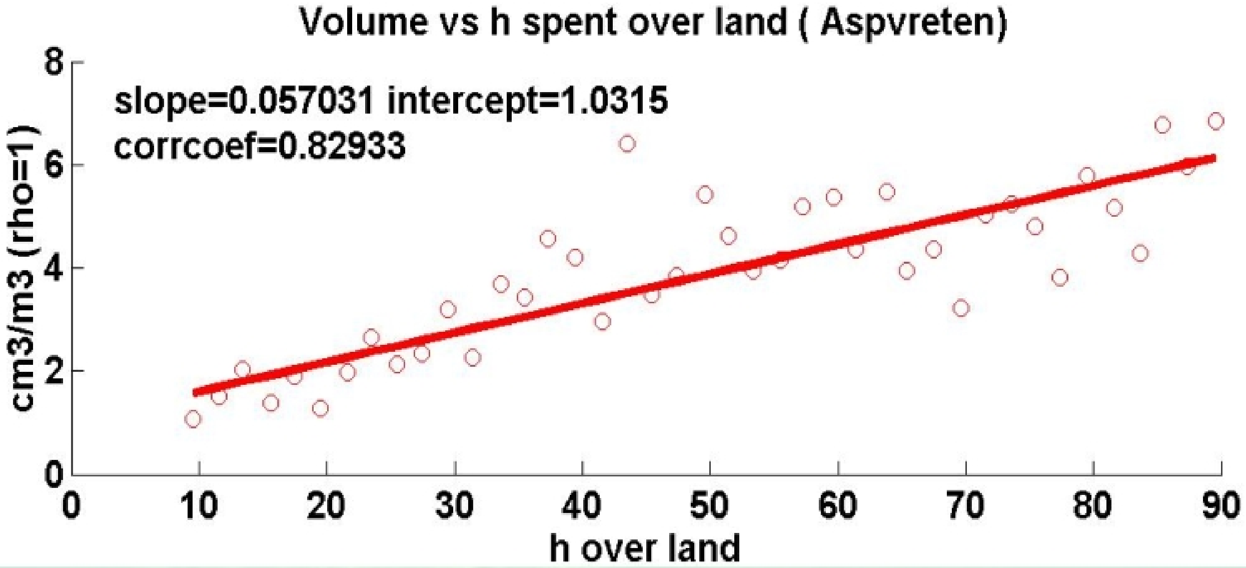
Strategies:

- Check basics - does the model work for anything?
  - Check other pollutants - SO_2, SO_4, NO_x, NO_y,
- Check emissions!
- Check PCM tracers - EC, levoglucosan, C14
- Check measurements - what do they mean?!
- Be humble.....

The End...

Other studies

The simplest result – all PM from forests:



See: Tunved et al., Science, 2006

Other studies

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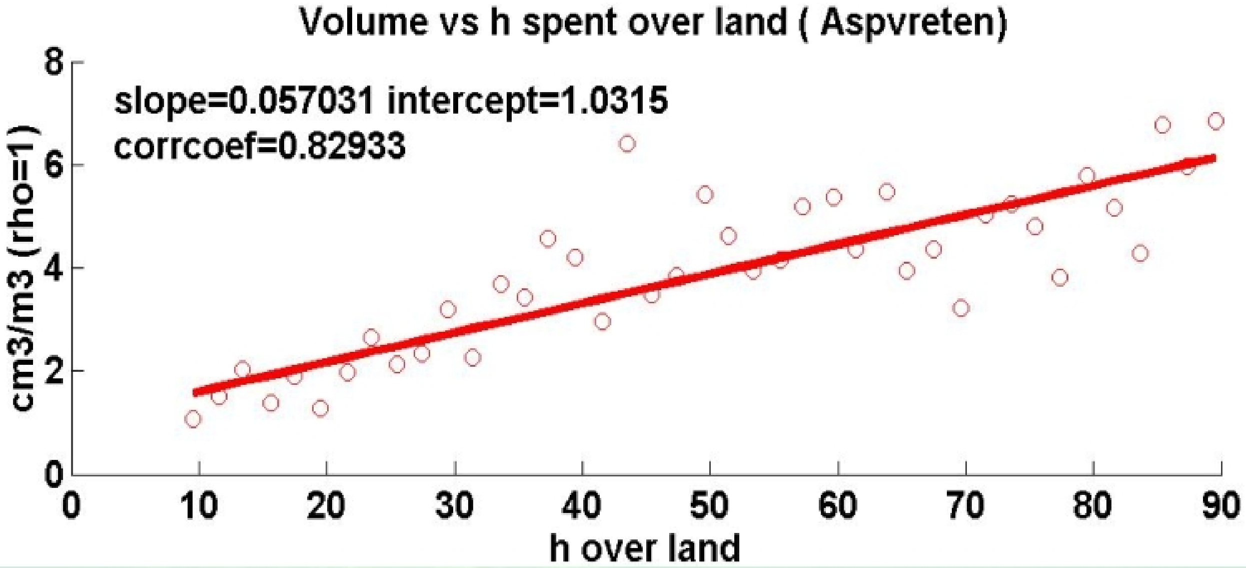


See: Tunved et al., Science, 2006

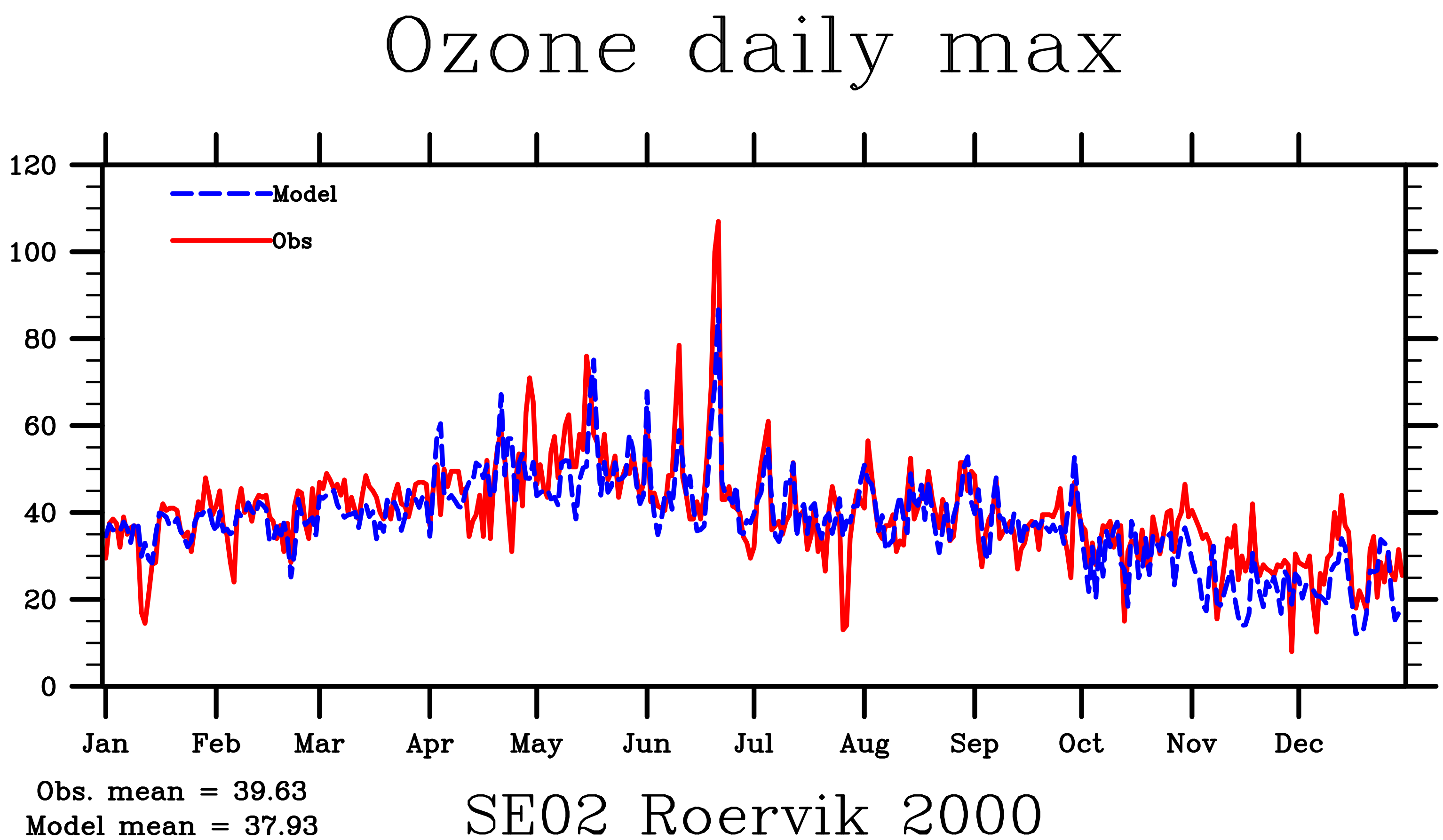
NB: Applies to clean air, selected air masses

Evaluation

Mainly by comparison with:

- More Complex models (e.g. for chemical schemes)
- Measurements - the main test!!

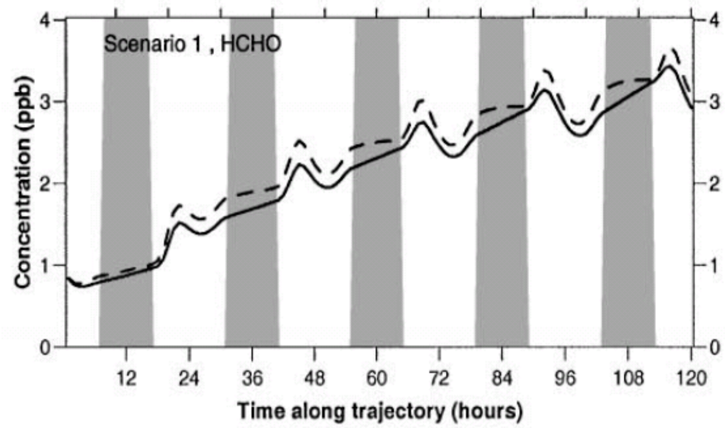
Ozone

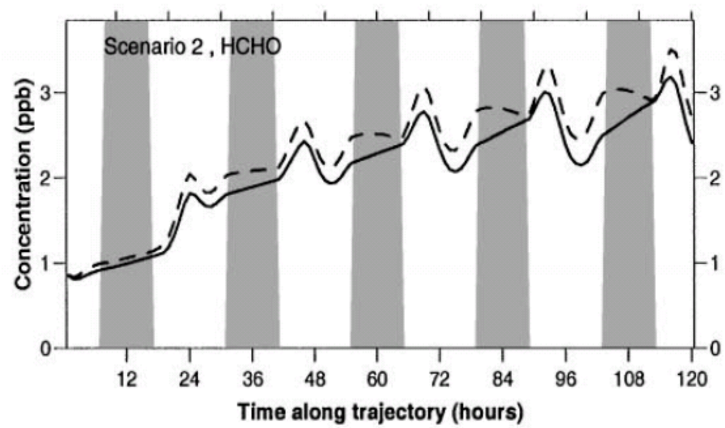


Obs. mean = 39.63
Model mean = 37.93
Correlation = 0.78

Model vs. Model

EMEP vs IVL (HCHO):

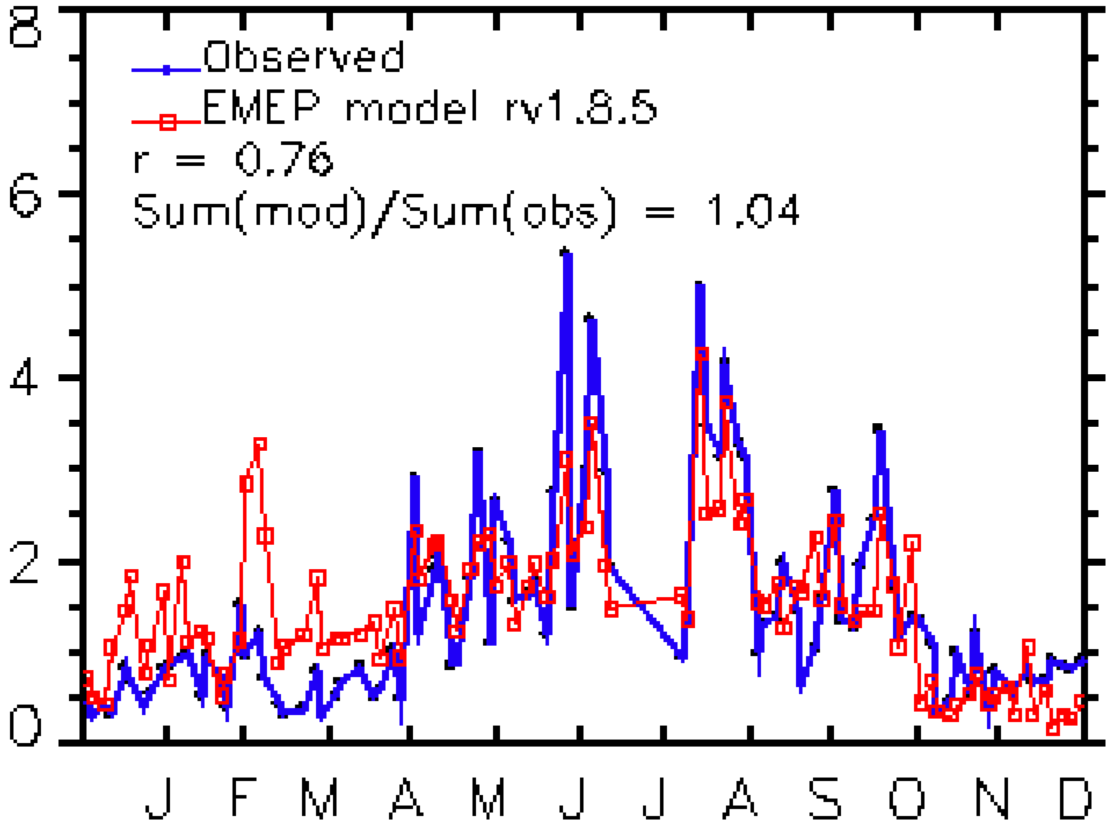




Andersson-Sköld & Simpson, Atmos.Env., 1999

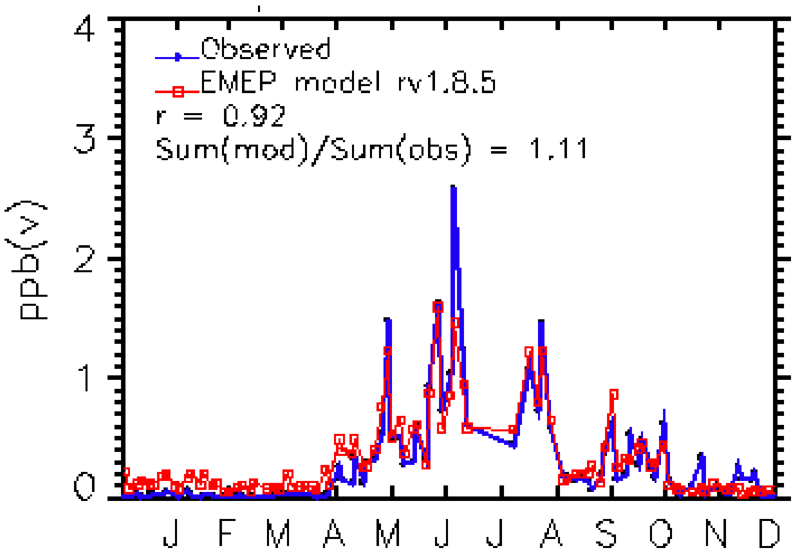
HCHO Cont. Field Comp:

Donon, France:



Isoprene

(Nice result for precursor too:)



Lessons?

- Combination - lab (via. MCM) + field data very powerful – tests kinetics, emissions and chemistry
- (New comparisons in progress, Tack SCARP, Tellus, FZJ!)