

Testing of SOA-models against chamber experimental data

Scope of the exercise:

- To see how well existing models of SOA formation can simulate chamber experiments
- Analyse reasons for the differences between models

Why use chamber data?

- Controlled conditions
- Chemistry can be separated from transport
- Disadvantages: Wall effects need to be considered, concentrations are typically higher than ambient

Reactants
Terpenes, isoprene, aromatics, large alifatic HC

Mechanisms to form condensable products

(Semi-)explicit

Generic species



Condensable products

Partitioning between gas- and particle-phase

Kinetic vs. equilibrium approach

Size-resolved model?

'Theoretically' calculated vs. empirically determined K_p 's

Condensed phase chemistry, reactive uptake

History:

The exercise was initiated on a workshop in Ispra, February 2007:

It was decided to focus on alpha-pinene and criteria for selection of data were established.

Subsequently:

- Collection of relevant data from smog chamber owners
- Contacts to modelers

A few selected data sets were made available to the participating modelers in March 2009.

Discussion of preliminary results on workshop in Arona (IT), April 2009

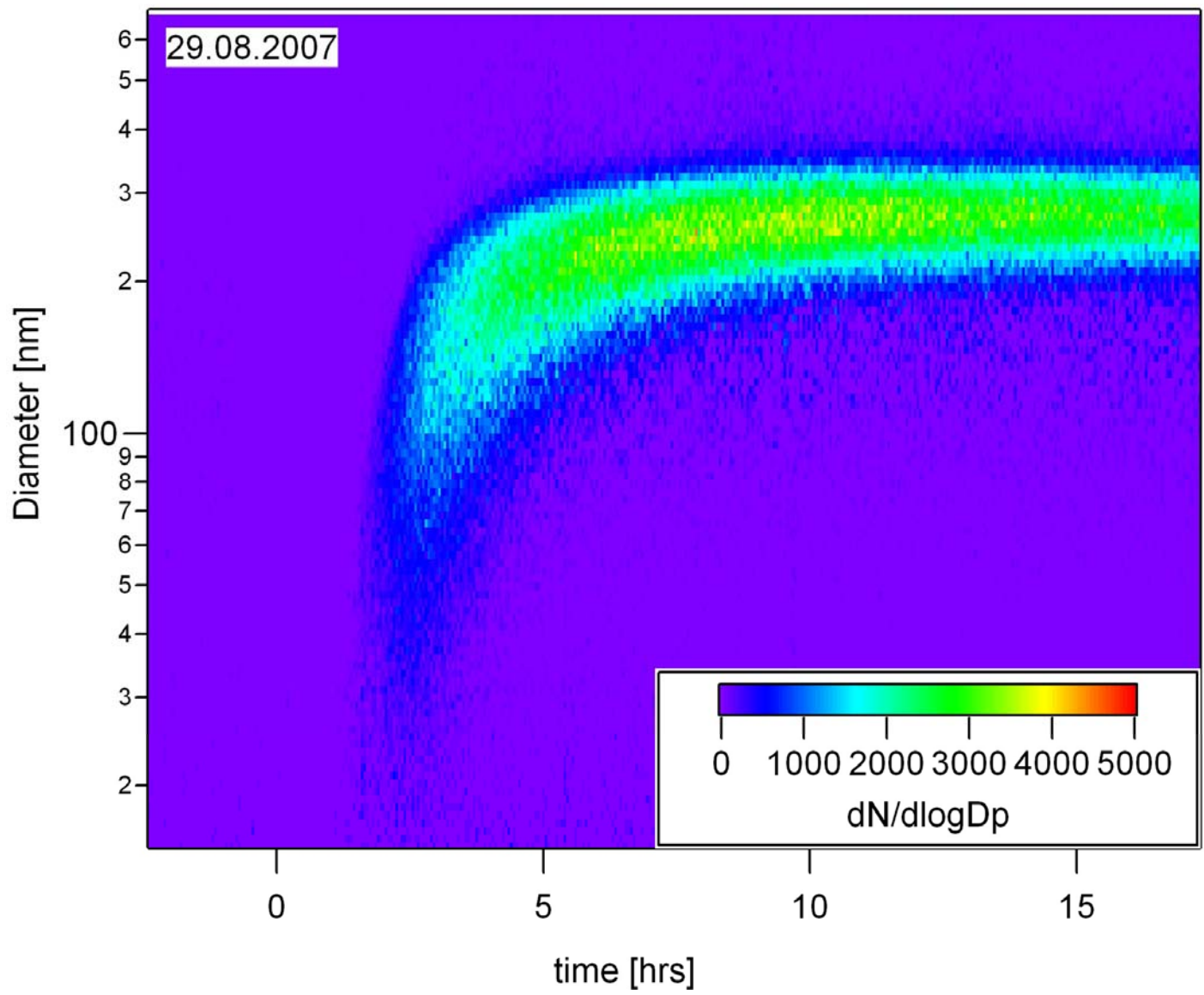
Criteria for selection of datasets:

- concentration of alpha-pinene as close as possible to atmospheric conditions.
- humidity at ambient levels (but a few experiments in dry air included for comparison).
- variation of [NO_x] and [NO_x]/[VOC] levels within the range of concentrations that may be found in ambient air (with other experimental parameters kept unchanged).
- repeated experiments in the same chamber should be included.
- experiments from different chambers but with the same (or very similar) conditions should be available.

Decisions:

- Simulations start when new particle formation has ceased
- All relevant experimental information is made available to the participating modelers; no 'blind' intercomparison.

Chamber	Experiment	NO ppb	NO₂ ppb	<i>a</i>- pine- ne ppb	Ozo- ne ppb	T (K)	RH%	Light
PSI	photooxi- dation	60	60	240		293	50	yes
PSI	photooxi- dation	60	60	240		293	60	yes
EUPH ORE	ozono- lysis (CO as OH scavenger)	0	0	109	190	293	3	no
EUPH ORE	ozonolysis , CO added	0	0	106	190	291	2	no
AIDA	ozonolysis	0	0	Step- wise (93, 95 and 188 ppbV)	296	303	44	no



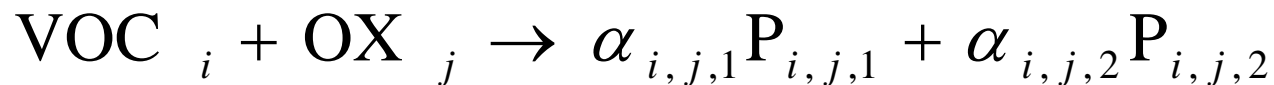
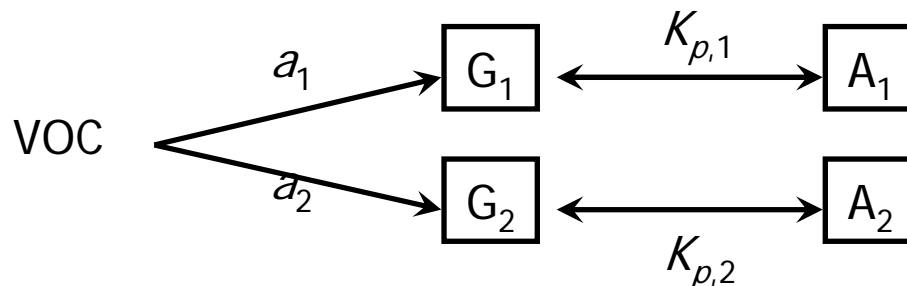
Models participating in first intercomparison:

- TM5 SOA model
- MAPSv1.2
- COSIMA
- Tsigaridis/Mircea/Kanakidou model
- EMEP SOA model
- BOREAM
- Gecko
- MALTE

TM5 SOA Box Model

CB-IV chemistry

SOA formation – 2 product model



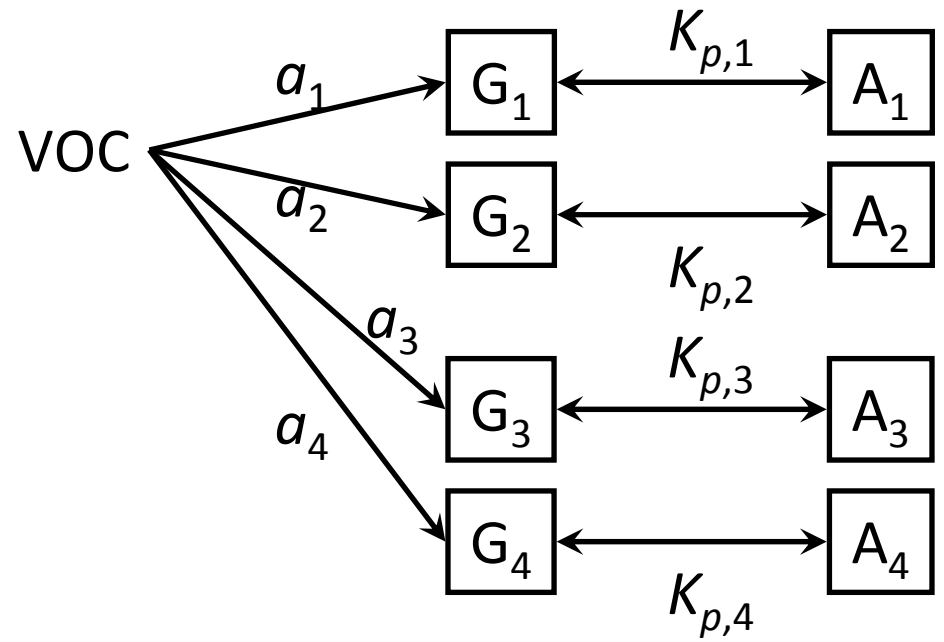
$$G_i = \frac{A_i}{K_{p,i} M_o}$$

The partitioning coefficient is T-dependent

Processes affecting SOA production

- Pre-existing aerosols
- Oxidant levels
- Temperature
- Gas-phase chemical composition (high/low NO_x)
- Relative humidity
- UV light
- Evaporated POA
- Aged SOA
- Others?

$$G_i = \frac{A_i}{K_{p,i} M_o}$$



Partitioning parameters

	α - pinene ^a	β - pinene ^a	toluene ^b	xylene ^b	isoprene ^c	β - caryophyllene ^d
$a_{i,1}$	0.125	0.026	0.071	0.038	0.232	0.20
$K_{p i,1}$	0.088	0.195	0.053	0.042	0.00862	0.05
$a_{i,2}$	0.102	0.485	0.138	0.167	0.0288	0.80
$K_{p i,2}$	0.0788	0.003	0.0019	0.0014	1.62	1.0×10^{-5}

^a: Oxidant is O₃ (Griffin et al., 1999a)

^b: Oxidant is OH and O₃ (Odum et al., 1997)

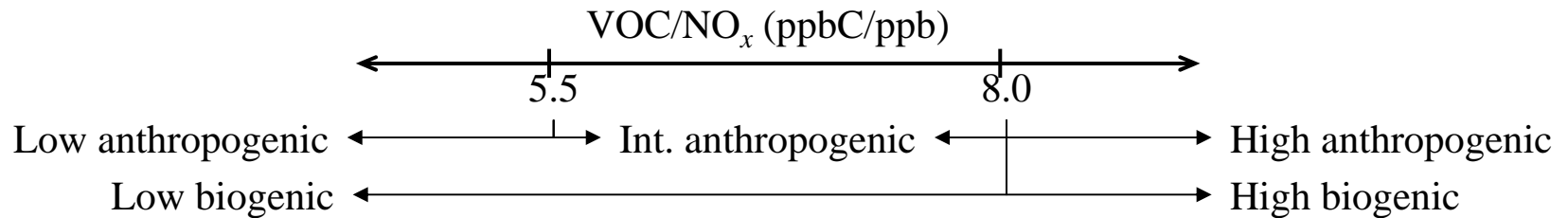
^c: Oxidant is OH (Henze and Seinfeld, 2006)

^d: Oxidant is OH and O₃ (Hoffmann et al., 1997).

Product 2 is further oxidized by OH, O₃, NO₃ to

give a non-volatile compound

NO_x dependence



- **α-pinene: Presto et al., 2005**
- **xylene: Song et al., 2005**

	α-pinene standard	α-pinene High VOC/NO _x	α-pinene Low VOC/NO _x
a _{i,1}	0.125	0.192	0.0138
K _{p i,1}	0.088	0.0637	0.0637
a _{i,2}	0.102	0.215	0.461
K _{p i,2}	0.0788	0.0026	0.0026

**NO_x dependent α and K_p
for α-pinene**

COSIMA

*Simulation based on a 2-component model -
one low-volatile (1) and one semi-volatile (2) product proxy*

Product parameters fixed beforehand (not fitted to measured data):

- Molar mass: $M1 = 186 \text{ g/mol}$, $M2 = 168 \text{ g/mol}$ (both α -pinene and limonene cases)
- Gas phase diffusion coefficients from Chapman-Enskog theory and Lennard-Jones parameters ($0.040 - 0.056 \text{ cm}^2/\text{s}$)
- Bulk density from AMS / SMPS measurements: 1.25 g/cm^3 (α -pinene), 1.3 g/cm^3 (limonene)
- Surface tension: $s1 = 80 \text{ dyn/cm}$, $s2 = 30 \text{ dyn/cm}$ (both α -pinene and limonene cases)

Kinetic treatment of uptake and release of gases from particles

MAPSv1.2

2-product approach

- ✓ Model for Aerosol Process Studies (MAPS).
- ✓ Developed at NCAR, USA.
- ✓ Box model with gas/aerosol chemistry.
- ✓ Gas phase photochemistry (SAPRC-97/99 mechanism).
- ✓ 65 gas species and 21 aerosol species (up to 64 size sections)
- ✓ 8 condensable organic compounds (for SOA calculations)
- ✓ Includes condensation, evaporation, deposition.
- ✓ Partitioning coefficients are T-dependent

Three SOA models tested:

Kamens 2001

Kamens 2007 (updated
chemistry and exploratory
oligomerization reactions

Volatility Basis Set - based
methods (Donahue et al., Lane
et al.)

MALTE – Model to predict new aerosol formation in the lower troposphere

- 1 or 0-dimensional model
- Chemistry (KPP-MCM)
- Aerosol dynamics (UHMA)
- Multicomponent condensation
- Several nucleation theories

$$[C]Vapour1 = Y1 * [Monoterpenes] * [O3], [OH], [NO3]$$

$$[C]Vapour2 = Y2 * [Monoterpenes] * [O3], [OH], [NO3]$$

Y1 = 0.05 (condensing on nano-sized inorganic clusters)

Y2 = 0.1 (involved in the general condensation mechanism)

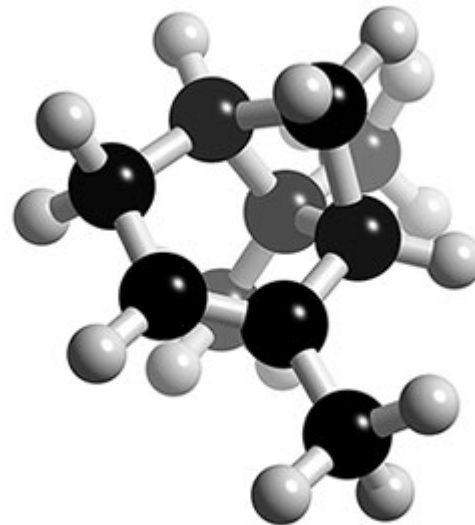
Only first order reaction products taken into account.

Change rate in particle volume = collision rate between particles and gas molecules x gas molecule volume x (gas concentration – gas saturation concentration)

BOREAM (Biogenic hydrocarbon Oxidation and Related Aerosol formation Model)

Quasi-explicit treatment of chemistry (~5000 reactions, 1300 species).

Partitioning follows a kinetic representation with coefficients calculated by a group contribution method.



The chemical scheme generator GECKO-A

GECKO-A = Expert system that

- assimilates physical and chemical data from laboratory experiments
- estimates the missing information based on structure/activity relationships

Input

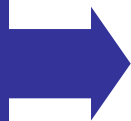
Hydrocarbons



**Automatic generator for
VOC oxidation scheme**

**Machinery :
structure/activity relationships**

Laboratory
data



Output

Explicit chemical
schemes

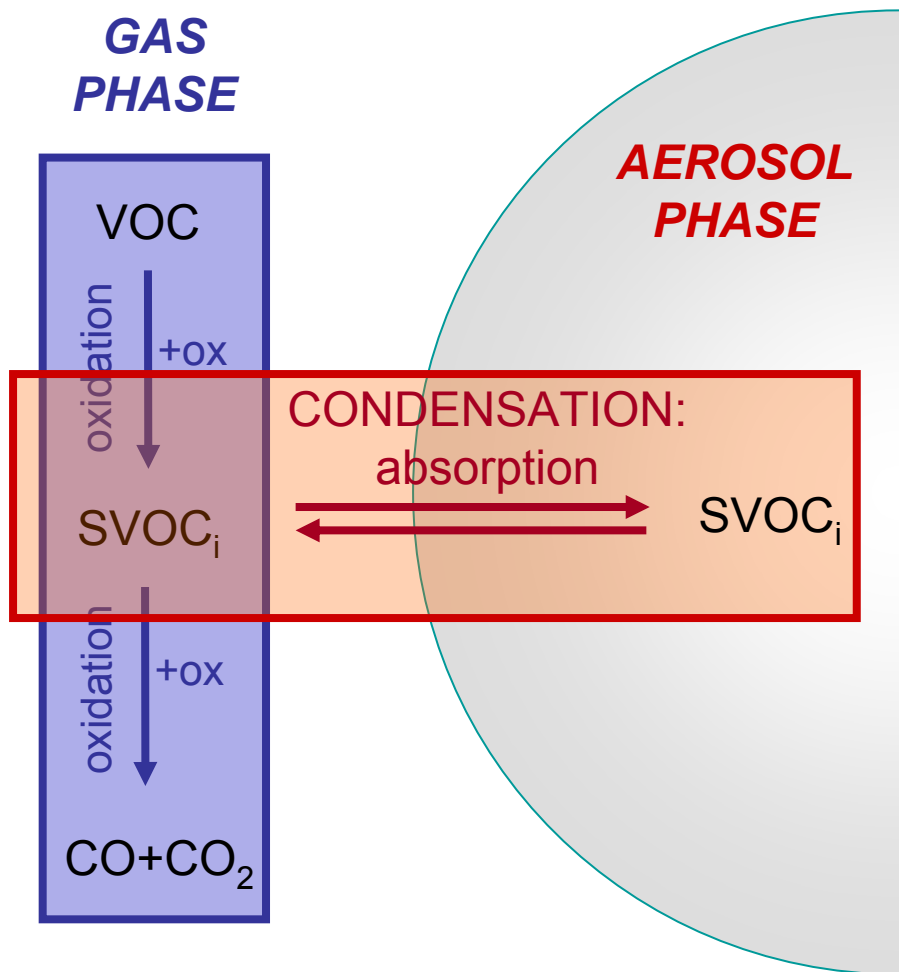
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Related data :
vapor pressure,
Henry's law coef.

...

The protocol currently used :

- Conceptually similar to the MCM3 mechanism
- Most SAR implemented were borrowed from SAPRC99, MCM and NCAR MM
- Described in Aumont et al., ACP, 2005



1. Gas phase oxidation schemes

Explicit description of the production and removal of SVOC in the gas phase based on GECKO-A

2. Gas/particle partitioning of SVOC

Phase equilibrium described on the basis of Raoult's law :

$$P_i = \gamma_i x_i P_i^{\text{vap}}$$

Assume a thermodynamic equilibrium between gas and particulate phases

P_i^{vap} are estimated for each intermediate using Myrdal & Yalkowsky (1997) structure/properties relationship

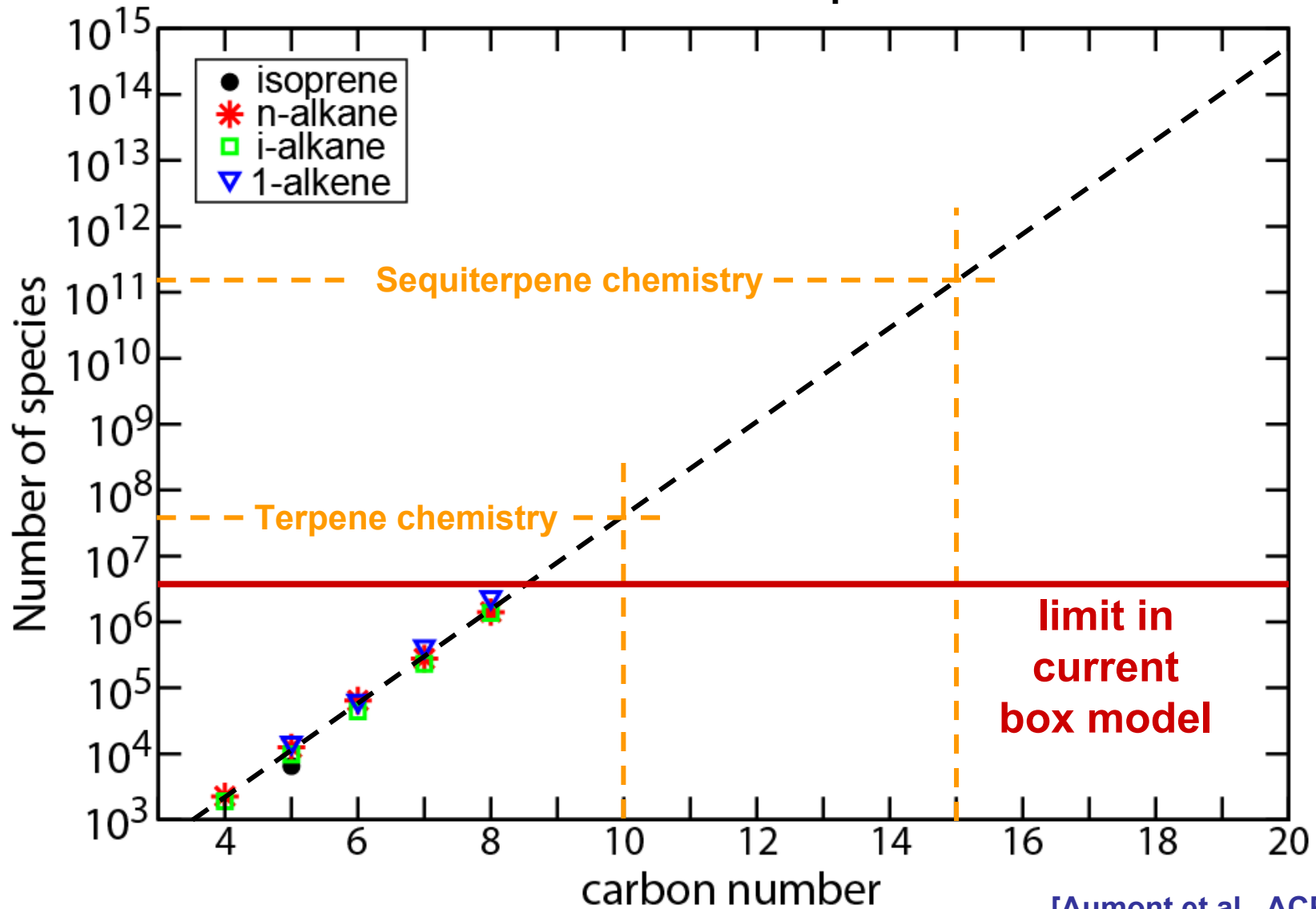
[Camredon et al., Atmos. Env., 2006]

Species with vapor pressure below 10-13 atm do not significantly contribute to the carbon budget.

No need to develop the gas scheme for such species.

Reduction of chemical scheme – Why ?

Number of species in the chemical mechanism as a function of carbon number in the parent HC



Preliminary results:

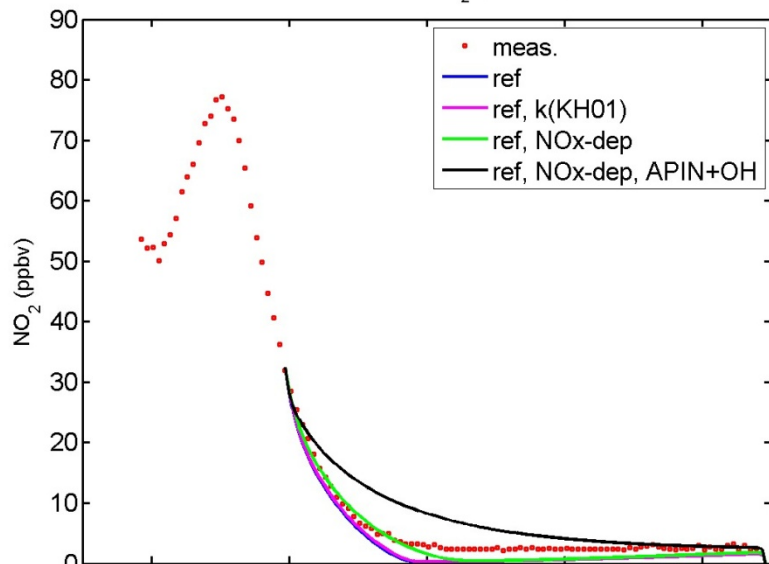
PSI photo-oxidation experiments:

SOA formation underestimated by nearly all models. Better agreement was obtained by reducing $J(\text{NO}_2)$. Spectral distribution different from sunlight?

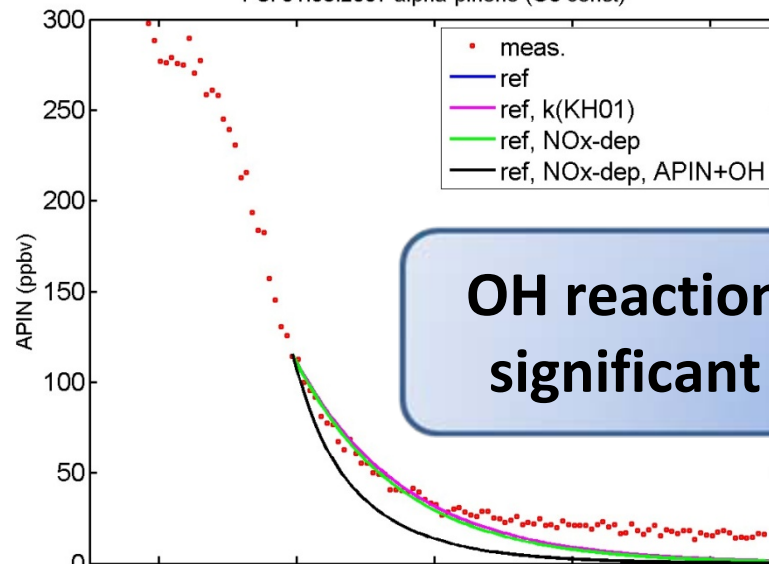
Reasonably agreement was obtained by TM5 model when NO_x -dependence of SOA yield was taken into account.

PSI: α -pinene photo-oxidation, 01.08.2007

PSI 01.08.2007 NO₂ (O₃ const)

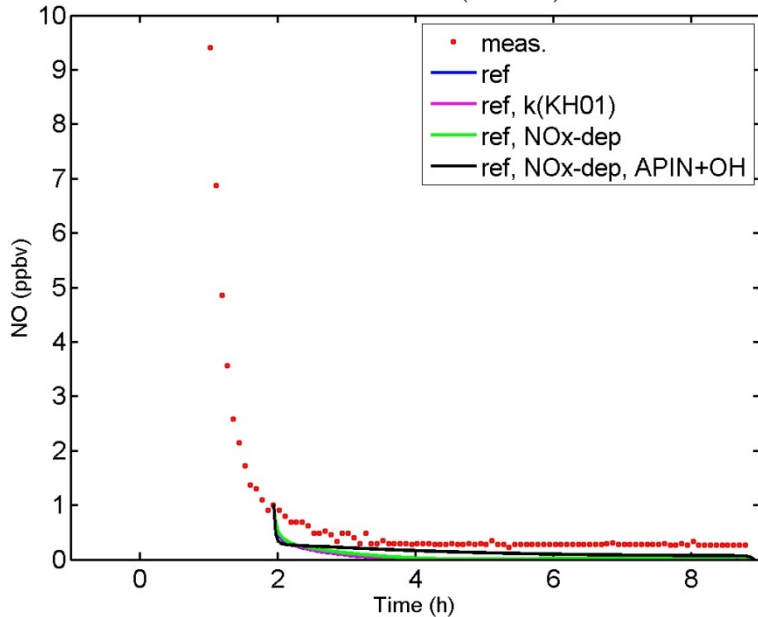


PSI 01.08.2007 alpha-pinene (O₃ const)

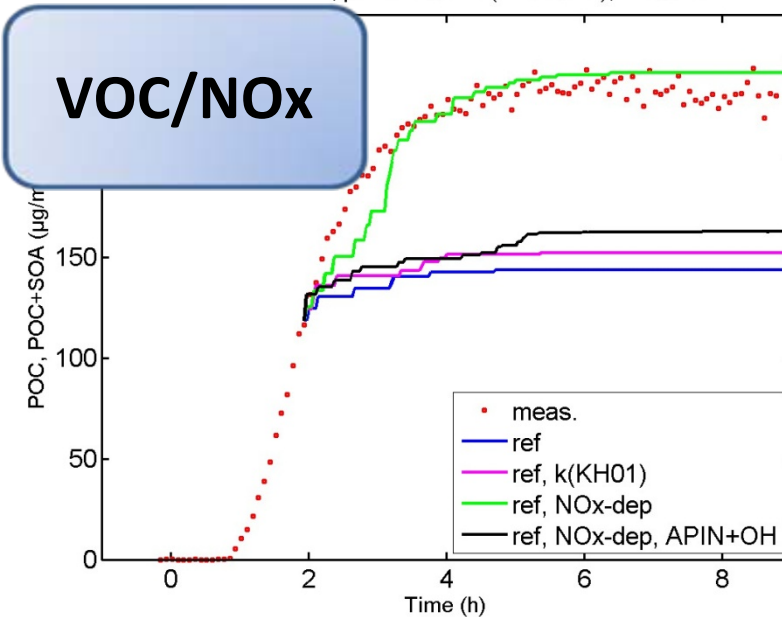


OH reaction significant

PSI 01.08.2007 NO (O₃ const)



PSI 01.08.2007, particulate OM (POC+SOA), O₃ const



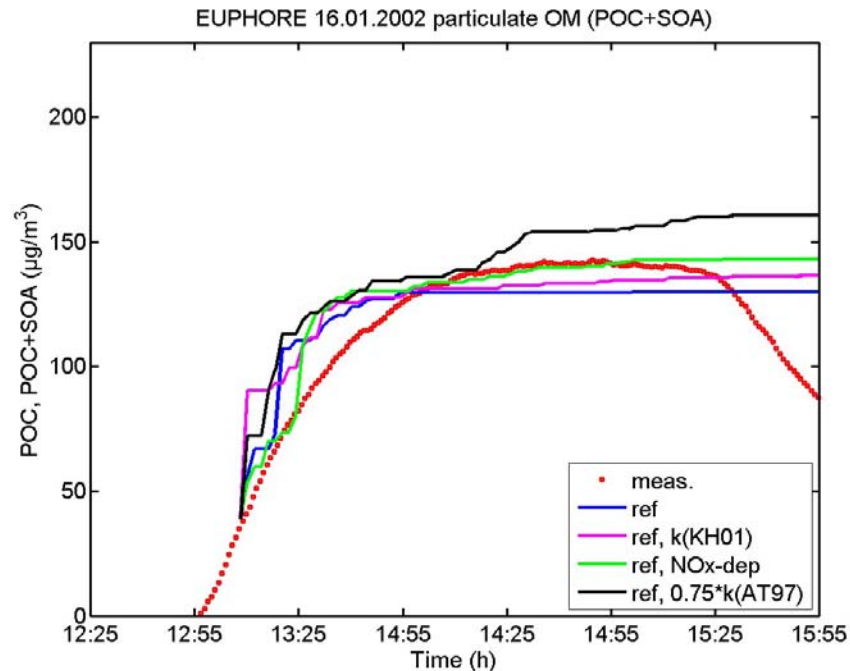
VOC/NO_x

EUPHORE ozonolysis experiments

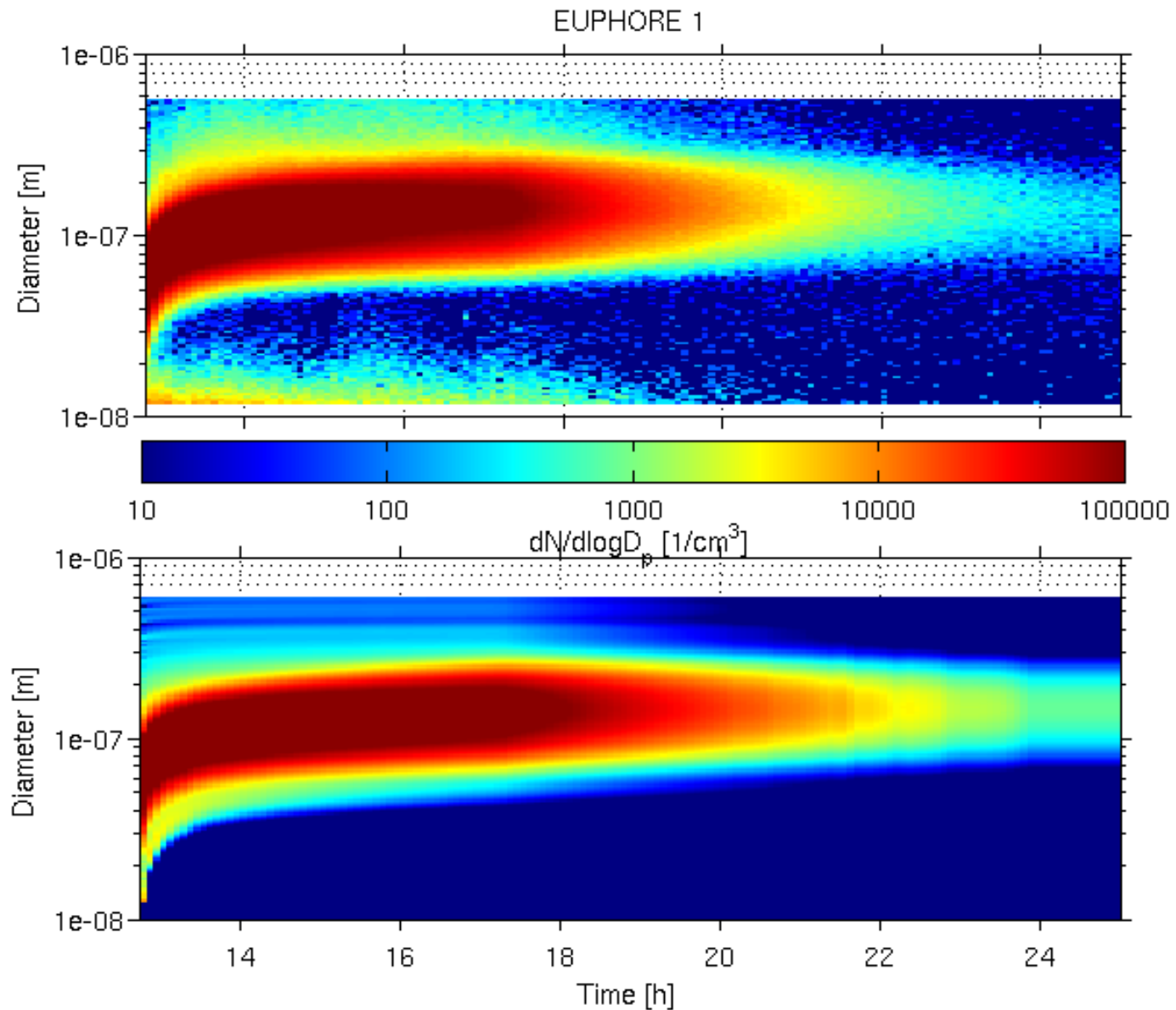
CO as OH scavenger

Quite good agreement for the 2-product models
COSIMA and MAPS; TM5 performs slightly
better with NO_x -dependence included

No systematical under- or overestimation of
SOA by models



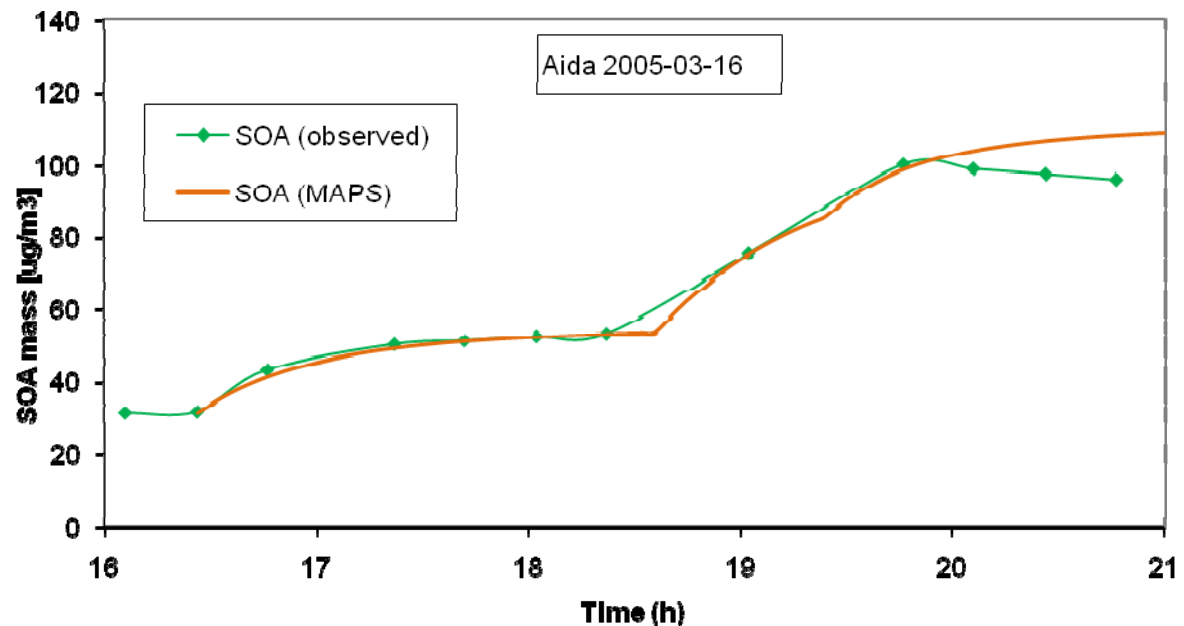
MALTE, EUPHORE experiment



AIDA

Good agreement with COSIMA and MAPS.

Explicit models strongly underestimate aerosol yields.



General observations:

- **models assuming gas-particle phase equilibrium seem to perform reasonably well, at least for some of the experimental conditions**
- **evidence of importance of $[\text{NO}_x]/[\text{VOC}]$**
- **'worst' cases of disagreements found for (nearly) explicit models**
- **wall-losses of semivolatile compounds seem to be important (COSIMA)**

Discussion at Arona workshop:

Detailed information about experimental conditions and characteristics of the chamber needed, particularly:

Wall loss rates for different types of compounds (vapour pressures, polarity)

Photolysis rates/spectral distribution of lamps

Future:

- Finalize present model intercomparison, providing requested information to modelers
- Planning of further SOA chamber data model intercomparison exercises?
- Mechanisms for interaction modelers/chamber 'owners'?