



# Secondary Organic Aerosol: Natural Background and Anthropogenic Contributions

Institute of Inorganic and Analytical Chemistry  
University of Mainz, Germany

*Thorsten Hoffmann*

*Jörg Warnke*

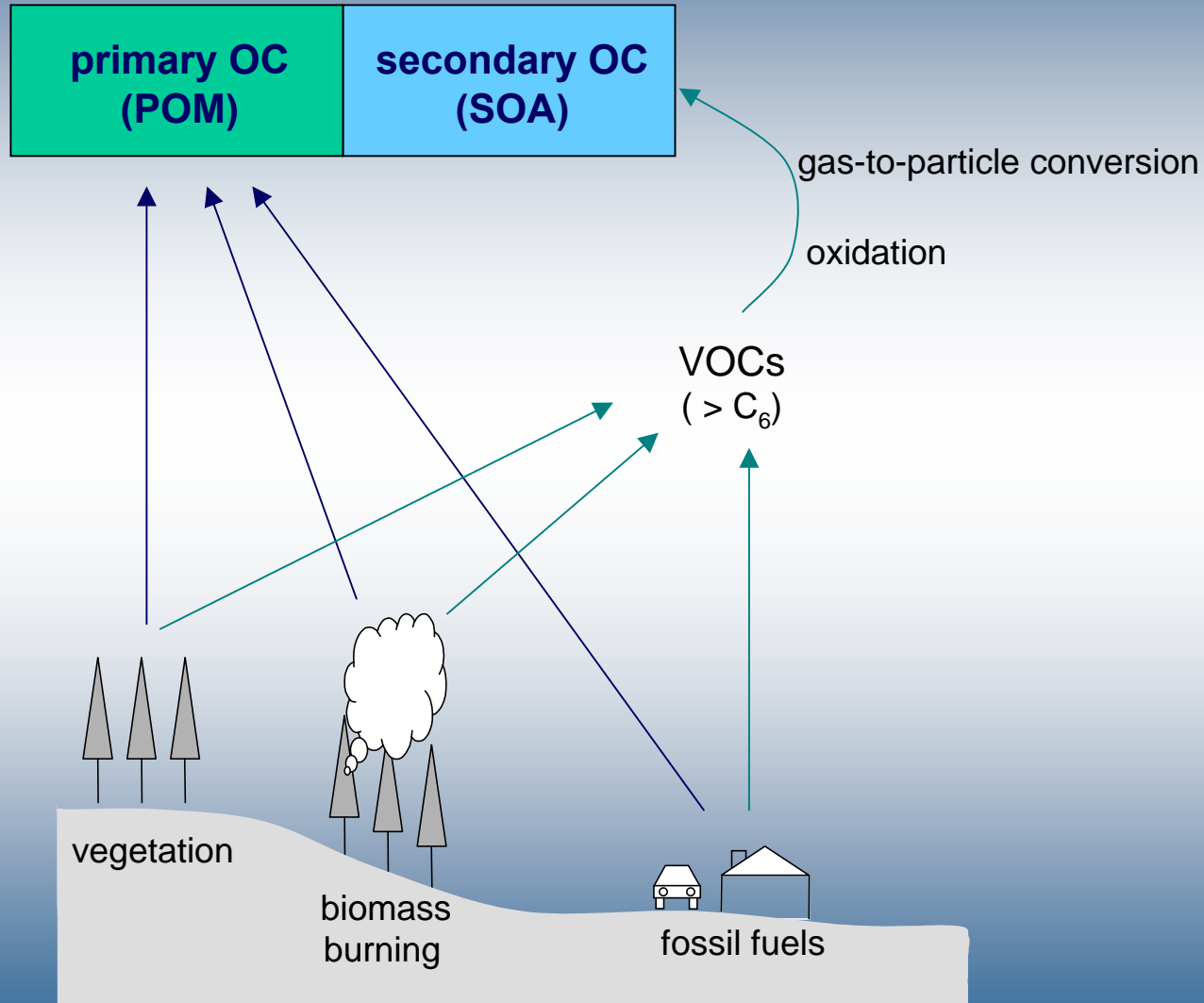
*Bettina Warscheid*

*Rolf Bandur*

## OUTLINE

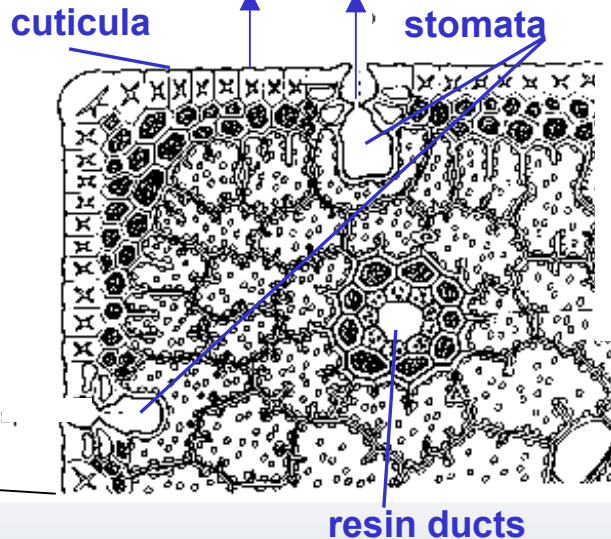
- Introduction
- New particle formation (infl. on particle number concentration)
- Gas/particle partitioning (infl. on particle mass)
- Quantification of the relative contribution of biogenic precursors (marker approach)

# Primary and secondary organic particles in the troposphere

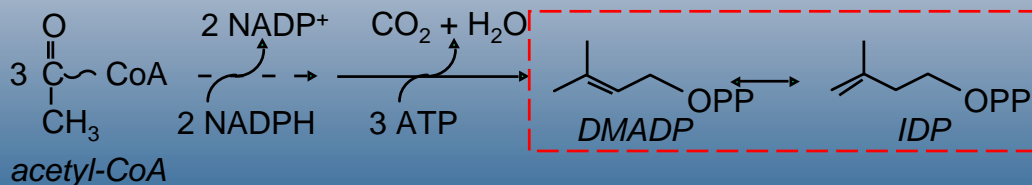
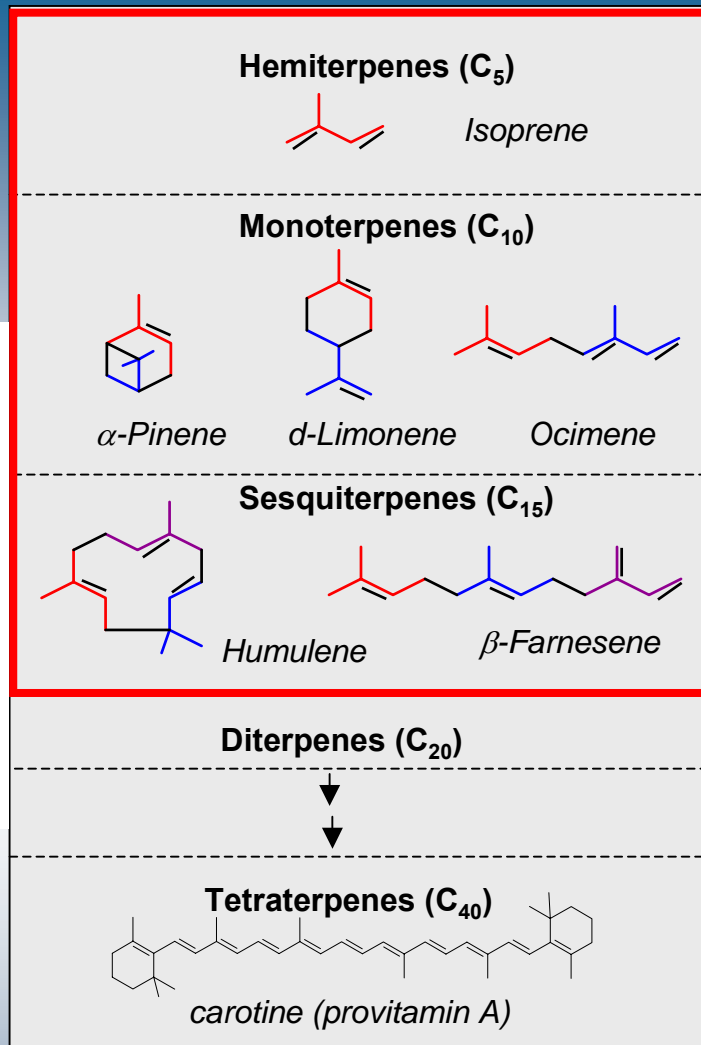


# Emission pathways and structures of biogenic VOCs

emission rate  
plant species  
temperature  
PAR  
physiological condition



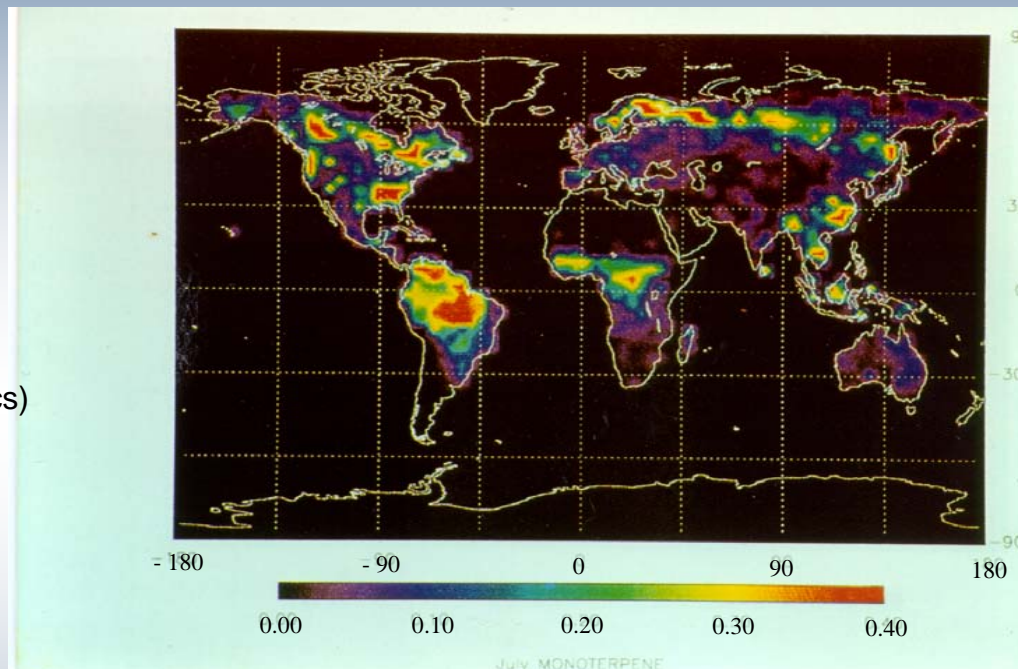
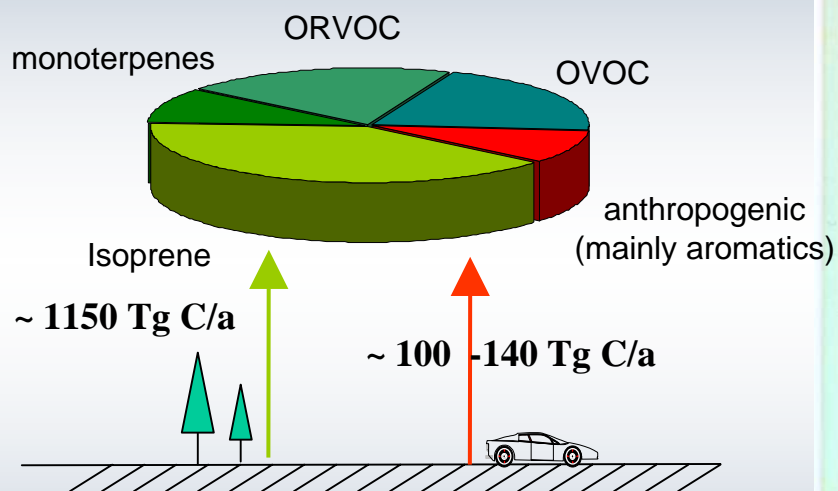
Pine (*Pinus sylvestris*)



**“active Isoprene”**

# Significance of VOCs for organic aerosol formation

VOC from natural sources ~ 90%

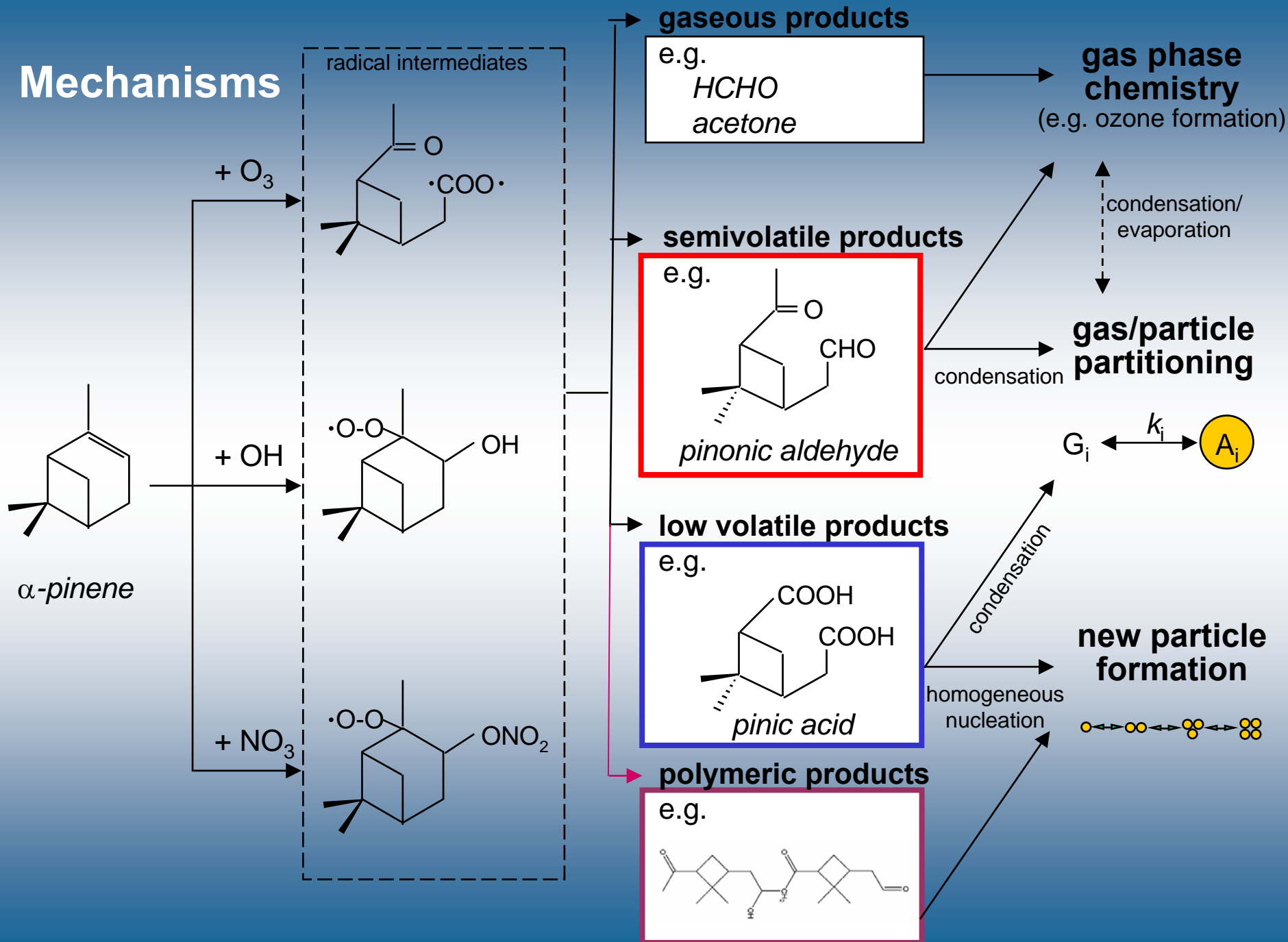


**Emission rates of biogenic VOCs**

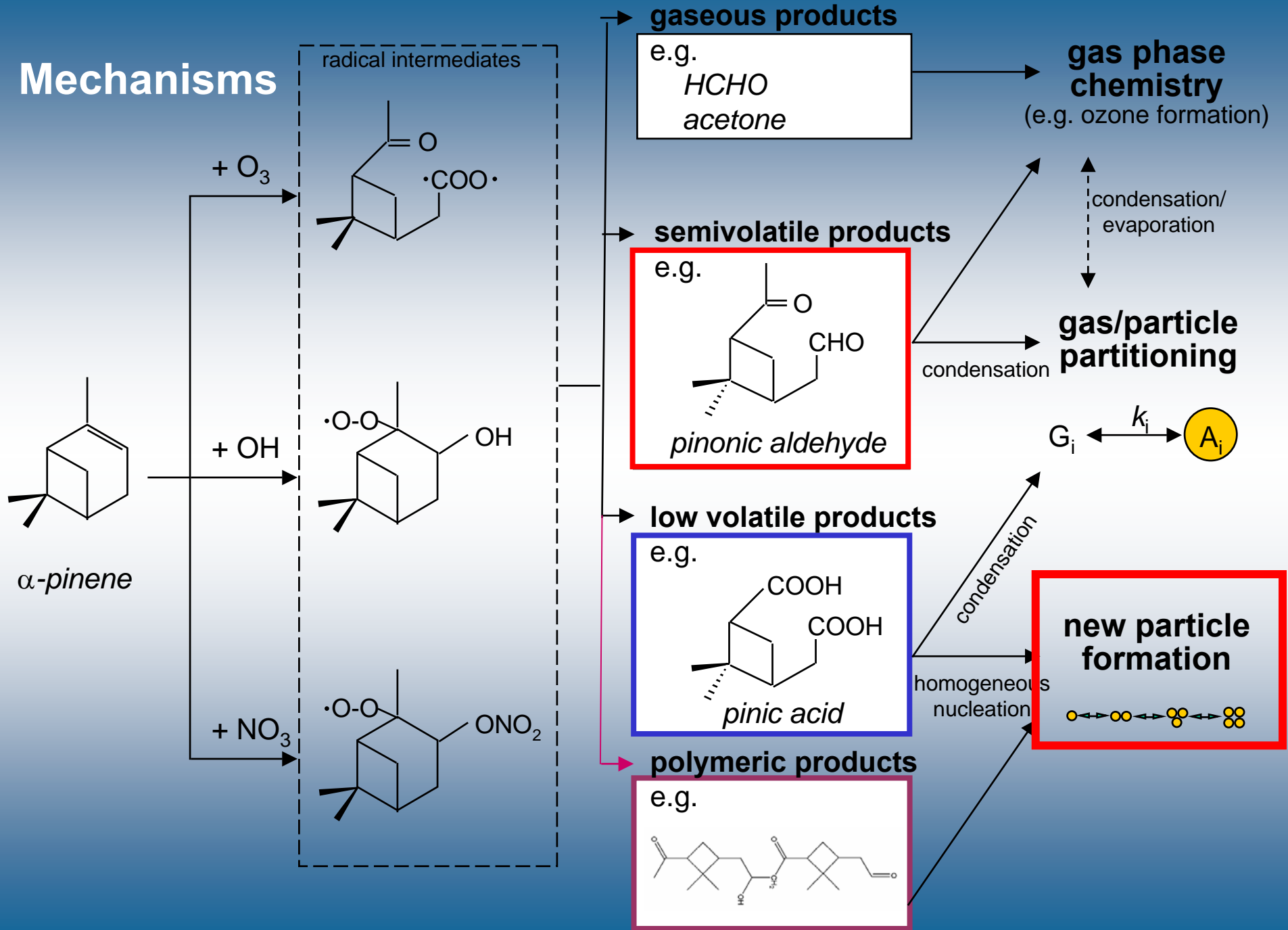
[g C m<sup>-2</sup> month<sup>-1</sup>]

Gunther et al. 1995

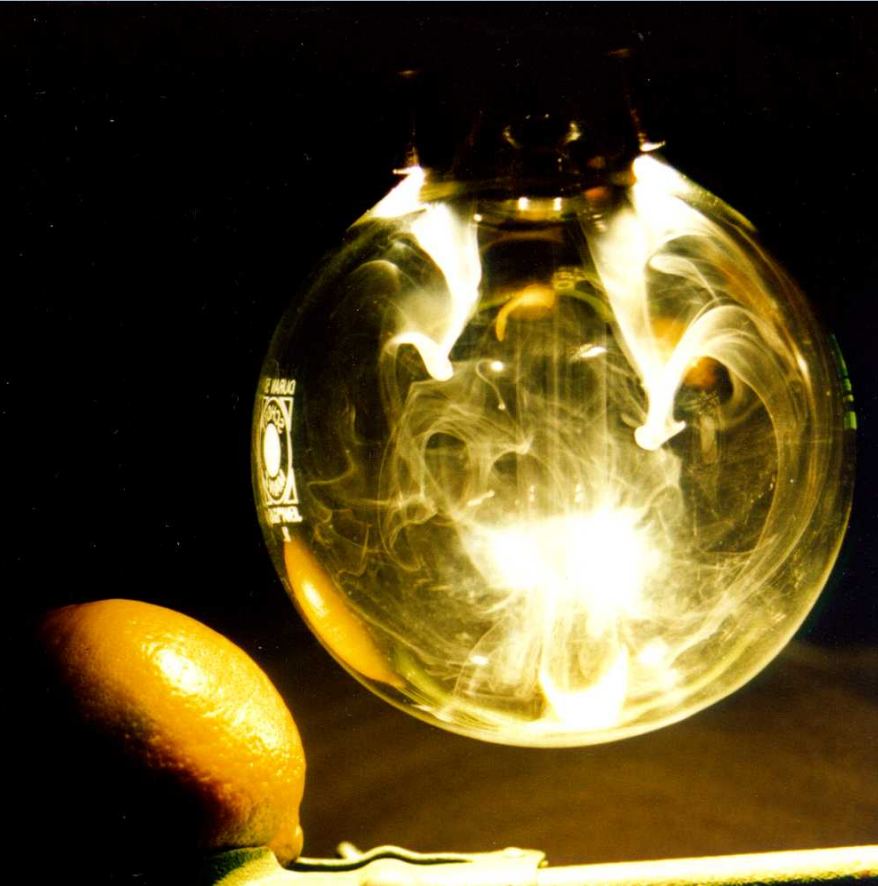
# Mechanisms



# Mechanisms



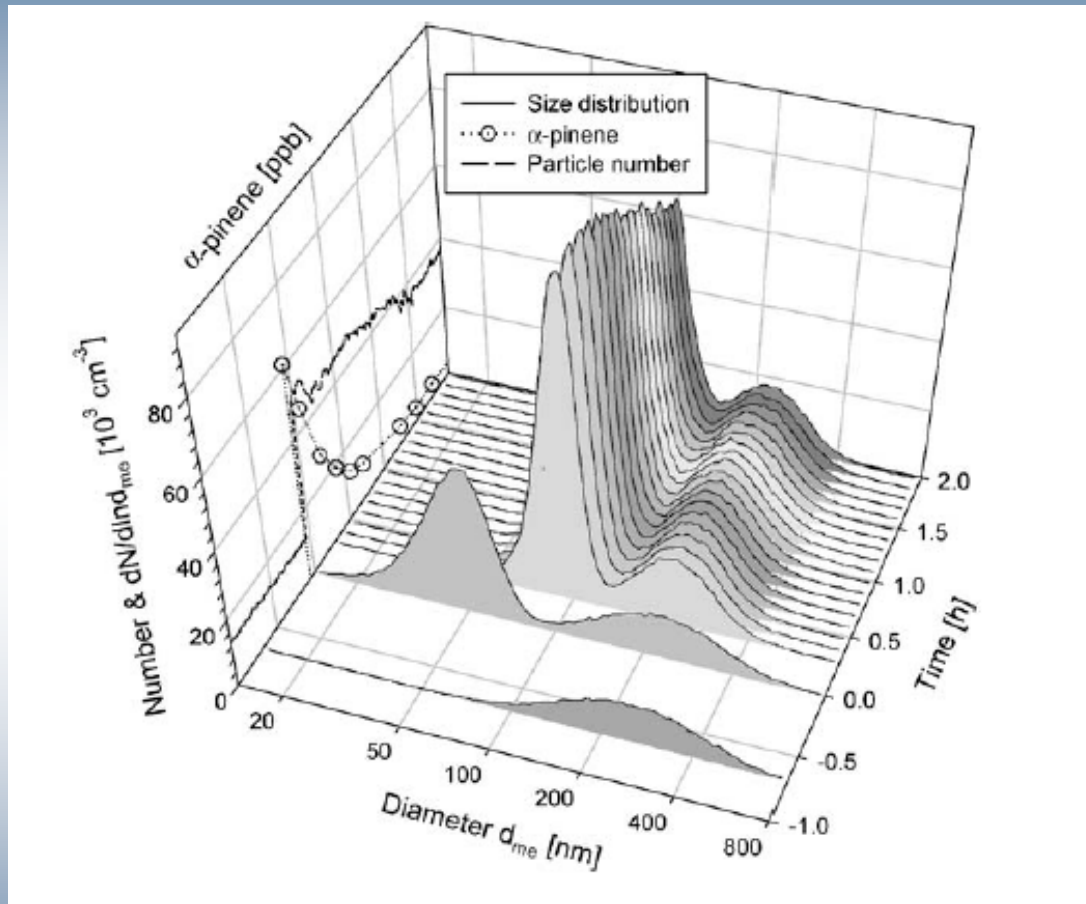
# Chamber studies



Demonstration experiment

EUPHORE chamber facility / Valencia, Spain

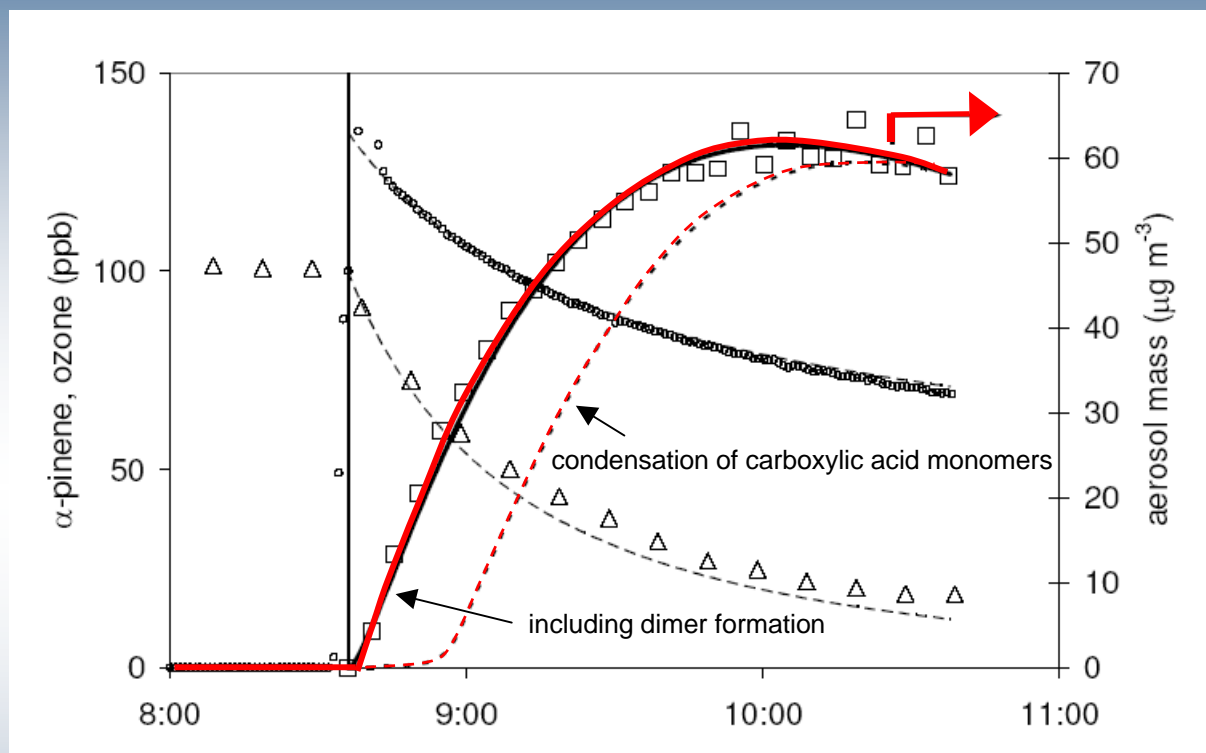
# Evolution of the size distribution and number concentration of Diesel soot and organic aerosol formed upon ozonolysis of alpha-pinene



Saathoff et al. (2004) *J. Aerosol Sci.*

⇒ natural VOCs show a much higher new particle formation potential than anthropogenic VOCs

## Comparison of experiments ( $\alpha$ -pinene/ $O_3$ ) and results from the MCM coupled with a representation of gas-to-aerosol transfer based on equilibrium absorptive partitioning



Time dependence of ozone (circles), pinene (triangles) and aerosol mass (squares) in OSOA experiment. Lines are results of simulations using present mechanism.

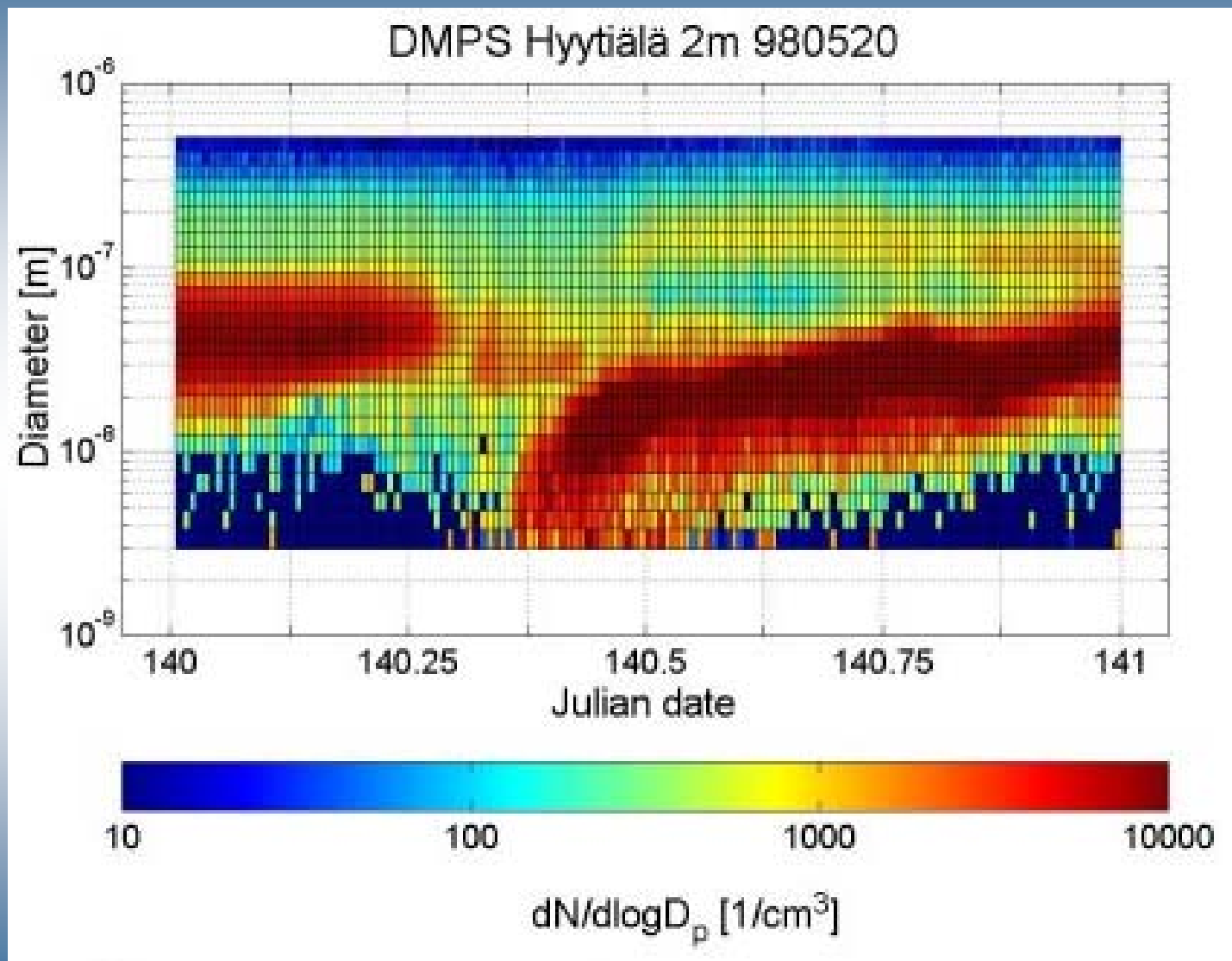
Jenkin (2004), *Atmos. Chem. Phys. Discuss.*

⇒ Inclusion of very low volatile products into absorption models improve model performance



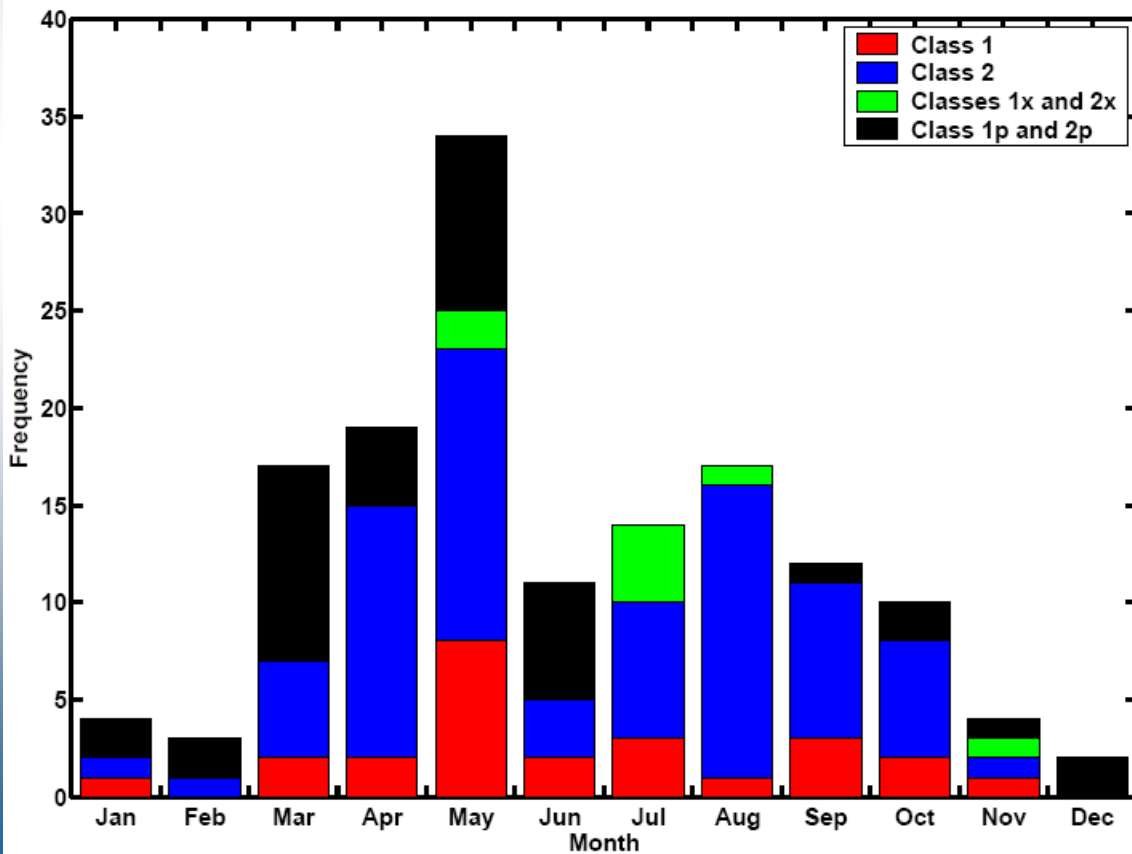
# Field studies

Field observations of new particle formation in rural areas



# Monthly distribution of particle Formation events 1998-2002

Värriö, northern Finland

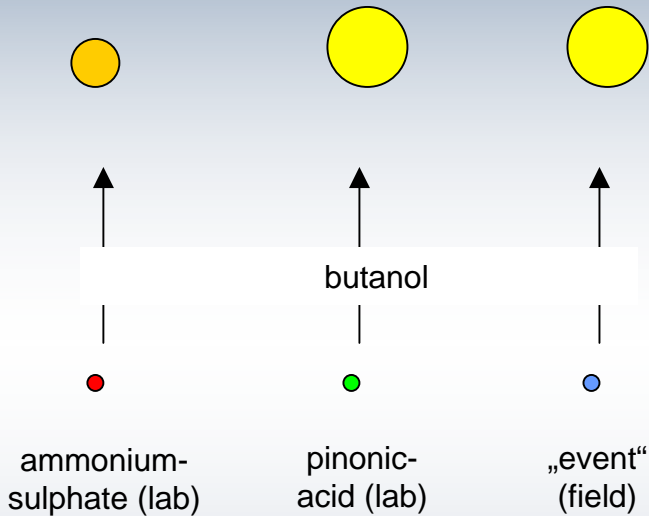


Vehkamäki et al. (2004) *ACPD*

⇒ increasing biological activity  
might produce the precursor gases

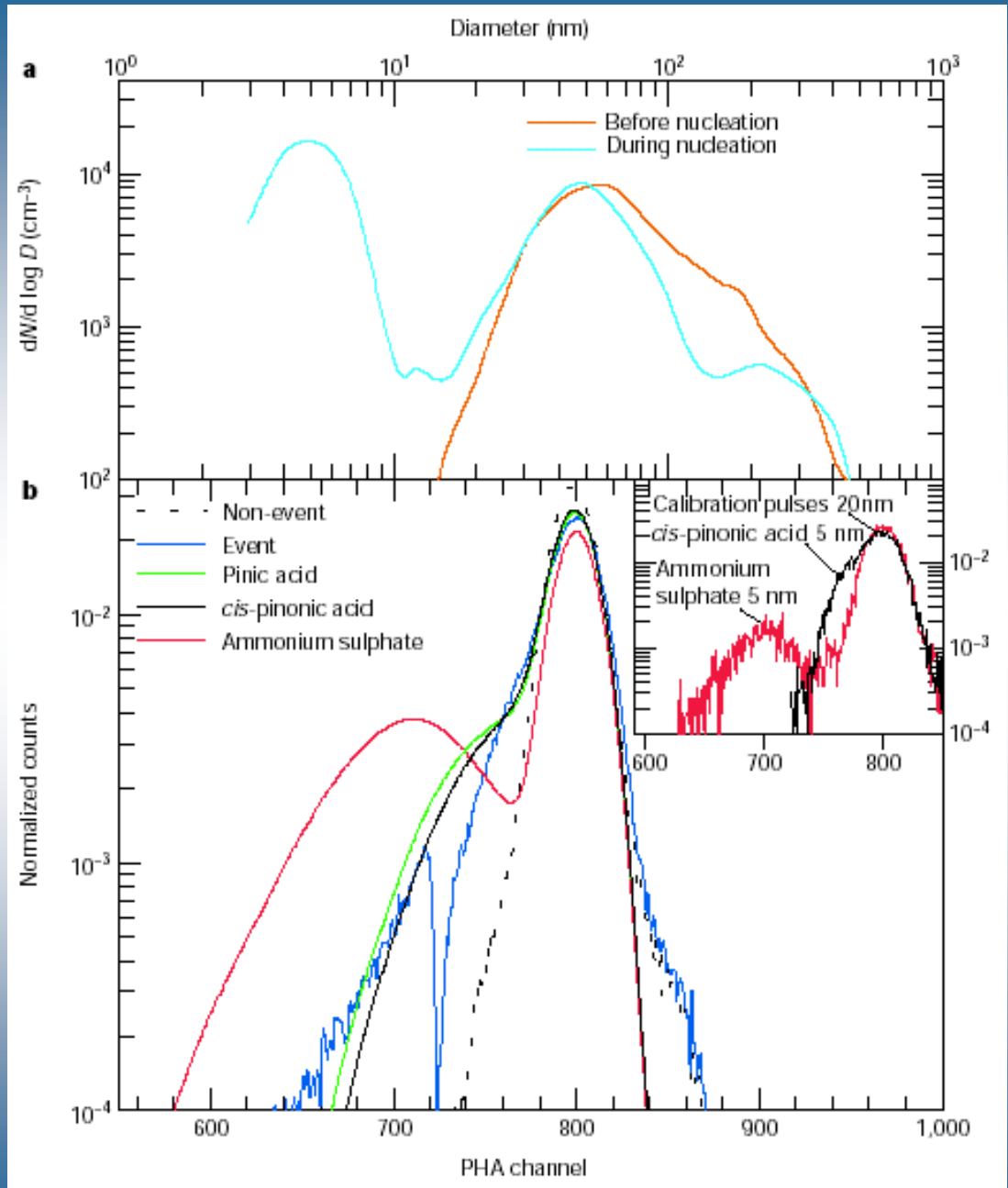
# Pulse height analysis of ultrafine particles

Hyytiälä, Finland



O'Dowd et al. (2002) *Nature*

⇒ actual nucleation mode particles have a solubility in butanol which is similar to biogenic SOA products



# 3 concepts to explain atmospheric new particle formation

TSCs ( $\text{H}_2\text{SO}_4 - \text{H}_2\text{O} - \text{NH}_3$ )

A) Kulmala, Pirjola and Mäkelä (2000) *Nature*, Kulmala et al. (2004) *JGR*

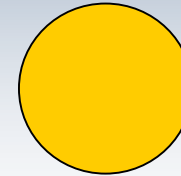
1) Formation of TSCs



~ 1 nm

2) condensation of low volatile organics

activation („nano-Köhler“)



B) Zhang and Wexler (2002) *JGR*

1) Formation of TSCs



2) heterogeneous reactions

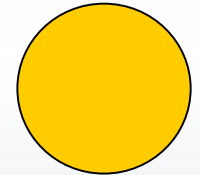
e.g. alkenes

e.g. alkyl sulfates



3) condensation of low volatile organics

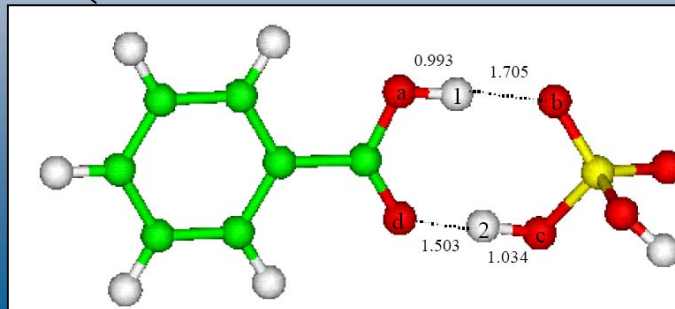
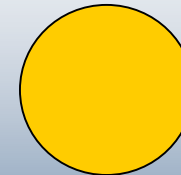
⇒ growth and lowering surface tension



C) Zhang et al. (2004) *Science*

heteromolecular  
homogeneous  
nucleation  
involving organic acids  
and sulphuric acid

condensation of low volatile organics



bonding energy ~ 20 kcal mol<sup>-1</sup>

$\text{H}_2\text{SO}_4 - \text{H}_2\text{O} \sim 10 \text{ kcal mol}^{-1}$

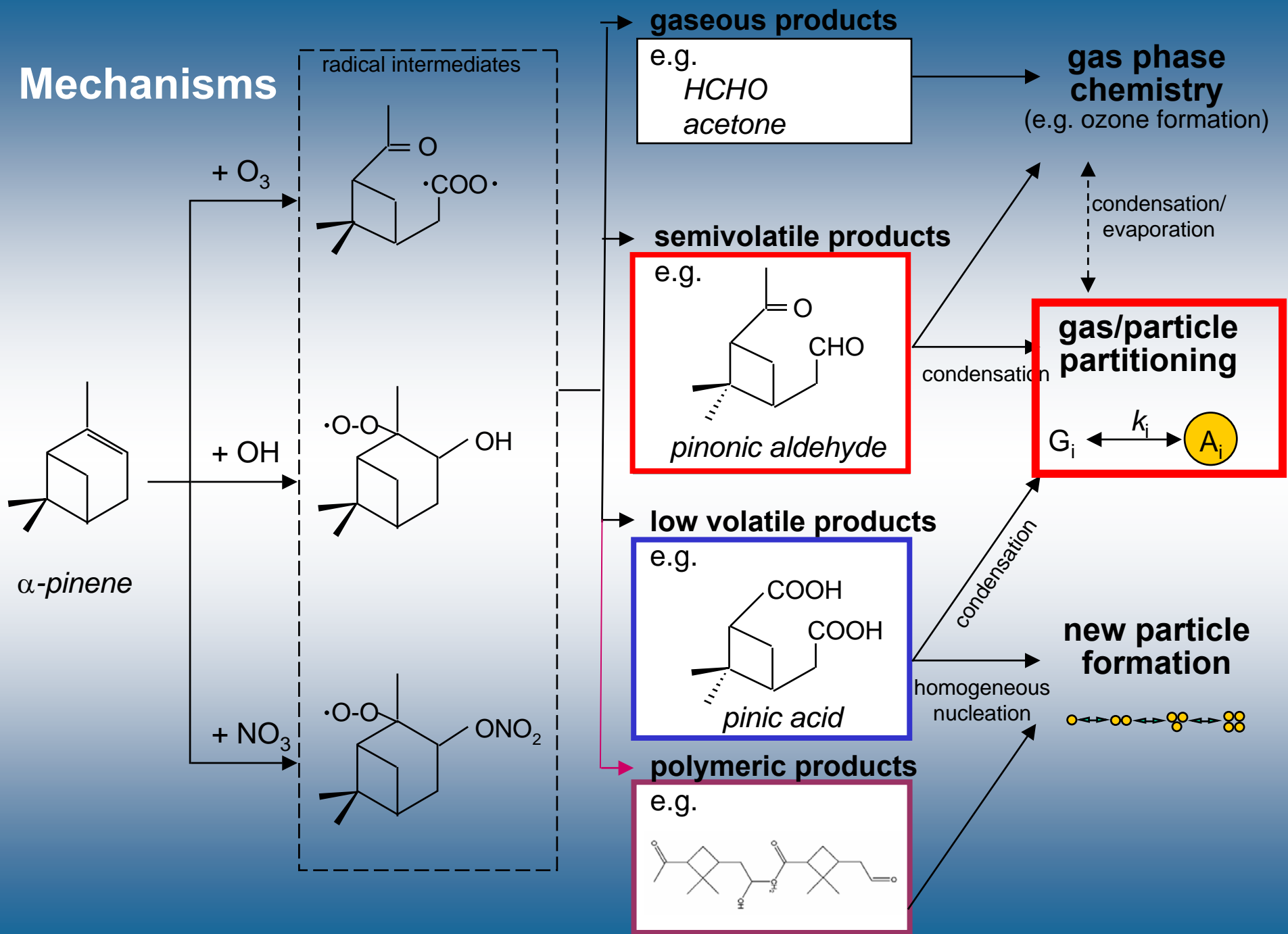
$\text{H}_2\text{SO}_4 - \text{H}_2\text{O} - \text{NH}_3 \sim 25 \text{ kcal mol}^{-1}$

# Conclusions I

## (new particle formation)

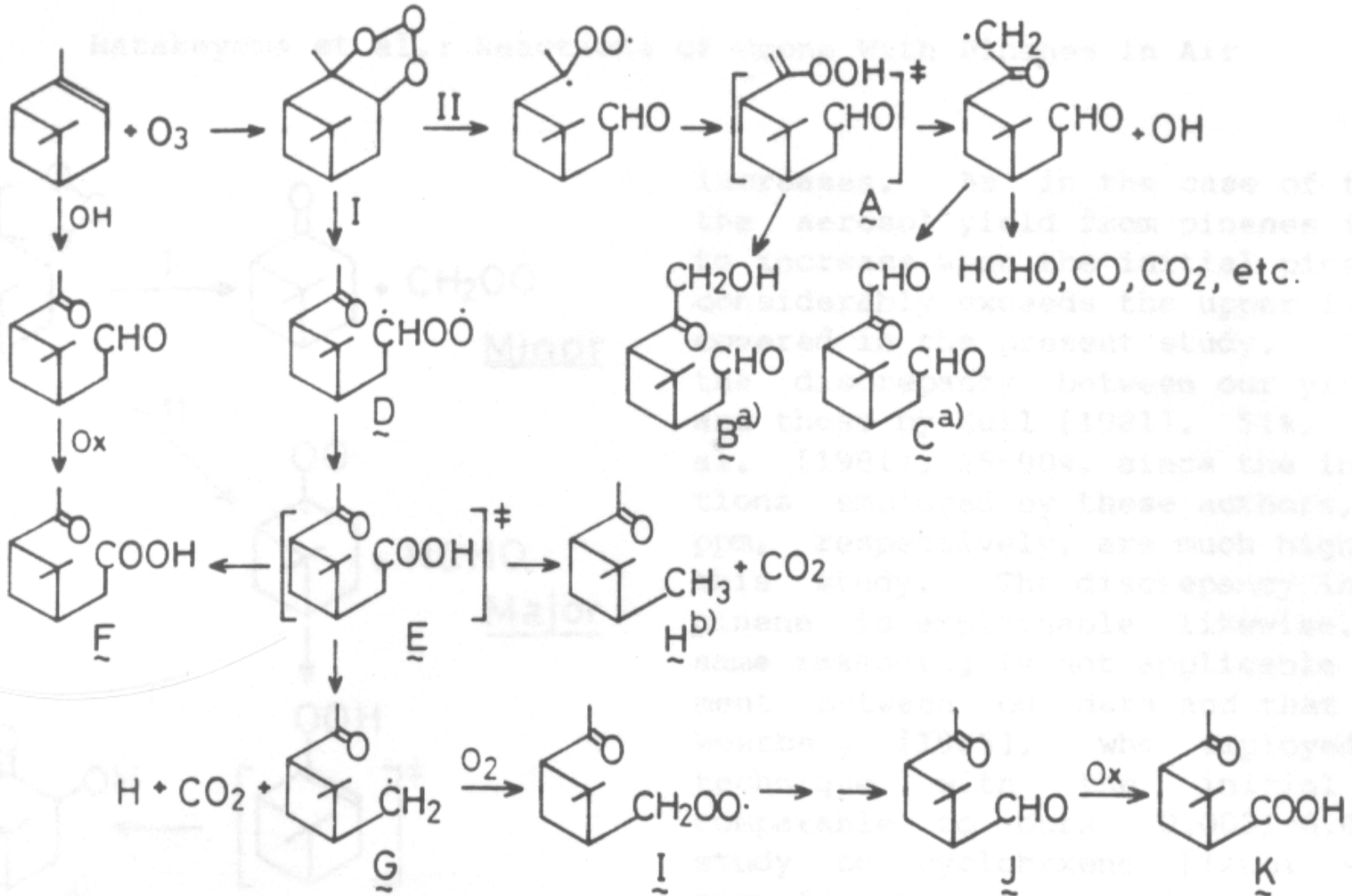
- ⇒ biogenic VOCs - higher new particle formation than anthropogenic VOCs
- ⇒ small amounts of very low volatile products are essential to explain chamber observations
- ⇒ in the ambient atmosphere probably „inorganic seeds“ are involved in the early steps of particle formation – however – particle growth is governed by secondary organic aerosol components

# Mechanisms

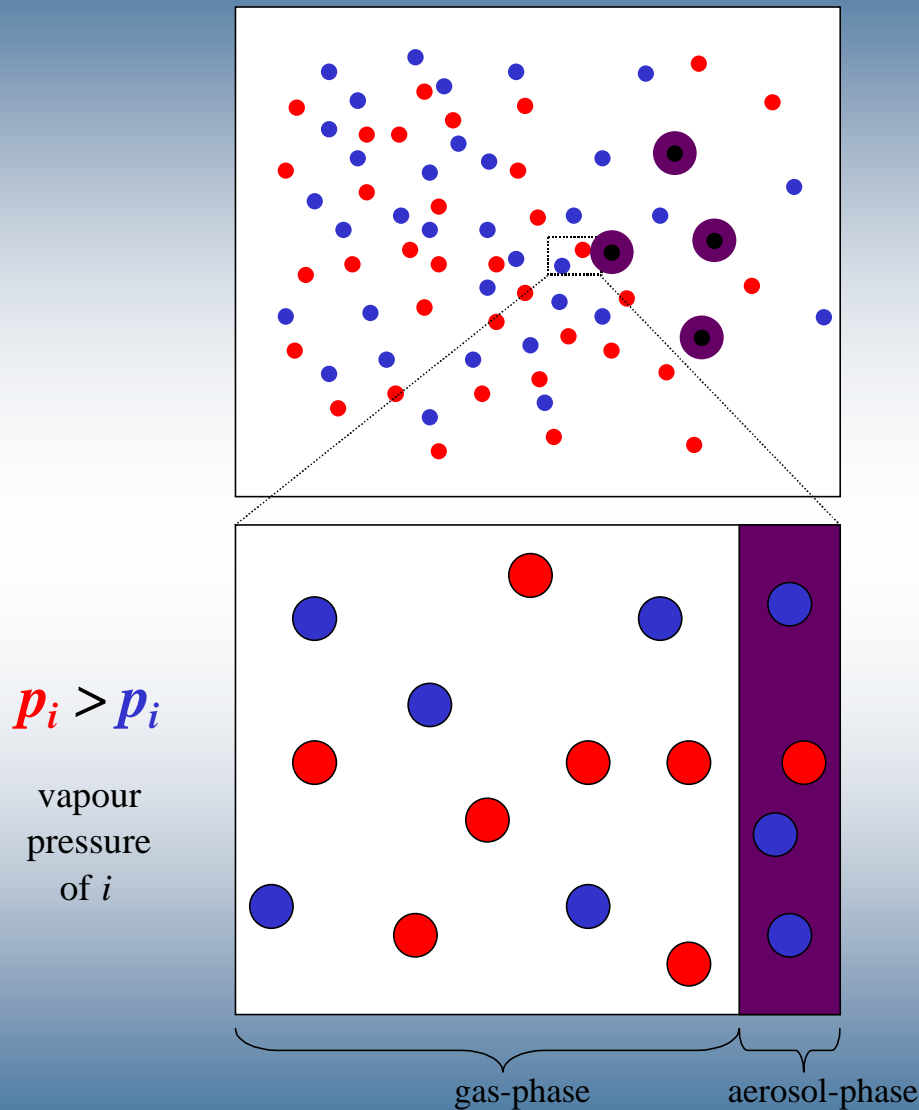


# Chemistry of SOA formation

## Chemical pathways to condensable species



# Physicochemical properties of condensing organics



$K_i$  partitioning coefficient  
[ $\text{m}^3 \mu\text{g}^{-1}$ ]

$M_o$  absorbing organic aerosol  
mass [ $\mu\text{g m}^{-3}$ ]

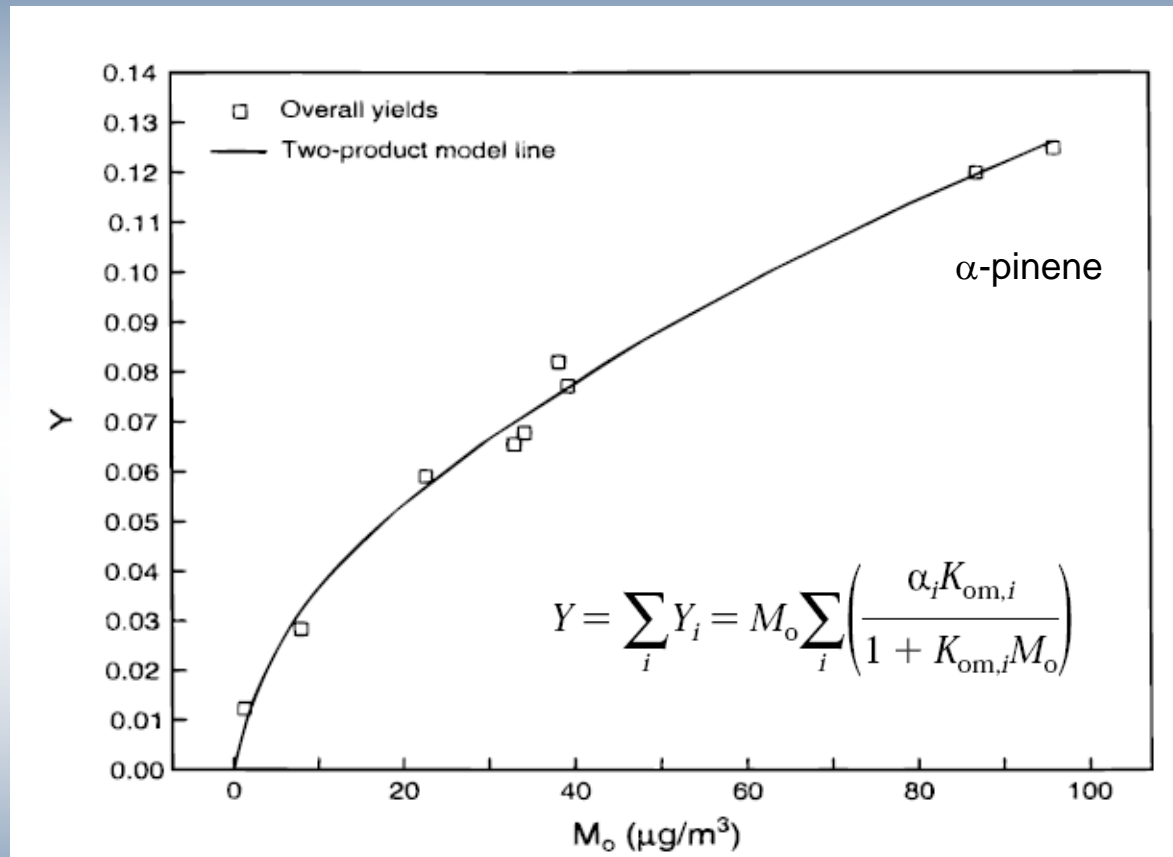
$A_i$  concentration of product  $i$   
in the aerosol-phase [ $\mu\text{g m}^{-3}$ ]

$G_i$  concentration of product  $i$   
in the gas-phase [ $\mu\text{g m}^{-3}$ ]

$$K_i = \frac{A_i}{G_i M_o}$$

$$K_i \sim 1 / p_i$$

# Odum et al. model



Odum et al. (1996)  
*Environ. Sci. Technol.*

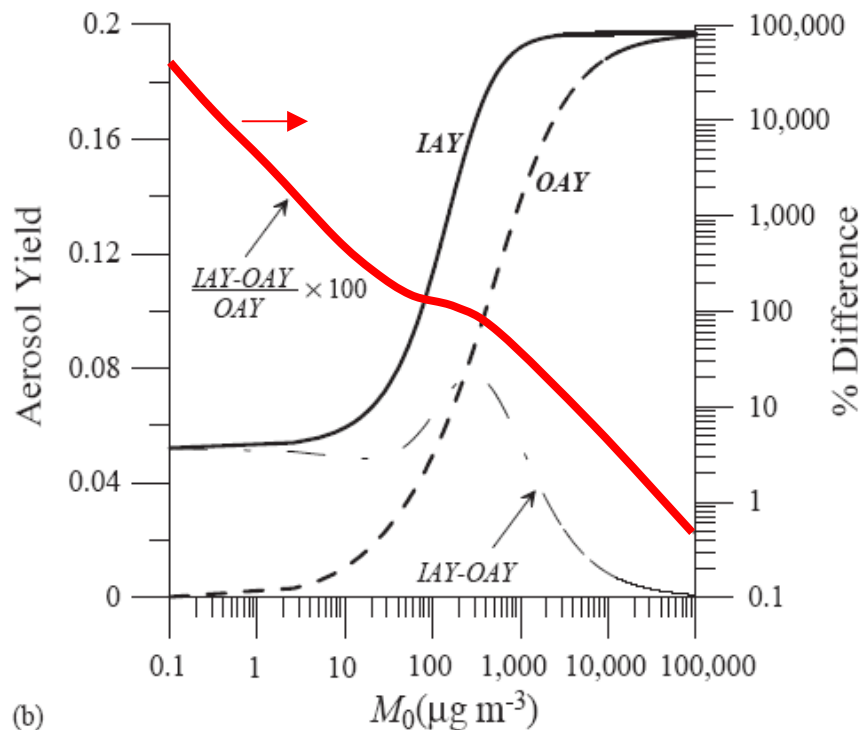
# Instantaneous secondary organic aerosol yields (IAY)

$$OAY = \frac{\Delta M_0}{\Delta ROG} = M_0 \sum_i \left( \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_0} \right)$$

Odum et al. (1996)  
*Environ. Sci. Technol.*

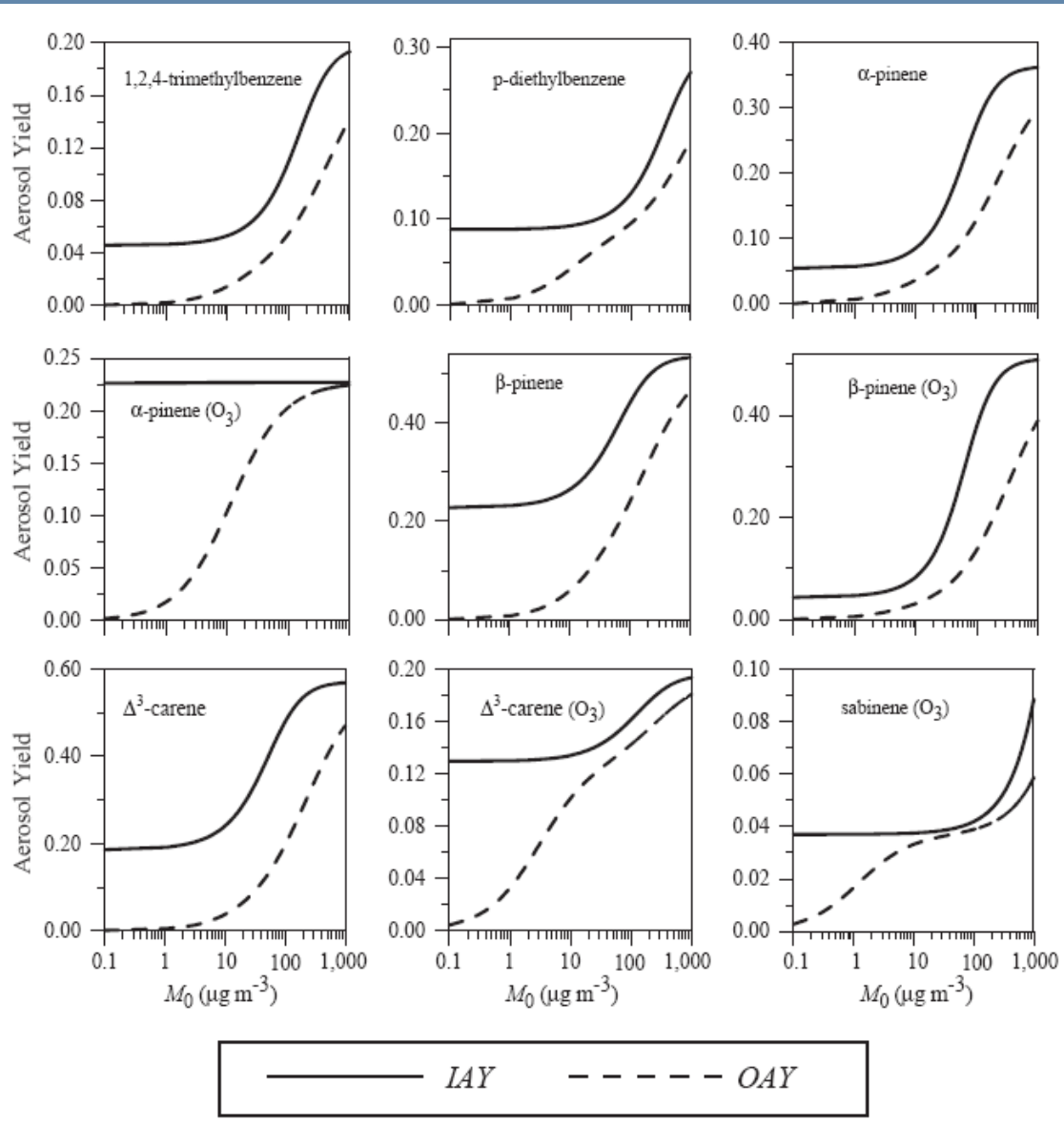
$$IAY = \frac{dM_0}{d\Delta ROG} = \frac{(\sum_i \alpha_i K_{om,i} / (1 + K_{om,i} M_0))^2}{\sum_i \alpha_i K_{om,i}^2 / (1 + K_{om,i} M_0)^2}$$

Jiang (2003)  
*Atmos. Environ.*



(6)

# Comparison of OAY (Odum) and IAY (Jiang)

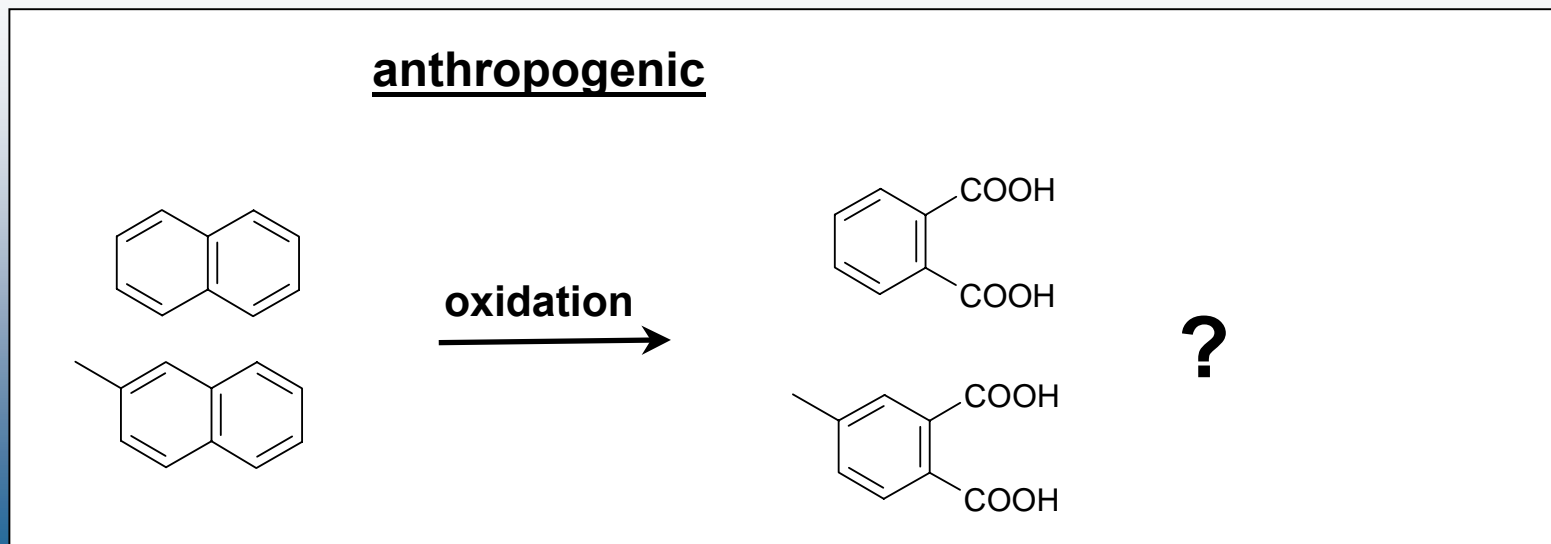
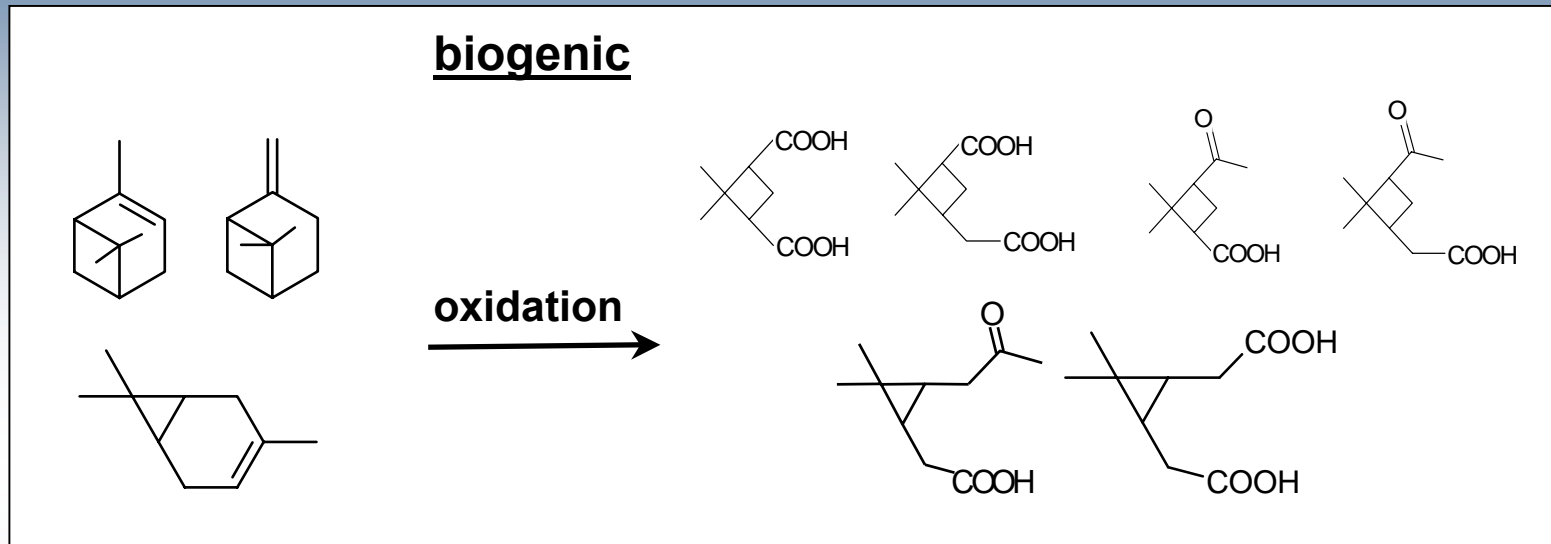


## Conclusions II

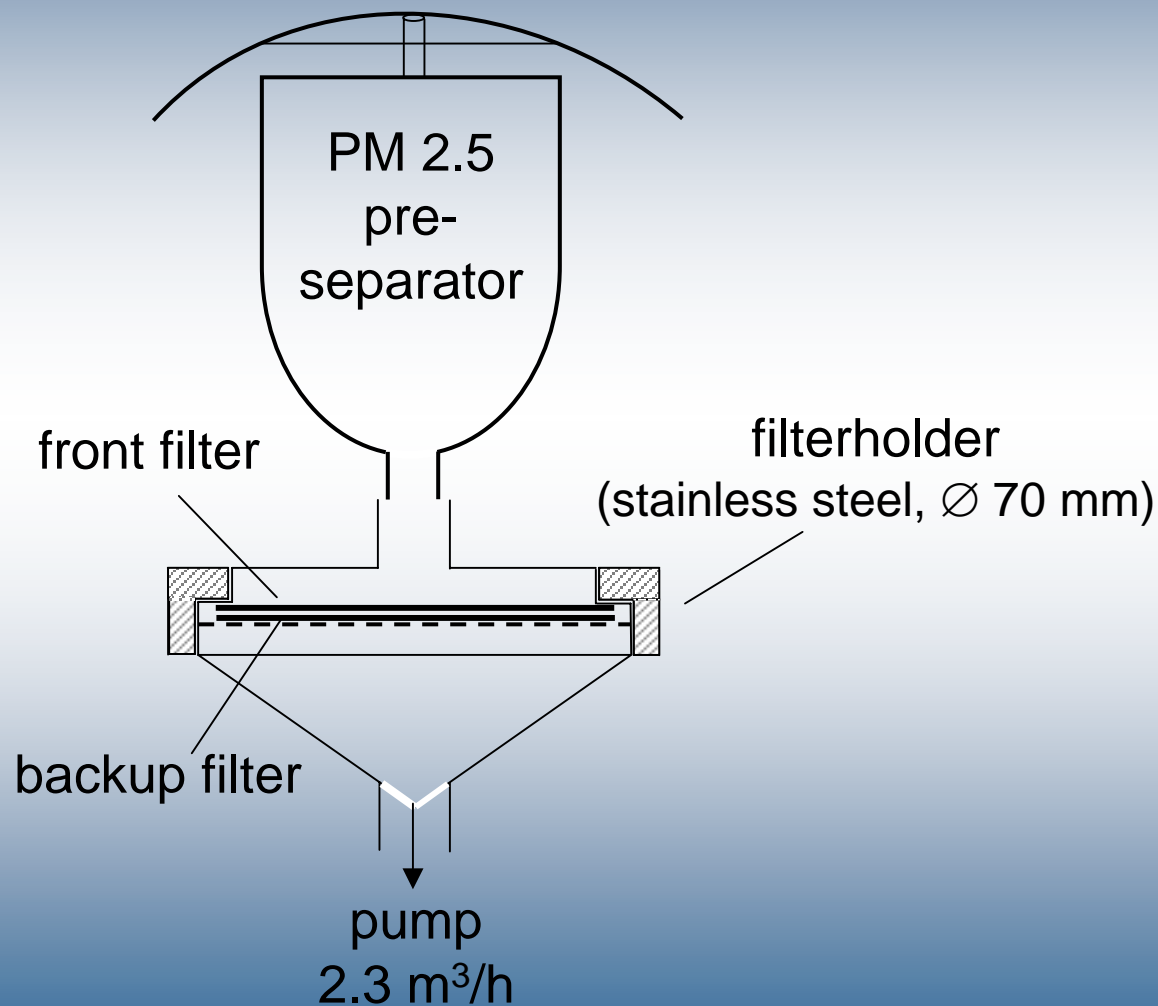
### (SOA process modelling)

- ⇒ there exists a general understanding of the physico-chemical processes leading to SOA formation (gas/particle partitioning)
- ⇒ integration into coupled models appears to be not satisfactory (need for precise laboratory data on  $K$ 's and  $\alpha$ 's)
- ⇒ small amounts of very low volatile products are also essential for the model predictions under ambient conditions

# Quantification of biogenic and anthropogenic SOA contributions

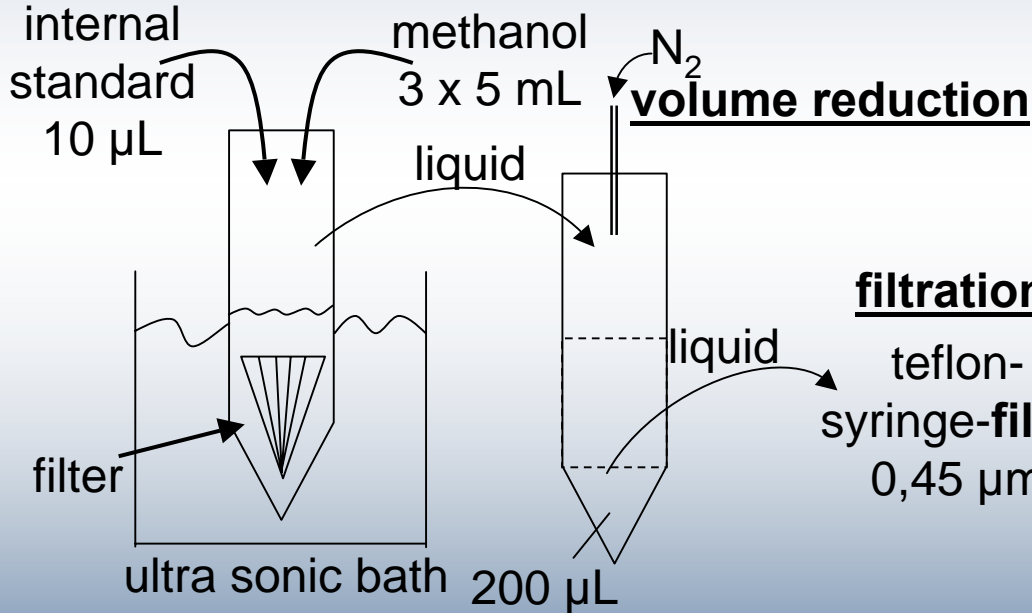


# Aerosol sampling set-up



# Sample preparation

## extraction



## filtration

liquid  
teflon-  
syringe-filter  
0,45  $\mu\text{m}$

## solvent evaporation

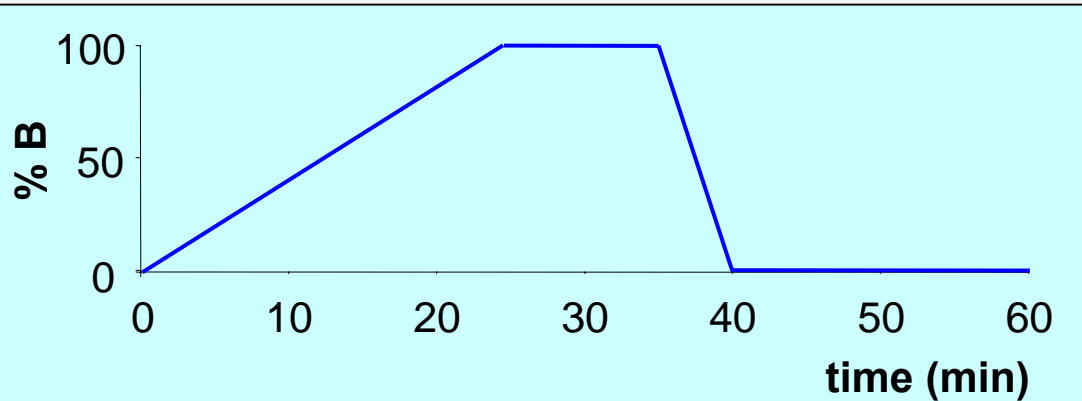
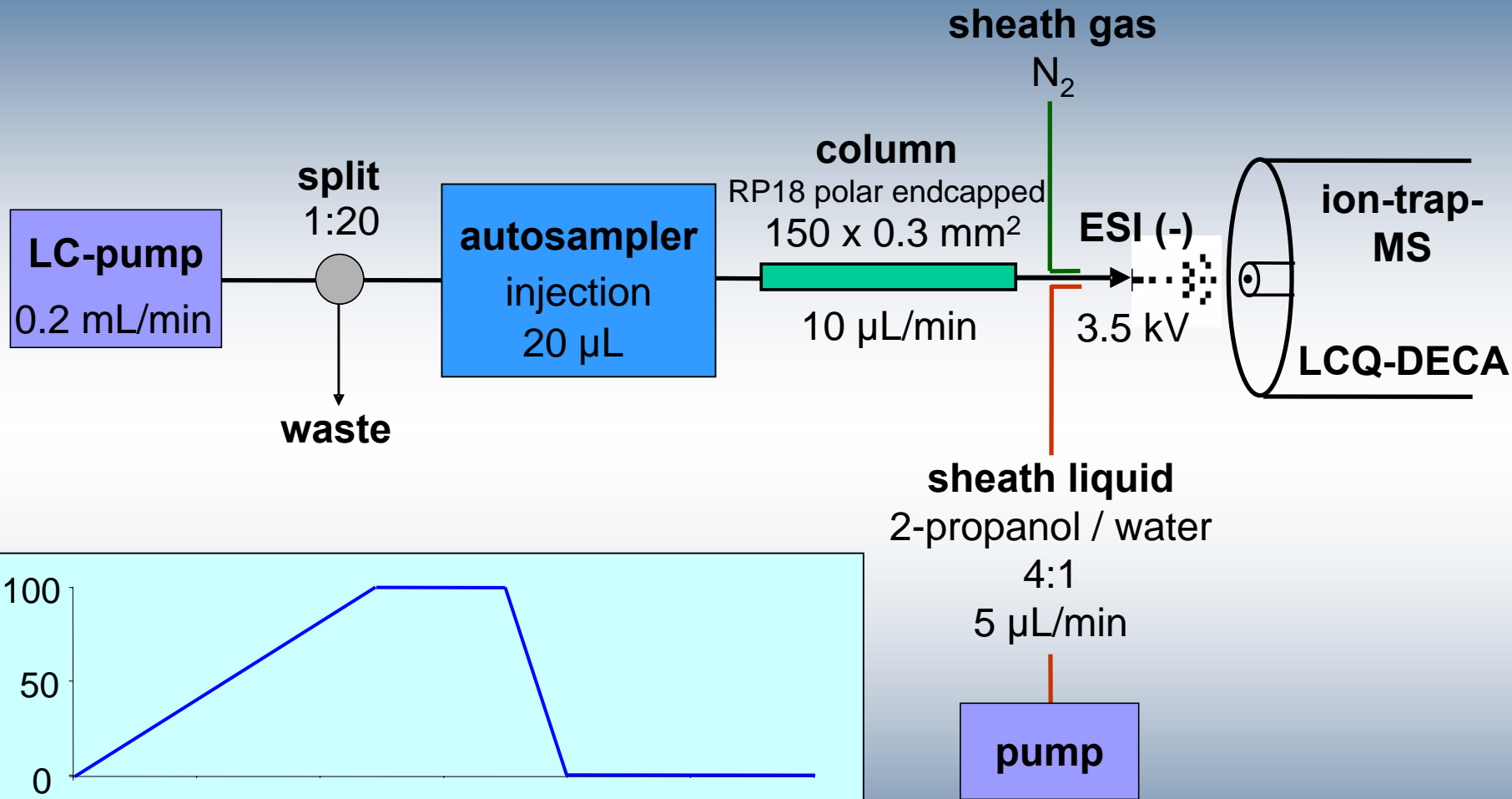
## resolving

+ 200  $\mu\text{L}$   $\text{H}_2\text{O}$   
(+ standard)

(dilution,  
standard-addition)

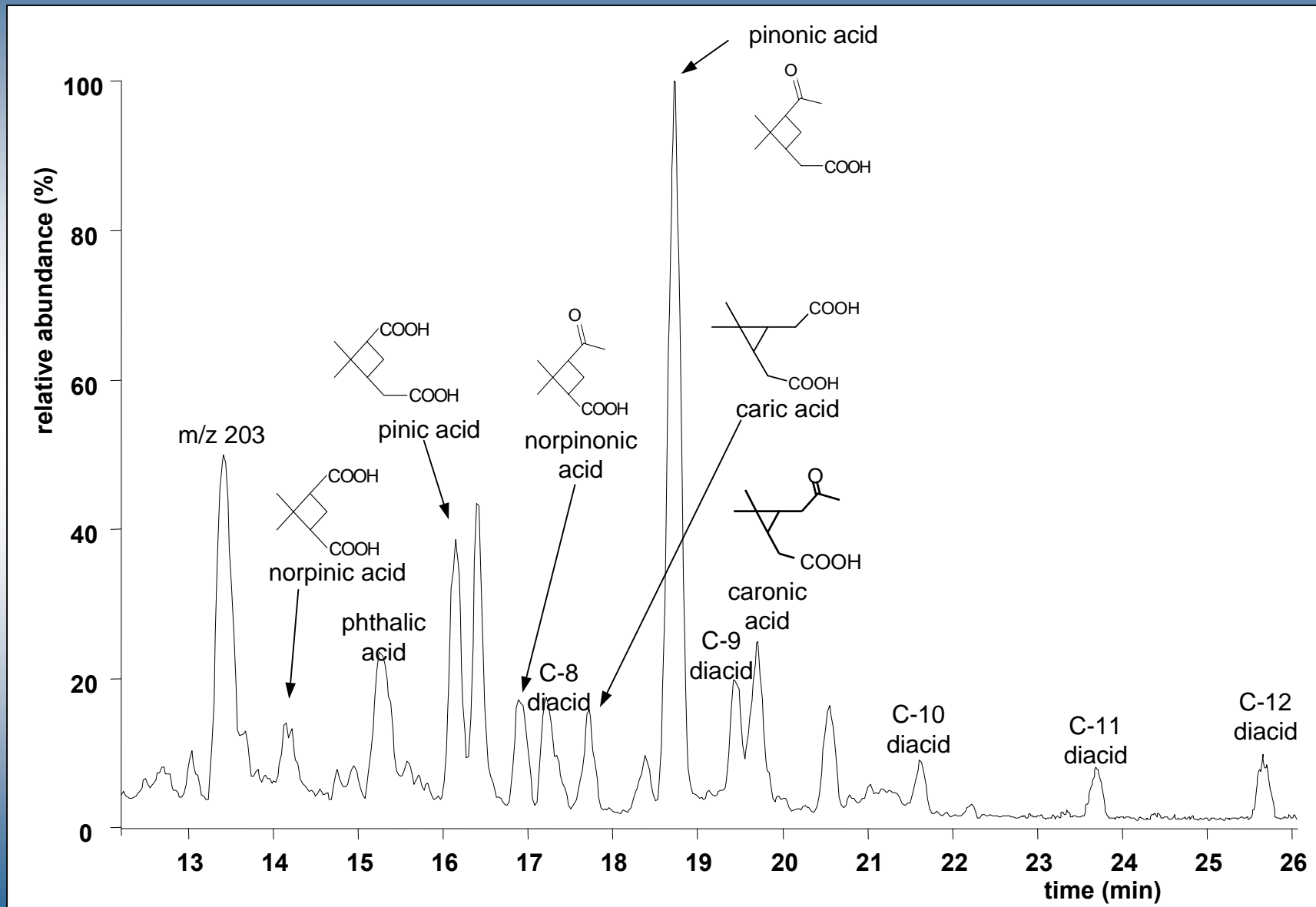
## injection

# HPLC-ESI-MS-method



Eluent A: 10 mmol HCOOH in H<sub>2</sub>O, 2.5% CH<sub>3</sub>CN  
Eluent B: CH<sub>3</sub>CN, 2.5% H<sub>2</sub>O

# Base peak chromatogram of an aerosol sample from Hyytiälä



# Field sites

BIOFOR, OSOA, QUEST, AFO2000



Hyytiälä, Finland

Melpitz, Germany

FZ Jülich, Germany

Bologna, Italy

# Calculating secondary organic aerosol (SOA) from concentrations of marker compounds

Calculation of SOA derived from ozonolysis of different terpenes in the troposphere by:

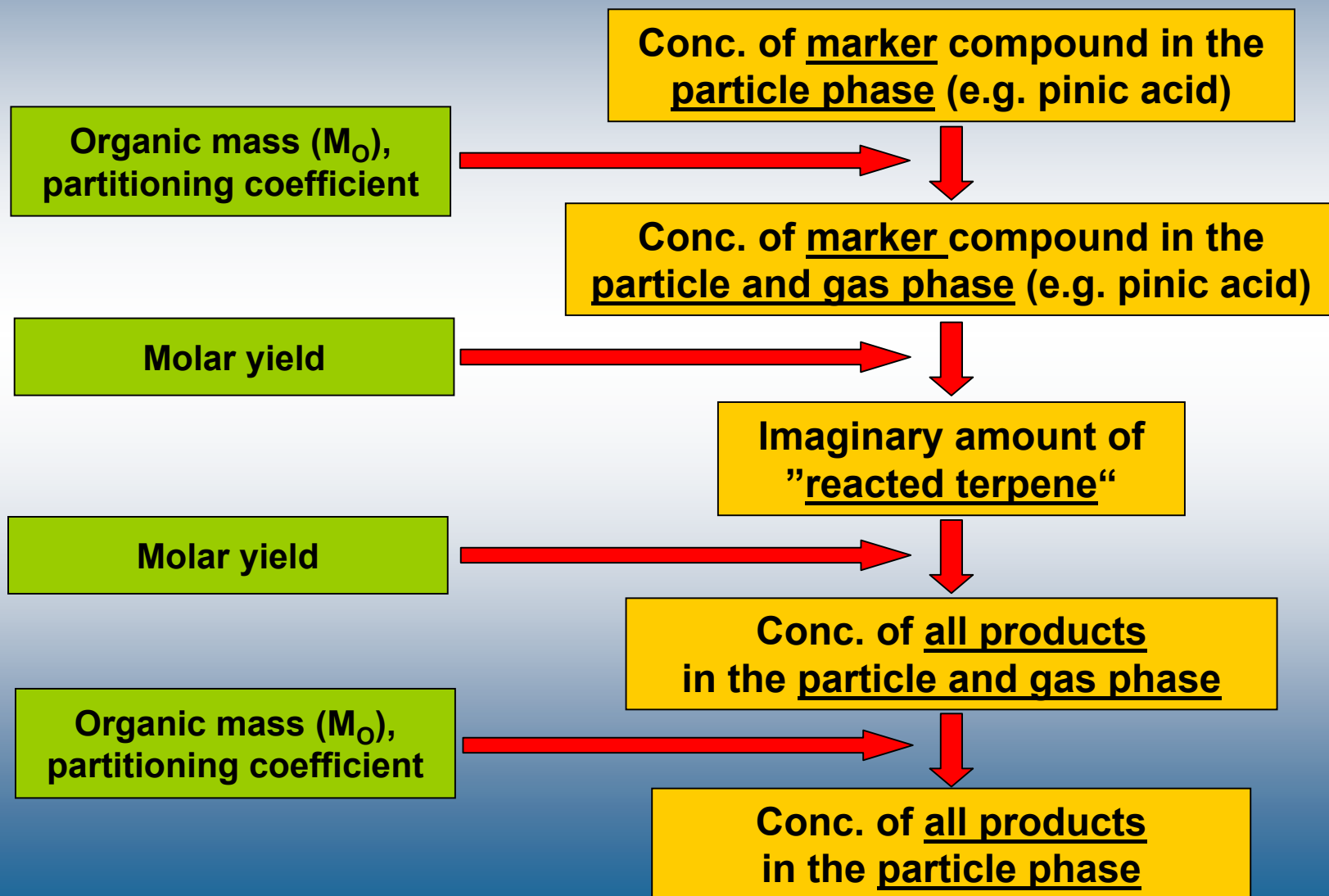
- using low volatile products as markers
- using the gas particle partitioning model after Pankow (1994) and Odum et al. (1996)
- using product yields of ozonolysis after Yu et al. (1999)

Pankow, J. F. (1994), Atmos. Environ. 28(2): 185-188.

Odum, J. R. et al. (1996), Environ. Sci. Technol. 30: 2580-2585.

Yu, J. Z. et al. (1999), J. Atmos. Chem. 34(2): 207-258.

# Scheme for calculating SOA from concentrations of marker compounds measured in the particle phase



SOA-precursors:

■  $\alpha$ -pinene

■  $\beta$ -pinene

■ 3-carene

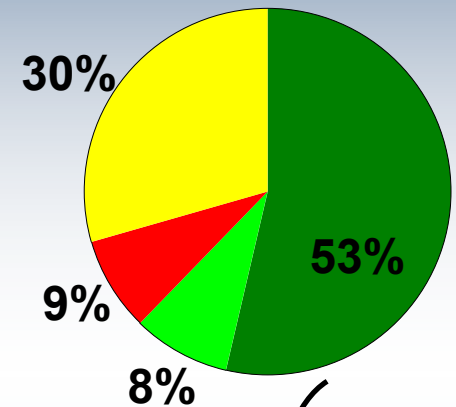
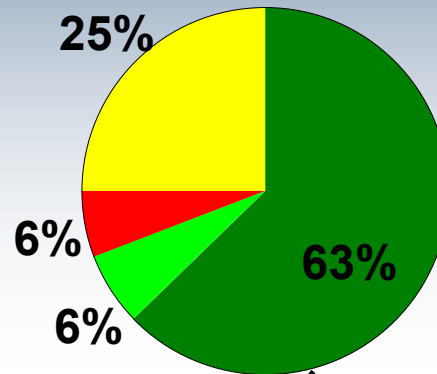
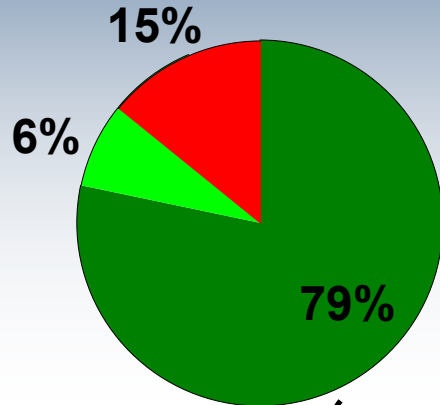
■ sabinene

Hyytiälä,  
early spring 2003  
73 ng/m<sup>3</sup>

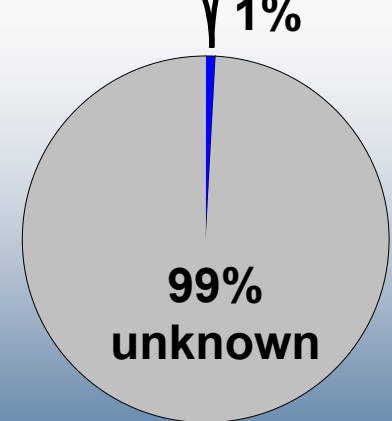
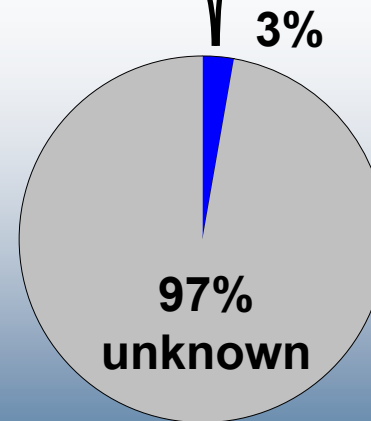
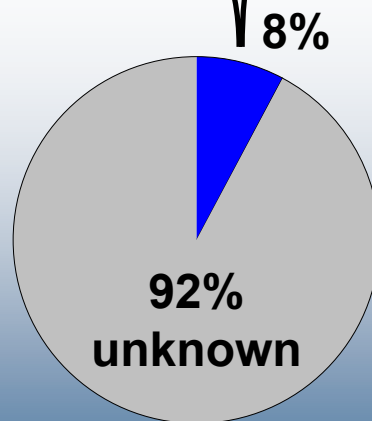
Jülich,  
summer 2003  
78 ng/m<sup>3</sup>

Jülich,  
summer 2002  
6 ng/m<sup>3</sup>

mean  
concentration  
and  
composition  
of estimated  
SOA from  
terpene  
ozonolysis



mean  
concentration  
of total SOA and  
fraction that  
can be assigned  
to ozonolysis  
of terpenes



910 ng/m<sup>3</sup>

3370 ng/m<sup>3</sup>

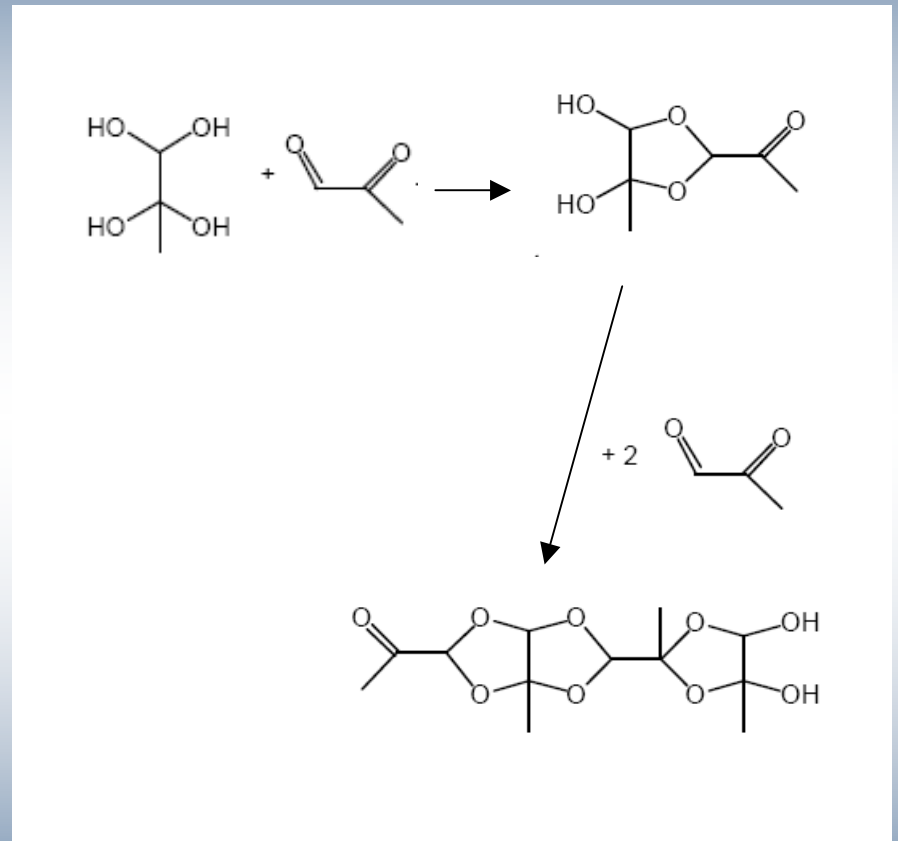
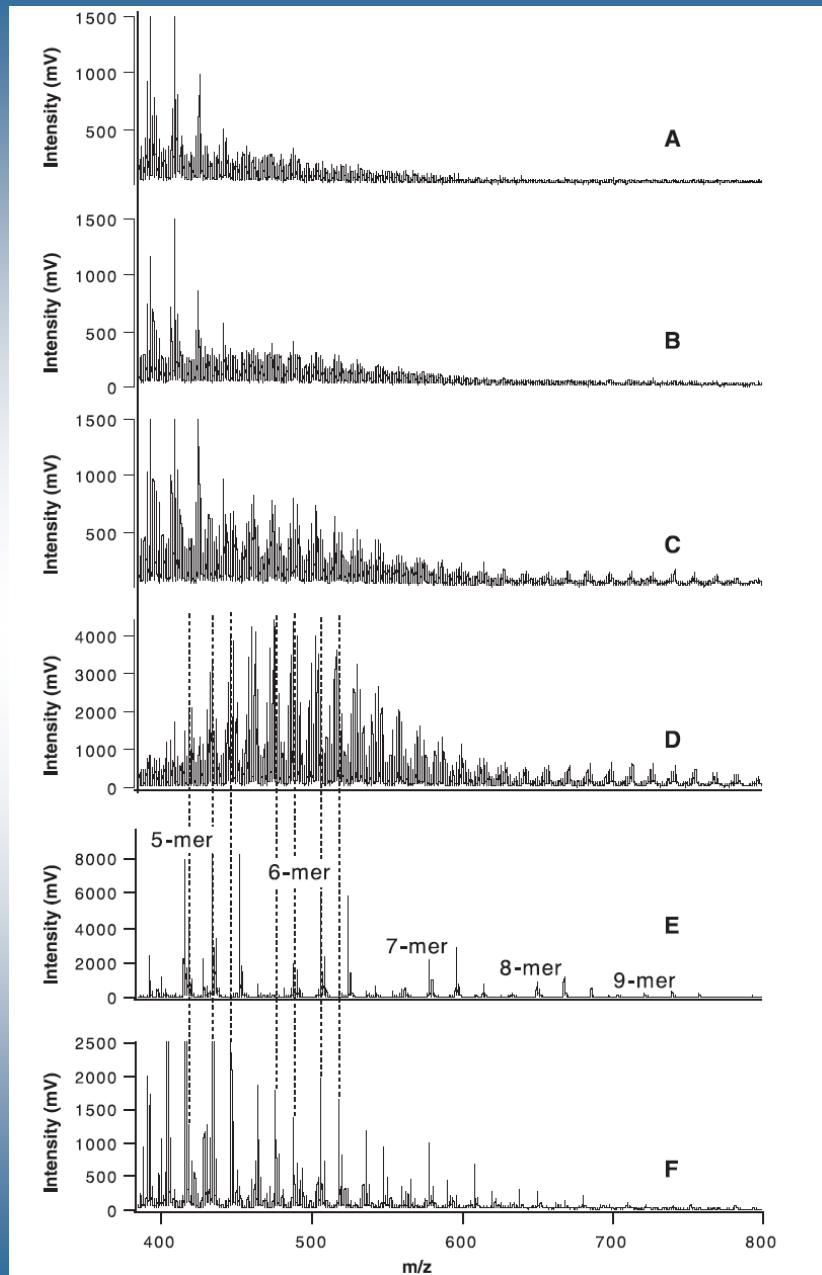
640 ng/m<sup>3</sup>

(estimation of total SOA by OC/EC tracer method)

# What is the missing SOA-mass?

- other important precursors
- second generation products
- polymers
- .....?

# Polymerisation and SOA



Kalberer et al. (2004),  
*Science*

## Conclusions III

### (relative contributions from biogenic and anthropogenic sources)

- ⇒ acidic oxidation products of biogenic VOCs are suitable tracer compounds for biogenic SOA formation (⇒ unique and low volatile tracers)
- ⇒ for anthropogenic VOCs less obvious SOA marker compounds exist
- ⇒ only a few percent of the atmospheric SOA can be explained by the known biogenic oxidation products (marker approach)

# Final conclusions

- ⇒ general understanding of SOA formation has tremendously improved, especially during the last decade (lab, field, modelling)
- ⇒ due to the complexity of the chemical and physical processes involved (number of VOCs, number of products, different oxidation pathways, heterogeneous processes etc.) there are still important gaps in our knowledge about natural and anthropogenic SOA formation
- ⇒ better analytical strategies for species analysis (time resolution, highly polar and higher molecular organics) are needed for future studies (lab and field)