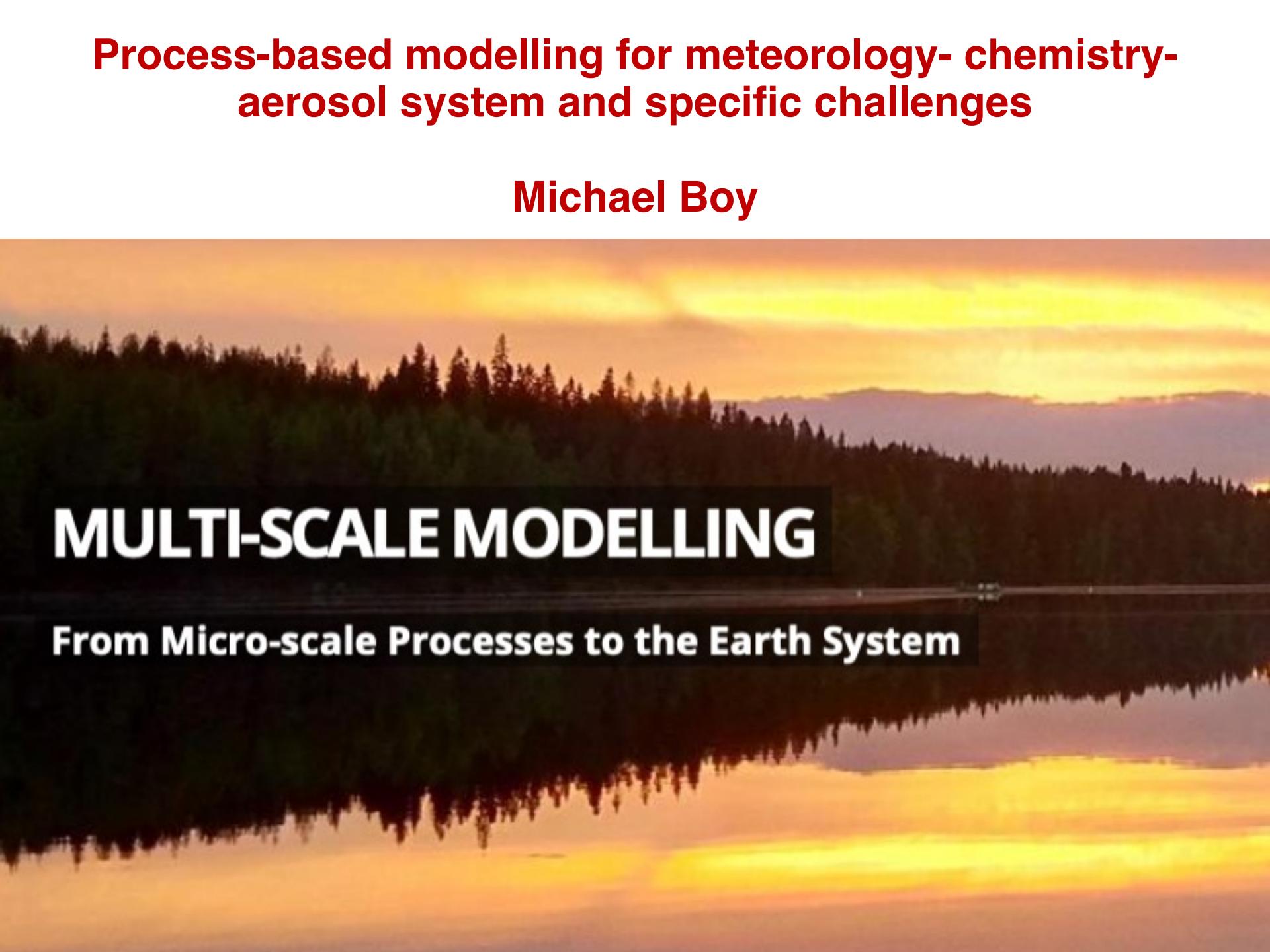


# **Process-based modelling for meteorology- chemistry-aerosol system and specific challenges**

**Michael Boy**

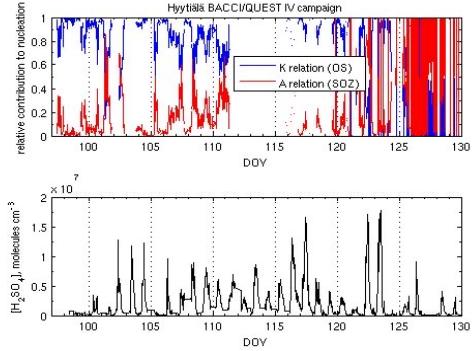
A photograph of a sunset over a forested landscape. The sky is filled with warm orange and yellow hues, reflected in a calm body of water in the foreground. A dense line of evergreen trees stands in the middle ground, silhouetted against the bright sky.

**MULTI-SCALE MODELLING**

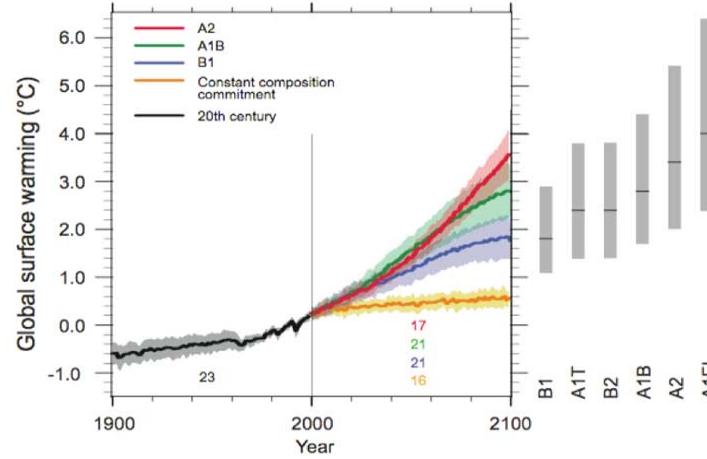
**From Micro-scale Processes to the Earth System**

# Why studying simple models and concepts?

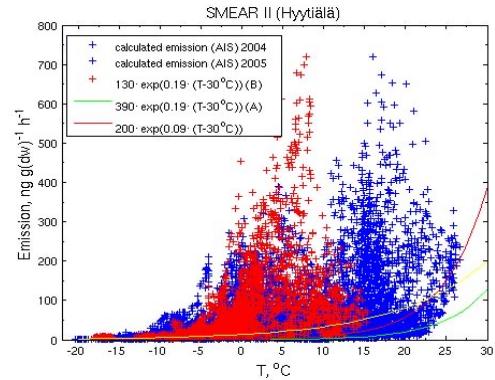
## Process investigations



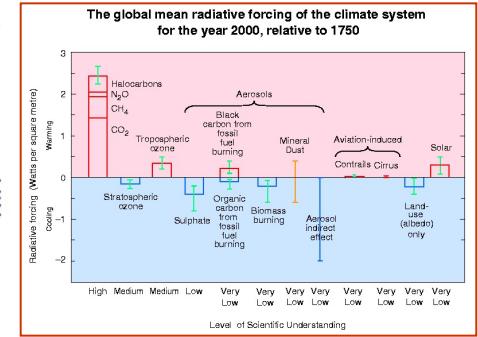
## Studies on transport phenomena



## Budget analyses



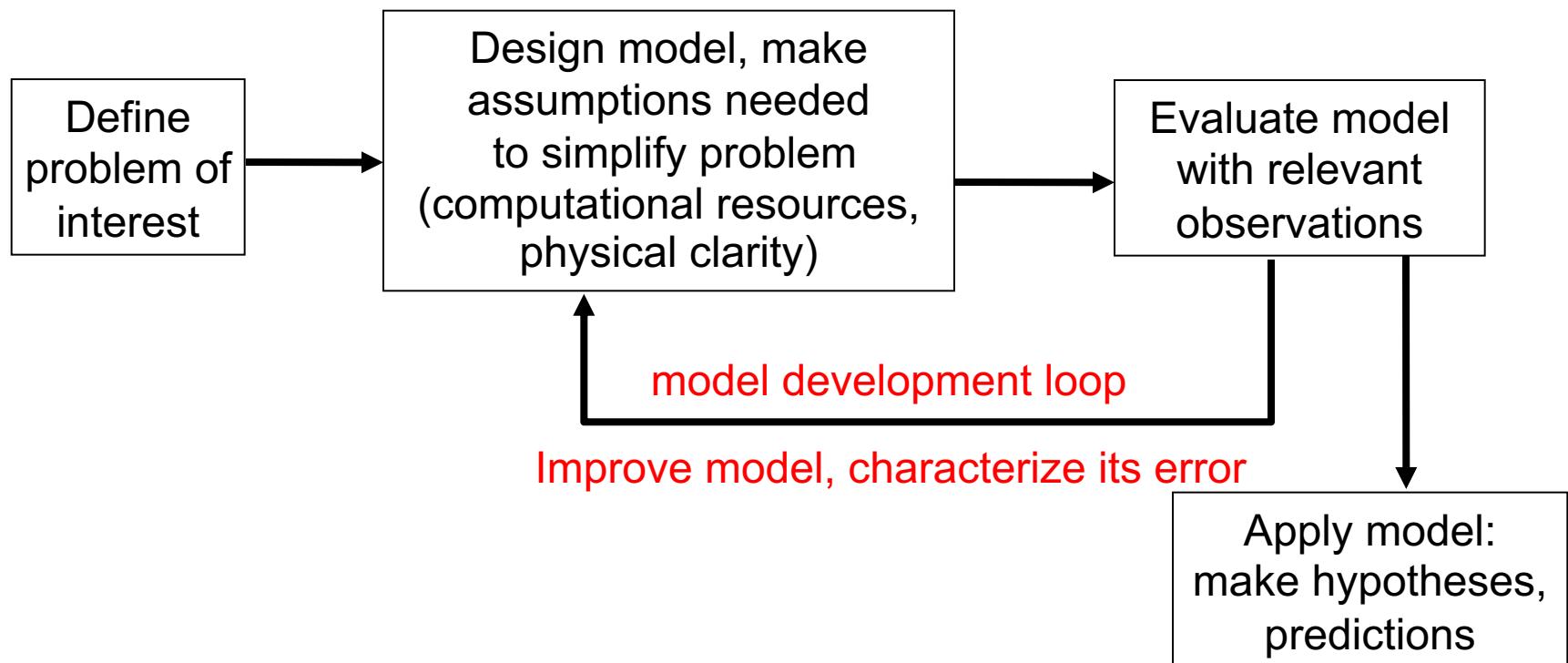
Test of understanding  
and quality of  
description



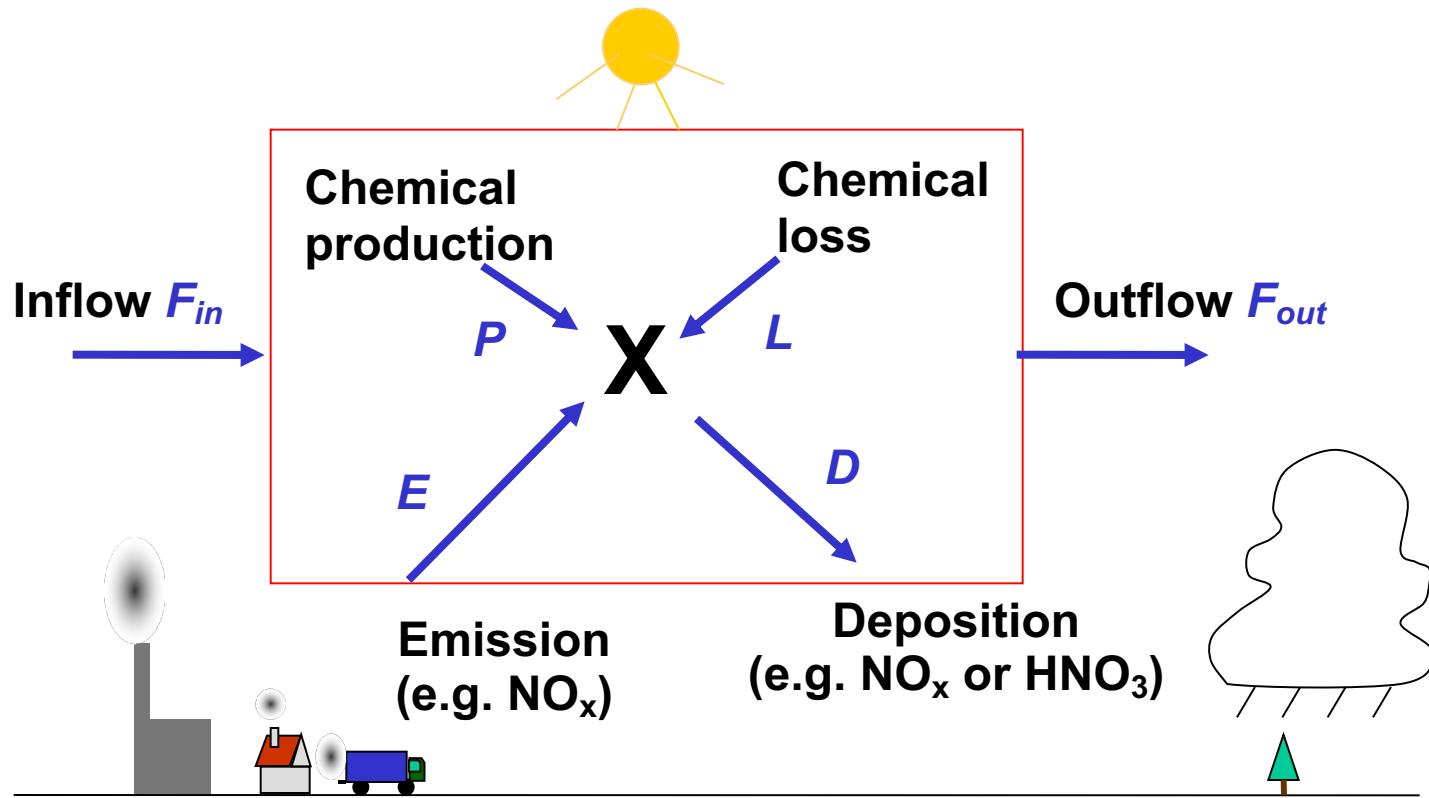
# Atmospheric species: budgeting from different processes

The atmospheric evolution of a species X is given by the **continuity equation**, which means by emissions, transport and sinks.

This equation usually cannot be solved exactly  $\Rightarrow$  need to construct **model** (= simplified representation of complex system)



# Box model



$$\text{Mass balance equation: } \frac{dm}{dt} = \sum \text{sources} - \sum \text{sinks} = F_{in} + E + P - F_{out} - L - D$$

**Atmospheric “box”: spatial distribution of X within box is not resolved !**

# Box model – possible applications

## ❑ Chamber experiments

- It can be difficult to quantify the wall loss effect, also you have a module in your model. Some chambers provide wall loss rates which you could apply. However, there is a difference for particles (size dependent) and gaseous compounds.

## ❑ Flow tube experiments

- Here the wall loss should be negligible as injected gases and particles “stay” in the middle of the tube.
- These experiments are one of the best way to apply a box model with very small time step (~ ms) as the experiments are normally only couple of seconds.

## ❑ Total atmosphere

- A good way for making simple first budget calculation for a compound when you know the main sink and source terms.

# Concept of atmospheric lifetimes

**Lifetime  $\tau_i$ :** is the time, a molecule resides in the atmosphere (box), until it is removed by a process i

$$\text{Atmospheric lifetime: } \tau = \frac{m}{F_{\text{out}} + L + D}$$

i) Removal by outflow or transport:  $F_{\text{out}}$

$$\text{Fraction lost by export: } f_{\text{exp}} = \frac{F_{\text{out}}}{F_{\text{out}} + L + D}$$

$$\text{Lifetime: } \tau_{\text{exp}} = \frac{m}{F_{\text{out}}} = \frac{1}{k_{\text{exp}}} \quad , \text{ k: loss rate constant}$$

ii) Removal by deposition (dry and wet):  $D$

$$\tau_{\text{dep}} = \frac{m}{D} = \frac{1}{k_{\text{dep}}} = \frac{1}{k_{\text{dep,dry}} + k_{\text{dep,wet}}}$$

**dry:** sedimentation and sticking to surfaces

**wet:** uptake by cloud liquid water and rain out

# Chemical Lifetime

iii) Removal by chemical reactions: L

Chemical lifetime:  $\tau_{chem} = \frac{m}{L} = \frac{1}{k_{chem,1}}$

First order loss ( $A \rightarrow B$ )



$k = 1.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$  at  $T = 298 \text{ K}$   
 $[NO] = 100 \text{ pptv} \cdot 2.5 \times 10^{19} \text{ molecules cm}^{-3}$

$\Rightarrow \tau_{chem,O_3,NO} = 6.5 \text{ h}$  for ozone

Several chemical reactions reducing a compound:

$$\frac{1}{\tau_{chem,total}} = \frac{1}{\tau_{chem,1}} + \frac{1}{\tau_{chem,2}} + \dots + \frac{1}{\tau_{chem,x}}$$
$$= k_{chem,1} + k_{chem,2}[C_j] + \dots + k_{chem,x}[C_j]^{x-1} = \sum_i k_{chem,i}[C_j]^{i-1}$$

1. order  
2. order  
x. order  
reaction

# Chemical Lifetimes of atmospheric compounds

(average for total atmosphere)

<i>Compound</i>	<i>Chemical lifetime</i>
Tropospheric O <sub>3</sub>	3-18 days **
Carbon monoxide (CO)	57 days*
Methane (CH <sub>4</sub> )	8.4 years **
SF <sub>6</sub>	3200 years **
Toluene (traffic, anthropog.)	2 days*
monoterpenes ( $\alpha$ -pinene)	1.6 hours*
CFCs (sprays, cooling, anthropog.)	45-1700 years **

\* [OH] = 1.0x10<sup>6</sup> molecules cm<sup>-3</sup> at room temperature assumed

\*\* IPCC, 2001

## Example

A chemical species is removed from the atmosphere by chemical reaction with a lifetime of 2 years, and by deposition with a lifetime of 1 year. What is its atmospheric lifetime?

$$\frac{1}{\tau} = \frac{1}{1\text{yr}} + \frac{1}{2\text{yrs}} = \frac{3}{2\text{yrs}}$$
$$\tau = 0.67\text{ yrs}$$

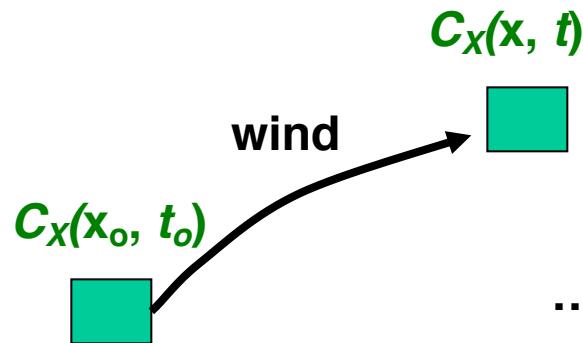
Further remark:

The chemical lifetime gives a measure for the speed of reaching an equilibrium ('steady state') of sources and sink in the atmosphere, if they are continuous.

⇒ ***The compounds with the shortest lifetime reach the equilibrium fastest:***

e.g. OH with a lifetime « 1 s.

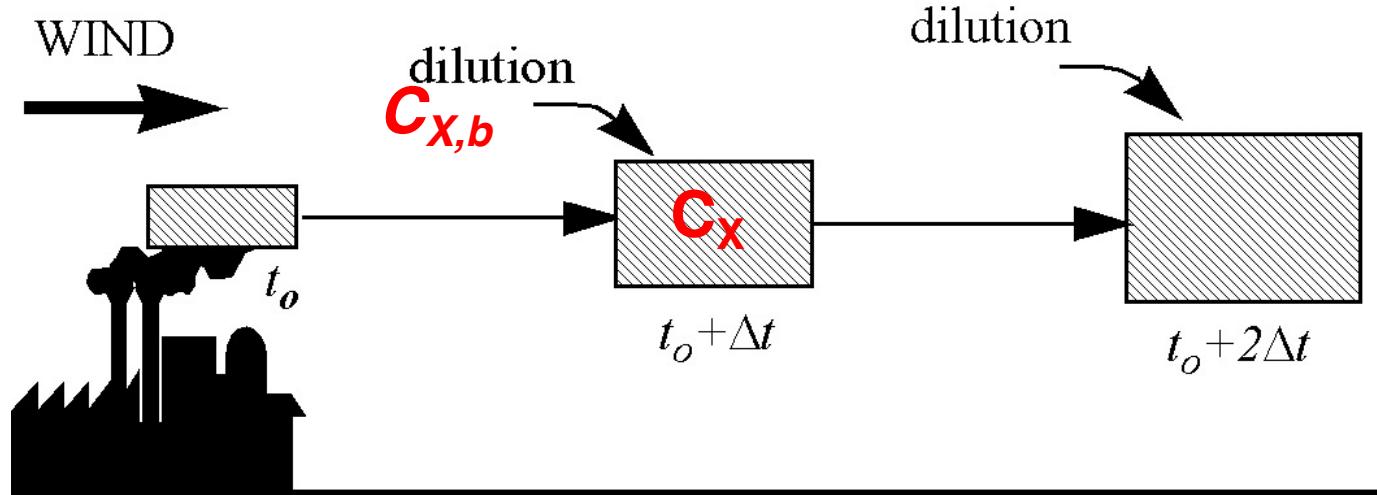
# FOLLOW AIR PARCEL MOVING WITH WIND



$$\frac{dC_X}{dt} = E + P - L - D$$

...no transport terms! (they're implicit in the trajectory)

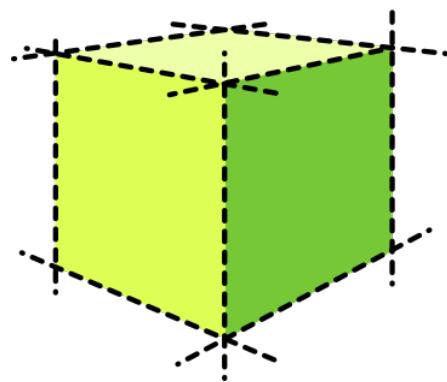
Application to the chemical evolution of an isolated pollution plume:



In pollution plume,

$$\frac{dC_X}{dt} = E + P - L - D - k_{dilution}(C_X - C_{X,b})$$

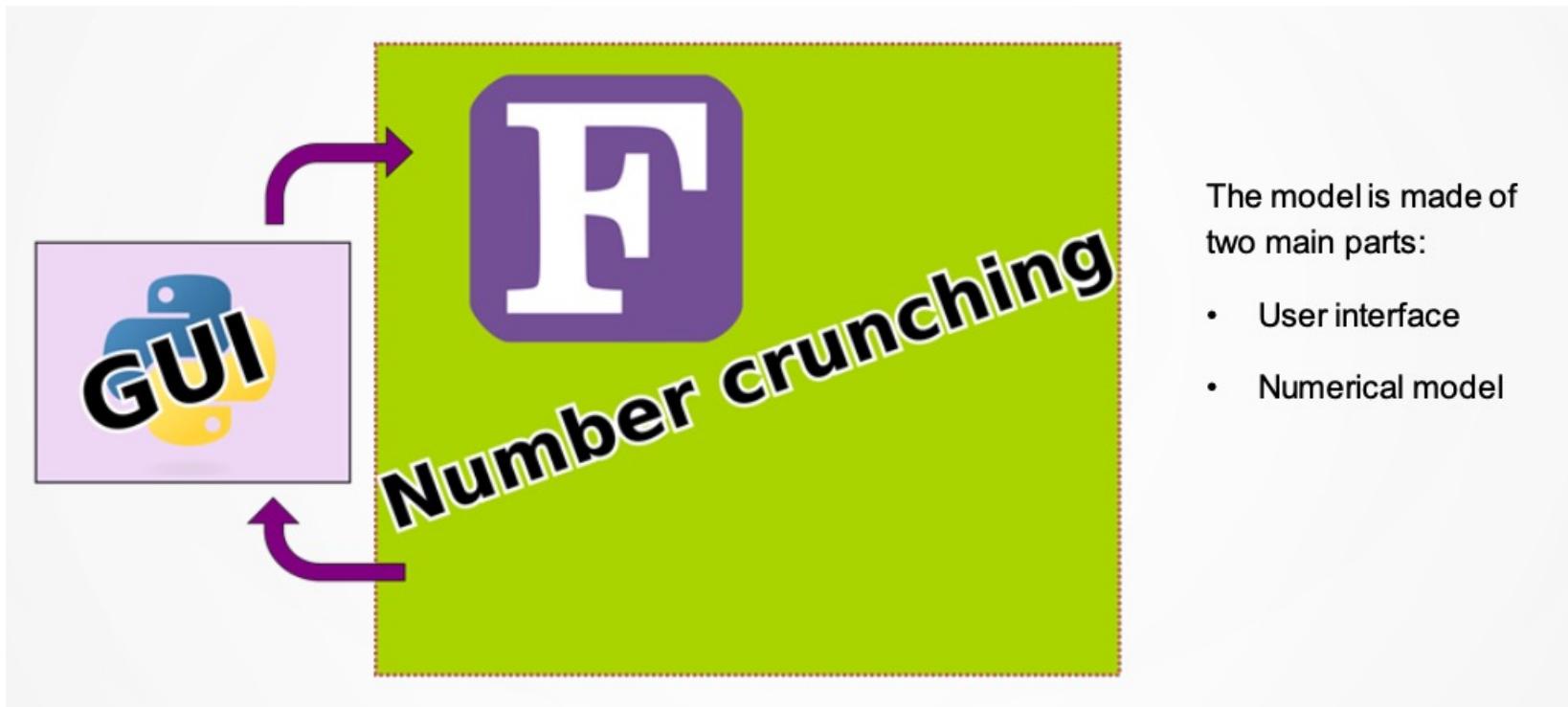
# Atmospherically Relevant Chemistry and Aerosol Box Model



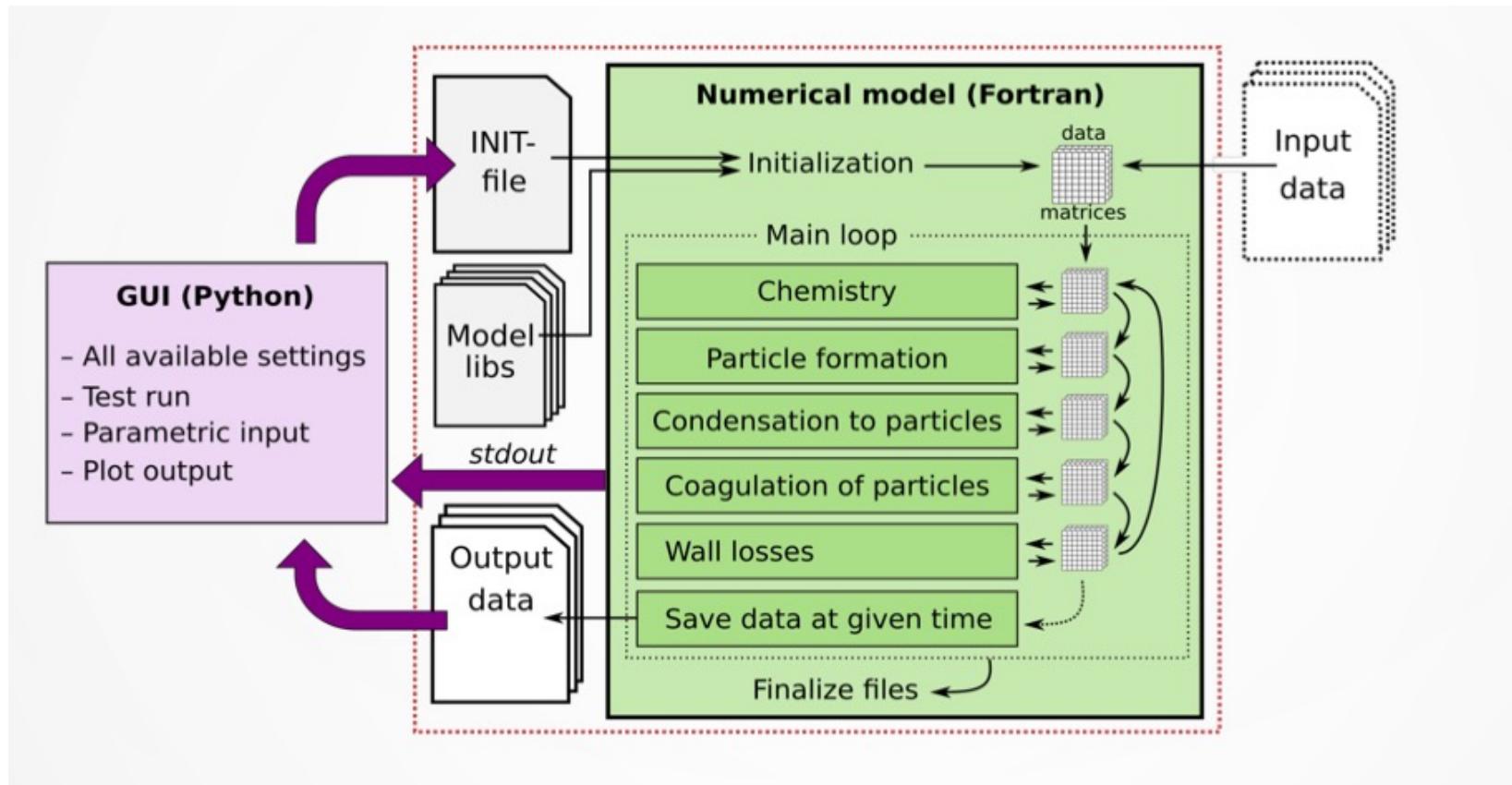
# ARCA box

Petri Clusius, Carlton Xavier, Lukas Pichelstorfer, Putian Zhou,  
Pontus Roldin, Tinja Olenius, Hanna Vehkamäki, Michael Boy

# Main structure of ARCA



# Main structure of ARCA



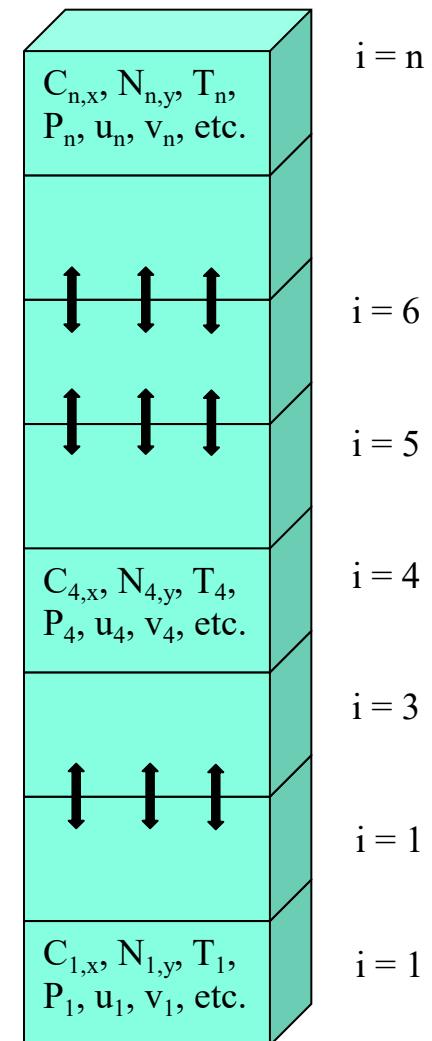
## Column model

Detailed chemistry and physics per box is possible as the computational costs are low compared to a regional model.

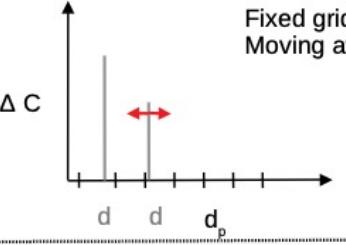
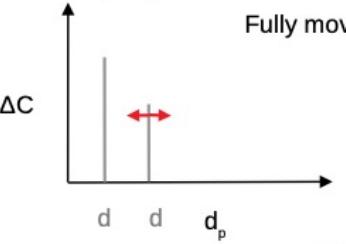
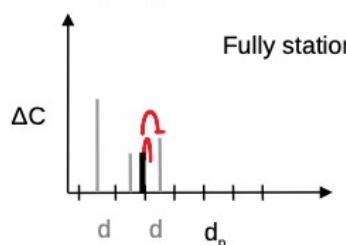
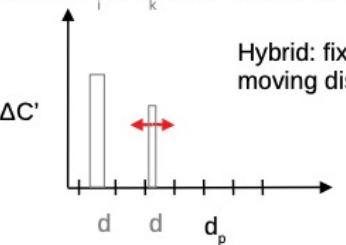
It is possible and suggested to parallelize the processes which are running unidirectional from other boxes (e.g. chemistry, aerosol dynamics).

Timestep can be in the order of second(s) if required individual modules require high temporal resolution.

Vertical mixing can be simulated with different approaches like the K-theory with different level of difficulty.



# Numerical techniques for representation of aerosol particle size distribution evolution

 <p>Fixed grid Moving average</p>	<ul style="list-style-type: none"> <li>+ limited numerical diffusion</li> <li>+ Max 4 equations for new volume + diameter</li> </ul>	<ul style="list-style-type: none"> <li>- Pits &amp; peaks in the PSD from merging bins</li> </ul>
 <p>Fully moving</p>	<ul style="list-style-type: none"> <li>+ Exact growth</li> <li>+ Exact coagulation</li> <li>+ Max 4 equations for new volume + diameter</li> </ul>	<ul style="list-style-type: none"> <li>- Number of bins is not controlled</li> </ul>
 <p>Fully stationary</p>	<ul style="list-style-type: none"> <li>+ Max 5 equations for new volume + diameter</li> </ul>	<ul style="list-style-type: none"> <li>- Numerical diffusion</li> </ul>
 <p>Hybrid: fixed grid – moving distribution</p>	<ul style="list-style-type: none"> <li>+ Very limited numerical diffusion</li> <li>+ Fixed number of bins</li> <li>+ No pits or peaks</li> </ul>	<ul style="list-style-type: none"> <li>- Equations turn to integrals</li> <li>- New volume: educated guess needed for dp-range</li> </ul>

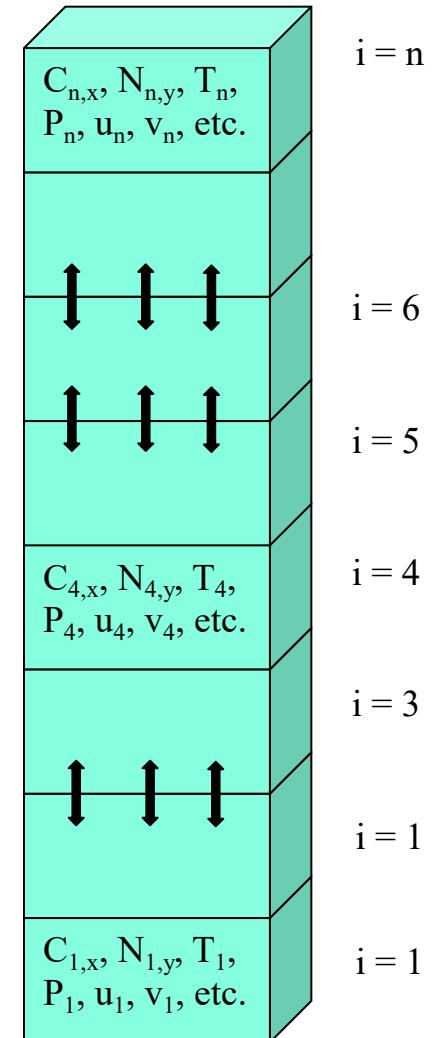
## Column model

Upper and lower boundaries need special attention:

The meteorological module solves the prognostic equations for the meteorological variables. The prognostic variables at the upper boundary of the model domain should be constrained with available data (e.g. ECMWF).

Upper boundary conditions for gases and aerosols has be set in a way that an outflow for all compounds with sources inside the column exist.

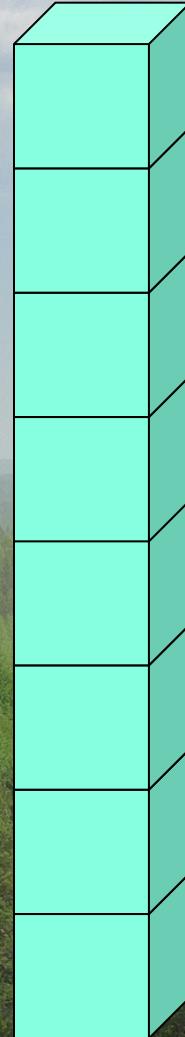
Deposition in the lowest level(s) depending how many levels are inside the rural or urban canopy.

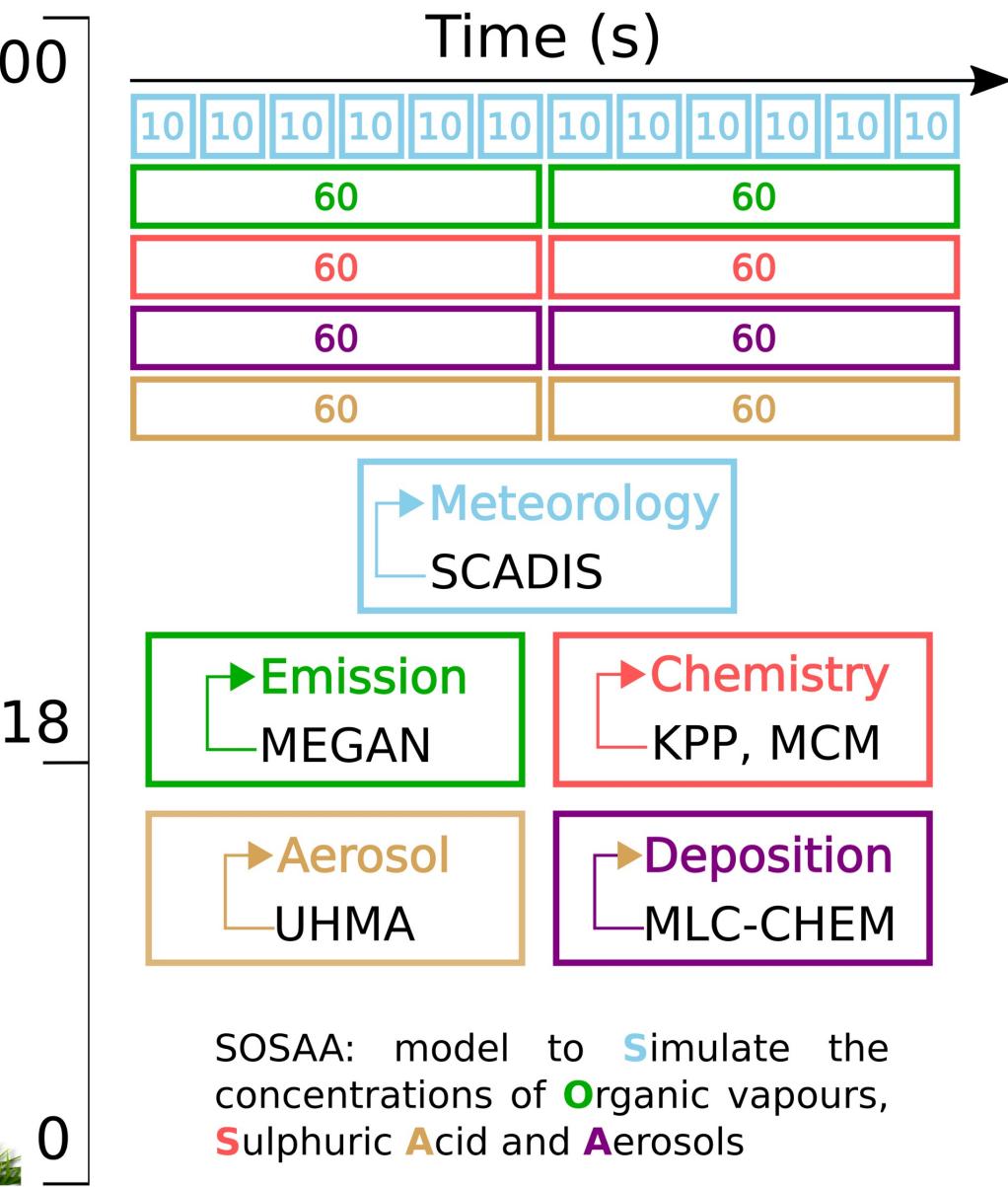
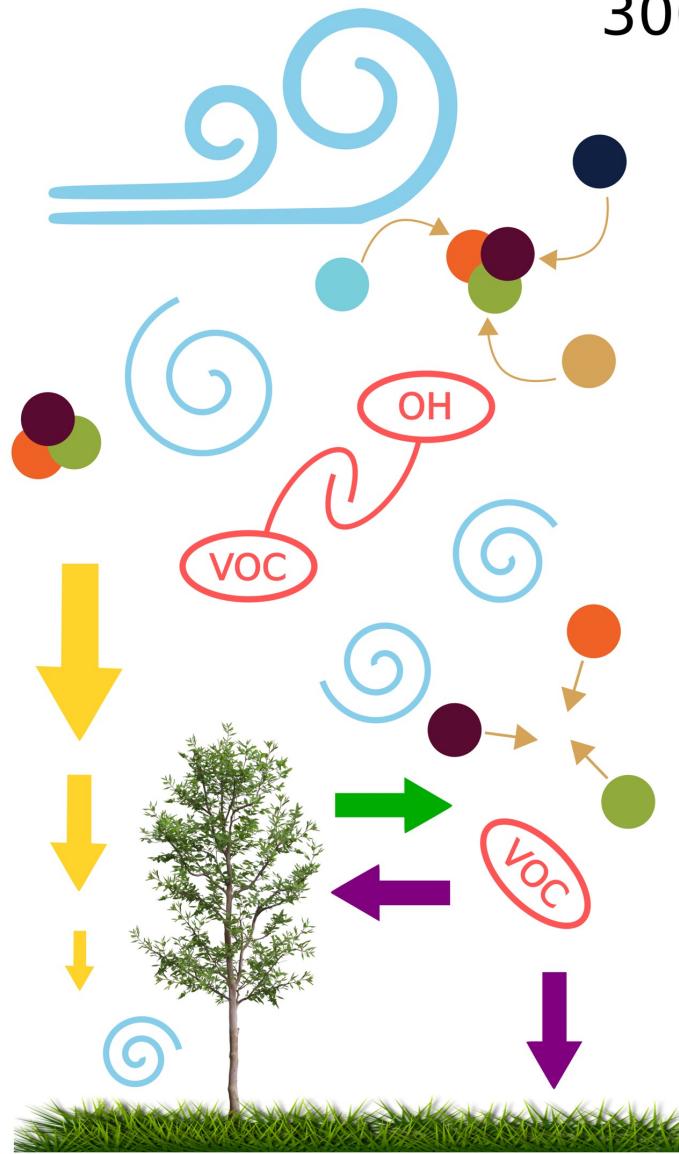


# When the application of a 1D-model makes sense?

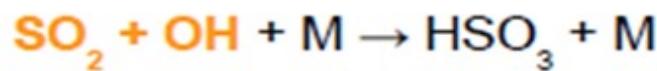
Homogeneous  
landscape in each  
direction

Less (no) impact  
from anthropogenic  
emission sources





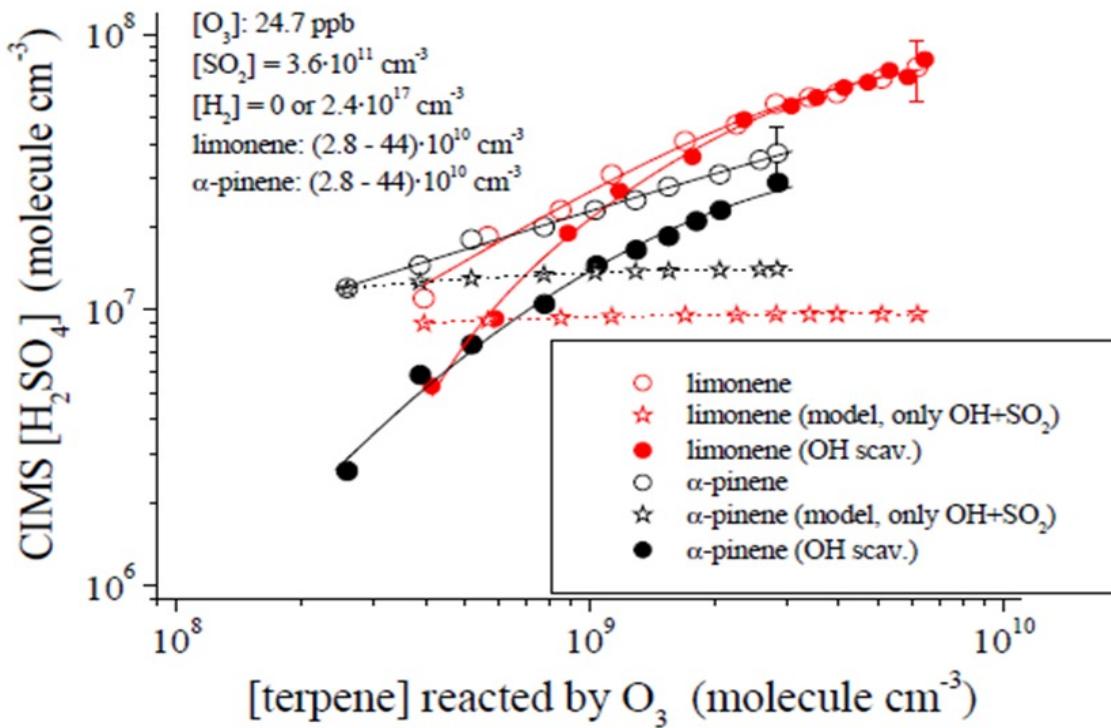
# 'Traditional' formation of H<sub>2</sub>SO<sub>4</sub>



**PROBLEM:** we underestimate the [H<sub>2</sub>SO<sub>4</sub>]

→ So, either the sink or source of H<sub>2</sub>SO<sub>4</sub> is wrong...

# Flow tube experiments suggests $\text{H}_2\text{SO}_4$ production in presence of an OH scavenger



## Experiment:

- RH = 22 %
- nearly constant  $[\text{OH}]_{\text{ss}}$  but rising  $[\text{sCl}]$  with increasing [olefin]
- $[\text{OH}]_{\text{ss}}$  lowered by two orders of magnitude adding OH scavenger

## Modelling:

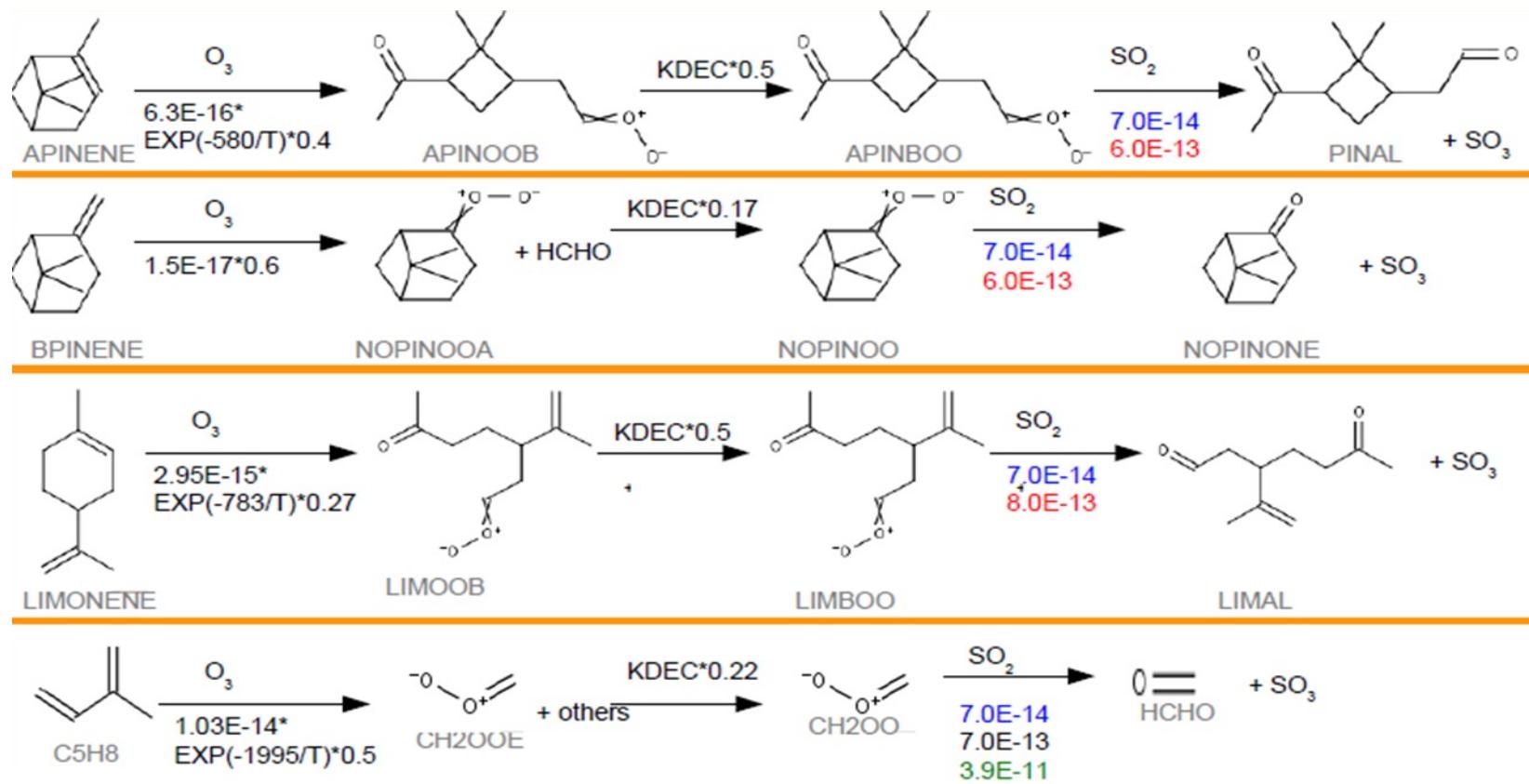
- only  $\text{OH} + \text{SO}_2$  for  $\text{H}_2\text{SO}_4$

Figure: Torsten Berndt

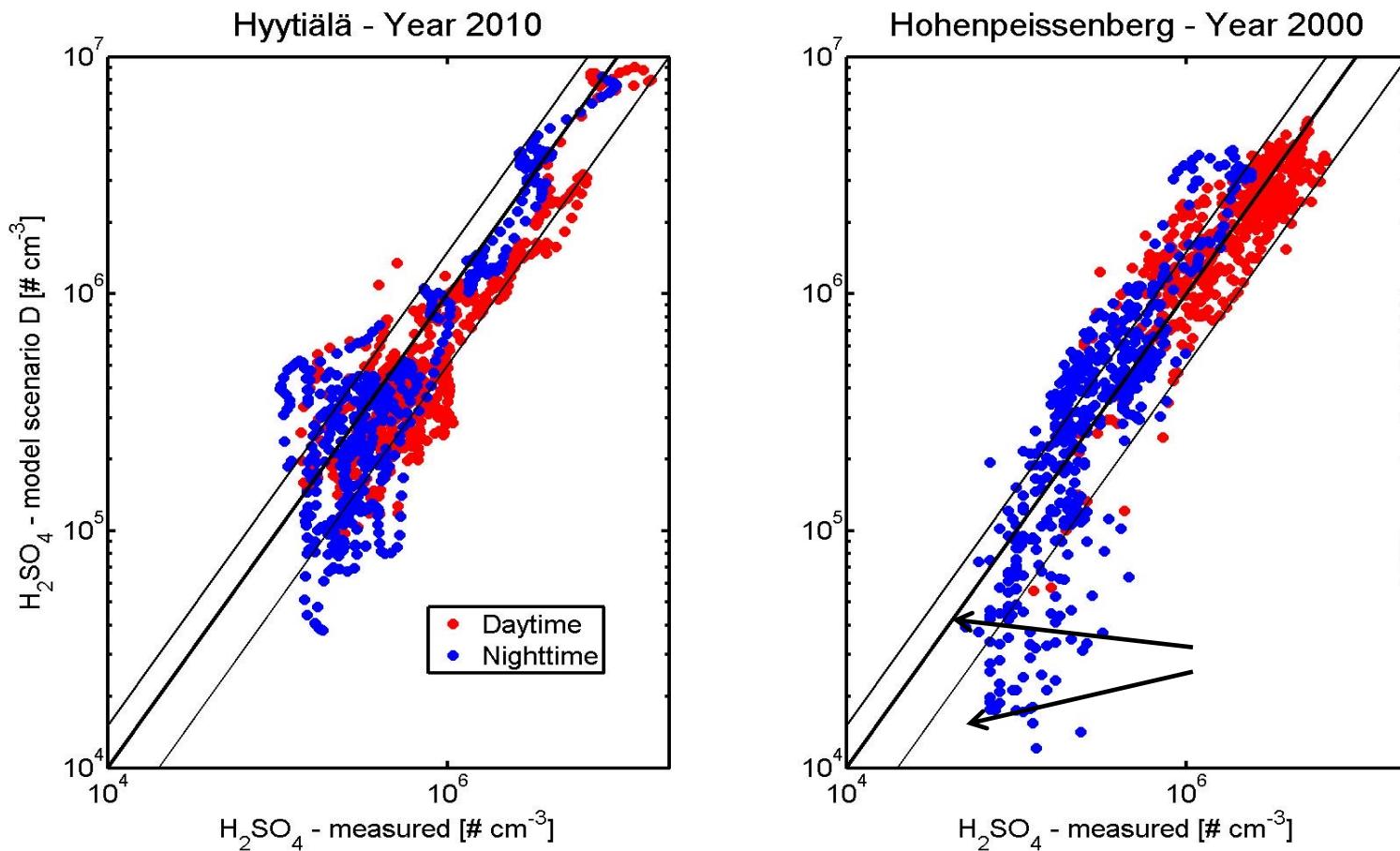
# sCI rate constants have changed significantly over time

Reaction rate constant from MCM v3.2

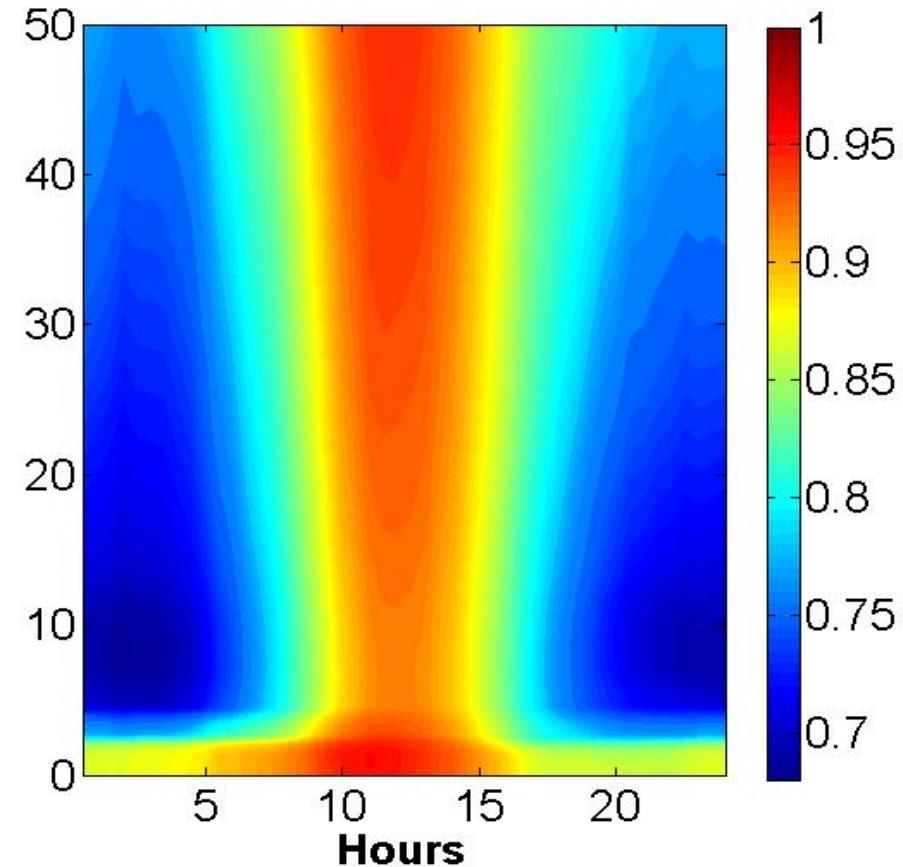
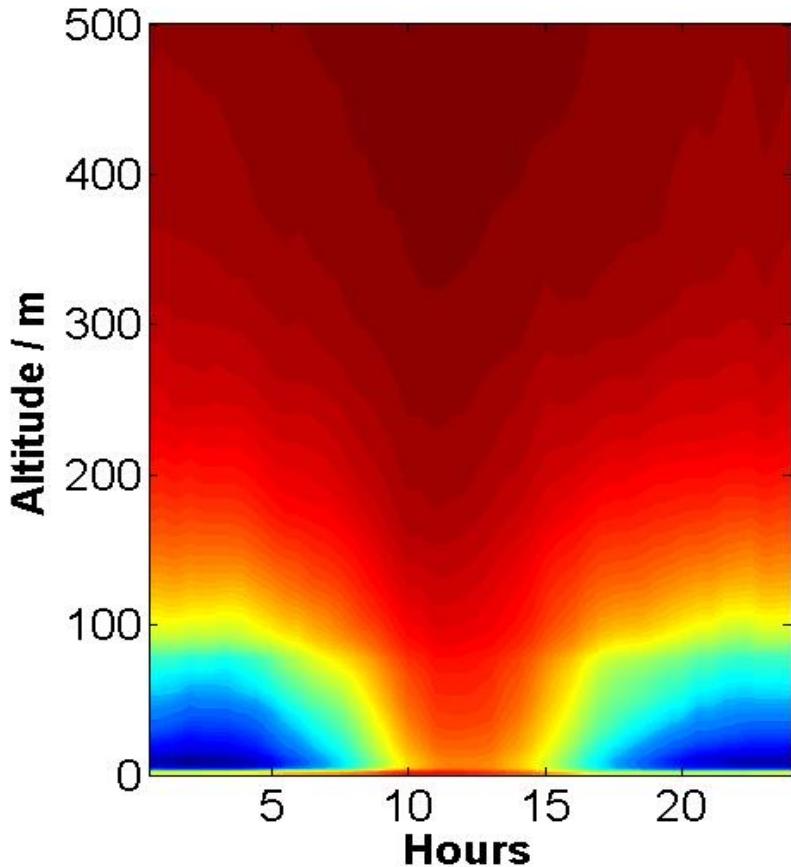
Reaction rate constant from Mauldin et al., Nature, 2012 Rate constant from Welz et al., Science, 2012



# SCI's are participating in SO<sub>2</sub> oxidation



$$R = [\text{H}_2\text{SO}_4]_{\text{OH}} / ([\text{H}_2\text{SO}_4]_{\text{OH}} + [\text{H}_2\text{SO}_4]_{\text{sCl}})$$



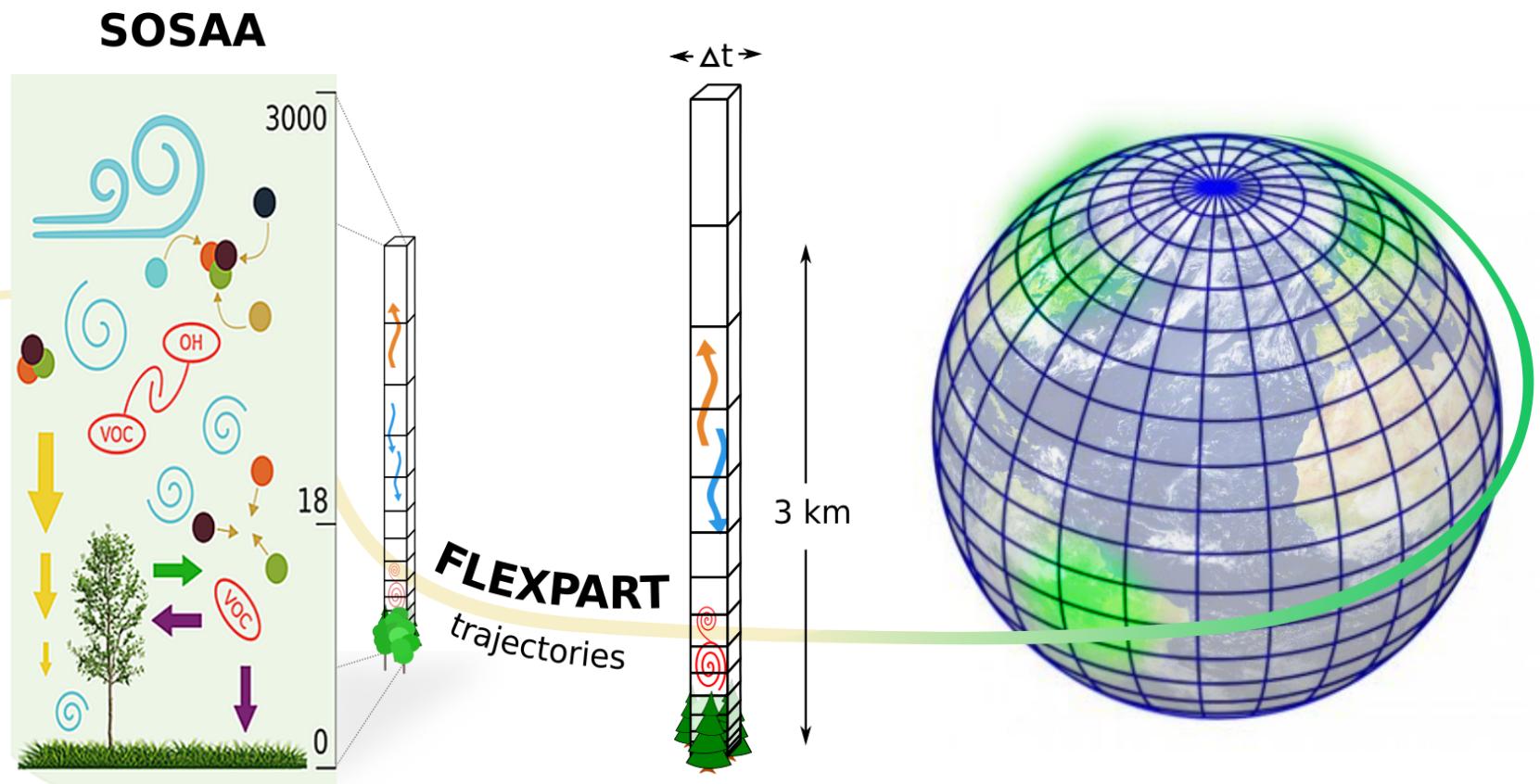
# There are many uncertainties

$\text{H}_2\text{SO}_4$  sink: CS

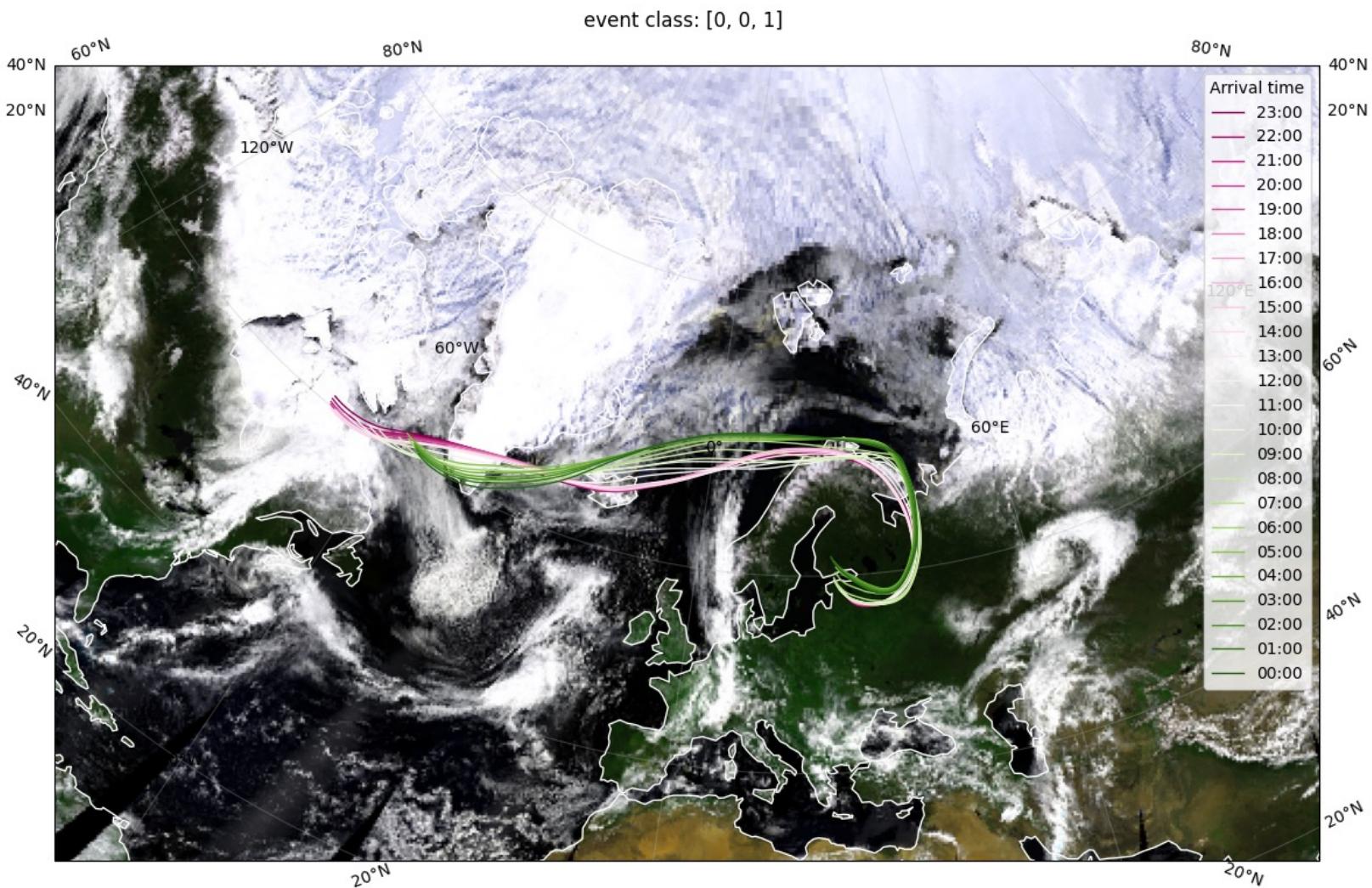
sCI chemistry:

- chemical mechanisms, pathways, products, yields, thermal life times, pressure dependency and reaction rate coefficients
- Maybe/probably the reaction rate constant for reaction between sCI and CO, NO,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$  can be expected to be different
- other sCI's

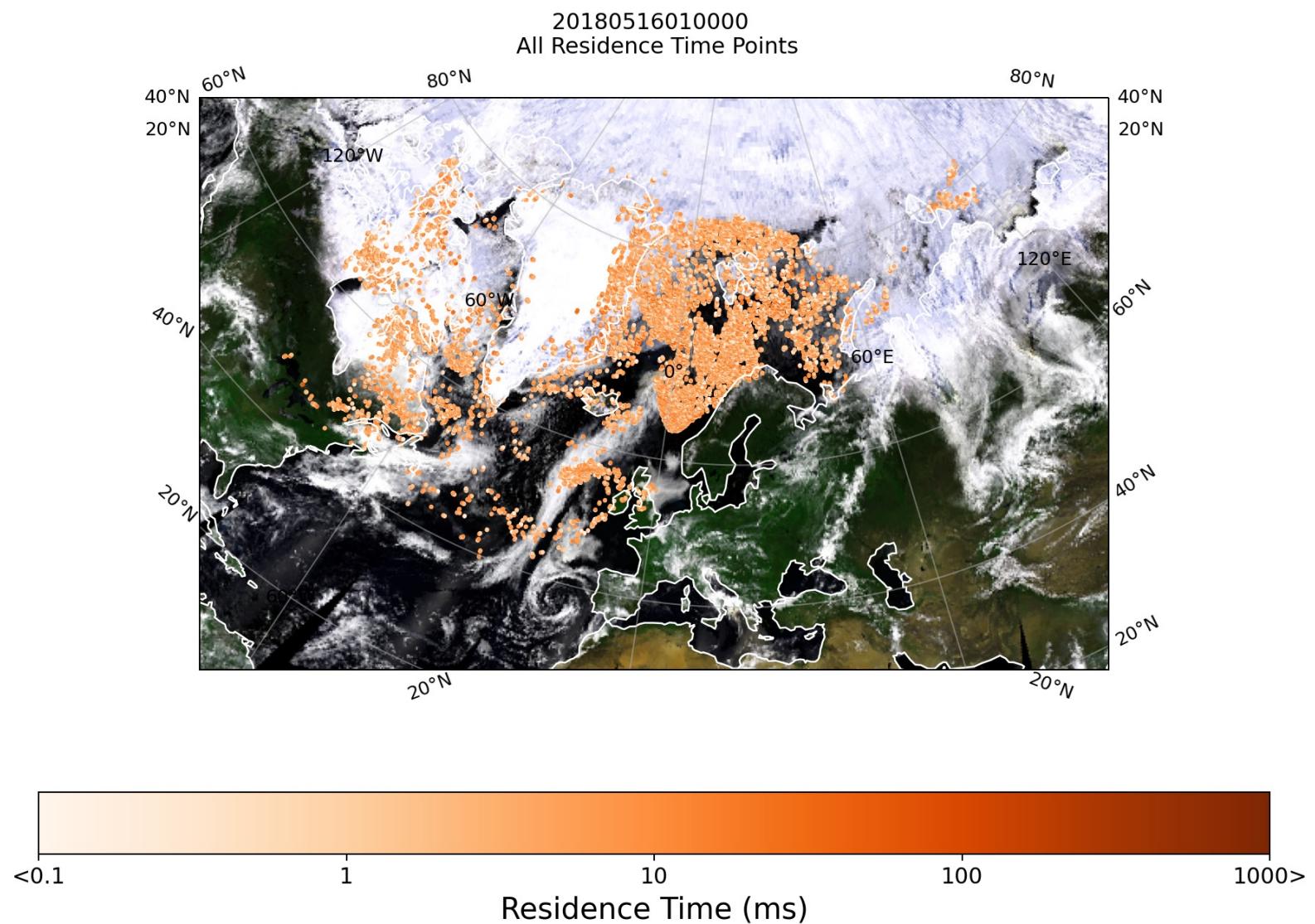
# SOSAA-FLEXPART simulations

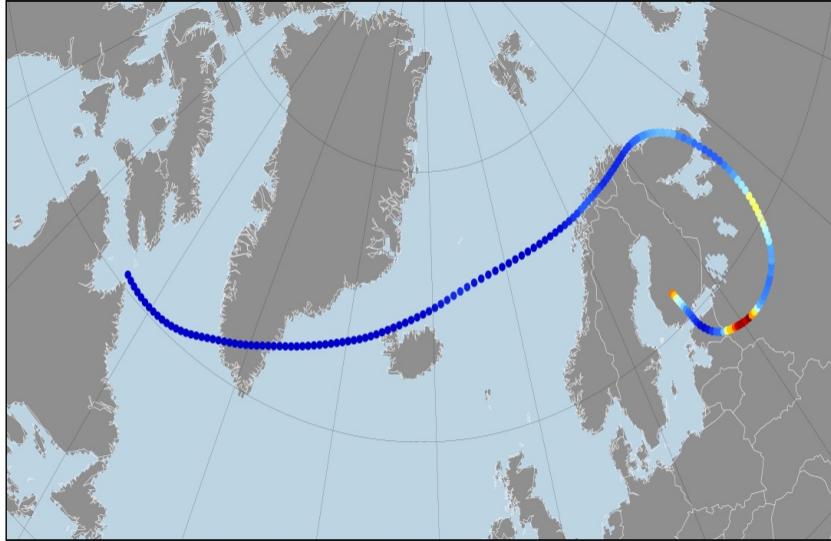


# 7 days backward trajectories for each hour



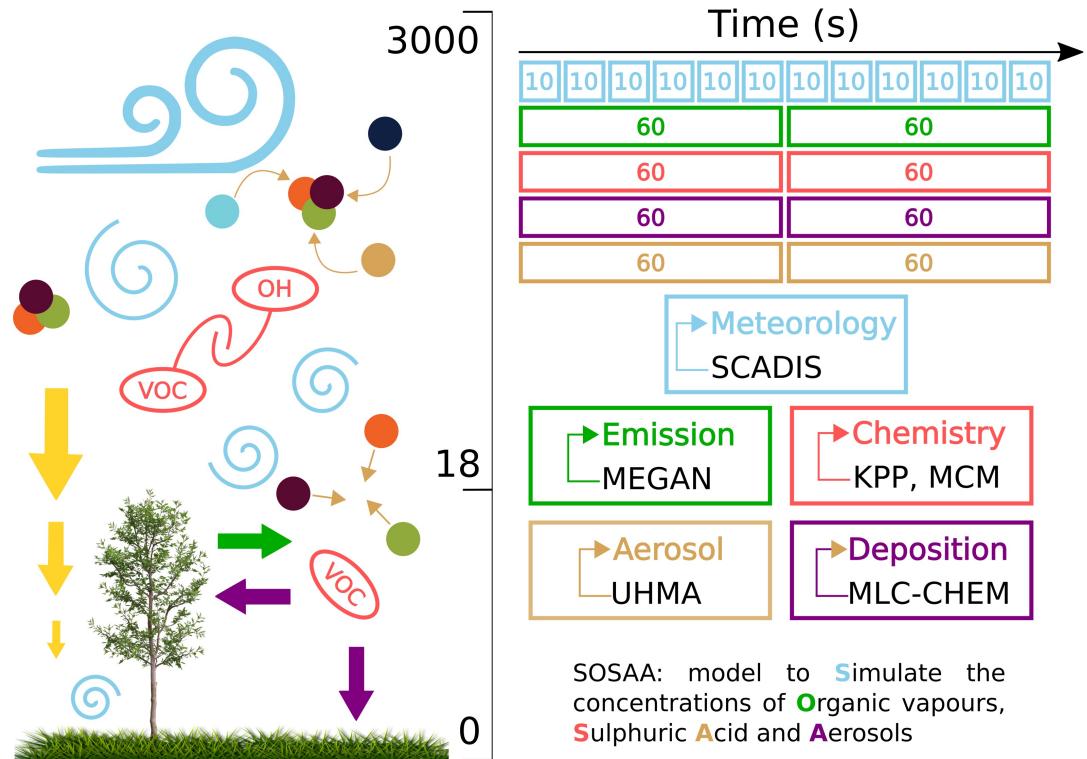
# Emssions are calculated based on the residence times





SOSAA simulations along the trajectories with input of emission and meteorological data.

Input of emissions for all gases and primary particles along the trajectories.

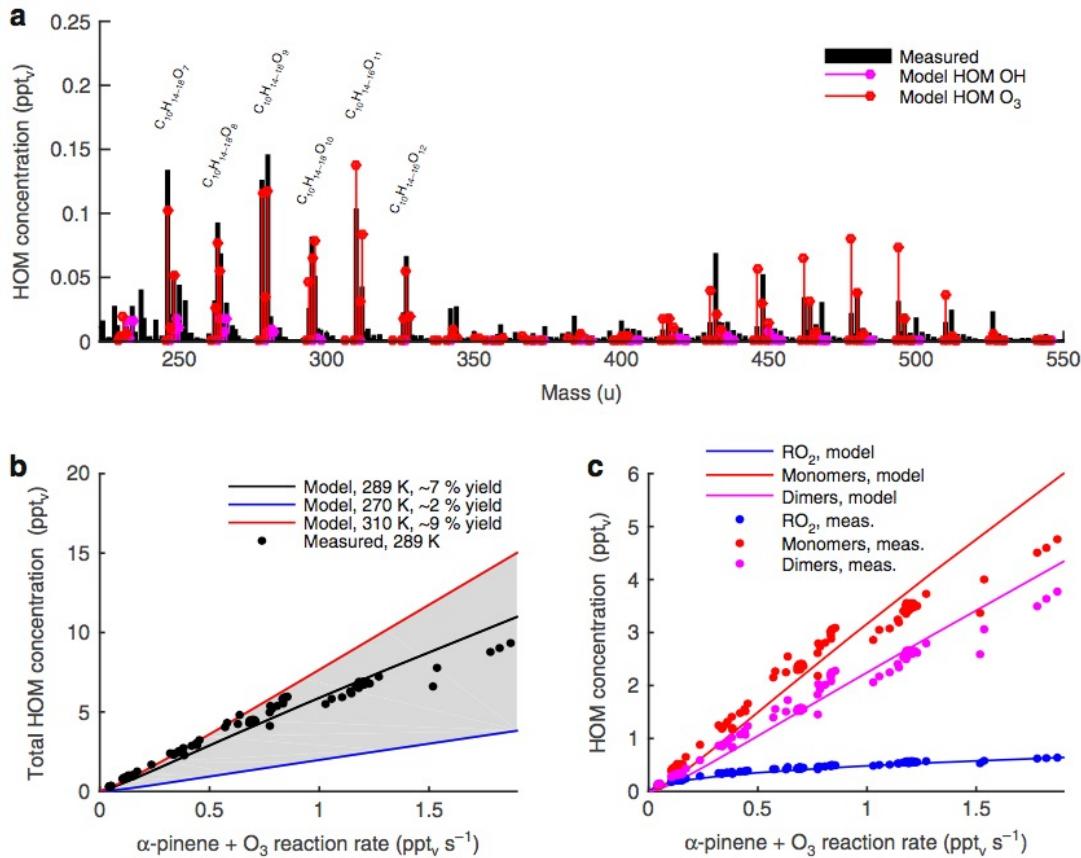


## ARTICLE

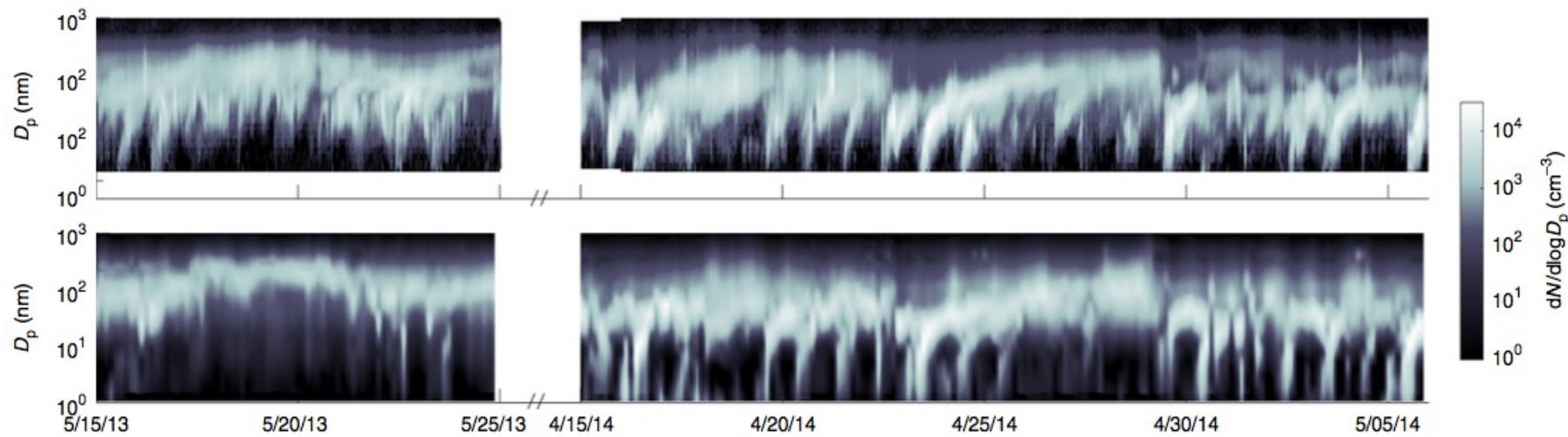
<https://doi.org/10.1038/s41467-019-12338-6> OPEN

## The role of highly oxygenated organic molecules in the Boreal aerosol-cloud-climate system

Pontus Roldin<sup>1\*</sup>, Mikael Ehn<sup>2</sup>, Theo Kurtén<sup>3</sup>, Tinja Olenius<sup>4</sup>, Matti P. Rissanen<sup>2</sup>, Nina Sarnela<sup>2</sup>, Jonas Elm<sup>5</sup>, Pekka Rantala<sup>2</sup>, Liqing Hao<sup>6</sup>, Noora Hytinen<sup>7</sup>, Line Heikkilä<sup>1</sup>, Douglas R. Worsnop<sup>2,8</sup>, Lukas Pichlerstorfer<sup>2,9</sup>, Carlton Xavier<sup>2</sup>, Petri Clusius<sup>2</sup>, Emilie Öström<sup>1</sup>, Tuukka Petäjä<sup>2</sup>, Markku Kulmala<sup>2</sup>, Hanna Vehkamäki<sup>2</sup>, Annele Virtanen<sup>6</sup>, Ilona Riipinen<sup>4</sup> & Michael Boy<sup>1,2</sup>



Modelled and measured HOM(g) concentrations during a JPAC α-pinene ozonolysis experiment . Panel a shows the modelled and measured HOM mass spectrum at an α-pinene+O<sub>3</sub> reaction rate of ~0.3 pptv s . Panel b modelled and measured total HOM concentration at various α-pinene+O<sub>3</sub> reaction rates. Panel c, concentrations of HOM peroxy radicals (RO<sub>2</sub>) and HOM closed shell monomers and dimers.



Measured (upper plot) and modelled (lower plot) particle number concentrations at the Station for Measuring Ecosystem-Atmosphere Relations II (SMEAR II) from the periods 15–25 May 2013 and 15 April to 5 May 2014.

# What to remember from this lecture?

- *Box models or zero-dimensional models are good tools to simulate chamber and flow tube experiments. However, wall loss effects can be difficult and special knowledge about the experimental setup is required to get it correct into the model.*
- *Applications of box models with the air flow for high emission point sources (e.g., chimney of coal power plant) are useful for short time scales.*
- *Single box-models can be used to make budgets or to describe the situation in a well mixed atmosphere.*
- *1D models like SOSAA can be applied locally at homogeneous landscape with less anthropogenic impact.*
- *Lagrangian models like our FLEXPART-SOSAA model system follow the air flow are useful for back trajectories or further development of an air mass (how does the particle number concentration will change during the simulated period).*