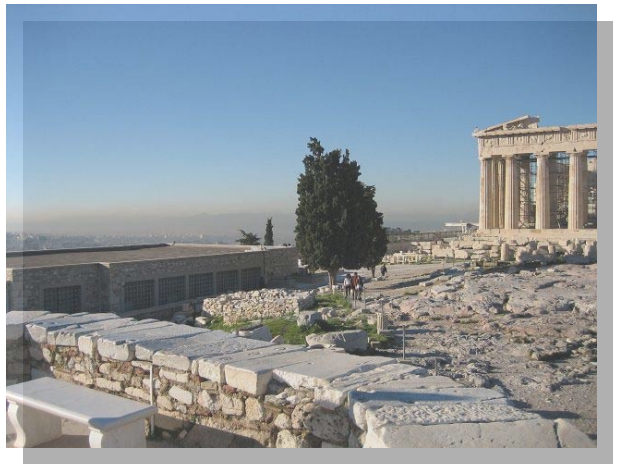
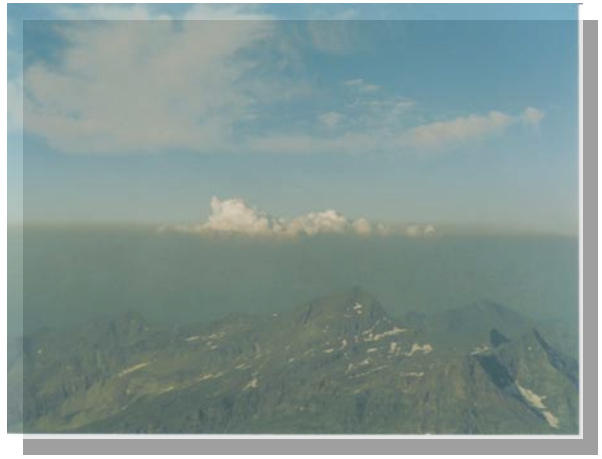
The impact of volatile organic compounds on the heterogeneous hydrolysis of N_2O_5





Bernhard Vogel, Nicole Riemer*, Heike Vogel

*Stony Brook University

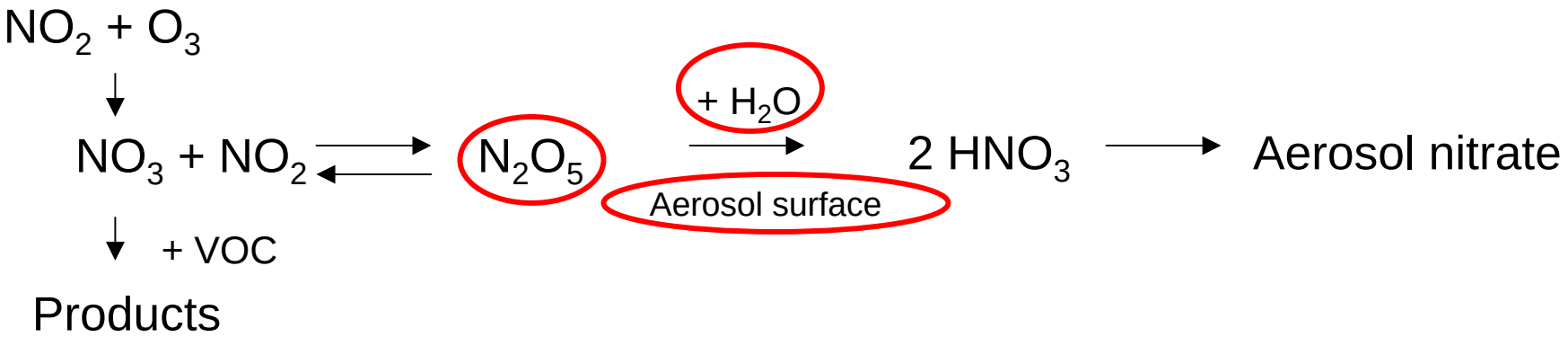
T. Anttila, Finnish Meteorological Institute
T. F. Mentel and A. Kiendler-Scharr, Forschungszentrum Jülich

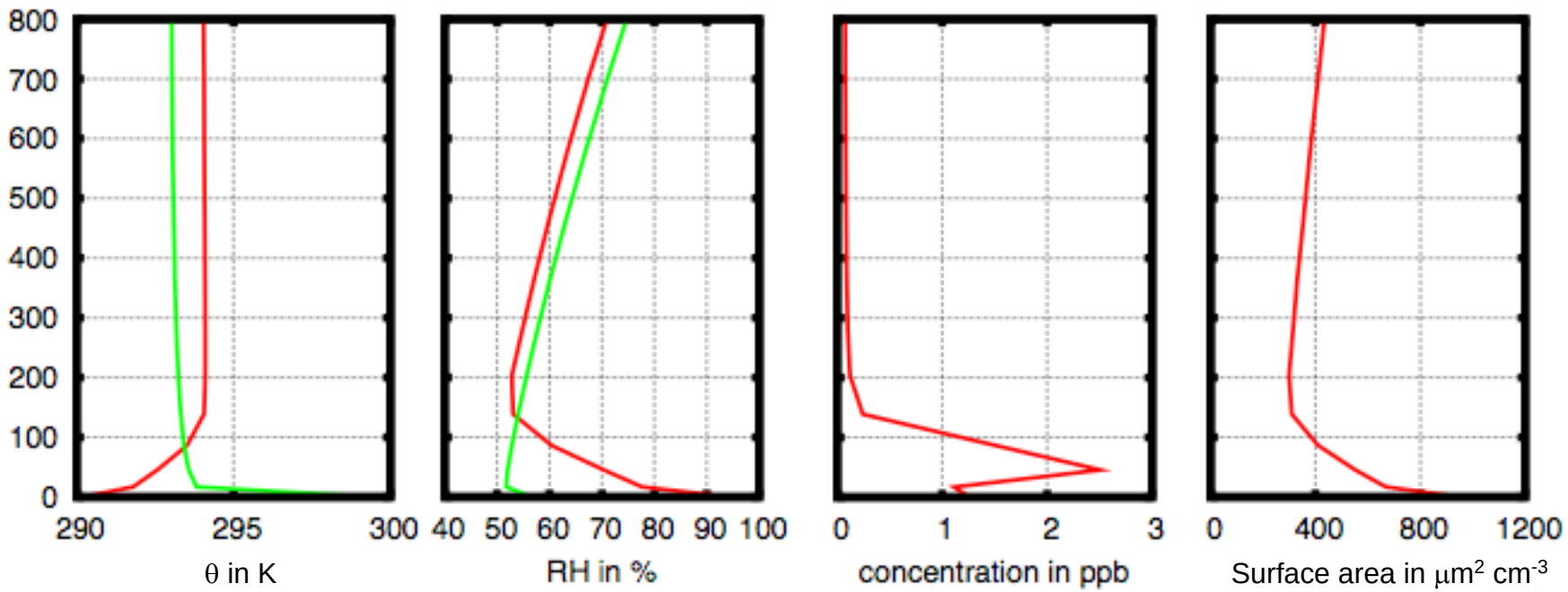
Relevance of the Heterogeneous Hydrolysis of N_2O_5 for Atmospheric Chemistry

- NO_x budget and particle nitrate is tied to N_2O_5 hydrolysis:
  - NO_x is removed, HNO_3 formed.
  - HNO_3 partitions between gas phase and aerosol phase.
- Laboratory studies show that reaction probability γ depends on aerosol composition.
- Aerosol nitrate or organic coatings can decrease γ.
- How important are these effects in the atmosphere?

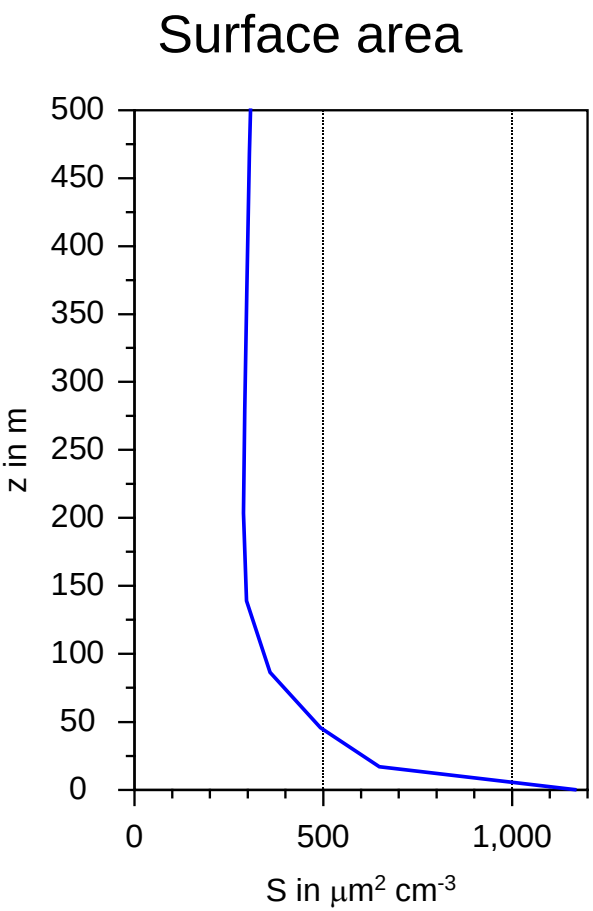
→ 1D process studies and 3D simulations

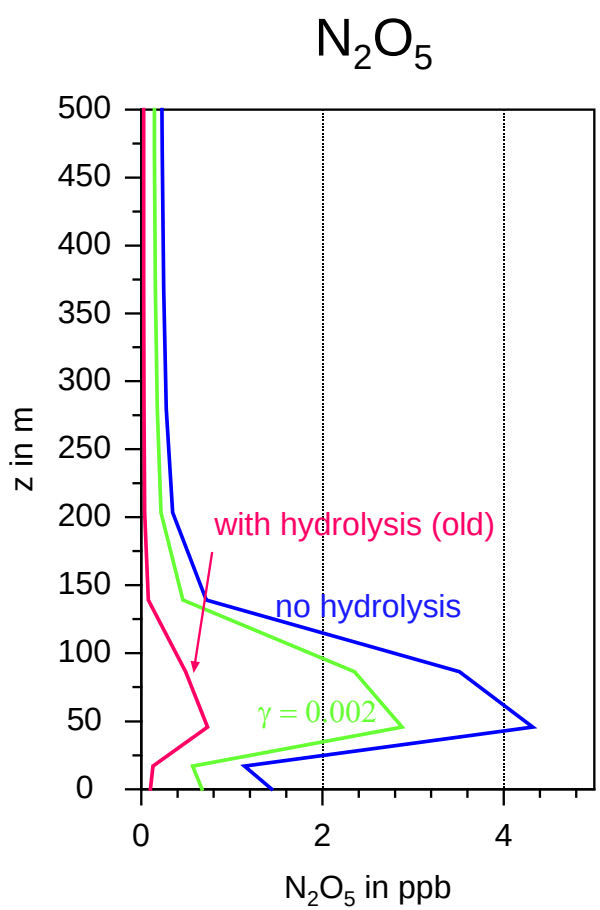
Interaction of Transport and Chemistry

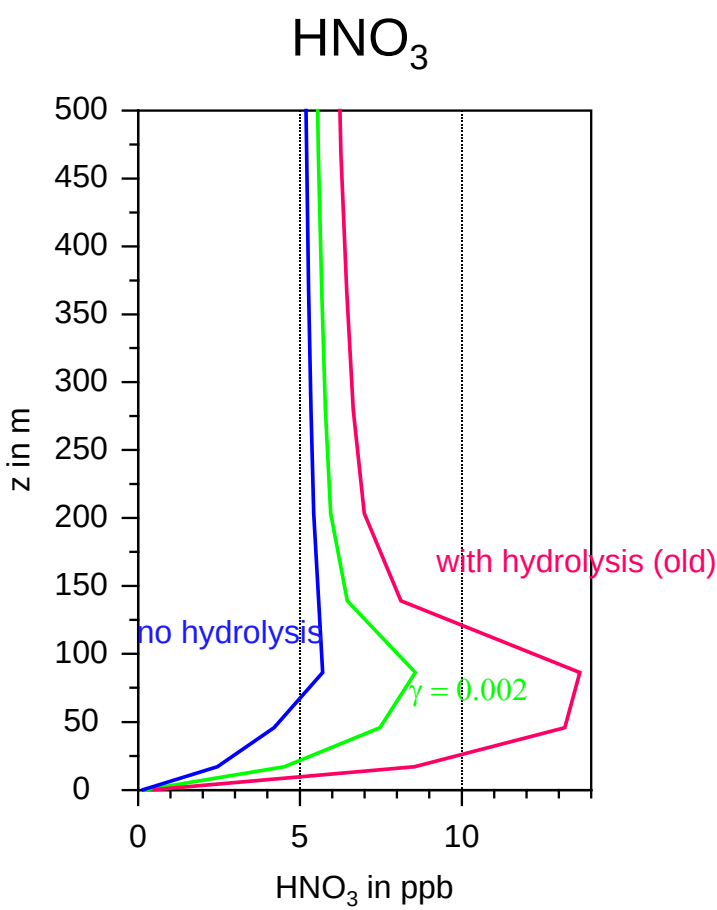




Starting Point







N_2O_5 hydrolysis on aerosols with organic coating

Hydrolysis as first order loss:

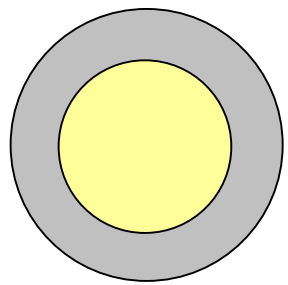
$$\frac{\partial[\mathrm{N_2O_5}]}{\partial t} = -k_{\mathrm{N_2O_5}} \cdot [\mathrm{N_2O_5}]$$

Reaction constant:

$$k_{\mathrm{N_2O_5}} = \frac{1}{4} \cdot c_{\mathrm{N_2O_5}} \cdot S \cdot \gamma$$

Resistor model for γ according to Anttila et al., JPC, 2006:

$$\frac{1}{\gamma} = \frac{1}{\gamma_{\mathrm{core}}} + \frac{1}{\gamma_{\mathrm{coat}}}$$



$\gamma_{\mathrm{core}}(m_{\mathrm{SO_4^{2-}}}, m_{\mathrm{NO_3^-}})$

Mentel et al., 1999
Riemer et al., 2003

$\gamma_{\mathrm{coat}}(H_{\mathrm{org}}, D_{\mathrm{org}}, R_p, R_c)$

Anttila et al., 2006

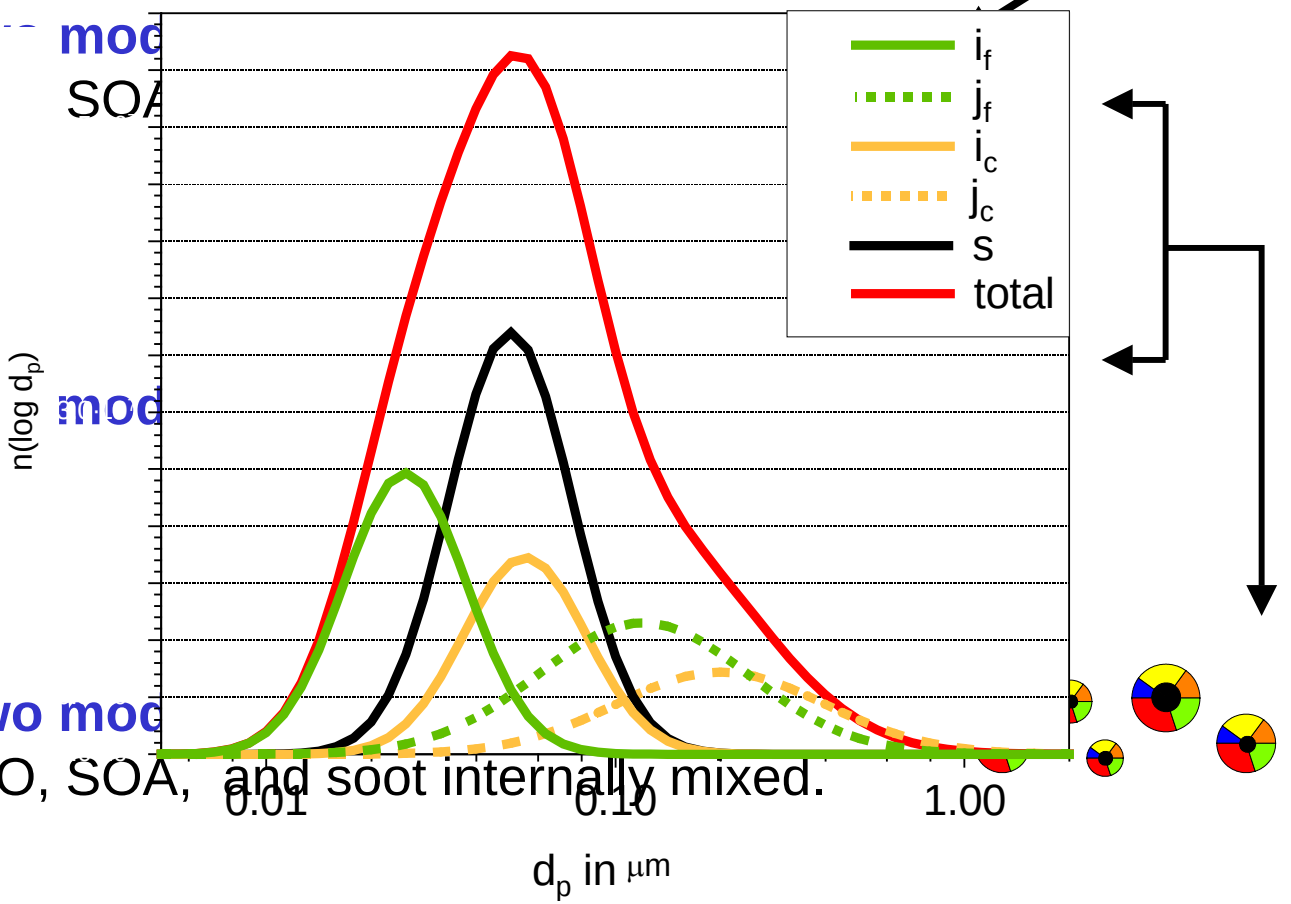
"Worst case scenario": Assuming that all SOA contribute to film formation

Treatment of the Aerosol Particles

Interaction of five modes:

Source: homogeneous **nucleation** of H_2SO_4/water

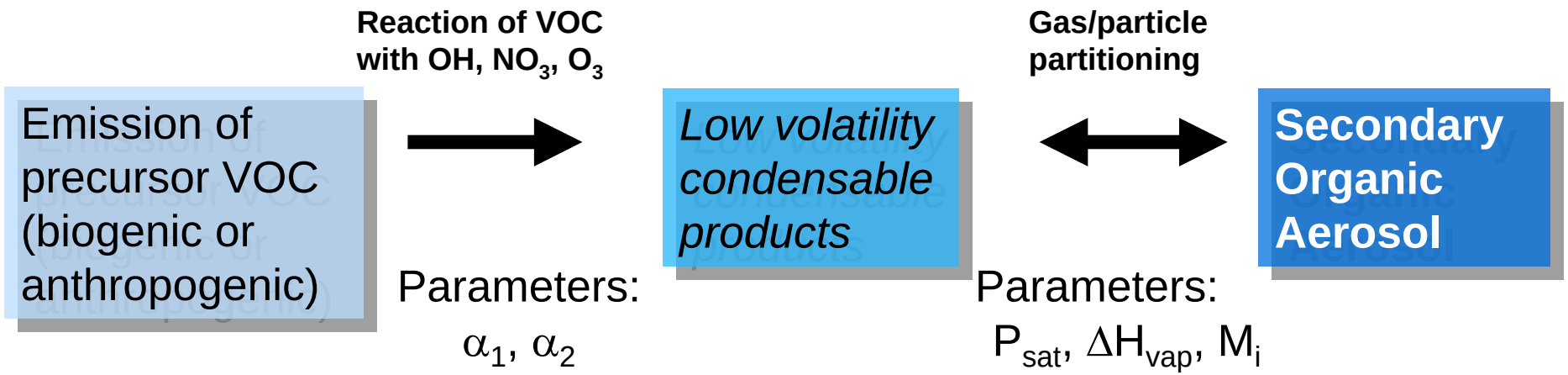
- **Tw[illegible] mod[illegible]**
  H_2 SO[illegible]
- **O[illegible] mod[illegible]**
- **Two mod[illegible]**
  H_2O, SOA, and soot internally mixed.



coagulation

Three modes for **mineral dust** particles + **three** modes for **sea salt** particles **+ pollen**

Treatment of SOA (SORGAM)



anthropogenic

Toluene, Xylene, Cresol
Higher Alkanes
Higher Alkenes

→ *CVARO1, CVARO2*
CVALK1
CVOLE1

↔ **SOAARO1,SOAARO2**
SOAALK1
SOAOLE1

biogenic

α-pinene
Limonene

→ *CVAPI1, CVAPI2*
CVLIM1, CVLIM2

↔ **SOAAPI1, SOAAPI2**
SOALIM1, SOALIM2

Nomenclature following Schell et al. JGR, 2001

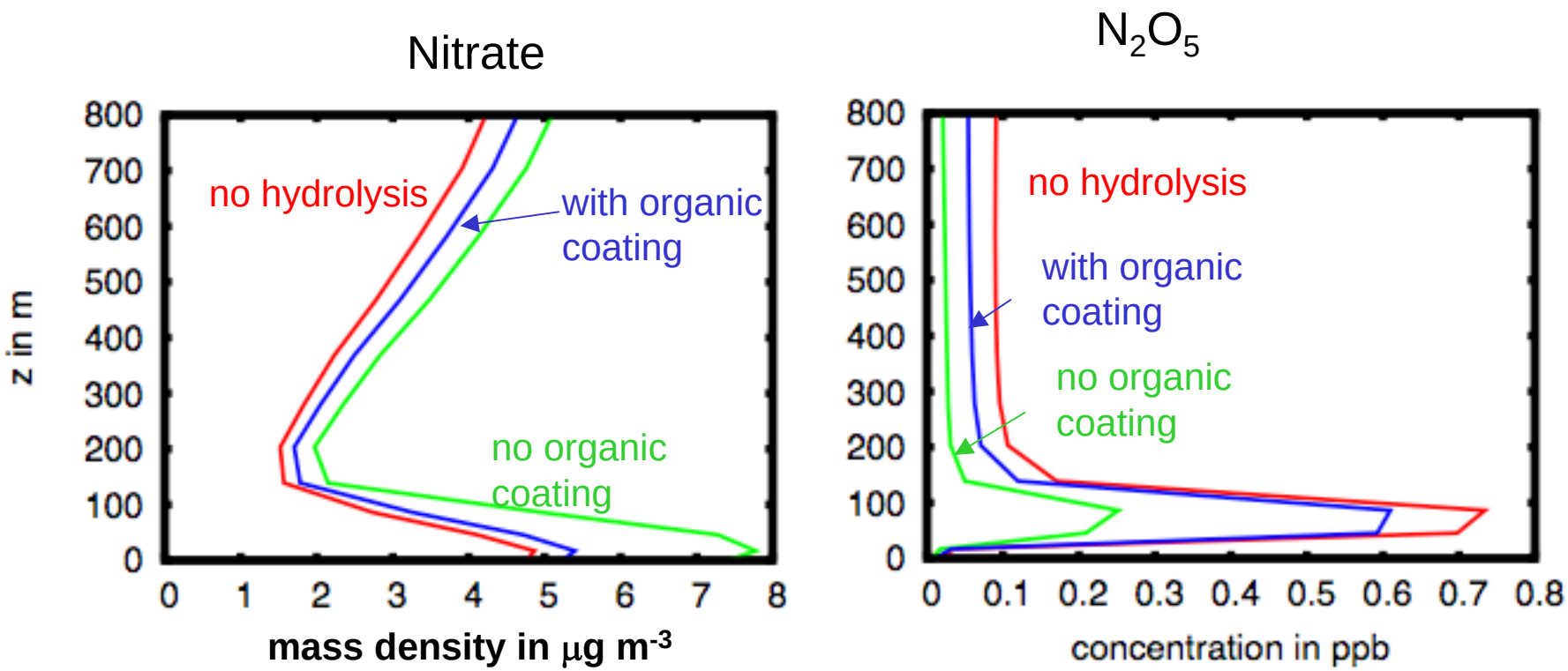
Results 1D

Three cases:

Run A: no Hydrolysis

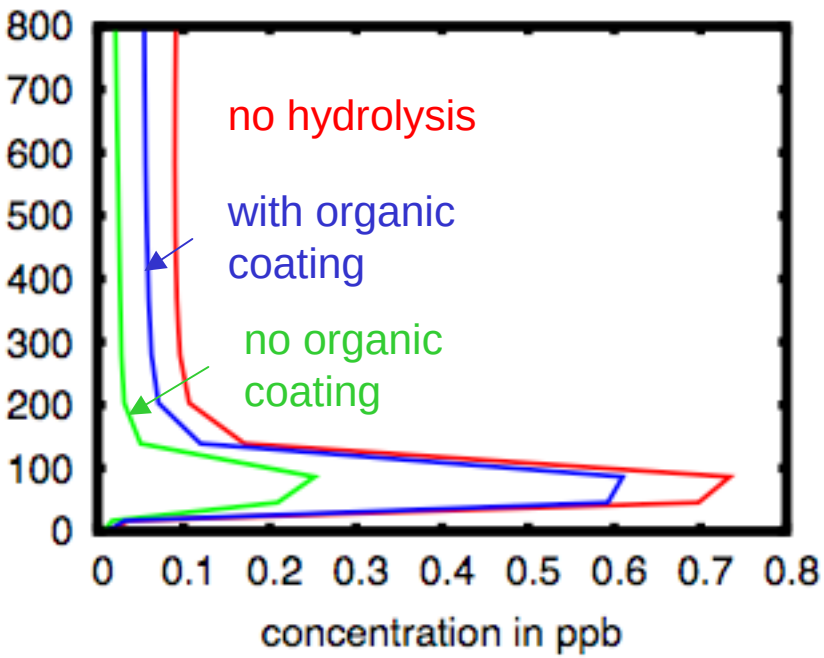
Run B: With Hydrolysis, organic coating effect neglected

Run C: With Hydrolysis, organic coating included

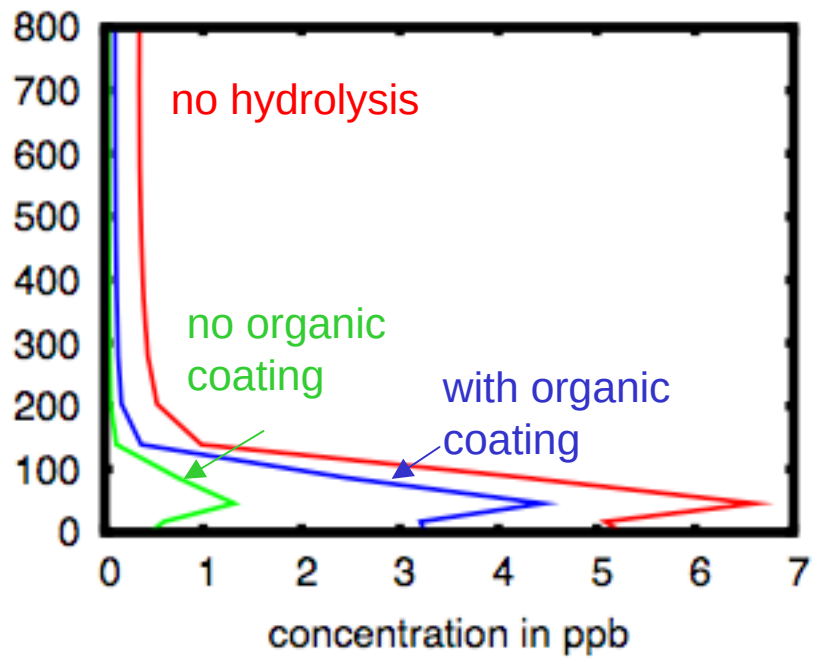


Low NO_x Versus High NO_x

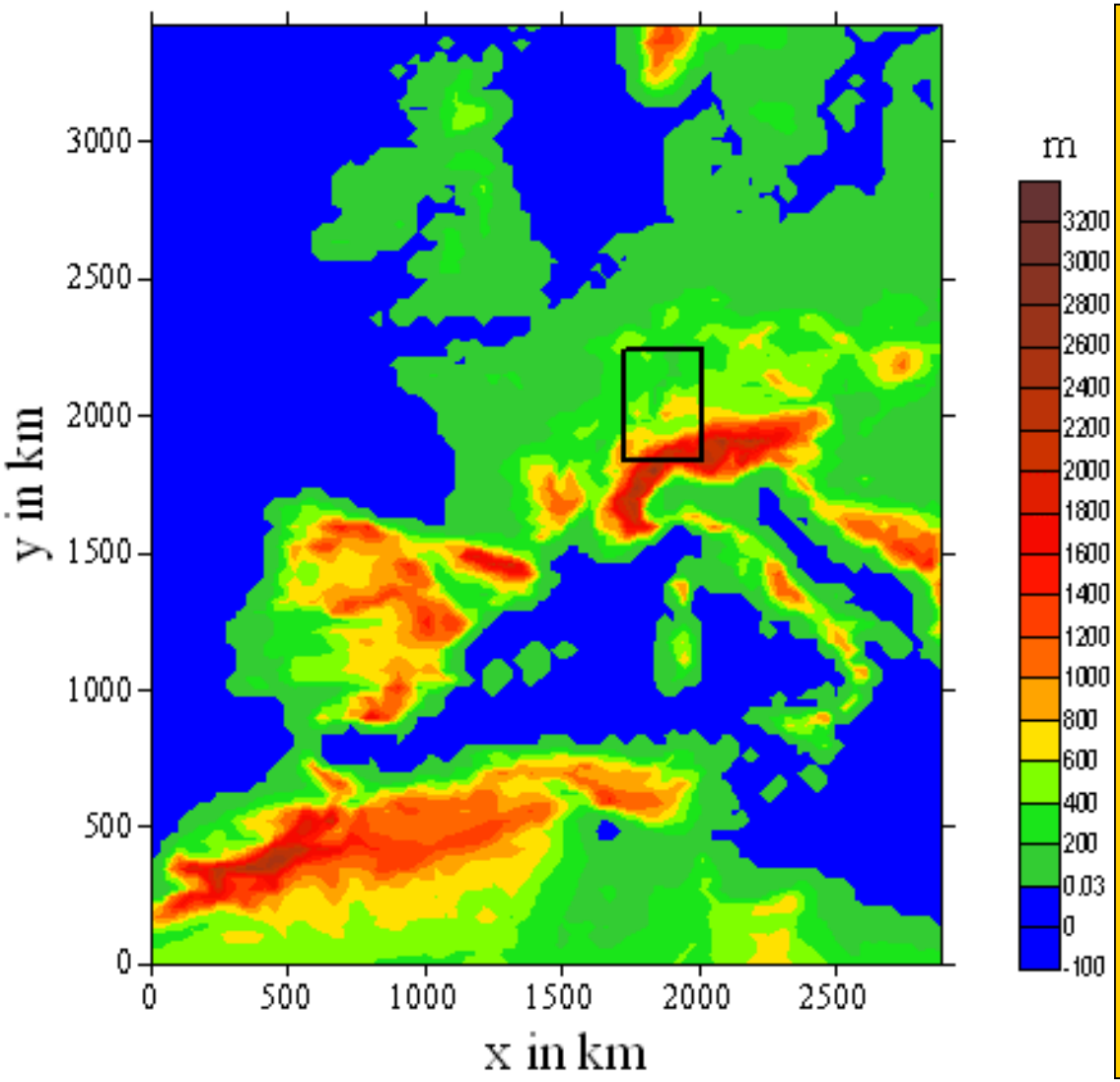
N_2O_5 (low NOx case)



N_2O_5 (high NOx case)



COSMO–ART (ART = Aerosols and Reactive Trace Gases)



Concept:

COSMO-ART is online coupled.

Identical methods are applied for all scalars as temperature, humidity, and concentrations of gases and aerosols to calculate the transport processes.

It has a modular structure.

Therefore COSMO-ART can (easily) be used in the forecast mode.

www-imk.fzk.de/tro/ACP/

Simulation period:

29.08.05 - 02.09.05

Simulation domain:

Southwest Germany + adjacent areas

Horizontal Resolution 7km x 7km

Input data:

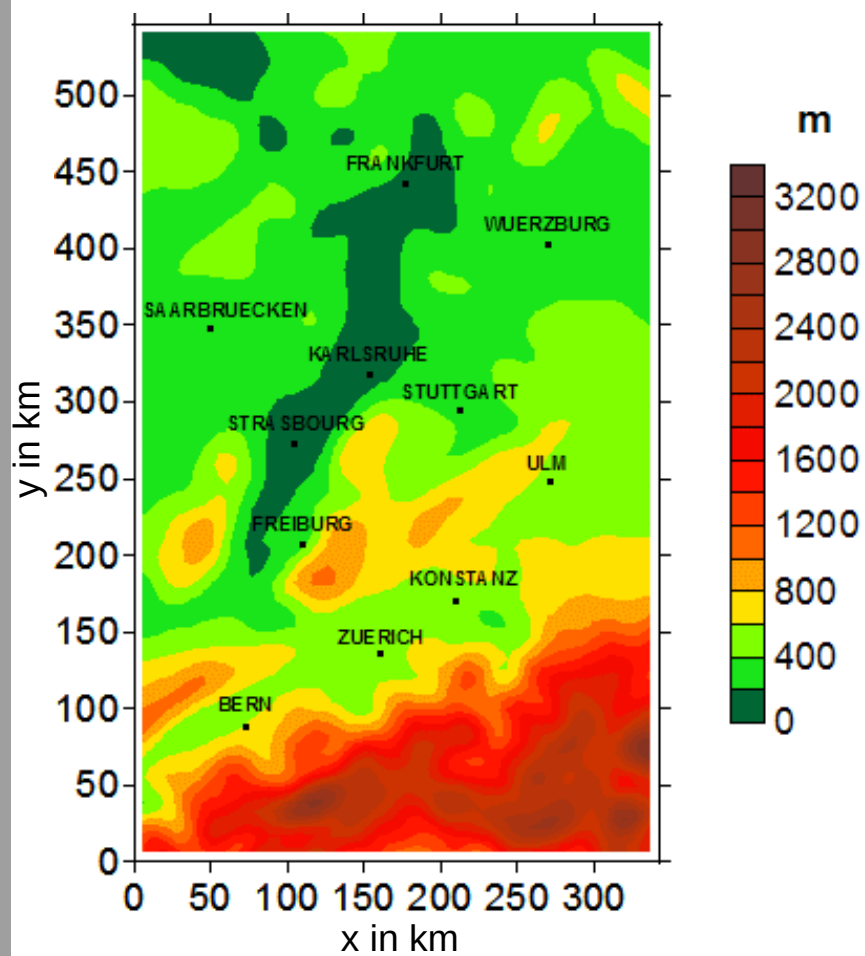
- Meteorology: GME Reanalysis (DWD)
- Emission data (IER,Stuttgart)
- Land use (JRC-IES,Ispra)

Run A: no hydrolysis

Run B: organic coating effect neglected

Run C: organic coating included

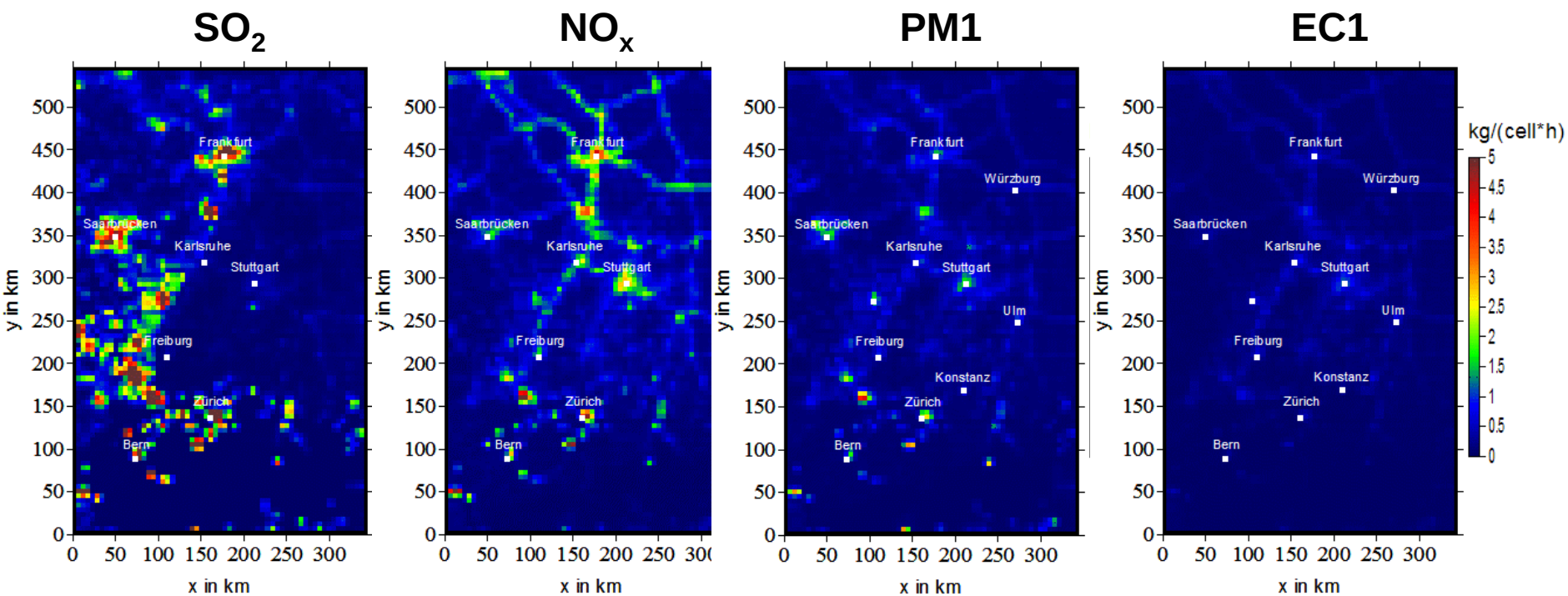
Model domain



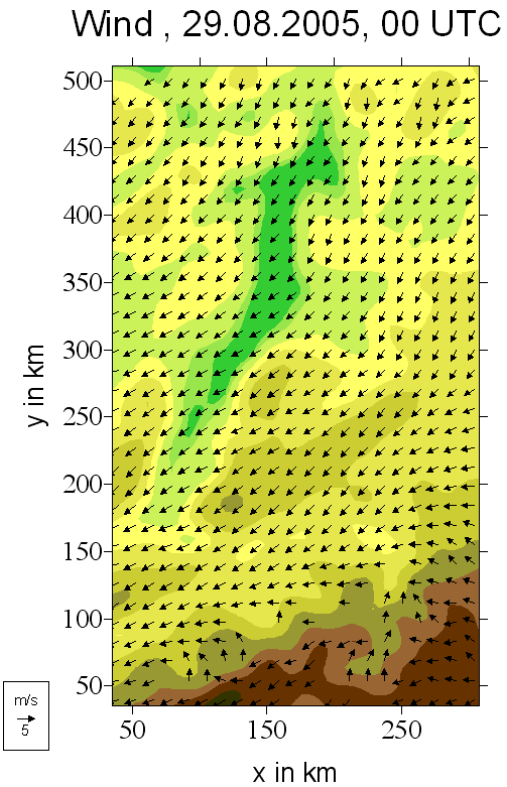
Emissions

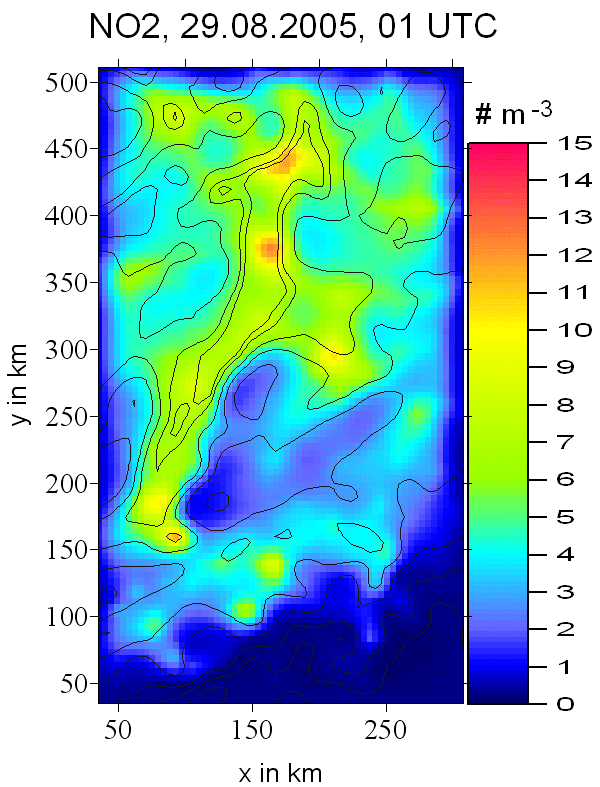
(Pregger et al., IER, Uni Stuttgart)

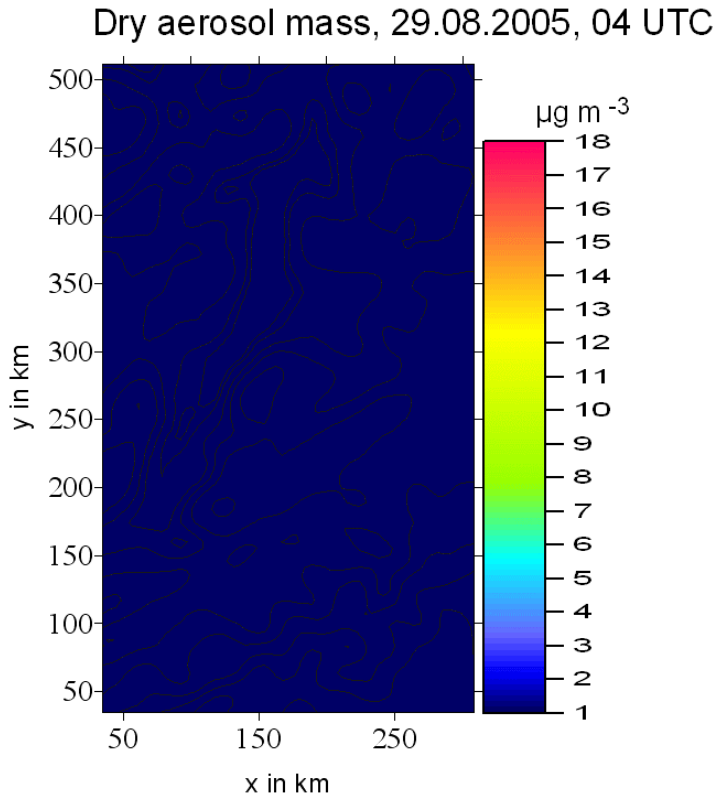
- Discrimination of point and area sources.
- Temporal resolution 1h, spatial resolution 7km x 7km
- 20 gas phase species (5 inorganic species, 15 VOC's)
- Primary particle emissions as EC and PM (1, 2.5, 10 μm)
- Biogenic emissions calculated online



Heteorgeneous Hydrolysis

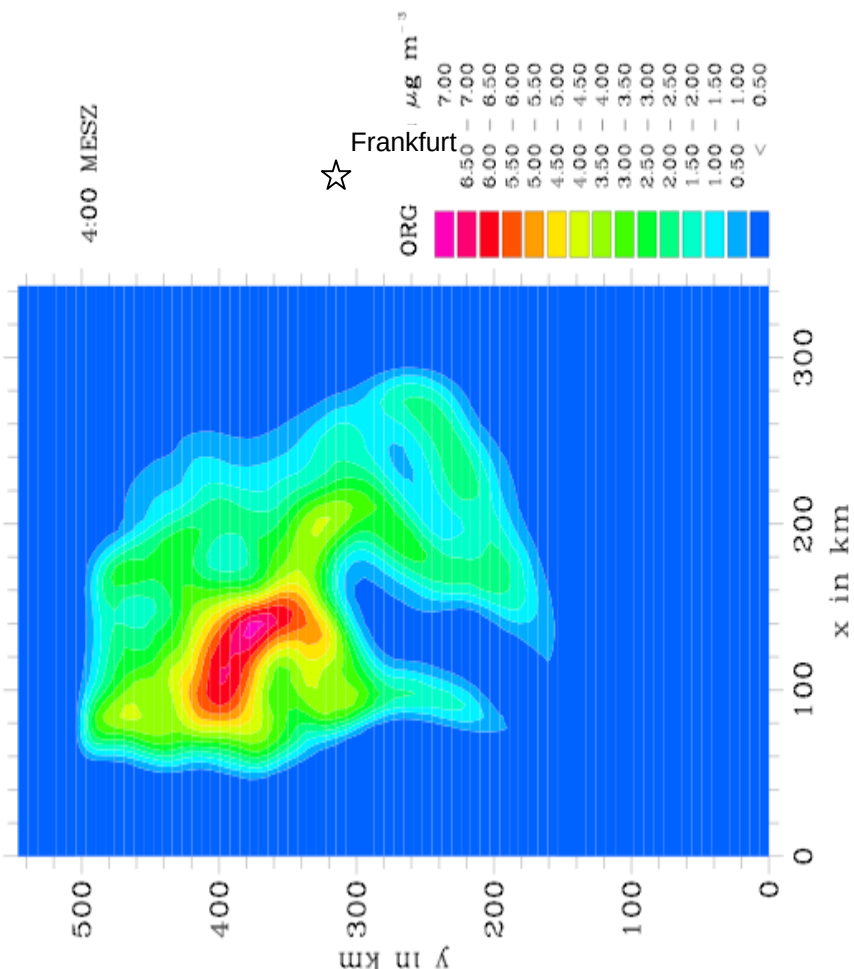




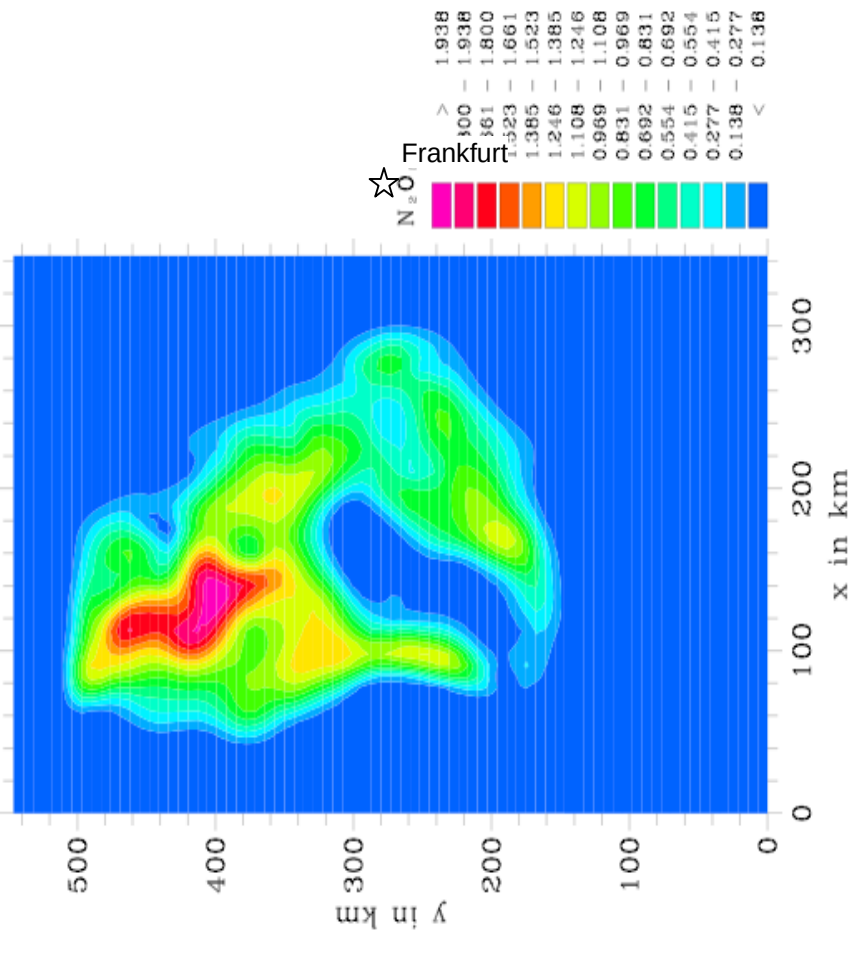


Impact on nitrate distribution

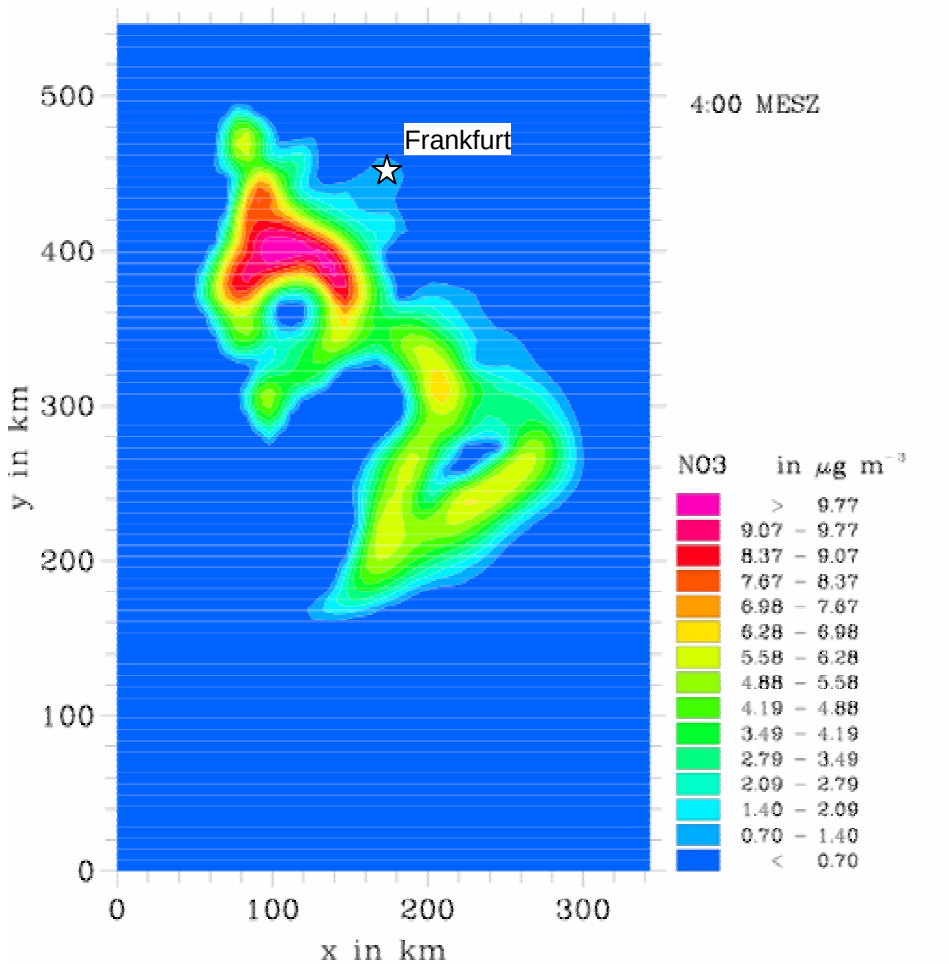
SOA in μg m^{-3}



N_2O_5 in ppb

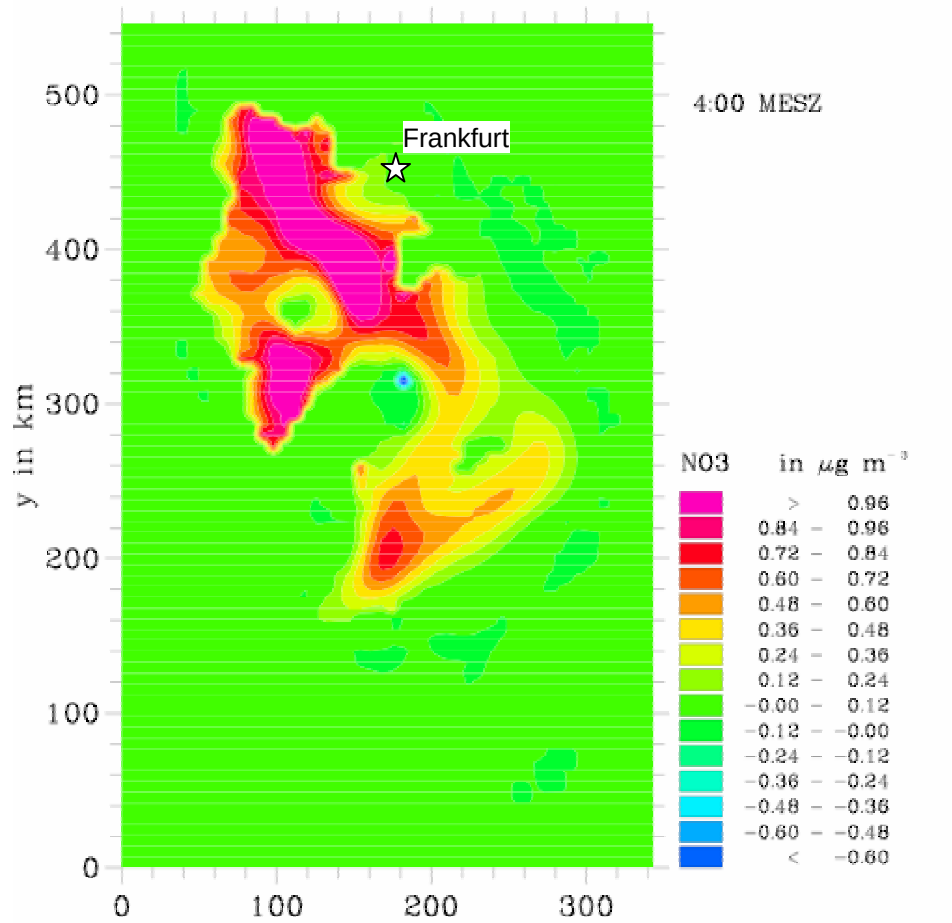


Impact on nitrate distribution

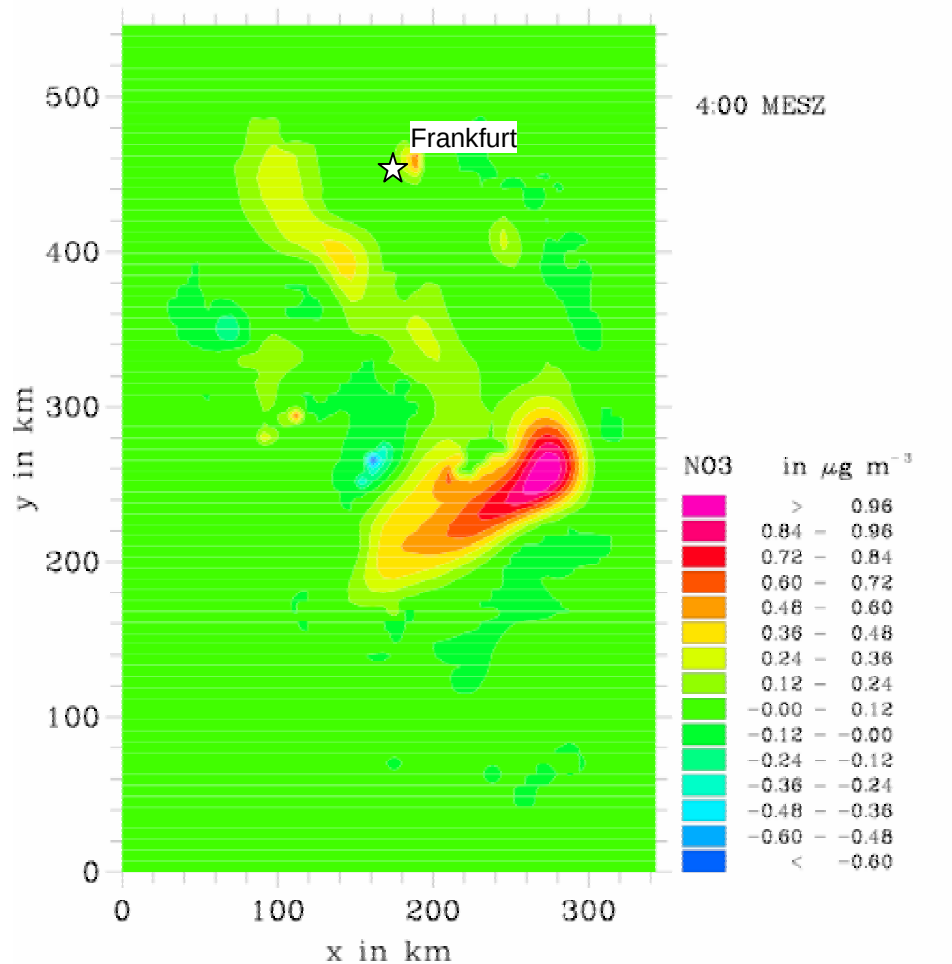


Run A: No Hydrolysis
Run B: With Hydrolysis, organic coating effect neglected
Run C: With Hydrolysis, organic coating included

Nitrate, Run B - Run A



Nitrate, Run C - Run A



Summary

- Aerosol and gas phase species involved in N_2O_5 hydrolysis have characteristic profile within the nocturnal boundary layer.
- 1D process studies show that organic films can suppress the hydrolysis significantly.
  - Impact on nighttime N_2O_5, NO_3, nitrate, VOC
  - Dependence on NO_x concentrations
- 3D results:
  - Up to 15% reduction of nitrate when organic film is accounted for.
  - Negligible impact in daytime ozone.