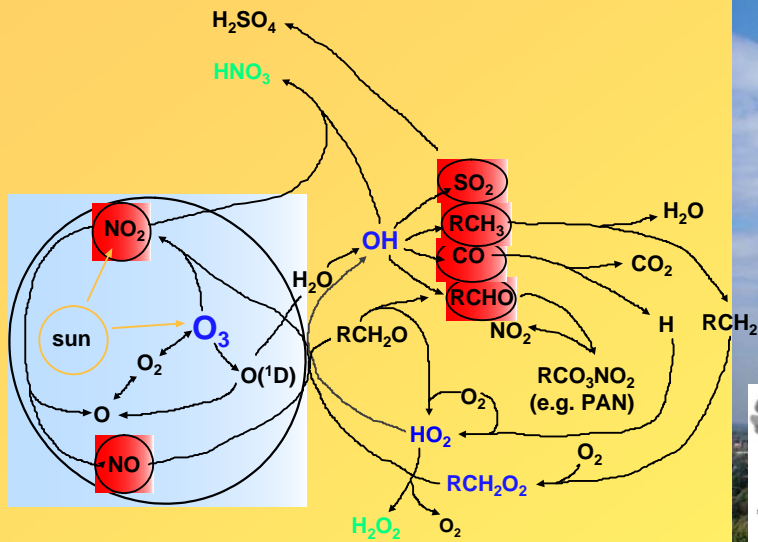
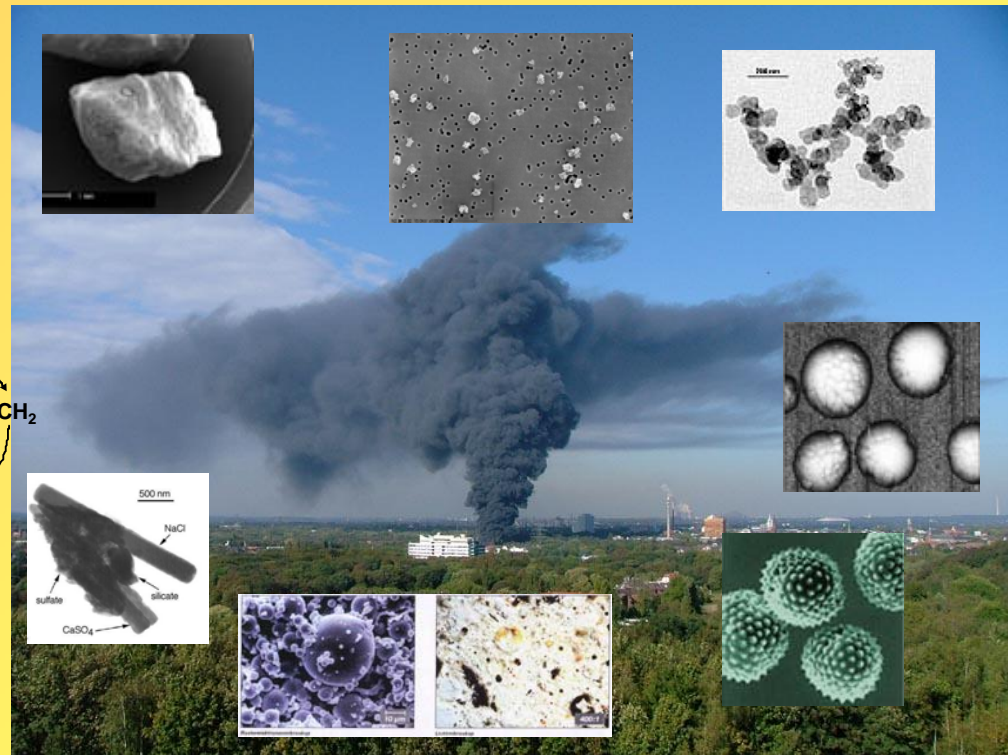


Modelling the Chemical Composition of Particles and Needs for Improvements in Chemical Mechanisms



Staehelin und Dommen (1994)



Bernhard Vogel

Institut für Meteorologie und Klimaforschung

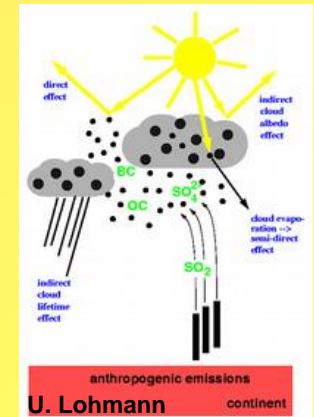
Aerosols and Climate

Aerosols have an impact on human health,

BUT they have also an impact on climate (and weather).

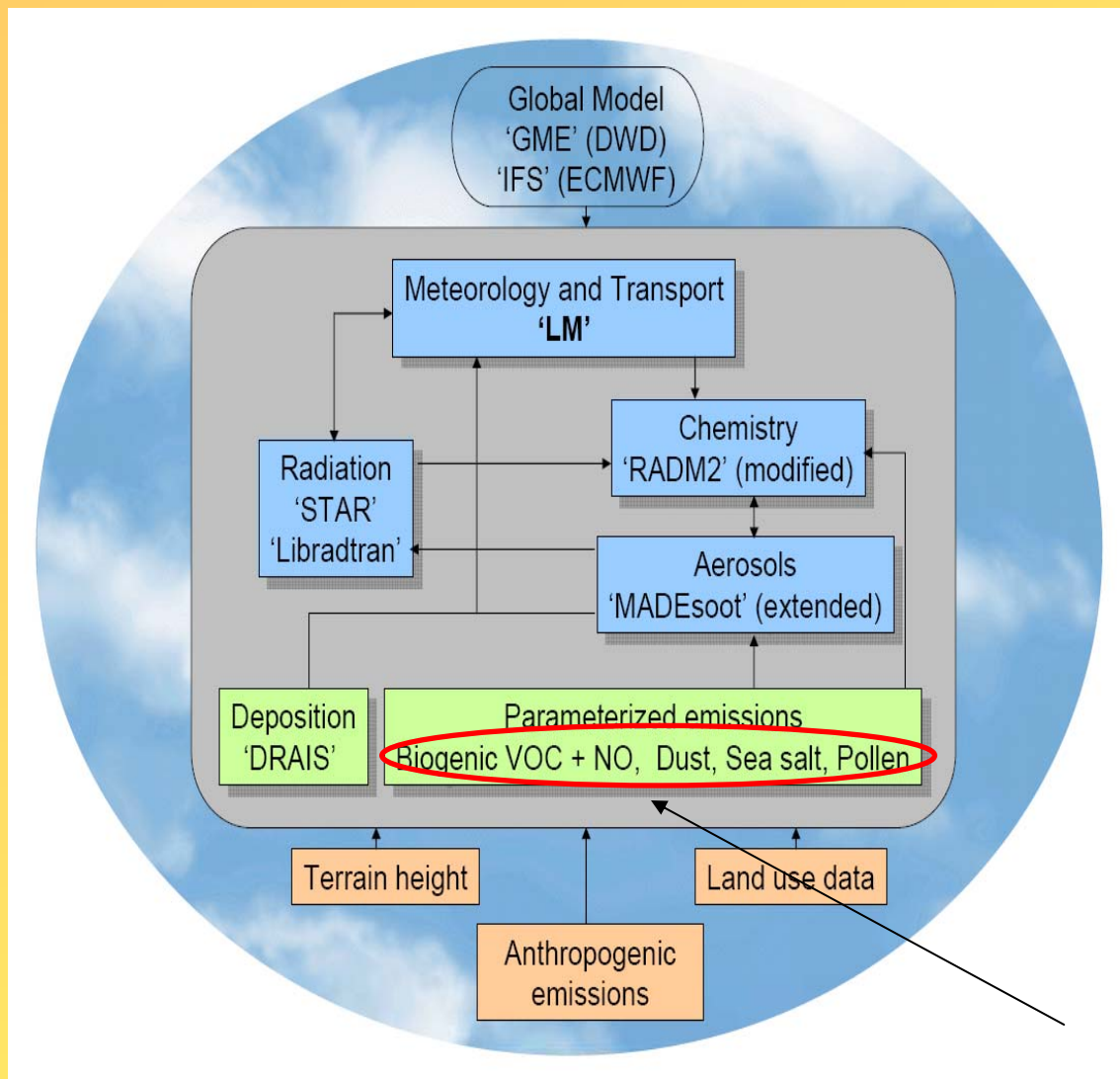
by:

modifying the atmospheric radiation (direct effect),
modifying cloud formation (indirect effect),
and mixtures of both.



LM-ART as an example of comprehensive CTMs.

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



Advantage:

LM is the **operational** weather forecast model of DWD. It is **continuously validated** with observations.

Concept:

Online coupled.

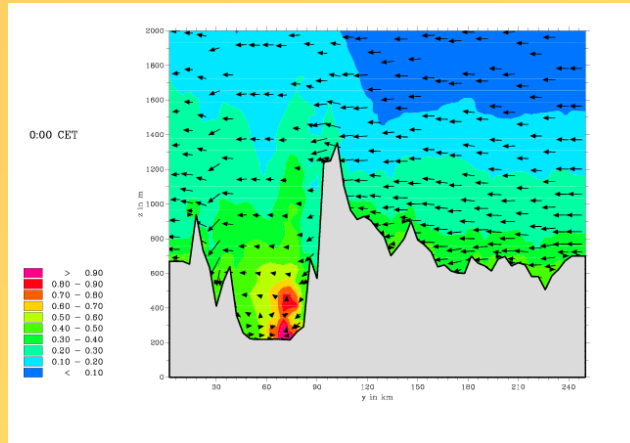
Identical methods are applied for all scalars as temperature, humidity, and concentrations of gases and aerosols to calculate the transport processes including **deep convection**.

It has a **modular** structure.

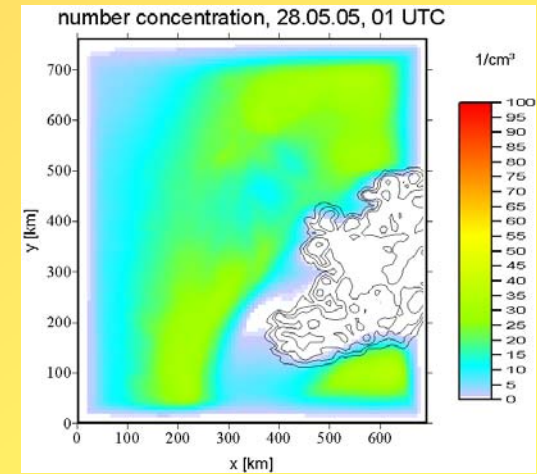
Therefore **LM-ART** can easily be used in the **forecast mode** by DWD (example: pollen forecast).

Applications of LM – ART

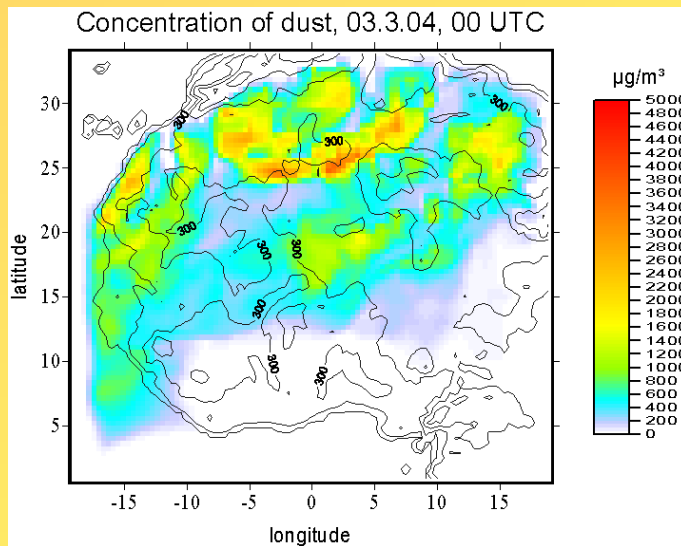
Soot containing particles



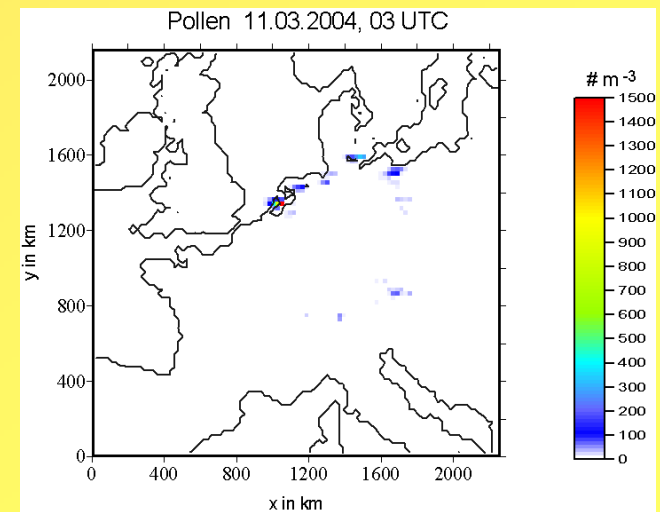
Sea salt



Mineral dust



Pollen



Calculation of the optical properties

$$b_{\text{ext},i} = \int_0^{\infty} \frac{\pi}{4} d_p^2 n_i(d_p) Q_e(d_p, m, \lambda) dd_p$$

$$b_{\text{ext}} = \sum_{i=1}^M b_{\text{ext},i}$$

M: Number of modes

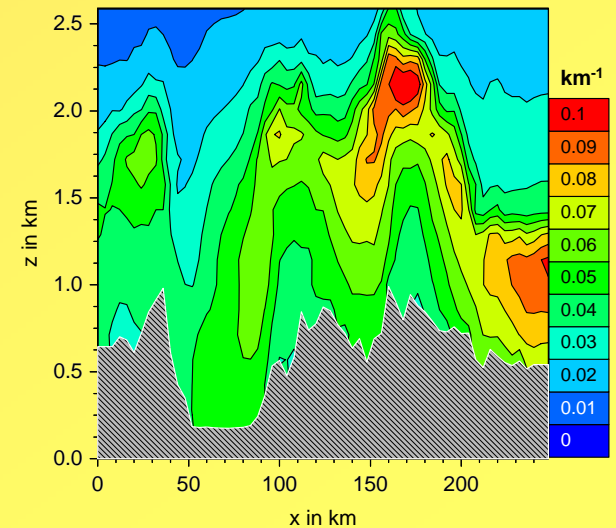
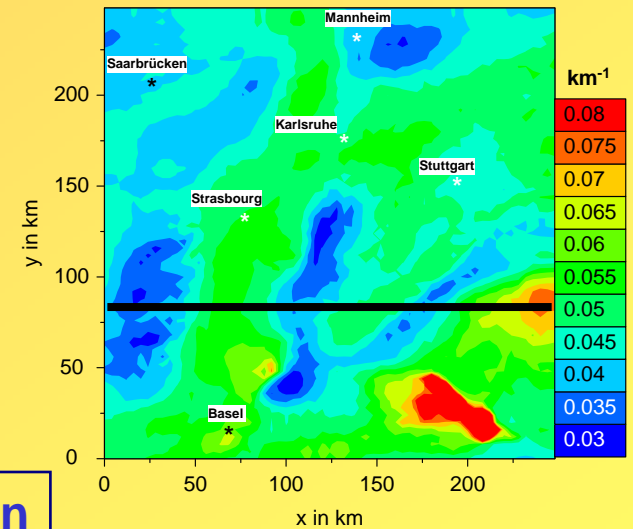
- d_p : Diameter of the particle
- $n_i(d_p)$: Size distribution
- Q_e : Extinction efficiency
- m : Refractive index
- λ : Wavelength of the incident radiation

Chemical Composition

Q_e is calculated using Mie theory (Bohren and Huffman, 1983).

The coated particles are assumed to consist of a centred soot core with a soluble shell.

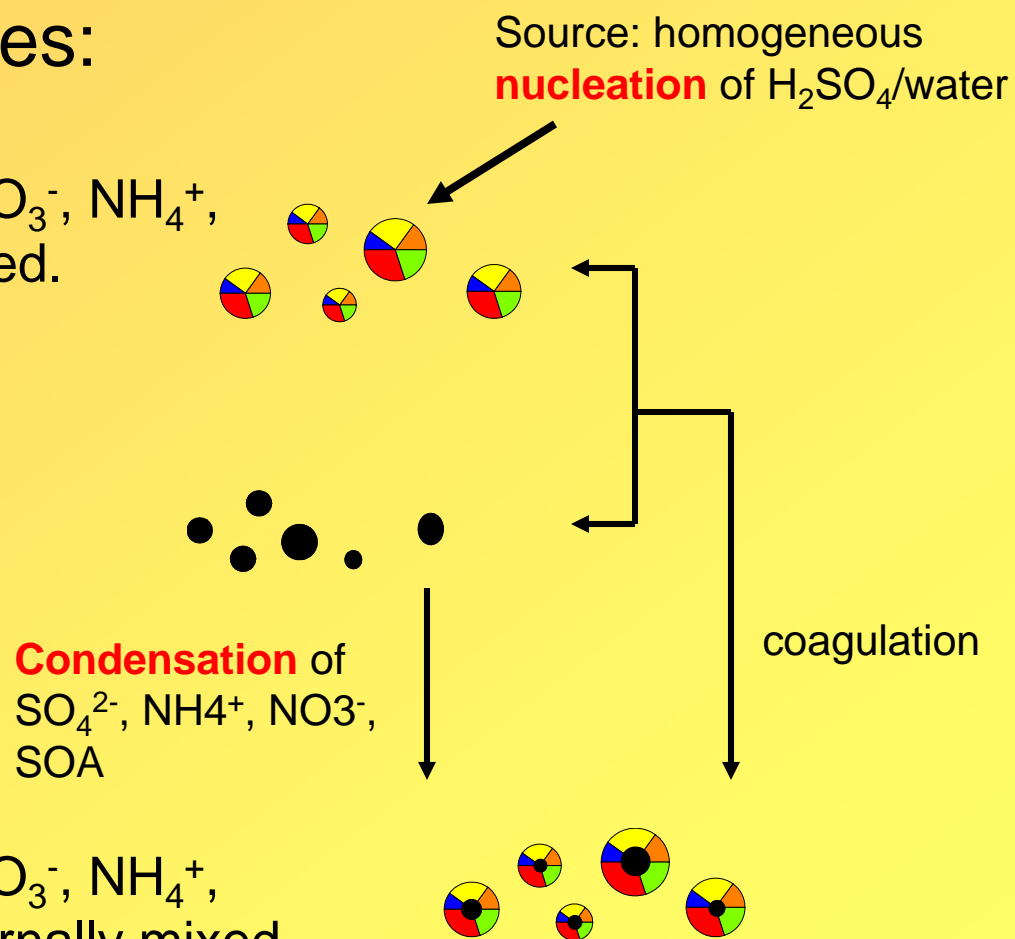
Mixing rule: weighted by mass fraction



MADEsoot

Interaction of five modes:

- **Two modes** for SO_4^{2-} , NO_3^- , NH_4^+ , H_2O , SOA, internally mixed.
- **One mode** for pure soot.
- **Two modes** for SO_4^{2-} , NO_3^- , NH_4^+ , H_2O , SOA, and soot internally mixed.



Three modes for **mineral dust** particles + Three modes for **sea salt** particles + + **Pollen**

Model Intercomparison

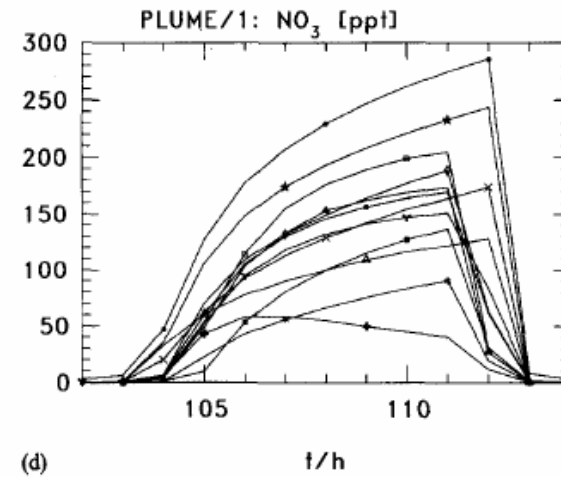
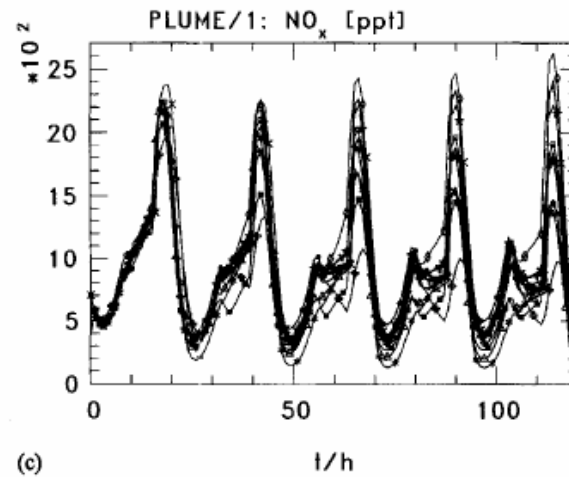
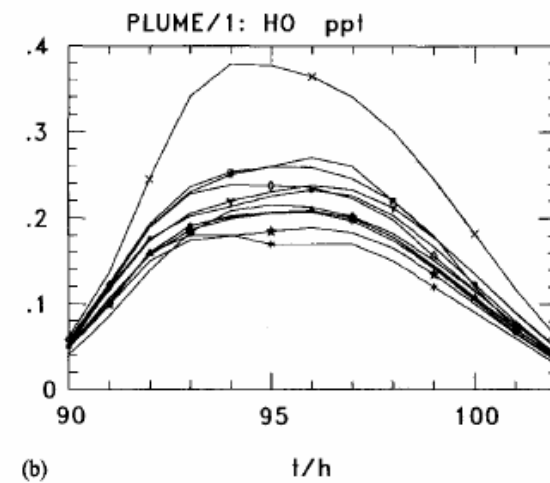
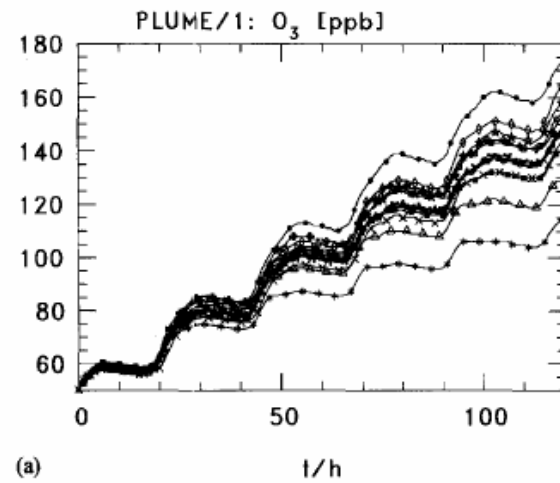
RADM2-IFU
RADM2-FZK^b
RADM2-KFA
Euro-RADM^b

CBM-IV-LOTOS
CB4-TNO
CB4.1^b

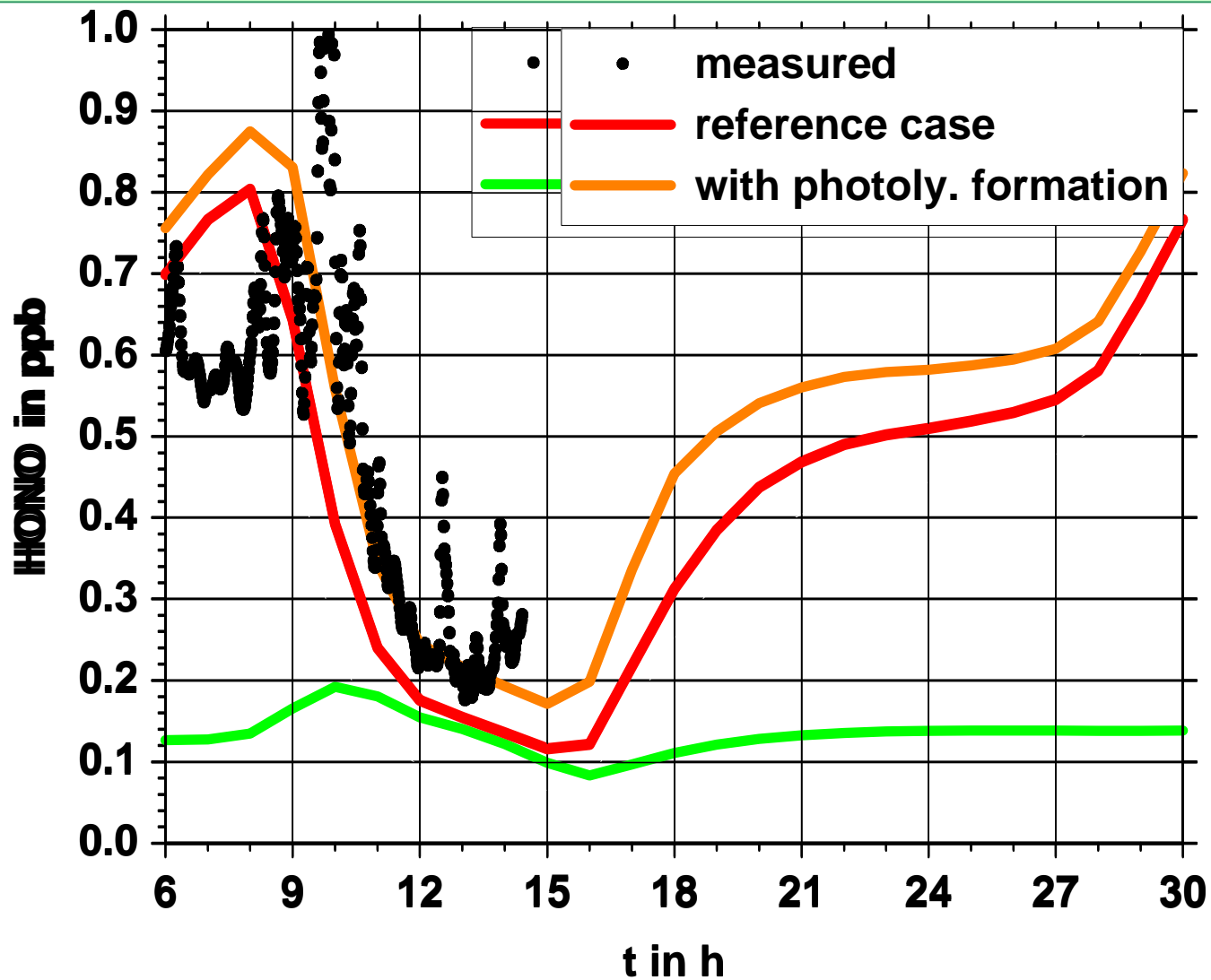
EMEP

ADOM

UiB
IVL
Ruhne

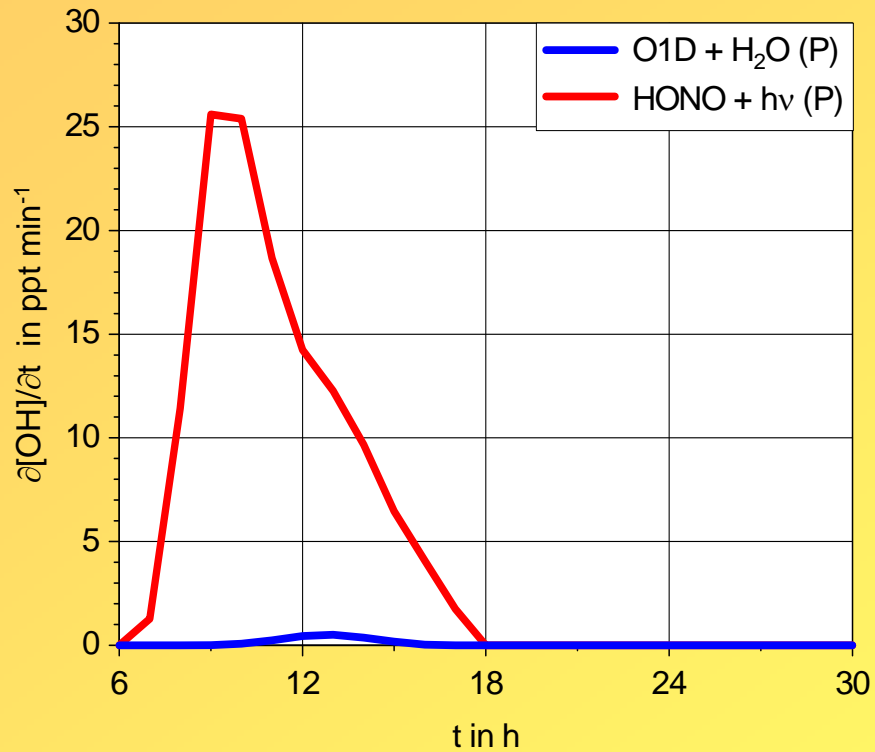


Relative importance of nitrous acid

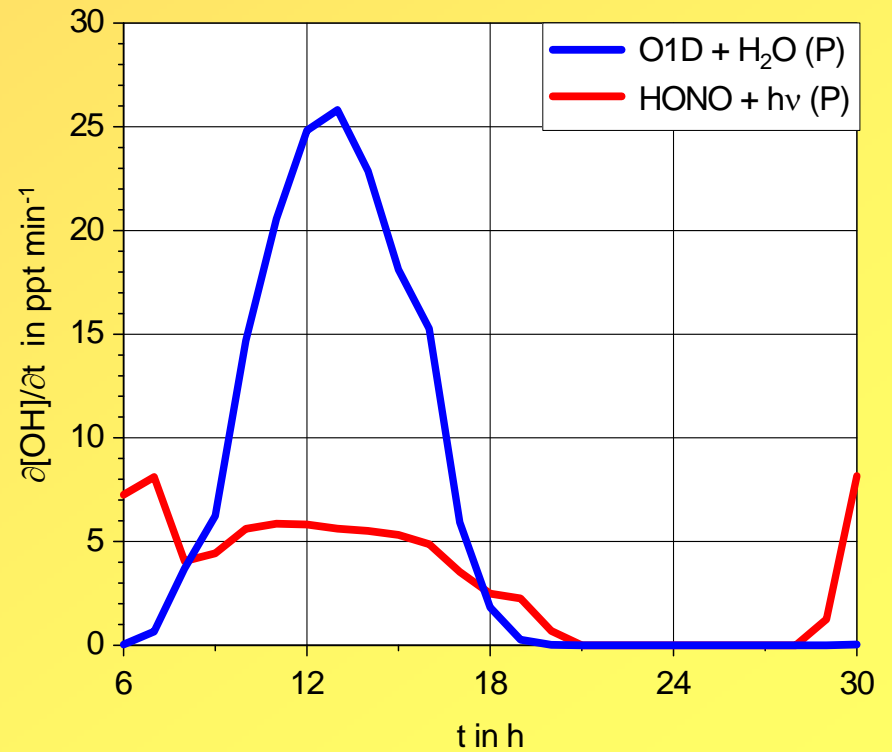


HONO and OH production

October



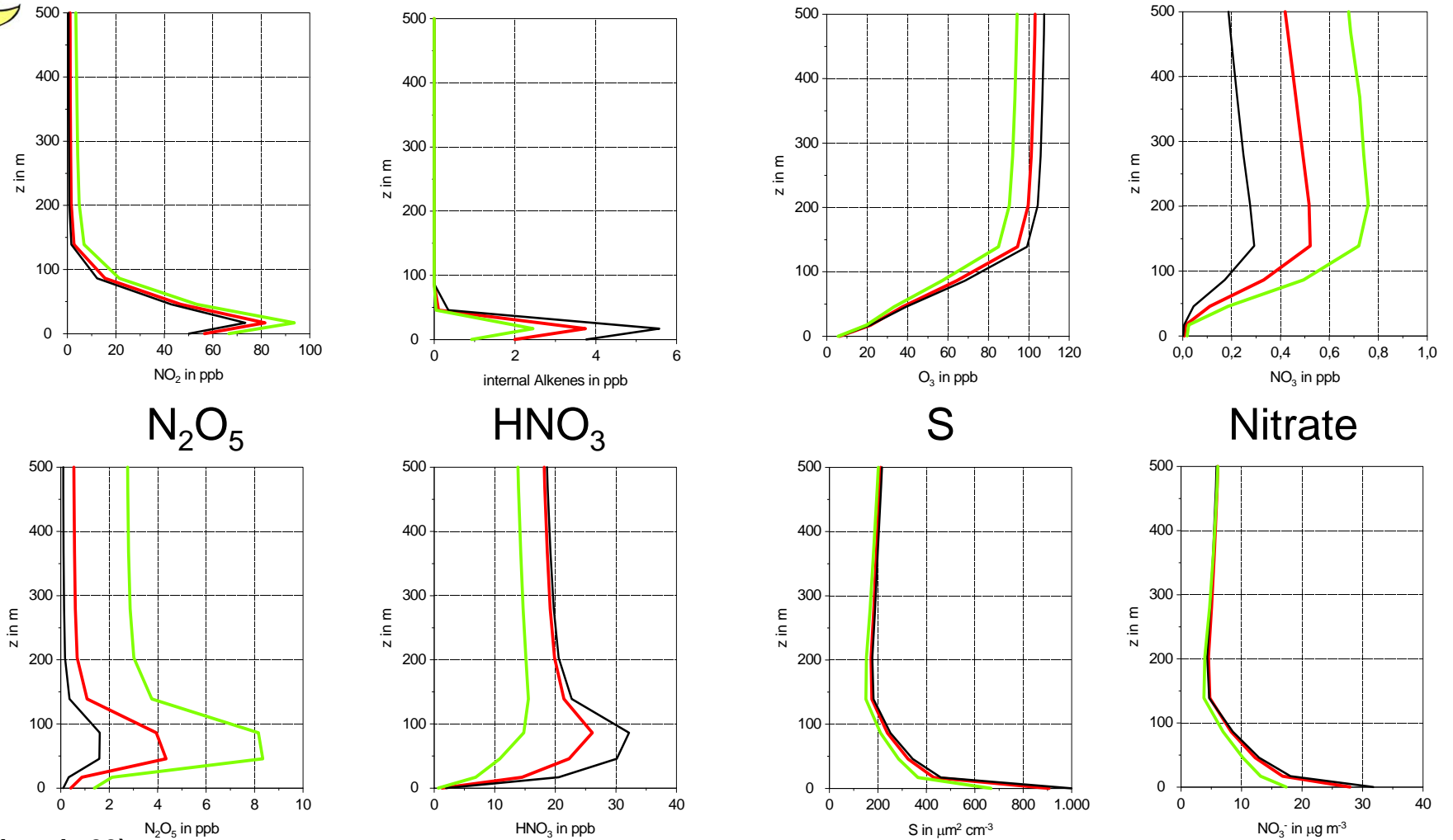
July



Heterogeneous hydrolysis of N_2O_5

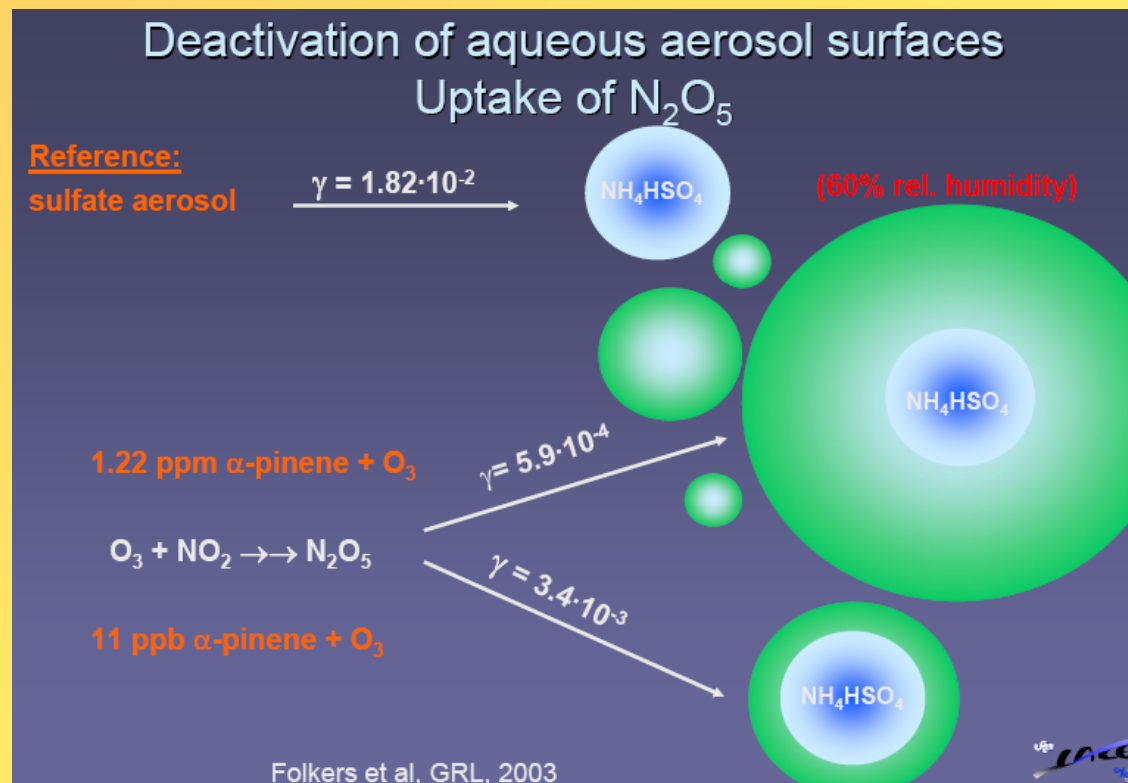


— no hydrolysis — hydrolysis — without nitrate effect



(Mentel et al., 99)

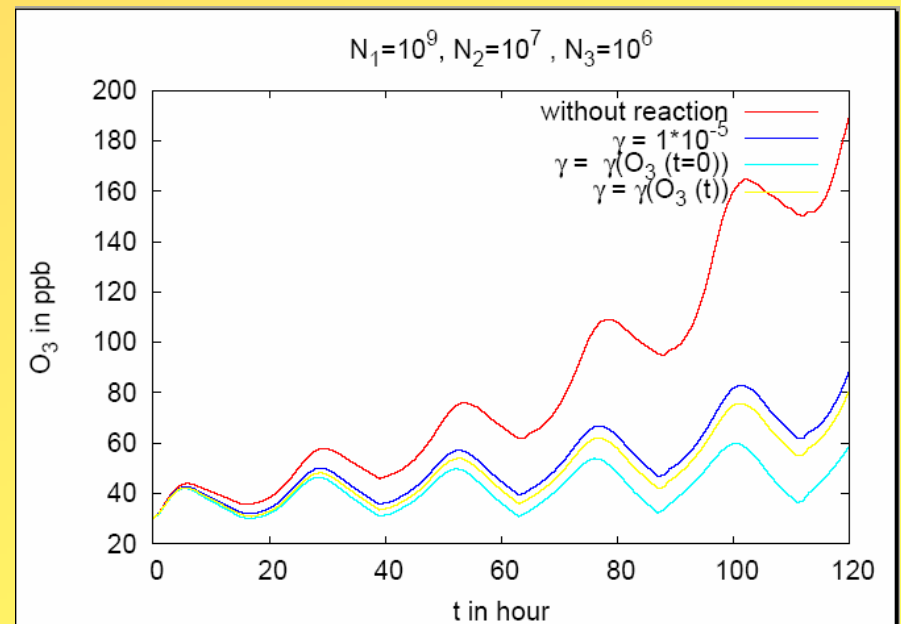
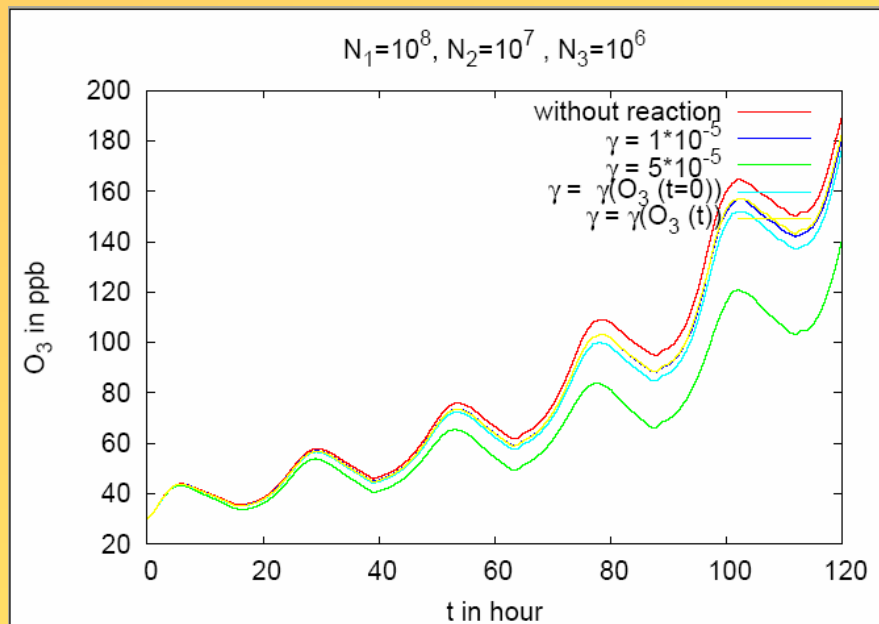
Organic compounds and hydrosolysis



(Ch. George)

Mineral dust and atmospheric chemistry

Different N_{i1} value



Bauer et al., 2004; Dentner et al., 1996; Chang et al., 2005

Summary

Transport

Emission (Composition of primary aerosol, gaseous precursors)

Gas phase chemistry (halogen species, organic compounds)

Nucleation (halogen species, organic compounds from the sea)

Condensation (halogen species, organic compounds from the sea)

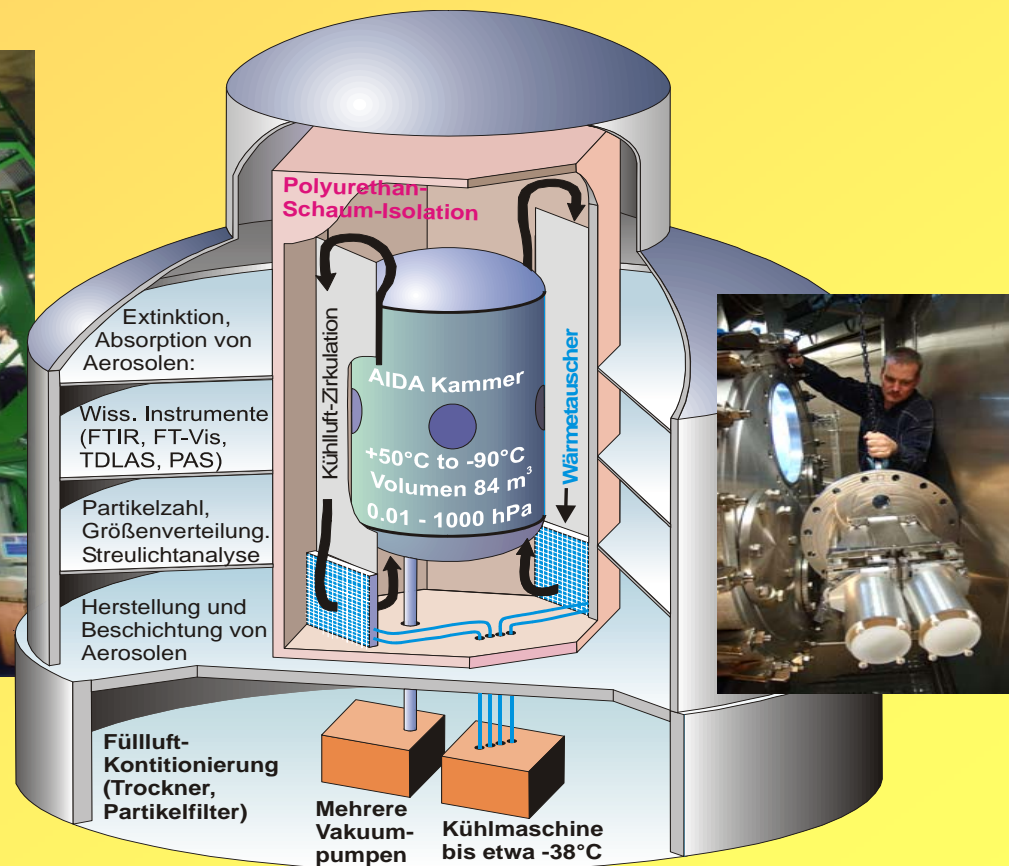
Heterogeneous reactions (great uncertainties e.g. mineral dust)

Reactions inside of particles (e.g. polymerization)

The AIDA chamber



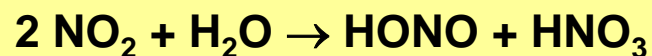
(80 m³, pressure and temperature down to stratospheric conditions)



Schurath et al., 2003

Methode:

- ✚ 1-D Simulationen mit KAMM/DRAIS inkl. MADE_{SOOT}
- ✚ Reaktion 1. Ordnung für die heterogene Produktion von HONO am Boden:



$$k_{\text{het}} = 3 * 10^{-3} \text{ m min}^{-1} * A \quad A = S/V = 0.1 \text{ m}^{-1} \quad (\text{Kurtenbach et al., 2001})$$

- ✚ Heterogene Reaktion am Aerosol wie oben. A ist jetzt die simulierte Oberflächendichte
- ✚ HONO Emissionen proportional NO Emissionen (0.8 %)
- ✚ **“Photolytische HONO Produktion“** proportional zu J_{NO_2}

Box Model simulation



From experimental study the initial uptake coefficient (γ_0) and the steady-state uptake coefficient (γ) are available

In this work, an initial uptake coefficient has been used, so possible surface deactivation processes are not taken in account.

The simulations have been carried out with:

1) **different values of uptake coefficient:**

- $\gamma = 1 * 10^{-5}$ (Bauer et al., 2004)
 $\gamma = 5 * 10^{-5}$ (Dentner et al., 1996)

- initial uptake coefficient calculated as $\gamma = \gamma(O_3)$
 $\gamma = 7.5 * 10^{-5} [O_3]^{-0.9}$ (Chang et al., 2005)
 $[O_3] = [O_3(t_0)]$; $[O_3] = [O_3(t)]$

2) **different dust particles concentrations** to test the sensitivity of O_3 reduction to particles size

Heterogeneous Reaction O₃ - Saharan Dust



- The reaction of O₃ with dust particles are treated as first order losses according to :

$$\frac{\partial [c]}{\partial t} = -k[c]$$

C is the concentration of O₃
K (s⁻¹) gives the net removal rate of O₃ to the dust surface

$$k = \int_{r_2}^{r_1} k_d(r)n(r)dr$$

n(r)dr (m⁻³) is the number density of particles between the aerosol radius *r* and *r* +*dr*

k_d(r) is the size-dependent mass transfer coefficient (m³ s⁻¹)

The **number distribution** is assumed to be a log-normal distribution:

$$n_i(\ln d_p) = \frac{1}{\ln \sigma_i} \frac{\overline{N}_i}{\sqrt{2 \cdot \pi}} \cdot \exp\left(\frac{-(\ln d_p - \ln d_{g,i})^2}{2 \cdot \ln^2 \sigma_i}\right)$$

d_g is the number median diameter
σ_i is the geometric standard deviation
N_i is the Reynolds averaged number density

Heterogeneous Reaction O_3 - Saharan Dust



- K_d is calculated using the *Fuchs and Sutugin (1970)* equation:

$$k_d = 4\pi r D_j \frac{0.75\alpha(1 + kn)}{kn^2 + kn + 0.283 \cdot kn \cdot \alpha + 0.75 \cdot \alpha}$$

D_j is the **gas-phase molecular diffusion coefficient** of a trace gas in air ($m^2 s^{-1}$) calculated following *Perry and Green, (1984)*

α ($0 < \alpha < 1$) is the dimensionless **mass accommodation coefficient**, defined as the number of molecules adsorbed by the surface divided by the number of collision with the surface

r is the **particle radius** (m)

Kn is ($= \lambda/r$) the dimensionless **Knudsen number** and λ is the effective **free path** of a gas molecule in air

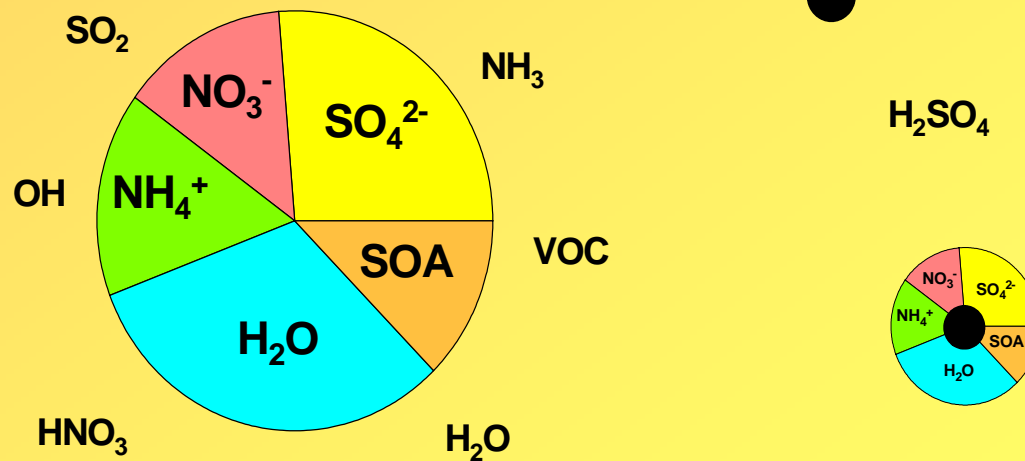
In this work we have substitute α with γ , which is the **uptake coefficient**

Nukleation, Kondensation und Koagulation



$c_{\text{krit}} = 0.16 \exp(0.1 T - 3.5 \text{RH} - 27.7)$ (Jaecker-Voirol & Mirabel, 89; Kerminen & Wexler, 94)

$d = 10 \text{ nm}$



The Aerosol Model MADEsoot

Eleven modes represent the aerosol population:

Two modes for SO_4^{2-} , NO_3^- , NH_4^+ , H_2O , SOA , internally mixed

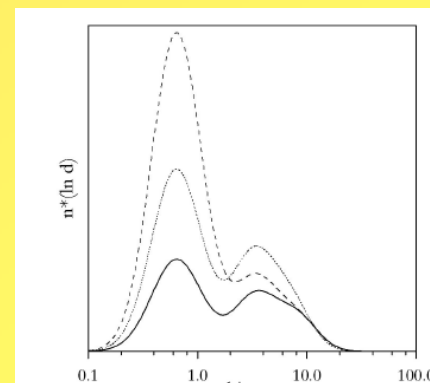
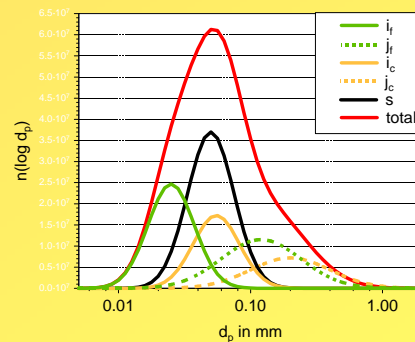
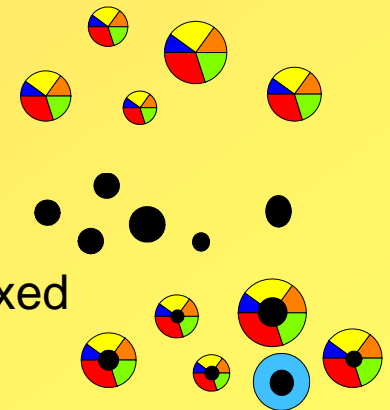
One mode for **pure soot**

Two modes for SO_4^{2-} , NO_3^- , NH_4^+ , H_2O , SOA , **soot**, internally mixed

Three modes for **mineral dust** particles

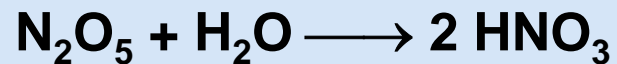
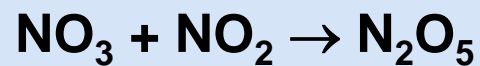
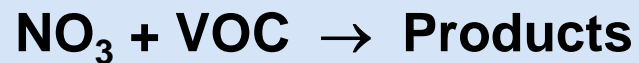
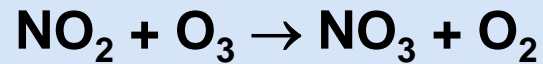
Three modes for **sea salt** particles

+ Pollen



Vogel et al., 2006;
Riemer et al., 2003;
Hoose, 2004
Lundgren, 2006

Einfluss der heterogenen Hydrolyse von N_2O_5 (Riemer et al., 2003)



$$\left. \frac{\partial [\text{N}_2\text{O}_5]}{\partial t} \right|_{\text{het.}} = -k_{\text{N}_2\text{O}_5} \cdot [\text{N}_2\text{O}_5]$$

$$k_{\text{N}_2\text{O}_5} = \frac{1}{4} \cdot c_{\text{N}_2\text{O}_5} \cdot S \cdot \gamma_{\text{N}_2\text{O}_5}$$

$$\gamma_{\text{N}_2\text{O}_5, \text{w}} = f \cdot \gamma_1 + (1-f) \cdot \gamma_2$$

$$\gamma_1 = 0.02, \gamma_2 = 0.002$$

$$f = \frac{m_{\text{SO}_4^{2-}}}{m_{\text{SO}_4^{2-}} + m_{\text{NO}_3^-}}$$

Mentel et al., 1999