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The International Union of Geodesy and Geophysics

2339-3

Workshop on Atmospheric Deposition: Processesand Environmental Impacts

Co-Sponsored by the International Union of Geodesy and Geophysics - IUGG

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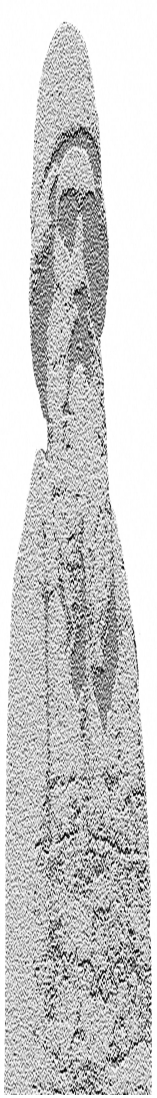
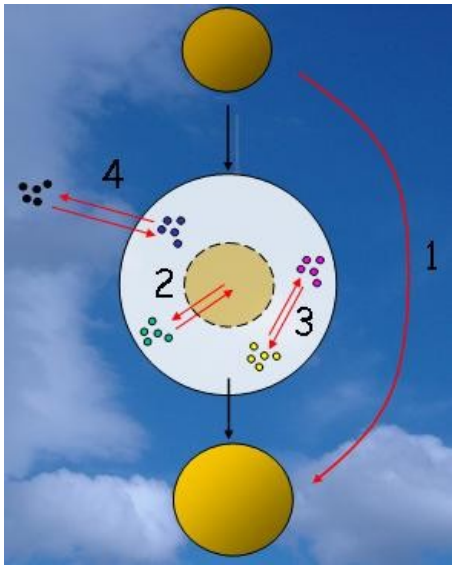
Wet deposition modelling

Holger Tost
Institut f. Physik der Atmosphare,
JGU, Mainz
Germany

tosth@uni-mainz.de



Wet deposition modelling



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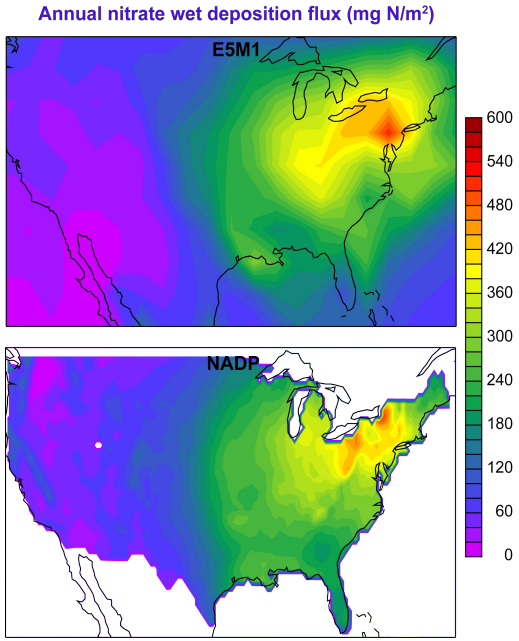

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Outline

- What is wet deposition modelling ?
  - What are requirements ?
  - What is the theoretical background?
- How to model wet deposition?
  - Trace gases
  - Aerosol particles
- Application examples
- Summary

What is wet deposition modelling?

Wet deposition
=
Removal of trace substances from the atmosphere by precipitation

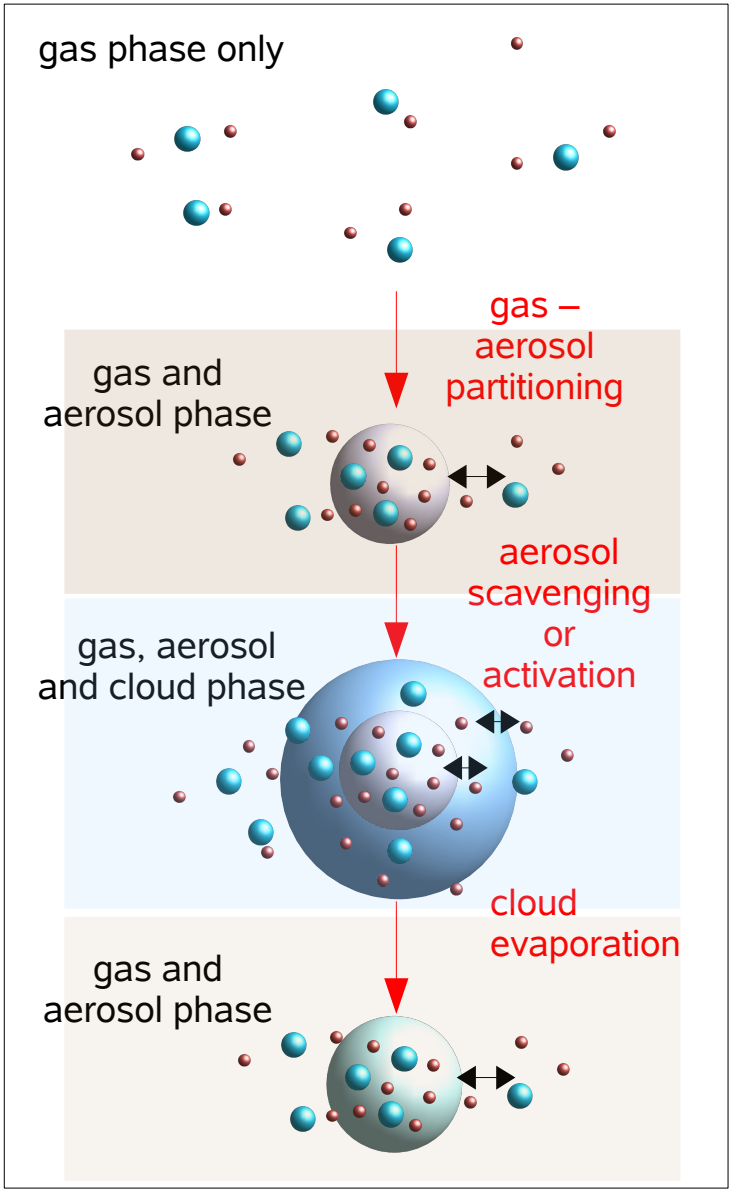
Trace gases

Aerosol particles

(Wet) Scavenging
=
Phase transition of compounds into the hydrometeor phase

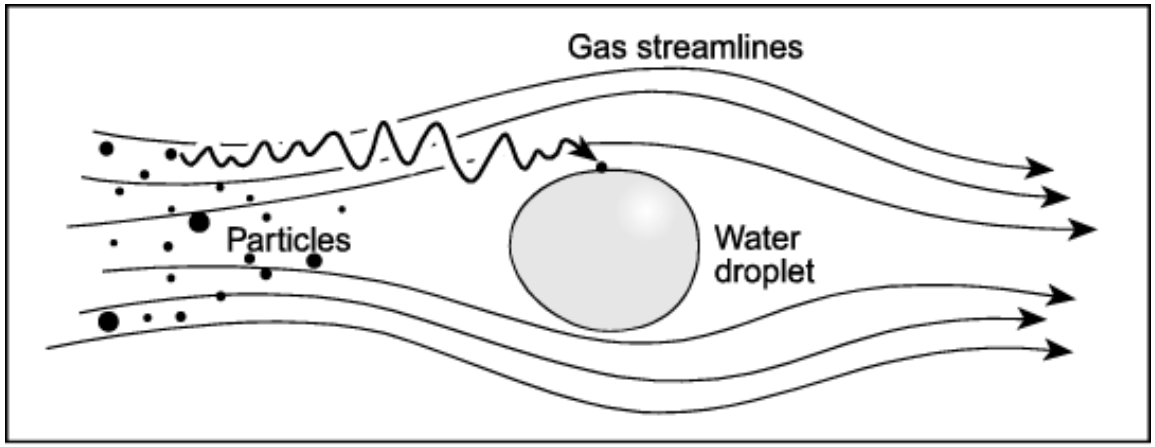
Processes in wet deposition I

- Nucleation scavenging
  - Phase change during the formation stage of a cloud
    - Incorporation of trace gases and aerosol particles during droplet formation
    - Diffusion of substances into cloud droplets
    - Chemical conversion in the cloud phase
    - Partial removal by conversion of cloud hydrometeors to precipitation
    - Partial release of chemically altered compounds into aerosol and gas phase



Processes in wet deposition II

- Impaction scavenging
  - Collection of trace compounds by precipitating hydrometeors
    - Vertically downward moving hydrometeors
    - Diffusion of substances into hydrometeors



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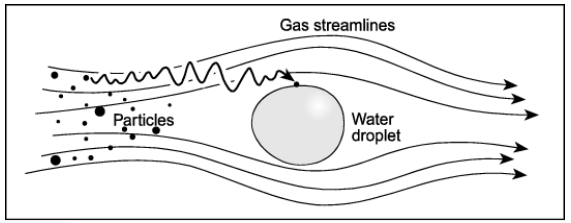

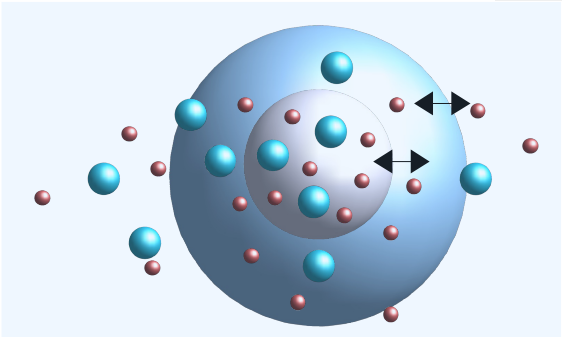

Processes in wet deposition II

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    - Vertically downward moving hydrometeors
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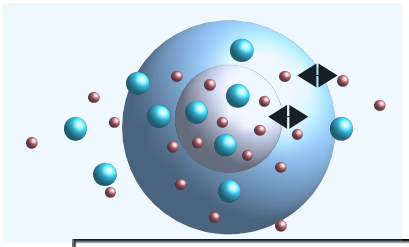
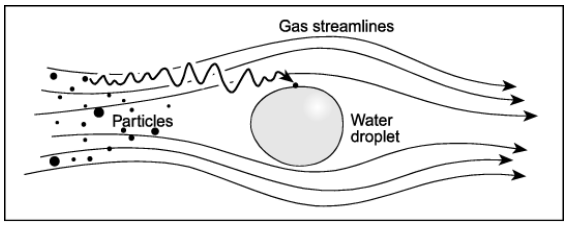
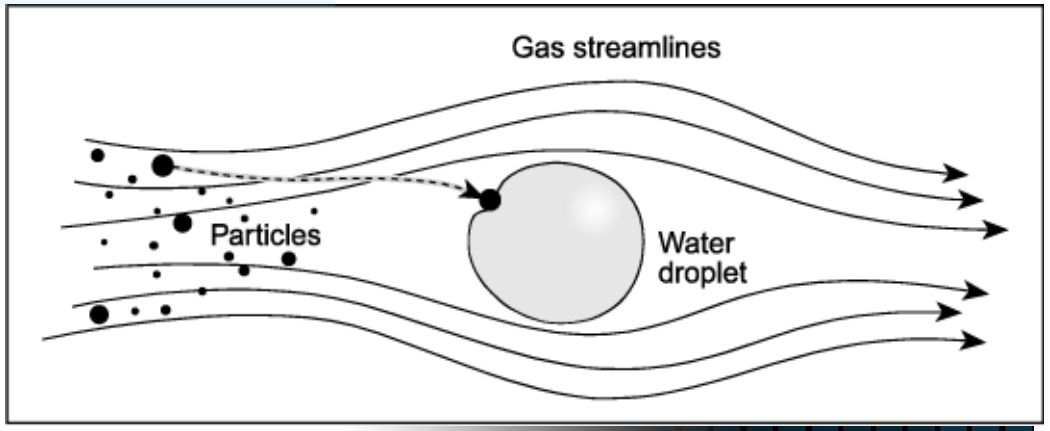
    - Chemical conversion in the precipitation droplets
    - Collection or flow around the droplet ?

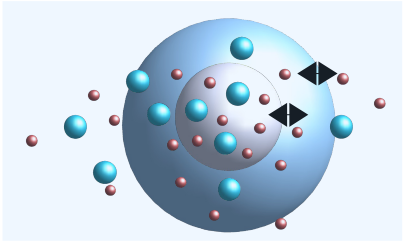


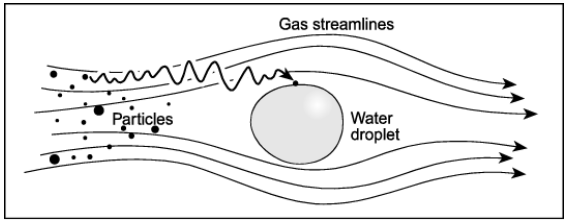


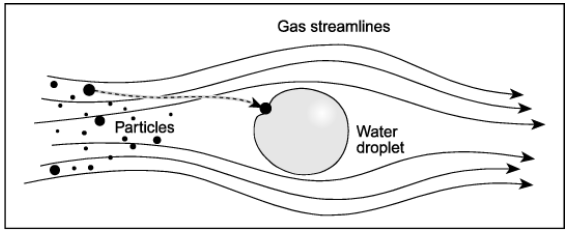


Processes in wet deposition II

- Impaction scavenging
  - Collection of trace compounds by precipitating hydrometeors
    - Vertically downward moving hydrometeors
    - Diffusion of substances into hydrometeors
    - Chemical conversion in the precipitation droplets
    - Collection or flow around the droplet ?
    - Partial release due to precipitation evaporation before the Earth's surface







Requirements I

- Good representation of precipitation
  - Phase state of precipitation
    - Rain, snow, graupel, hail, ice crystals
  - Production pathways of precipitation
    - Melting, condensation, evaporation, sedimentation
  - Vertical information about precipitation
    - Formation altitude, changes of precipitation by microphysical processes in dependency of altitude

Requirements II

- Good representation of the trace compounds
  - Emission
  - Transport
  - Chemical conversion
  - Other competing sink processes

Requirements IIb

- Wet deposition is one of the last processes in the life cycle of atmospheric compounds
  - All previous errors / uncertainties propagate into the results from this process!
  - Episodic (and not continuous) sink of atmospheric substances
- Good results only, if:
  - Precipitation matches reality.
  - Trace substance atmospheric distribution matches reality.

Theoretical background

Trace gases dissolve in a liquid phase due to Henry's law

- Deriving Henry's law from thermodynamics:
  - 2nd law of TD for a single component:

$$\underbrace{dU}_{\text{internal energy}} = \underbrace{T}_{\text{temperature}} \cdot \underbrace{dS}_{\text{entropy}} - \underbrace{p}_{\text{pressure}} \cdot \underbrace{dV}_{\text{volume}}$$

  - For a mixture of compounds:

$$\underbrace{dU}_{\text{internal energy}} = \underbrace{\frac{\partial U}{\partial S}}_{=T} \cdot \underbrace{dS}_{\text{entropy}} - \underbrace{\frac{\partial U}{\partial V}}_{=p} \cdot \underbrace{dV}_{\text{volume}} + \sum_{i=1}^{k} \left(\frac{\partial U}{\partial n_i} dn_i \right)$$

Henry's law

- Coordinate transformation from *S*, *V*, n_i to *p*, *T*, n_i:
  - Resulting in Gibbs free energy:

$$\underbrace{dG}_{\text{Gibbs free energy}} = \underbrace{U}_{\text{internal energy}} + pV - TS$$

  - For a mixture of compounds:

$$\underbrace{dG}_{\text{Gibbs free energy}} = \underbrace{\frac{\partial G}{\partial p}}_{=V} \cdot \underbrace{dp}_{\text{pressure}} - \underbrace{\frac{\partial G}{\partial T}}_{=S} \cdot \underbrace{dT}_{\text{temperature}} + \sum_{i=1}^{k} \left(\underbrace{\frac{\partial G}{\partial n_i}}_{=\mu_i} dn_i \right)$$

  - Chemical potential μ_i:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j} \quad \text{or} \quad \mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j}$$

Henry's law

- Chemical potential μ_i can be separated into a part only dependent on p and one depending on p and T:

$$\mu = \mu^0(T) + RT \ln \frac{p}{p_0}$$

- For an individual component, this is modified by taking the partial pressure into account:

$$\mu_i = \mu_i^0(T) + RT \ln(p) + RT \ln(x_i) = \mu_i^0(T) + RT \ln(p_i)$$

μ^0 is the temperature dependent chemical potential at standard pressure

Henry's law

- Analogously the chemical potential μ_i can also be determined for an ideal solution:

$$\mu_l = \mu_l^0(T, p) + RT \ln \chi$$

- In the next step, equilibrium is assumed between gas phase and solution:

$$\mu_{gas} = \mu_{liquid}$$

$$\mu_i^0(T) + RT \ln(p_i) = \mu_i^*(T, p) + RT \ln(\chi_i)$$

Henry's law

- Solving this equation towards p_i yields:

$$\mu_i^0(T) + RT\ln(p_i) = \mu_i^*(T, p) + RT\ln(\chi_i)$$

$$\ln\left(\frac{p_i}{\chi_i}\right) = \frac{\mu_i^0(T) - \mu_i^*(T, p)}{RT}$$

$$p_i = \chi_i \cdot \exp\left(\frac{\mu_i^0(T) - \mu_i^*(T, p)}{RT}\right)$$

$$p_i = K_i(p, T) \cdot \chi_i$$

What does this mean for scavenging ?

$$p_i = K_i(p, T) \cdot \chi_i$$

- Gaseous and aqueous phase ratio of a compound are constant at a given temperature and pressure (in equilibrium).
- Knowing gas phase concentrations the uptake into the liquid phase can be determined, if this coefficient $K_i(p,T)$ is known.
- This quantity is generally known as Henry coefficient.

How to model wet deposition ?

Henry's law

- Apply Henry's law, based on the liquid water content of the corresponding grid box

$$p_i = K_i(p, T, LWC) \cdot \chi_i$$

$\longrightarrow$ partitioning of gaseous compounds between gas and aqueous phase

Henry's law

- Based on this approach, many models use a constant value for the scavenging into the aqueous phase.

$$C_g = C_g^0 \cdot \exp\left(-\lambda \Delta t\right)$$

- This is acceptable if:
  - Small temperature and pressure ranges
  - Non – interacting compounds
  - Well chosen values for λ

Wet deposition from nucleation scavenging

- Nucleation scavenging = material dissolved in the cloud phase
- Only the fraction of the cloud water that forms precipitation, can remove (and hence wet deposit) material!
- Take only freshly formed precipitation water into account for scavenging, or remove only the precipitating fraction of the scavenged material!
- Consideration of cloud processing !

Problems I

- Equilibrium approach:
  - Diffusion limitations for typical droplet size → equilibrium time is often longer than typical model time step
  - Diffusion limitations inside the droplet, e.g. theoretical difference between droplet surface and droplet interior
  - Falling droplets are even further away from equilibrium

  → Correction: Taking the diffusion limitation explicitely into account
  → Time dependent process → mathematically: numerical solution

Problems I

$$k_{mt} = \bar{v} / \left(r \cdot \left(\frac{r}{\lambda} + \frac{4}{3\alpha} \right) \right) \qquad D_g = \frac{\bar{v} \cdot \lambda}{3}$$

Schwartz, 1986

Transfer rate for gaseous compounds into cloud droplets

$$v_t = \frac{D_g}{2r} \cdot \left(2 + 0.6 \sqrt{\frac{2 \cdot r \cdot u}{\nu}} \left(\frac{\nu}{D_g} \right)^{1/3} \right)$$

Frössling, 1938

Transfer rate for gaseous compounds into falling rain droplets

$$k_{\text{exf:f}} = k_{mt} \cdot LWC$$
$$k_{\text{exf:b}} = k_{mt} \cdot H_x$$

Forward and backward “reaction” (=transfer) rates

Problems I

- Equilibrium approach:
  - Diffusion limitations for typical droplet size → equilibrium time is often longer than typical model time step
  - Diffusion limitations inside the droplet, e.g. theoretical difference between droplet surface and droplet interior
  - Falling droplets are even further away from equilibrium

  → Correction: Taking the diffusion limitation explicitely into account
  → Time dependent process → mathematically: numerical solution
- Ideal solution:
  - Highly concentrated solutions do not follow the laws for ideal solutions any more → molecule – molecule – ion interactions

  → Correction: Use of activities instead of concentrations

Problems II

- Clouds and precipitation droplet distribution:
  - Not all droplets have the same size
  - Mean transfer rate is not equal to transfer rate for droplets with mean radius
  - Assumptions of droplet distributions for clouds and precipitation
    - Limited number of points in the distribution for which to calculate the transfer rates
- Relevant for:
  - Cloud and precipitation droplets
  - Trace gases and aerosol particle scavenging

Problems III$_a$

- Aqueous phase chemistry:
  - Equilibrium processes in the liquid phase:
    - Acid base reactions:
      - Dissociation of various compounds:

$$HA \Leftrightarrow H^+ + A^-$$

$$p_i = K_i(p, T) \cdot \chi_i$$

- The uptake of HA is increased due to the dissociation.

Problems IIIa

- Aqueous phase chemistry:
  - Equilibrium processes in the liquid phase:
    - Acid base reactions:
      - Dissociation of various compounds:

$$HA \Leftrightarrow H^+ + A^-$$

$$p_i = K_i(p, T) \cdot \chi_i$$

- The uptake of HA is increased due to the dissociation.

$$HA \Leftrightarrow H^+ + A^-$$
$$HB \Leftrightarrow H^+ + B^-$$

- The system is modified to a coupled system, depending on the H+ concentration

Problems IIIa

- Replacement of $K_i(p,T)$ by an effective Henry coefficient, which takes dissociation into account.

$$p_i = K_i^{eff}(p,T) \cdot \chi_i$$

  - Requires dissociation constants
  - Requires a fixed pH value

$$HA \Leftrightarrow H^+ + A^-$$

  - Treatment as an uncoupled system

Problems IIIb

- Aqueous phase chemistry:
  - Irreversible Redox chemistry in the liquid phase:
    - e.g. S(IV) oxidation:

$$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O$$

$$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-}$$

$$H_2SO_4 \Leftrightarrow H^+ + HSO_4^-$$

$$H_2SO_4(g) \Leftrightarrow H_2SO_4$$

$$SO_2 + H_2O \Leftrightarrow H^+ + HSO_3^-$$

$$SO_2(g) \Leftrightarrow SO_2$$

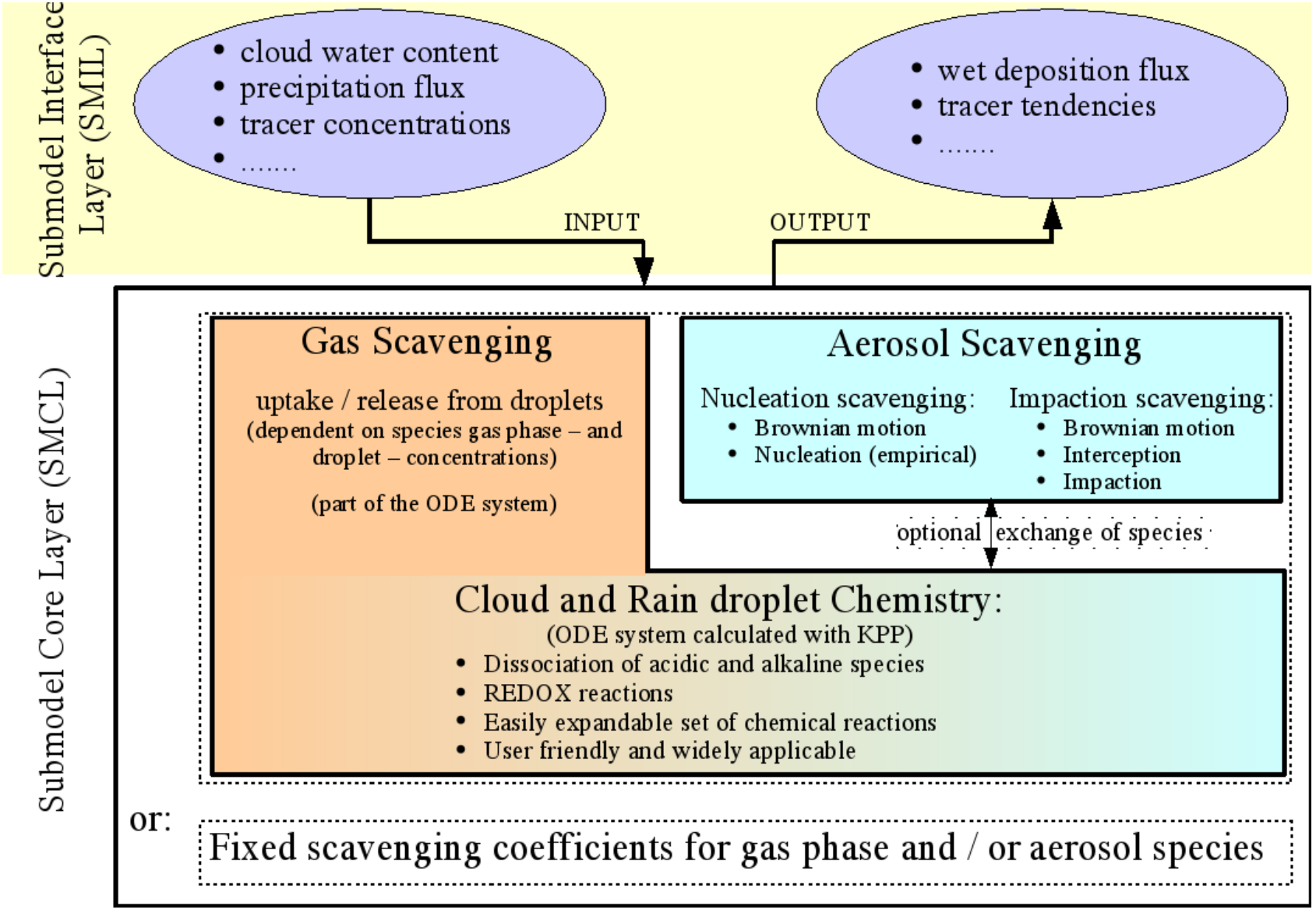
$$H_2O_2(g) \Leftrightarrow H_2O_2$$

$$p_i = K_i(p, T) \cdot \chi_i$$

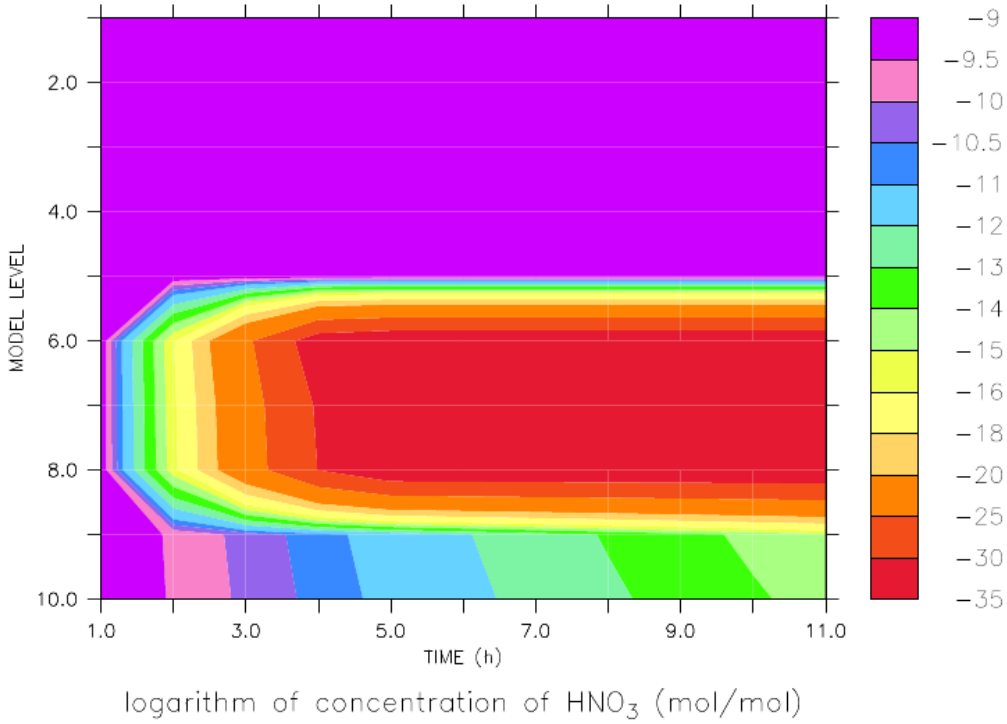
Problems IIIb

- Aqueous phase chemistry:
  - Explicit treatment of aqueous phase chemistry
  - Set of coupled differential equations including the interactions (= reactions) of all compounds in the aqueous phase
  - Computationally expensive
  - Interactive pH calculation
  - Combination of aerosol and gaseous material in the cloud / precipitation phase

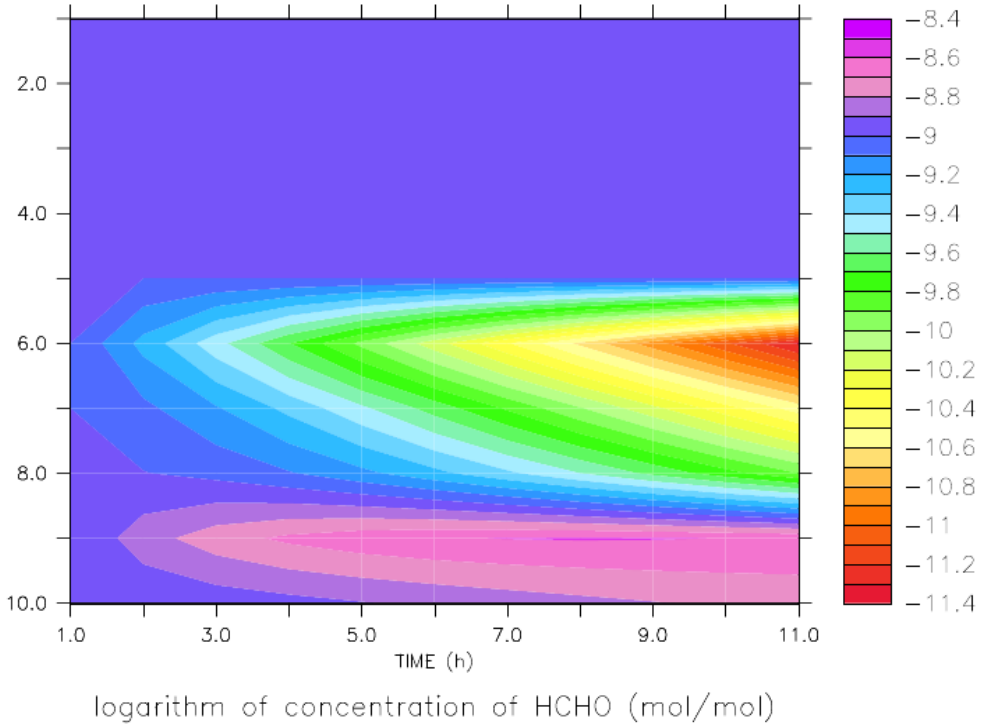
Problems IIIb



Problems IIIb



Two examples of 1D aqueous phase chemistry modelling



Aerosol scavenging

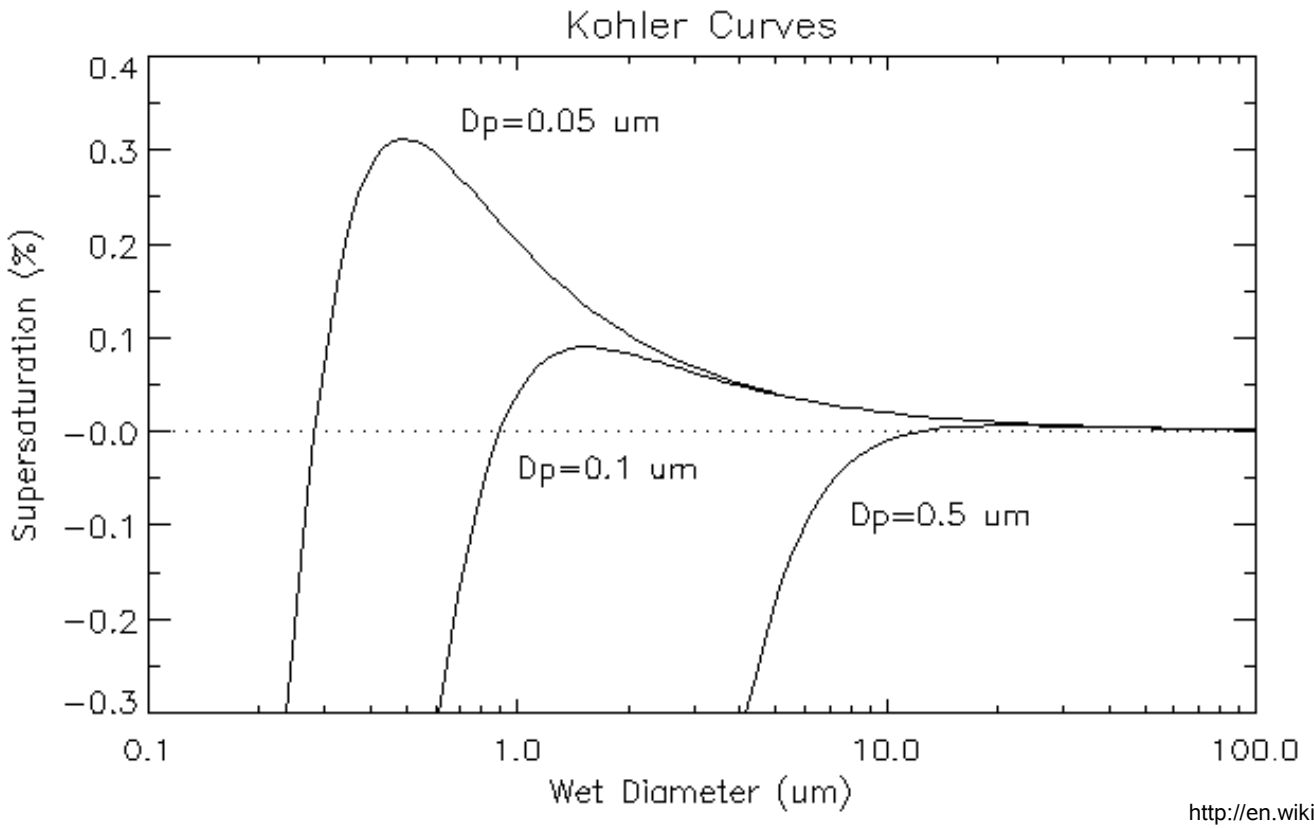
- Different aspects for aerosols than for gaseous compounds:
  - Nucleation scavenging
    - Activation of aerosols into cloud droplets
    - Diffusion of aerosols into cloud droplets
  - Impaction scavenging:
    - Capturing of aerosols by falling hydrometeors (in the streamline flow)
    - Diffusion of aerosol particles into the falling hydrometeors

"Blue" processes also relevant for gas phase

Aerosol activation

- Köhler – Equation:

$$\ln\left(\frac{p_w(D_p)}{p^0}\right) = \frac{4 M_w \sigma_w}{R T \rho_w D_p} - \frac{6 n_s M_w}{\pi \rho_w D_p^3}$$

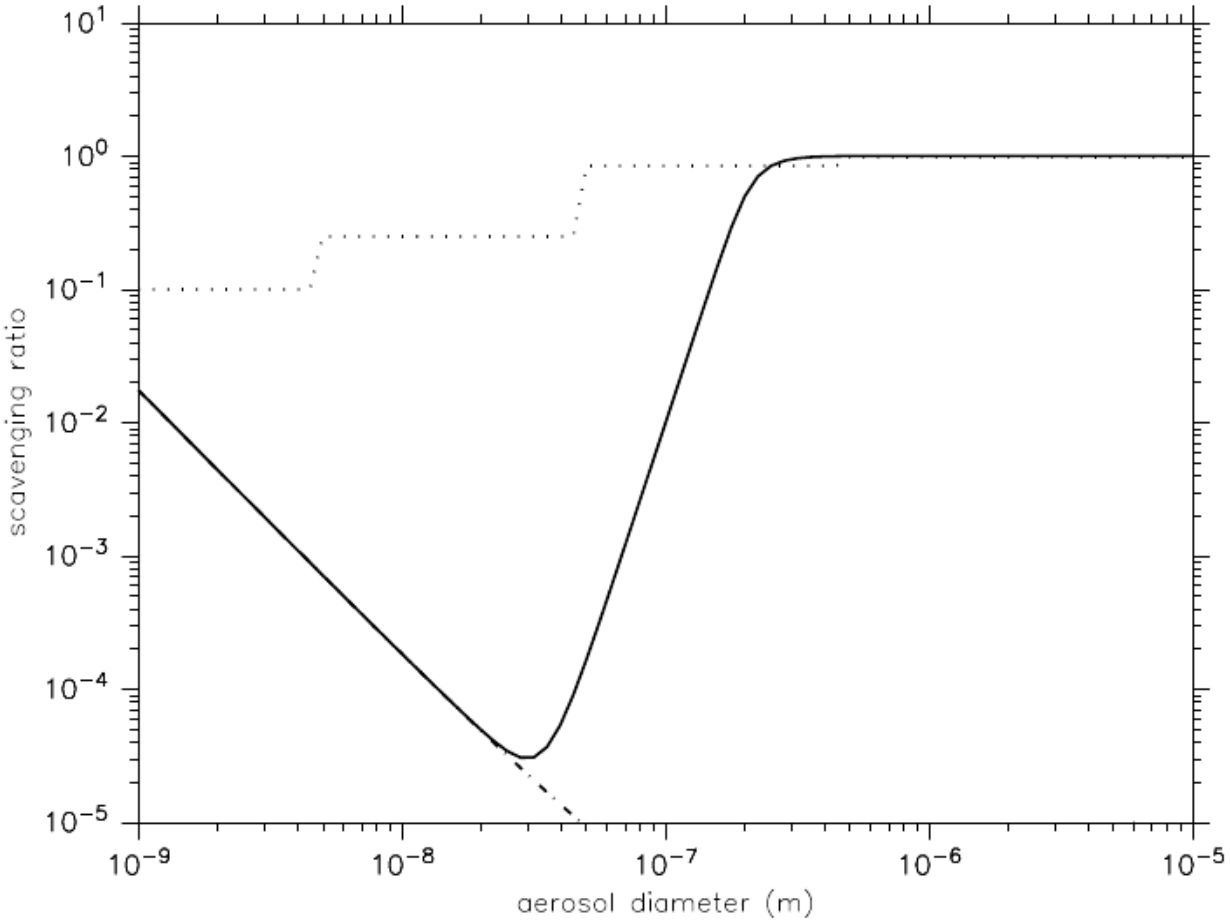


http://en.wikipedia.org/wiki/Köhler_theory

Aerosol activation

- Practically, this means that aerosols activate (=are nucleation scavenged) after reaching a critical size, which depends on their chemical composition
- Sophisticated models with aerosol – cloud interactions calculate explicitely the fraction of activated aerosols, since it determines the number of cloud droplets.
- Simplified models often use a constant fraction of aerosols assumed to be activated and hence nucleation scavenged.
- Intermediate complexity: a function depending on aerosol size, e.g. empirically fitted.

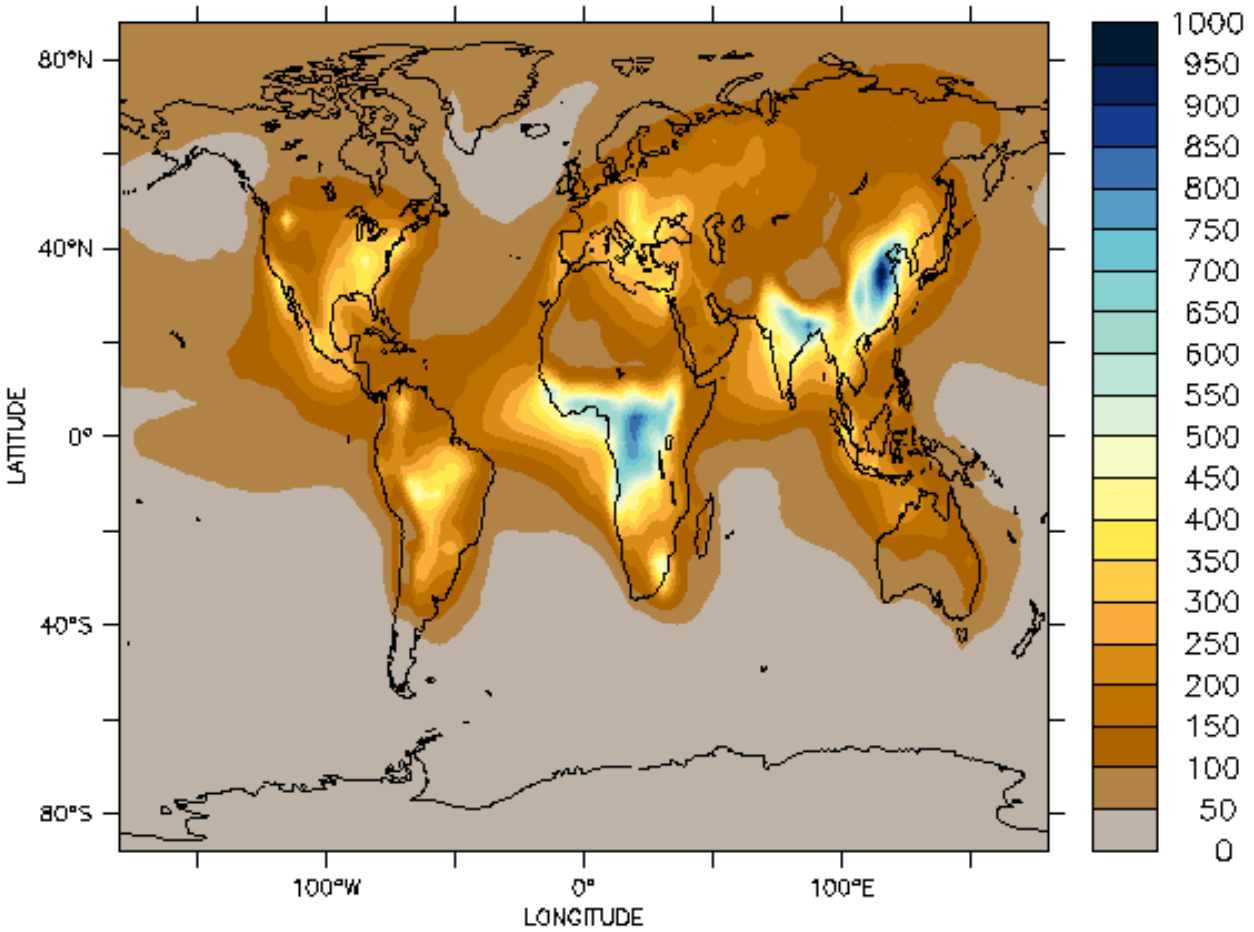
Aerosol activation



Tost et al., ACP, 2006

Empirically fitted schemes for aerosol nucleation scavenging

Activated Aerosols at PBL height with 0.4 % supersaturation



CCN (0.4% S_{sat}) at boundary layer height (cm^{-3})

Annual average value

Tost et al., ACPD, 2012

Aerosol Impaction Scavenging

- Various physical processes to be parameterised:
  - Diffusion
  - Interception
  - Inertia
  - Electrical charges
  - Thermophoresis
- Results in an overall collection efficiency

Aerosol Impaction Scavenging

$$E = \frac{4}{ReSc}(1 + 0.4Re^{1/2}Sc^{1/3} + 0.16Re^{1/2}Sc^{1/2}) +$$

Diffusion

$$4\Phi(\omega^{-1} + (1 + 2Re^{1/2})\Phi) +$$

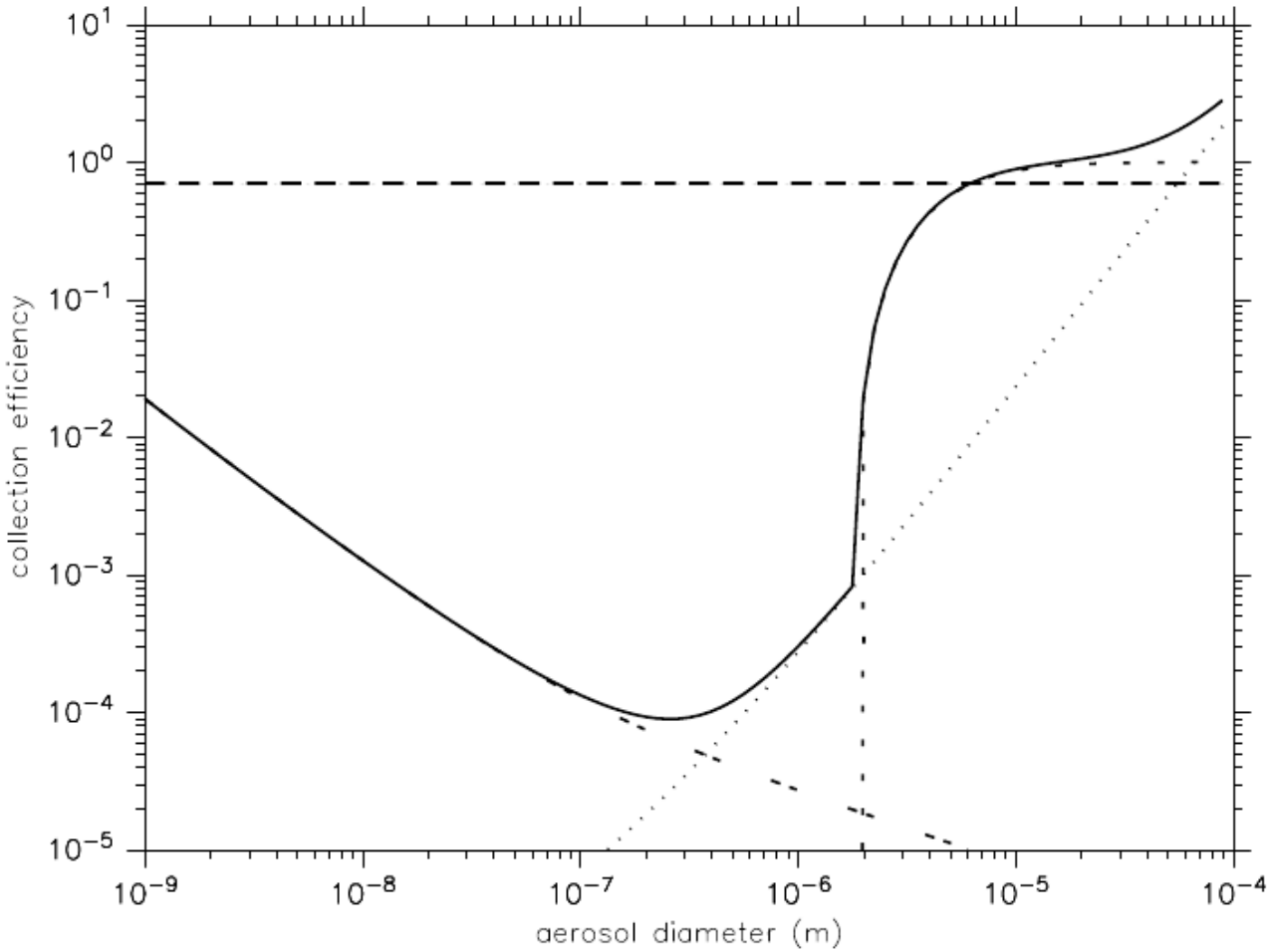
Interception

$$\left(\frac{St - S^*}{St - S^* + 2/3}\right)^{3/2}$$

Inertia

$$S^* = \frac{1.2 + \frac{1}{12}\ln(1 + Re)}{1 + \ln(1 + Re)}$$

Aerosol Impaction Scavenging

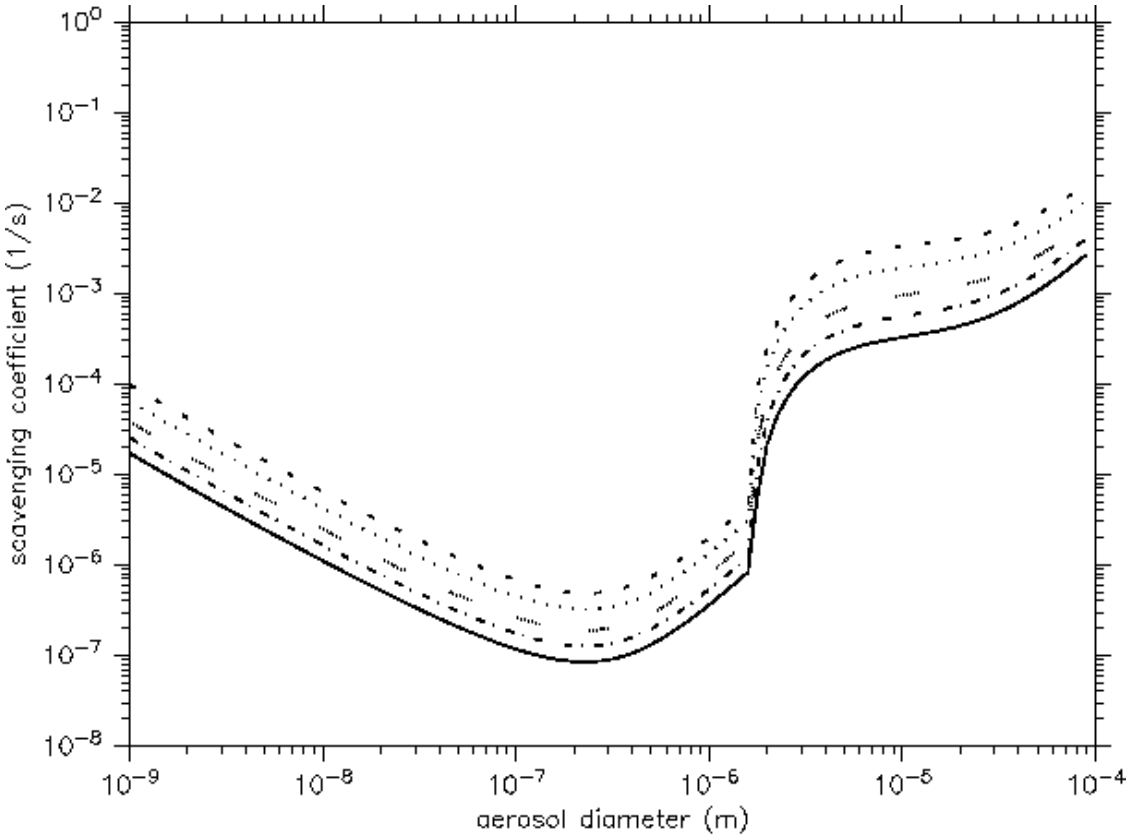


Tost et al., ACP, 2006

From collection to scavenging efficiency

$$\Lambda = \frac{E}{r_{\text{rain}}} \cdot 0.75 \cdot F_{\text{rain}}$$

For various rain rates this results in different scavenging coefficients Λ.



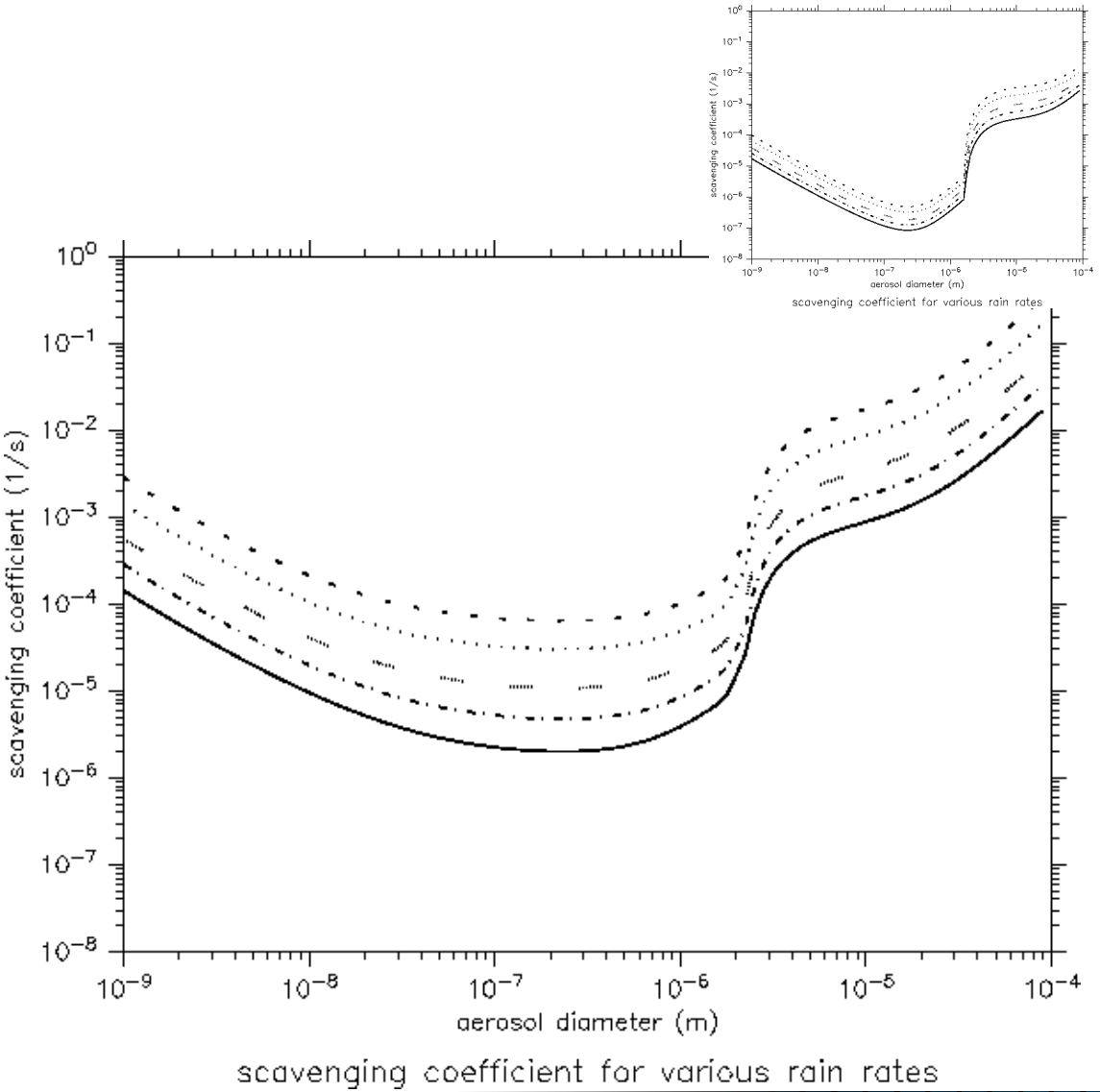
scavenging coefficient for various rain rates

$$C(t_0 + \Delta t) = C(t_0) \cdot \exp(-\Lambda_B \cdot \Delta t)$$

From collection to scavenging efficiency

Using a rain drop distribution (for the rain rates) this changes the picture.

For various rain rates this results in different scavenging coefficients Λ.



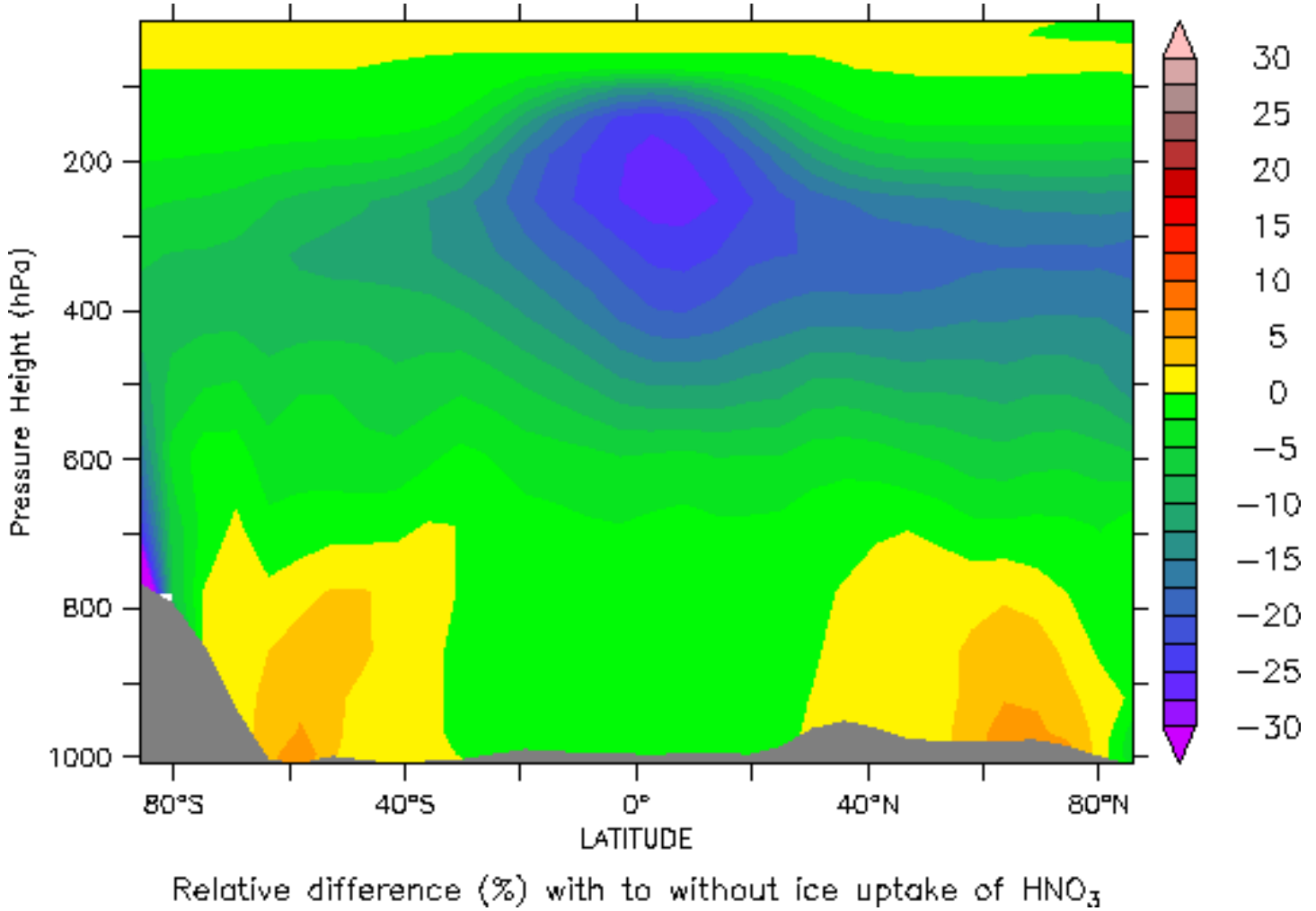
$$C(t_0 + \Delta t) = C(t_0) \cdot \exp(-\Lambda_B \cdot \Delta t)$$

The big “unkown”
The Ice Phase

Scavenging by the ice phase

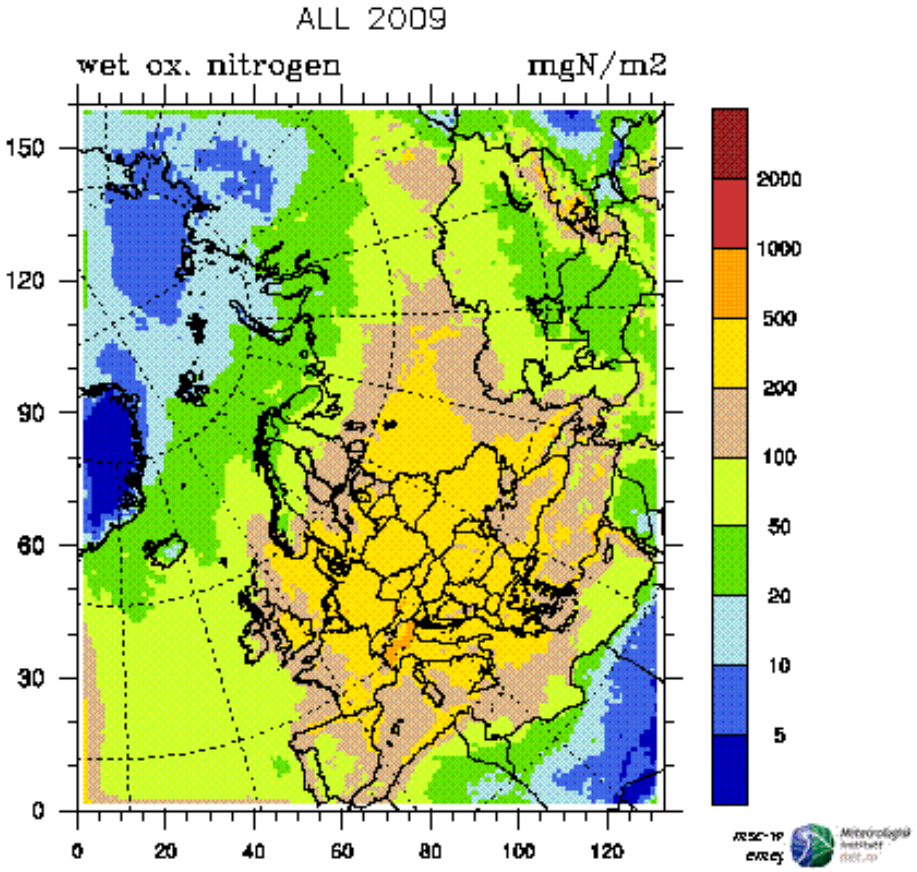
- Higher uncertainty
  - Less data
  - Complex structures of crystals
  - Ice changes structures depending on temperature range
  - Scavenging depends on the freezing type
  - Some compounds stay in the hydrometeors during freezing others are driven into the gas phase

HNO3 uptake by the ice phase



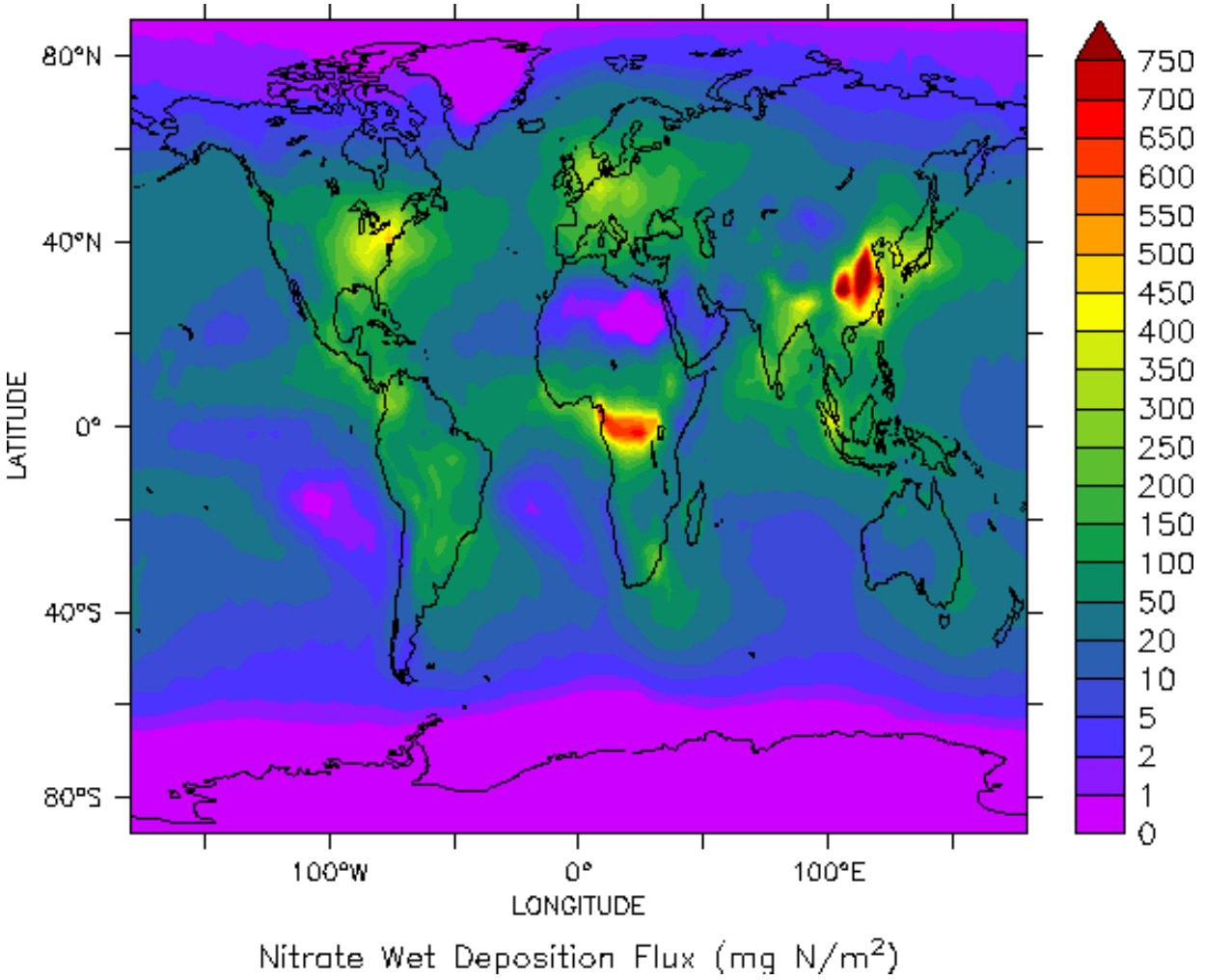
Model applications

EMEP nitrogen wetdeposition

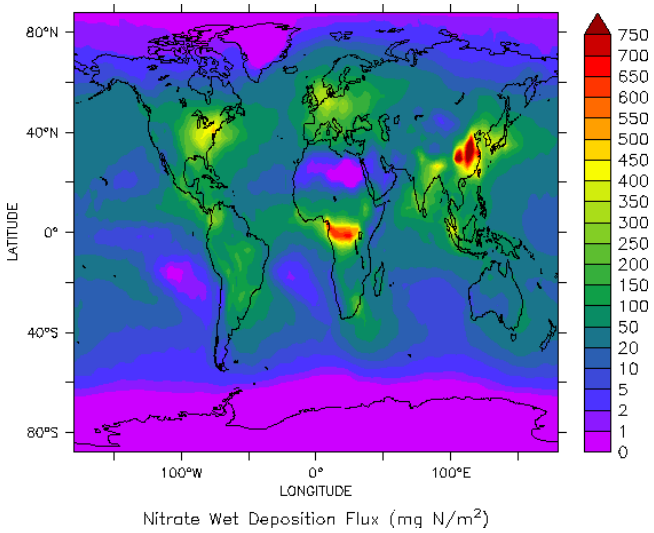


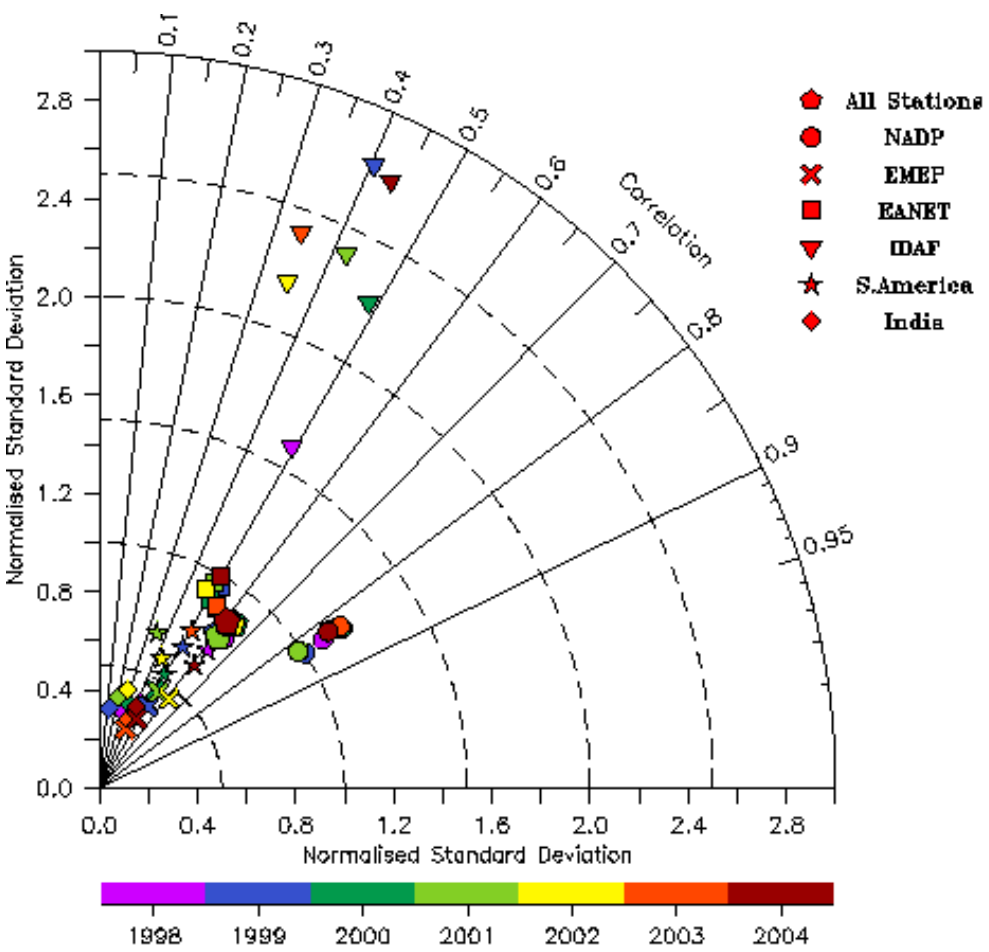
From http://webdab.emep.int/Unified_Model_Results/

Global NOy wet deposition modelling

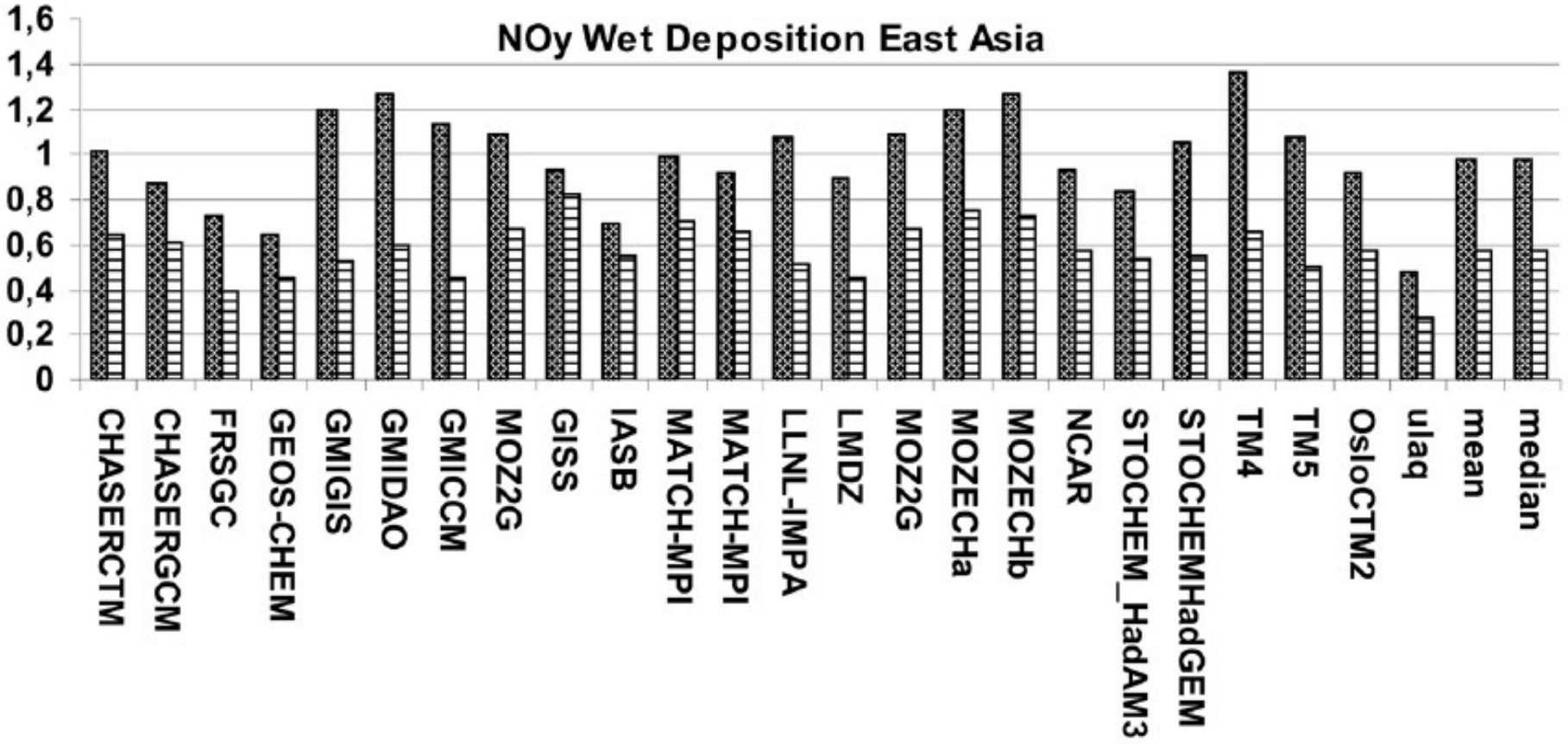


Global NOy wet deposition modelling





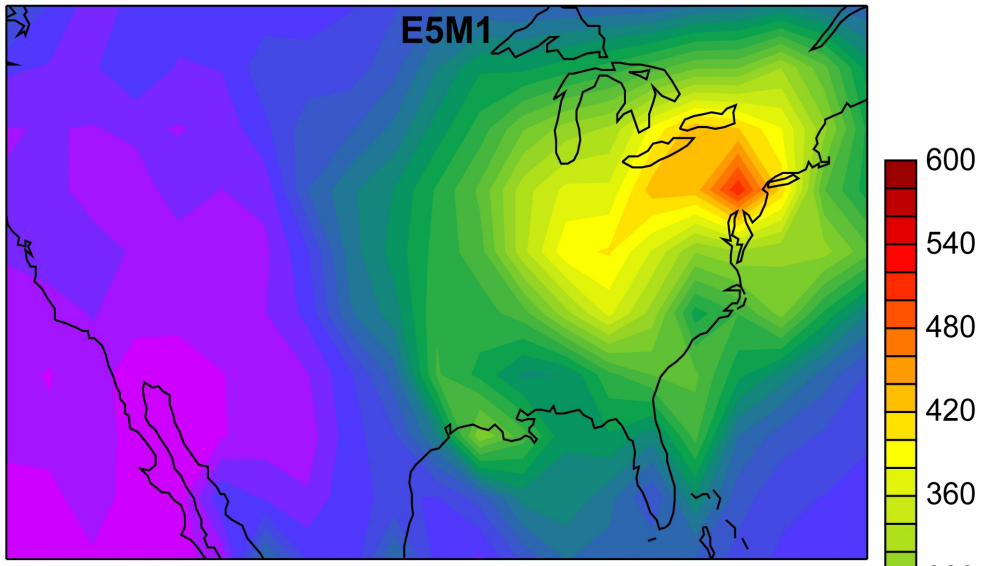
Models differ substantially in wet deposition

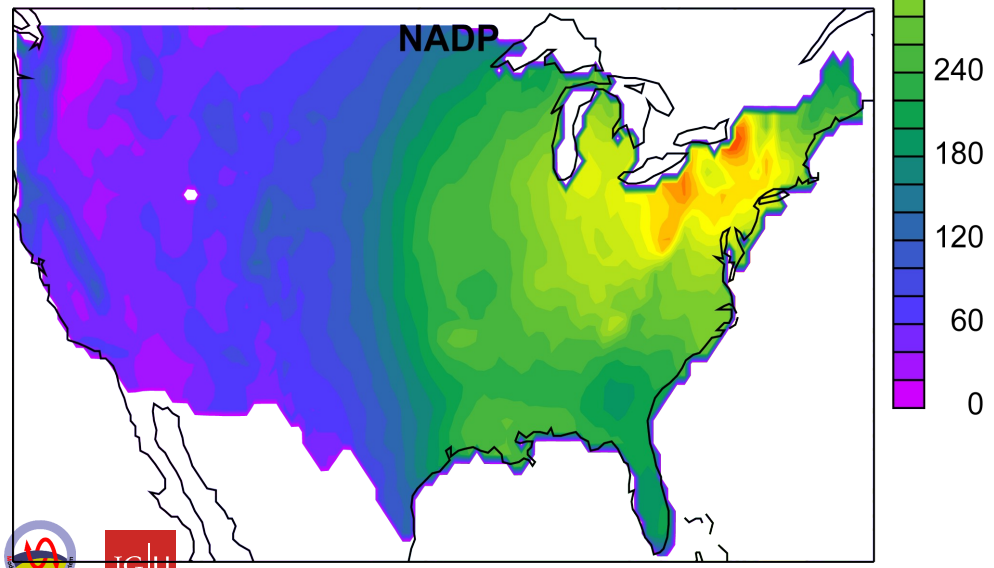


(Dentener et al., GBC, 2006)

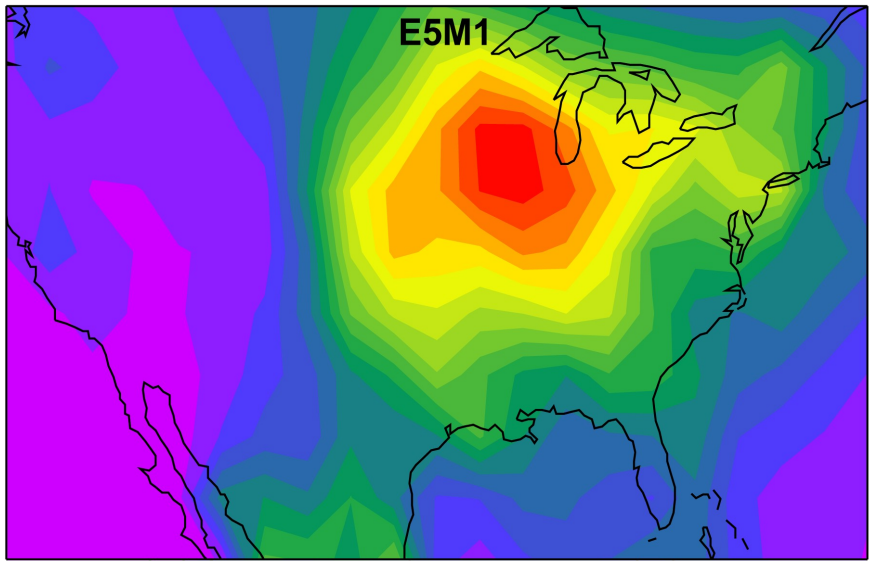
N wet deposition in the USA

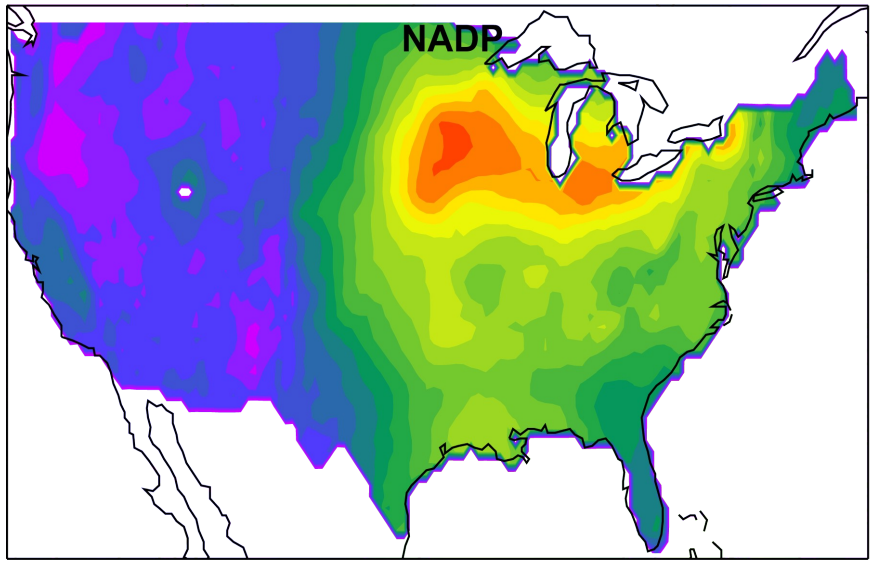
Annual nitrate wet deposition flux (mg N/m²)

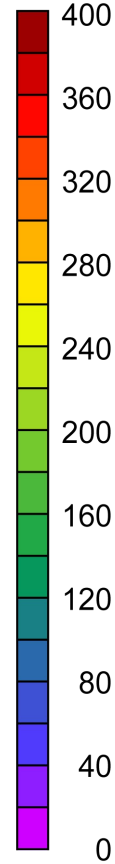




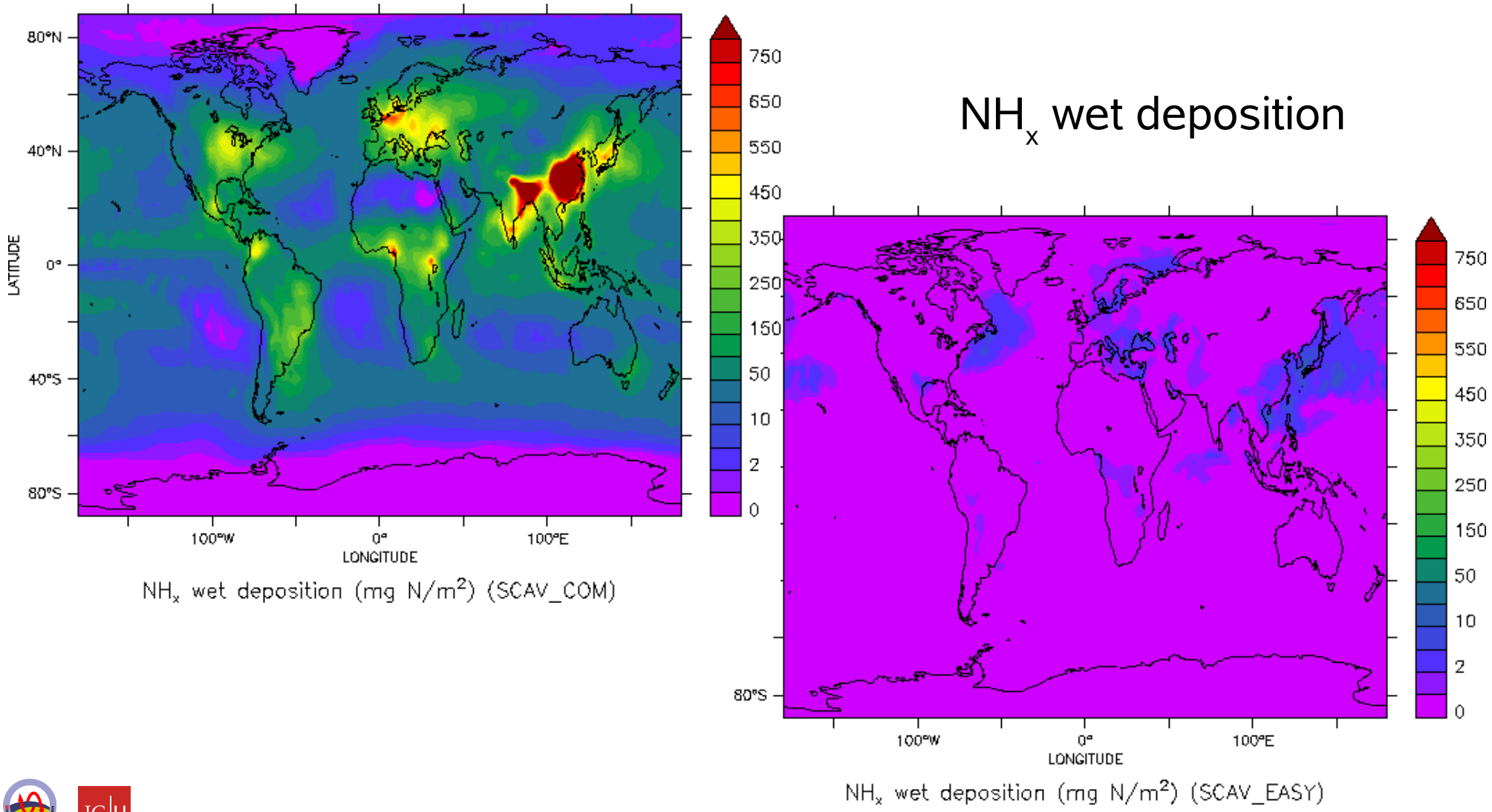
Annual ammonium wet deposition flux (mg N/m²)



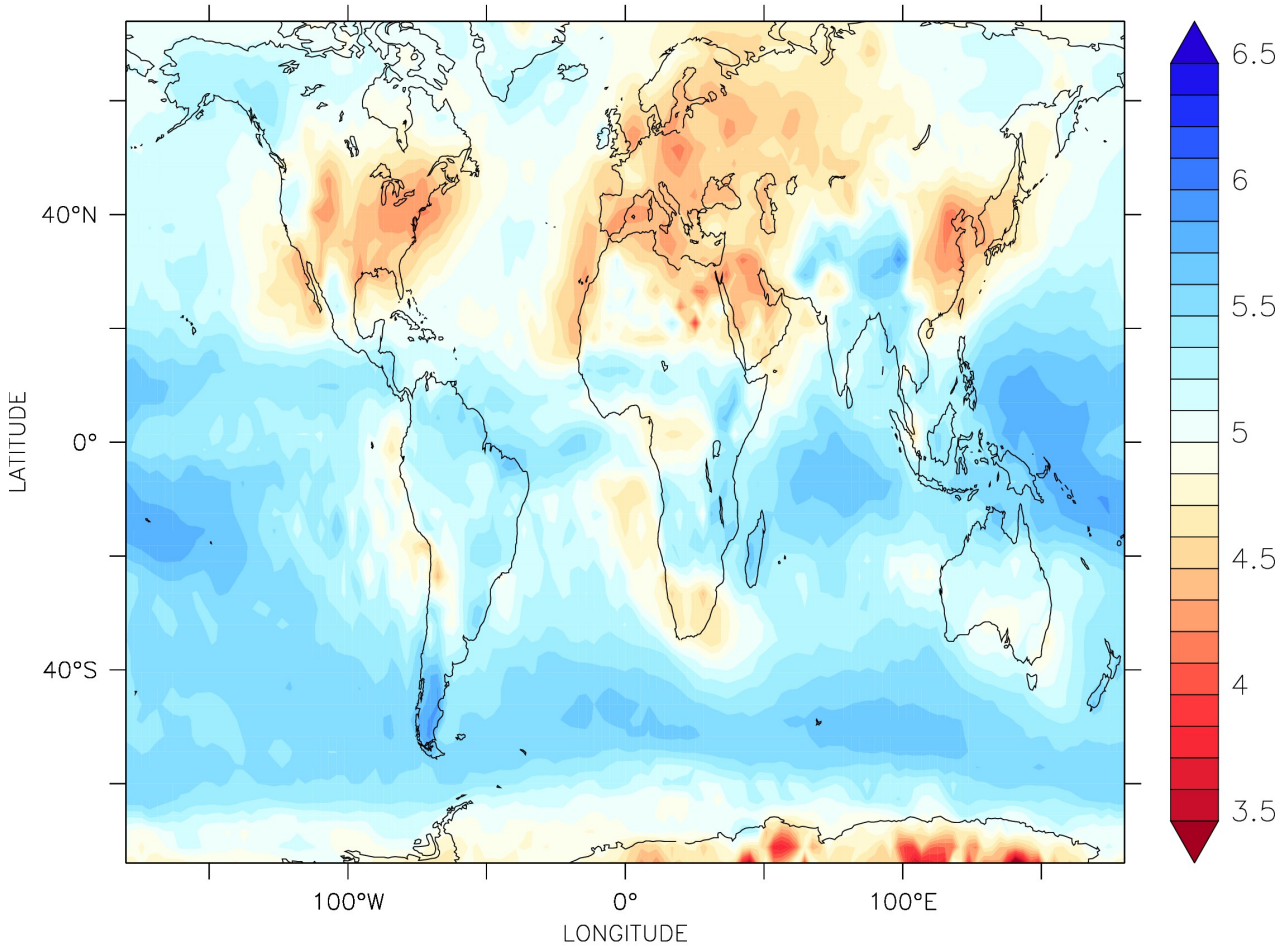




The importance of dissociation

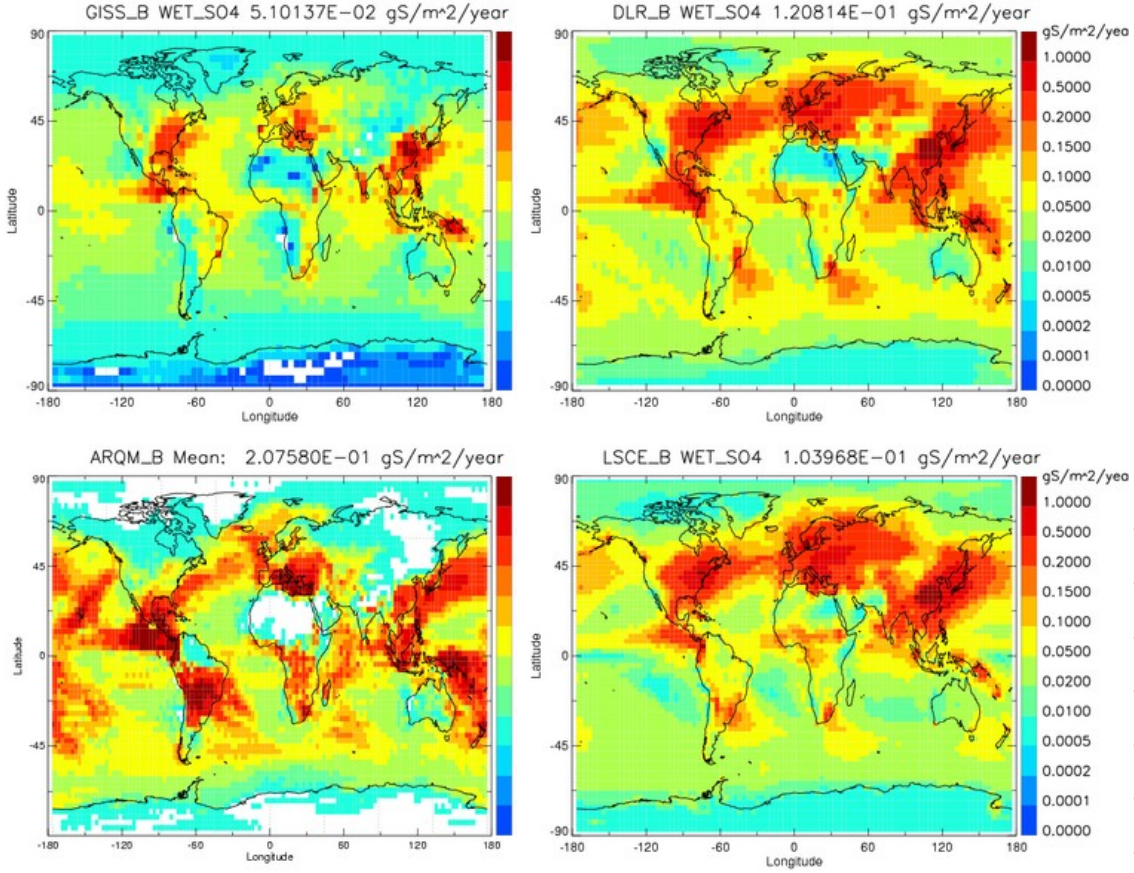


Precipitation pH



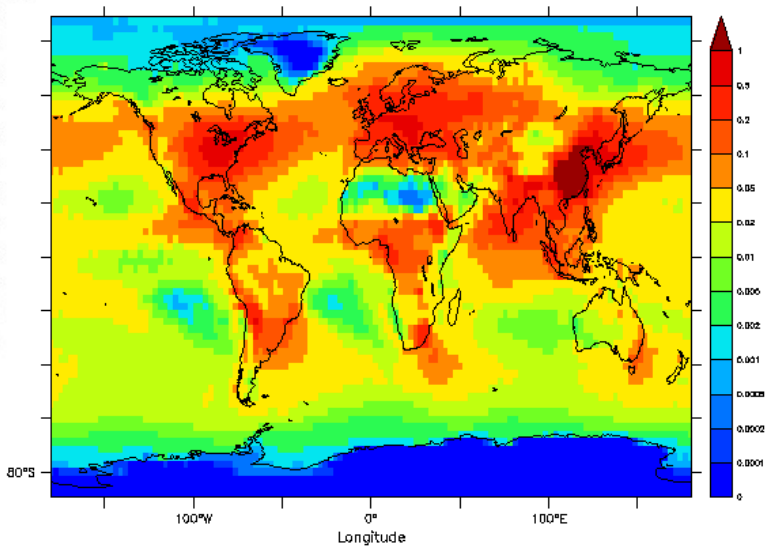
pH value of precipitation

Sulphate wet deposition



AEROCOM web site

ECHAM5/MESSy



Mean sulphate wet deposition flux (g S/(m^2 yr))

Summary

- Gaseous compounds follow Henry's law for solubility.
- Aerosol scavenging is based on physical processes (activation, impaction).
- Wet deposition is complicated due to many processes involved.
- Global modelling can take some into account, but current models treat wet deposition with a wide range of complexity.
- The ice phase is still hot topic of investigation.