Aerosols in Enviro-HIRLAM

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Todays programme

Aerosols
Feedbacks1
Feedbacks2
Exercises

Definitions

An aerosol is a *dispersion of solid and liquid particles suspended in gas*

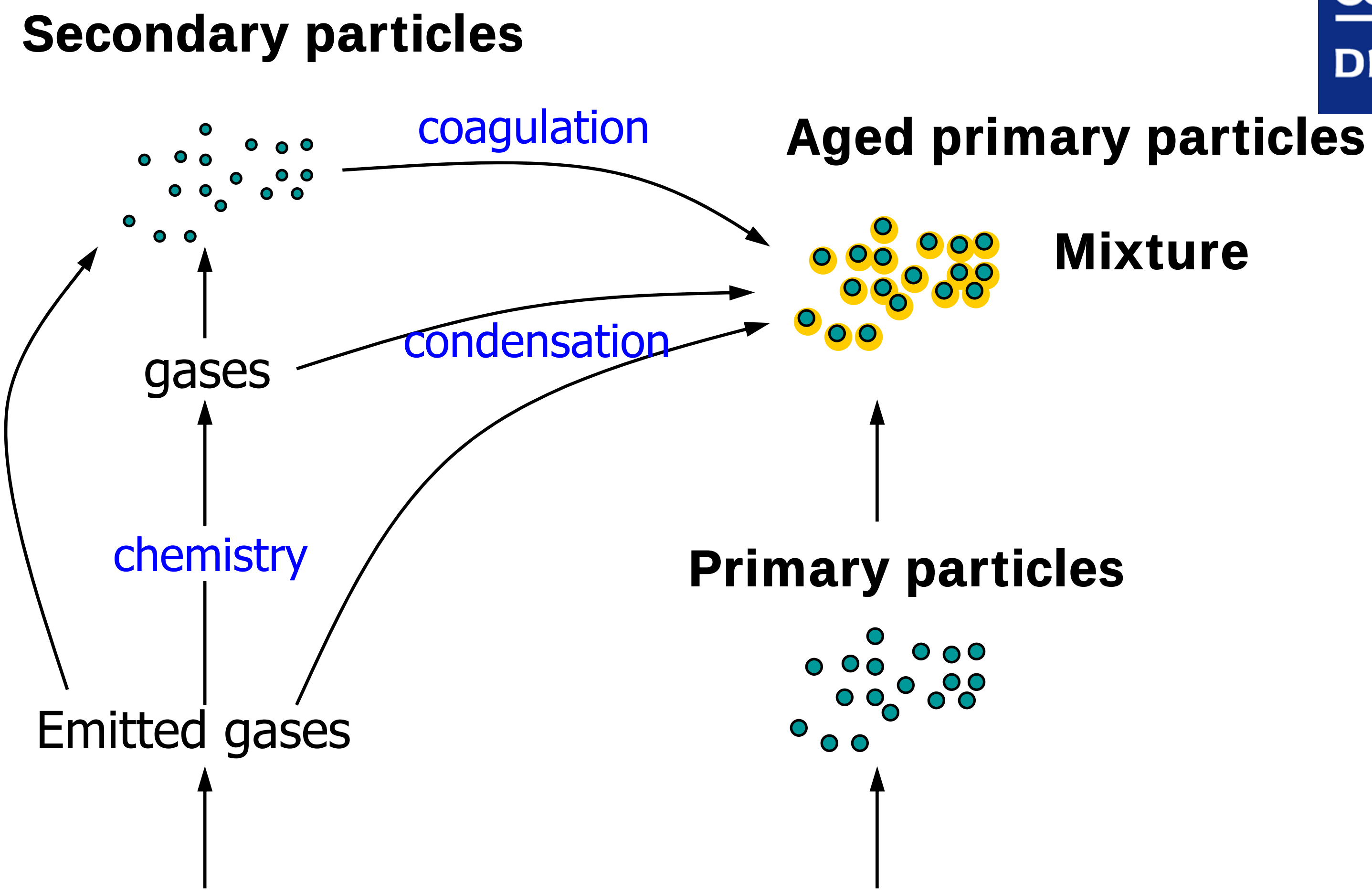
Primary particles are emitted *directly into the atmosphere*

Secondary particles are *formed in the atmosphere*

The distribution and properties of aerosols is described by:

- Spatial distribution
- Mass, number and size distribution
- Composition

Sources of aerosols



Secondary particles

coagulation

Aged primary particles

Mixture

gases

condensation

chemistry

Primary particles

Emitted gases

Carslaw, ISSAOS, 2008

Sources of aerosols

Both *natural* and *anthropogenic* sources

Primary: ***Dust*** (including re-suspended), combustion products of ***elemental and organic carbon*** (biomass burning, wildfires, vehicles), ***sea spray***, primary ***biological particles*** (spores, etc)

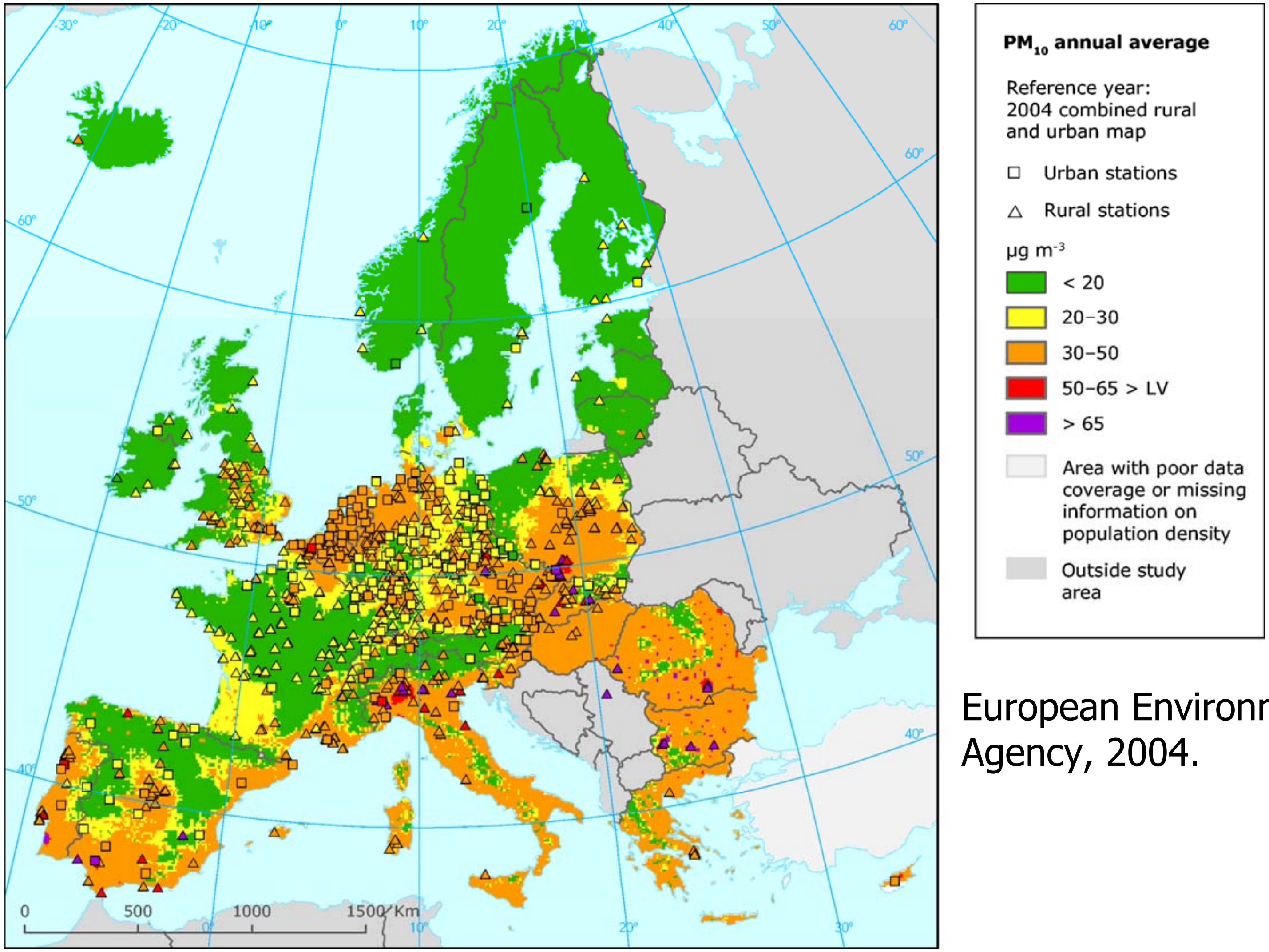
Secondary: Ammonia → ***ammonium*** (dissolution)

SO_2, Dimethyl sulfide → oxidation → ***sulfate*** (H_2SO_4)

Nitrogen oxides → oxidation → ***nitrate*** (HNO_3)

Volatile organic compounds (VOCs) -> oxidation -> low vapor pressure organic products ***(secondary organic aerosol, SOA)***

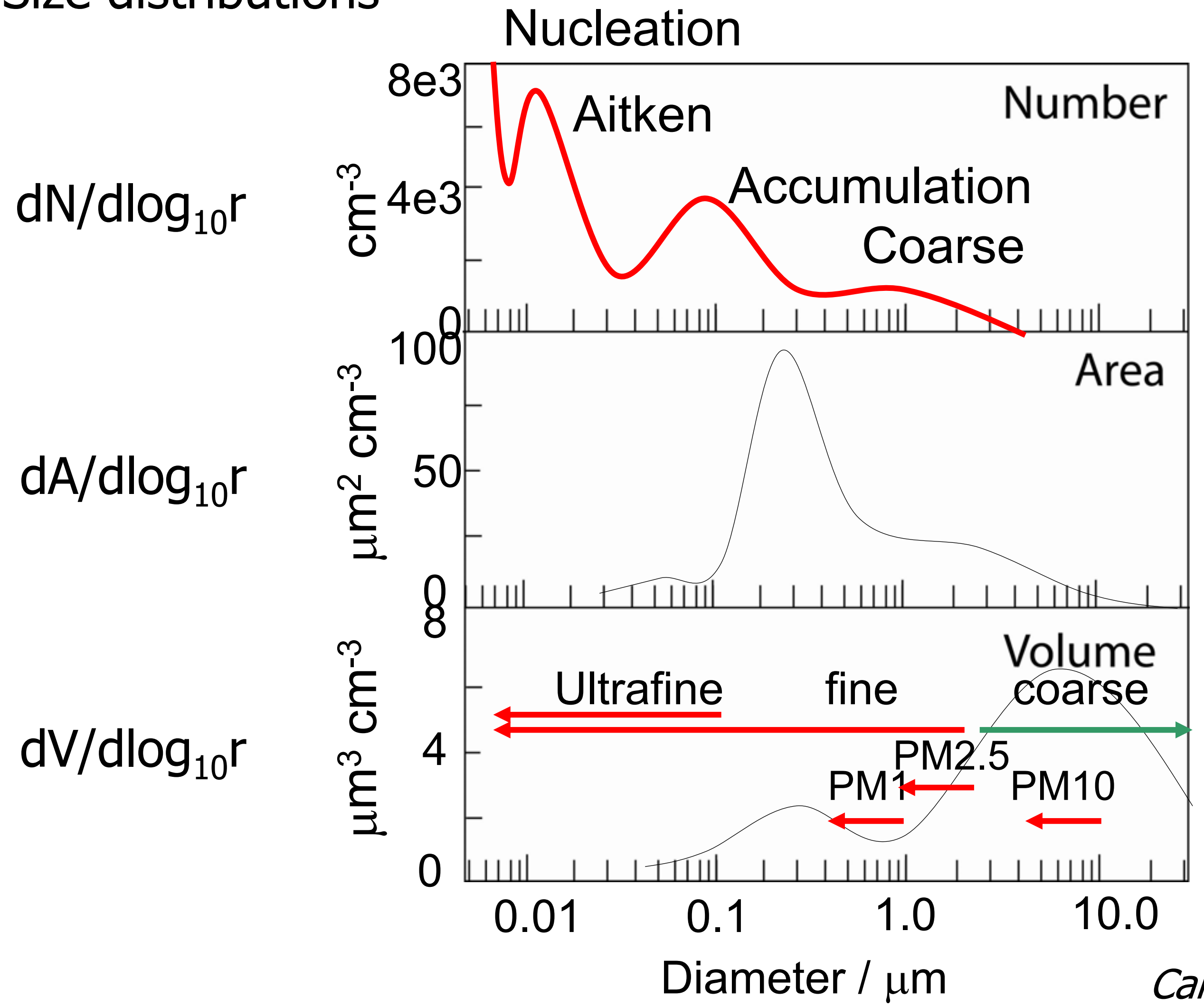
Annual average particulate mass less than 10 µm



European Environmental Agency, 2004.

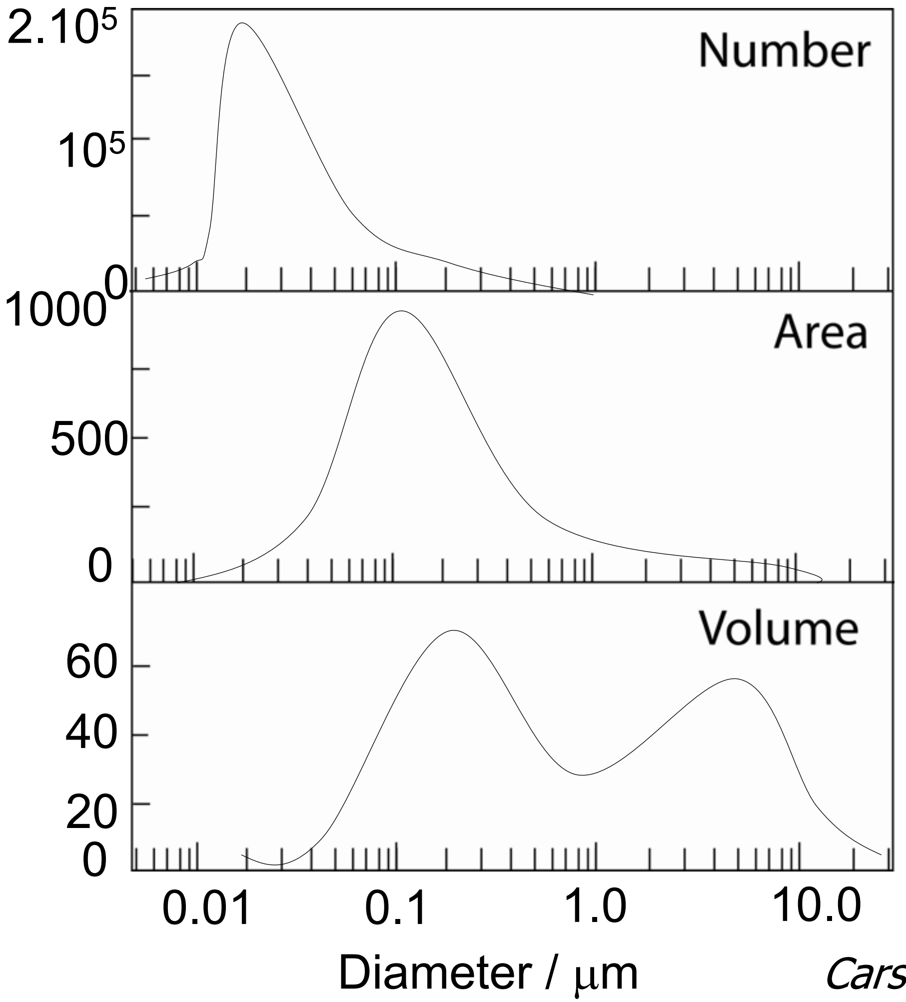
	Number concentration (cm^{-3})	$PM_{2.5}$ mass concentration ($\mu g\ m^{-3}$)	PM_{10} mass concentration ($\mu g\ m^{-3}$)
Urban	10^5 - $4x10^6$	8 - 100	30 - 300
Polluted continental	$2x10^3$ - 10^4	2 - 8	10 - 40
Remote continental	50 - 10^4	0.5 - 2.5	2 - 10
Marine	100 - 400	1 - 4	10

Size distributions



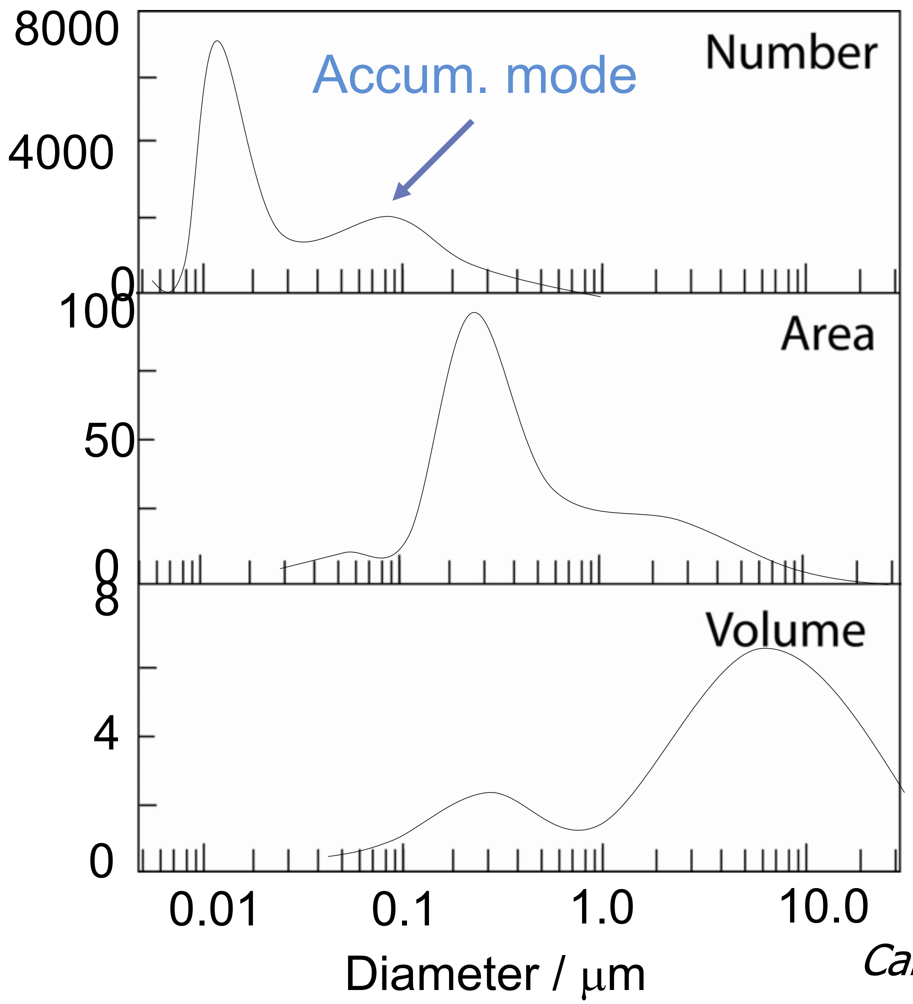
Carslaw, ISSAOS, 2008

Size distributions: Urban



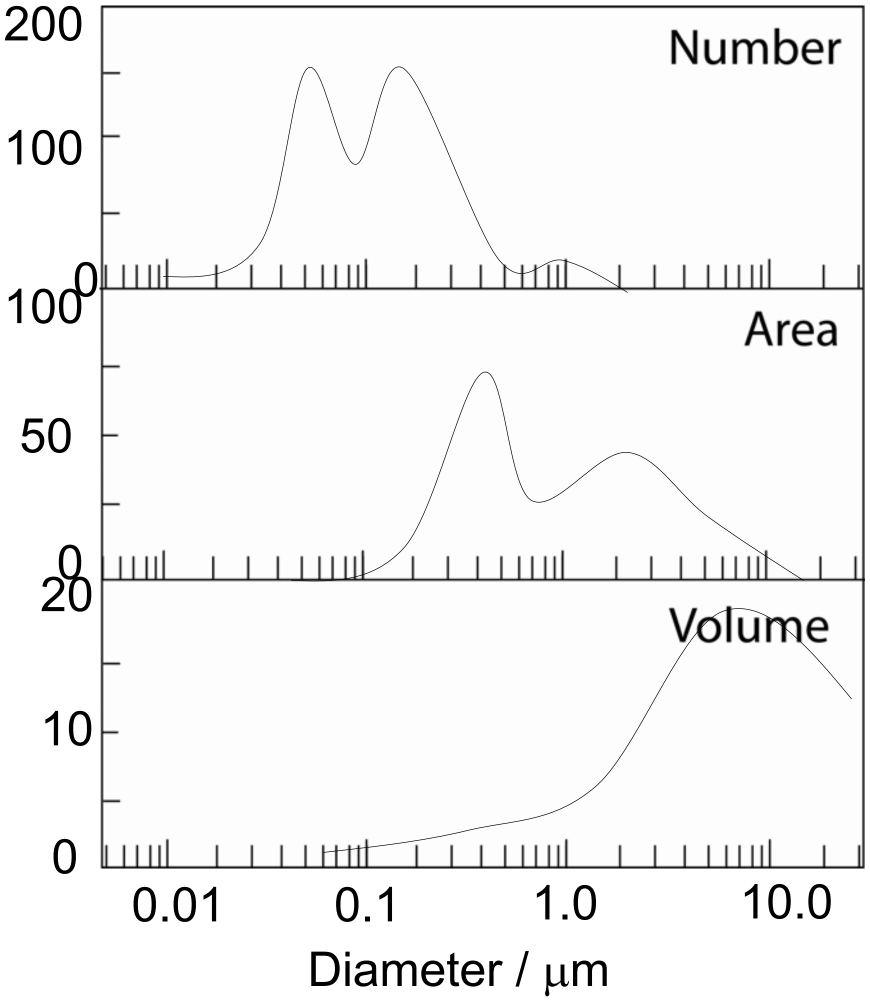
Carslaw, ISSAOS, 2008

Size distributions: Polluted continental

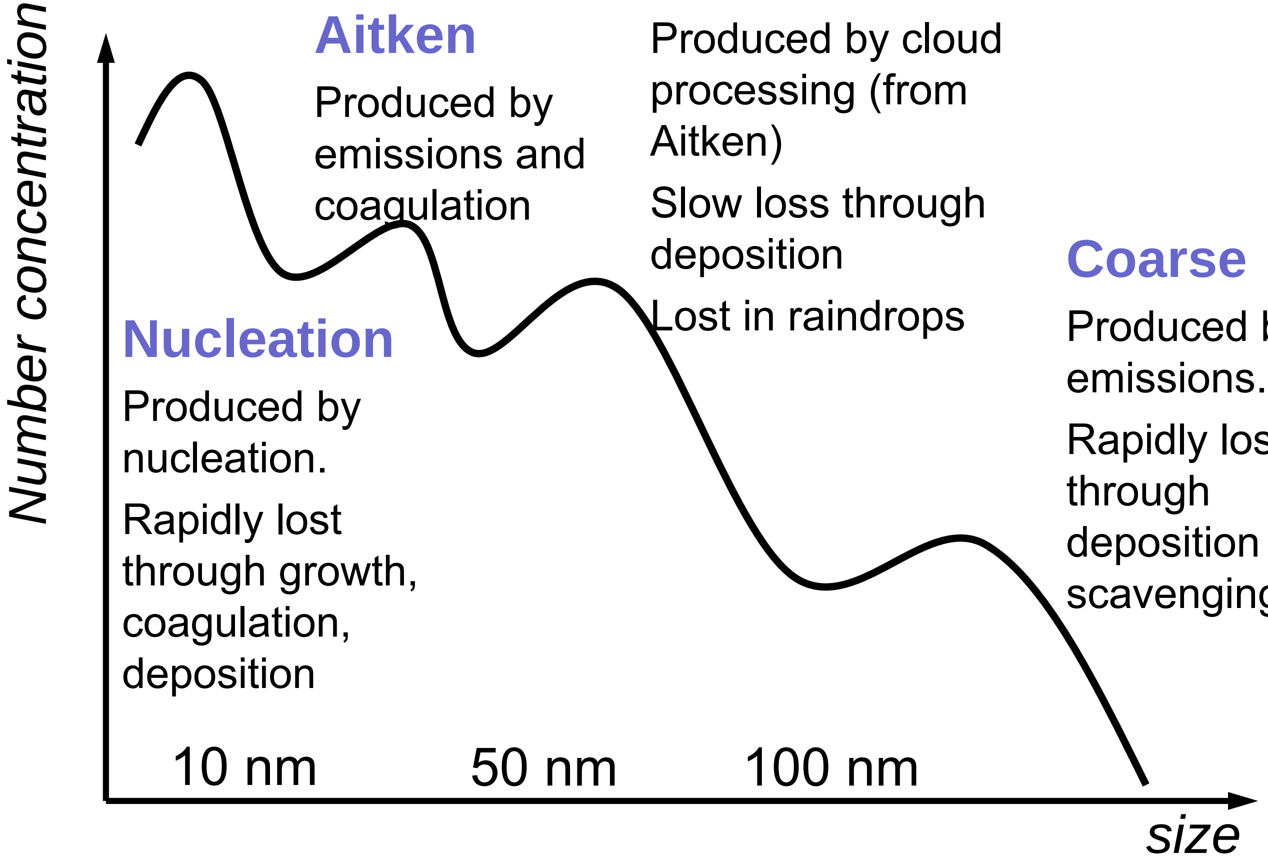


Carslaw, ISSAOS, 2008

Size distributions: Marine



Heintzenberg et al., Tellus, Ser. B, 52B, 1104–1122, 2000.



Nucleation

Produced by nucleation.

Rapidly lost through growth, coagulation, deposition

Aitken

Produced by emissions and coagulation

Accumulation

Produced by cloud processing (from Aitken)

Slow loss through deposition

Lost in raindrops

Coarse

Produced by emissions.

Rapidly lost through deposition and scavenging

Carslaw, ISSAOS, 2008

Aerosol composition

FINE

H, NH_4, SO_4, NO_3

Organic carbon

Elemental carbon

Metals

(Fe, Pb, Cd, V, Zn etc)

COARSE

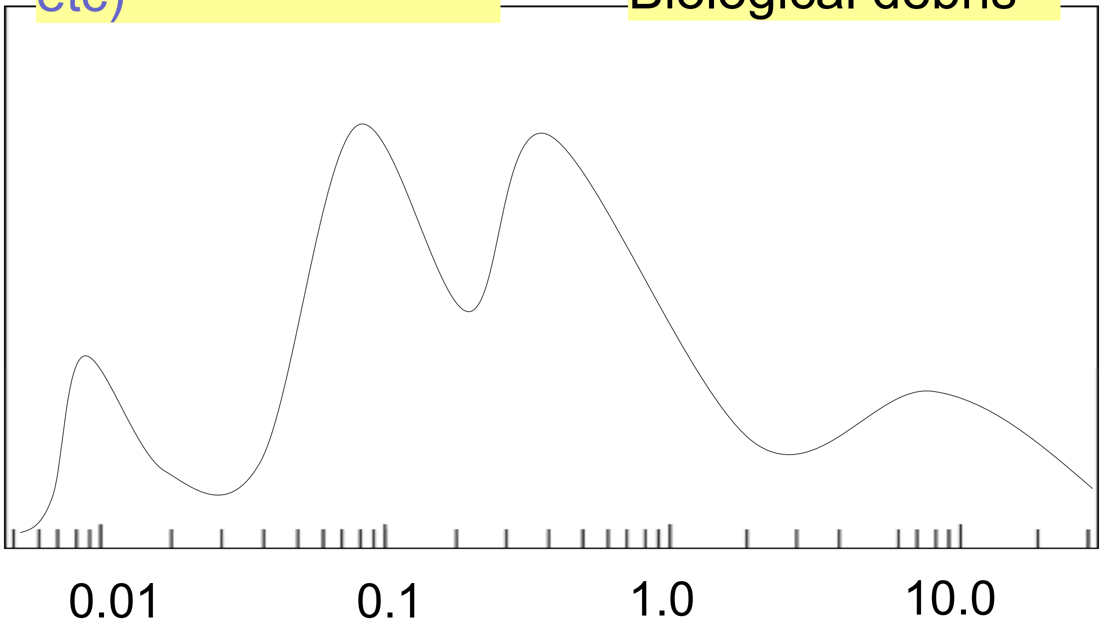
Dust ($CaCO_3$, Mg, Si, Al, Fe)

Coal dust

NaCl

Pollen, spores

Biological debris

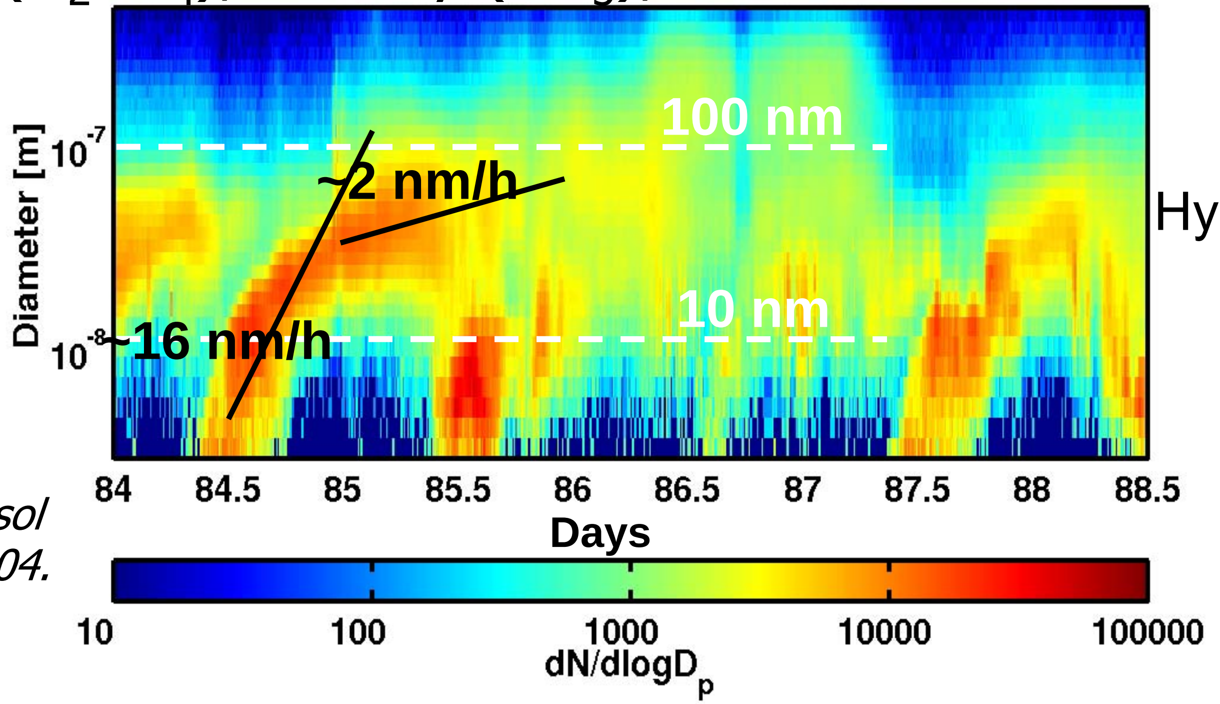


Carslaw, ISSAOS, 2008

Aerosol processes of importance

Nucleation:

- Formation of new particles through gas-to-particle conversion
- Occurs in almost every part of the atmosphere
- Binary (H_2SO_4), ternary (NH_3), ion-induced



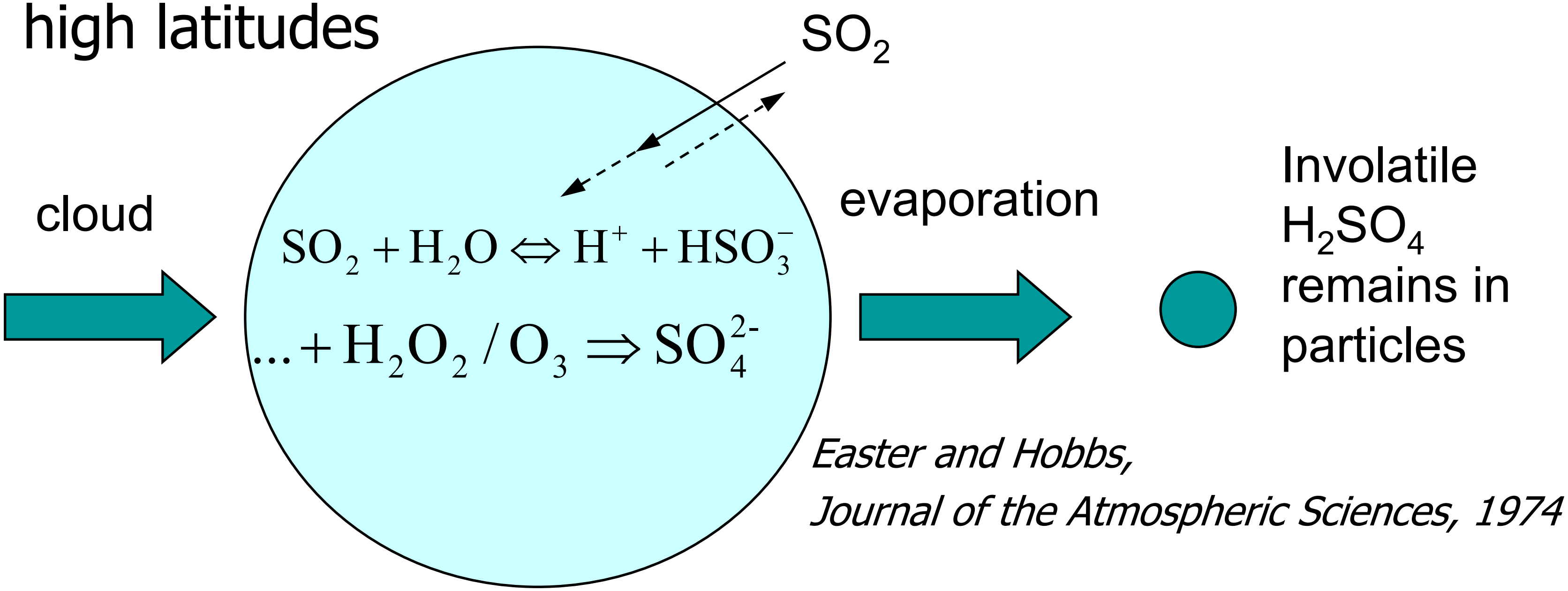
Hyytiälä, Finland

Kulmala, et al., Journal of Aerosol Science, 35, 2004.

Aerosol processes of importance

Cloud processing

- $SO_2 + H_2O_2 \rightarrow SO_4$ dominates in summer
- $SO_2 + O_3 \rightarrow SO_4$ dominates in winter and high latitudes



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

$$\ldots + H_2O_2 / O_3 \Rightarrow SO_4^{2-}$$

Involatile H_2SO_4 remains in particles

Easter and Hobbs, Journal of the Atmospheric Sciences, 1974

Carslaw, ISSAOS, 2008

Aerosol processes of importance

Aerosol ageing

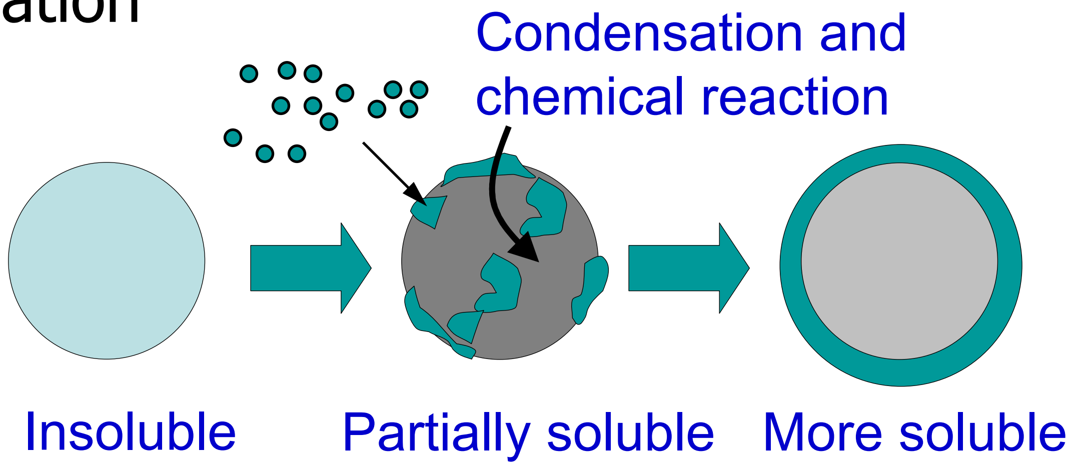
Some primary particles are initially insoluble

They become partly soluble through

(1)Coagulation

(2)Chemical transformation

(3)Condensation

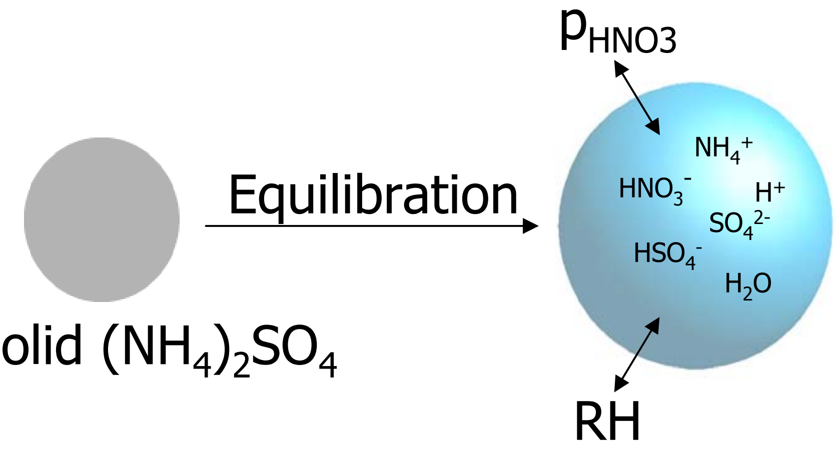


Carslaw, ISSAOS, 2008

Aerosol processes of importance

Equilibration

Gaseous H_2O, HNO_3



p_{HNO3}

Equilibration

Solid $(NH_4)_2SO_4$

NH_4^+

HNO_3^-

H^+

SO_4^{2-}

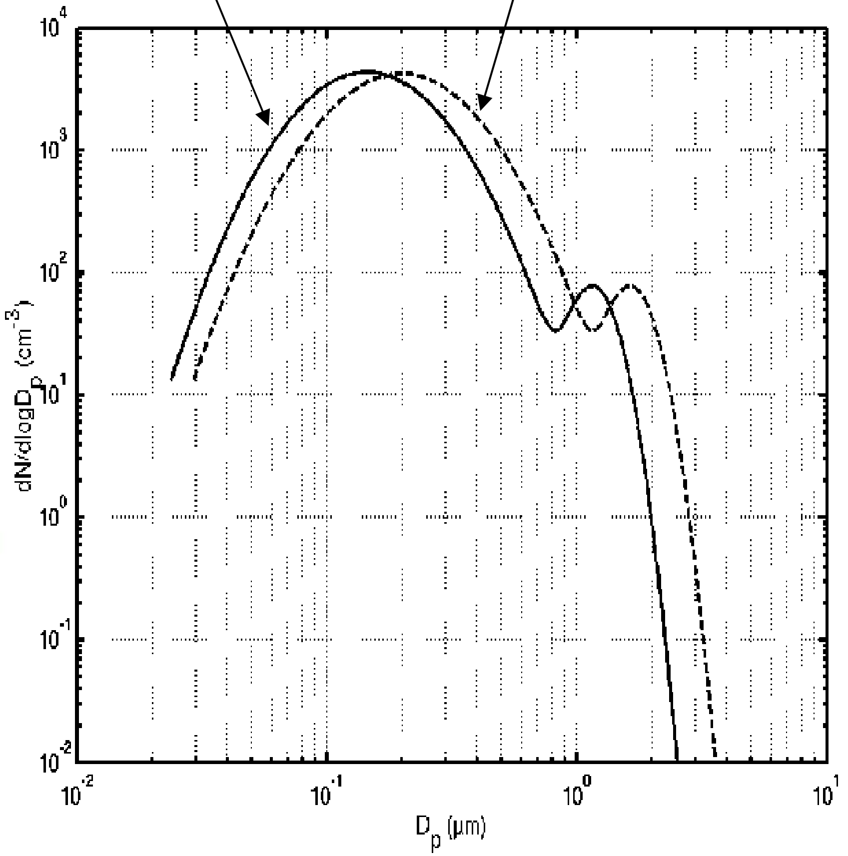
HSO_4^-

H_2O

RH

After equilibration

Initial distribution



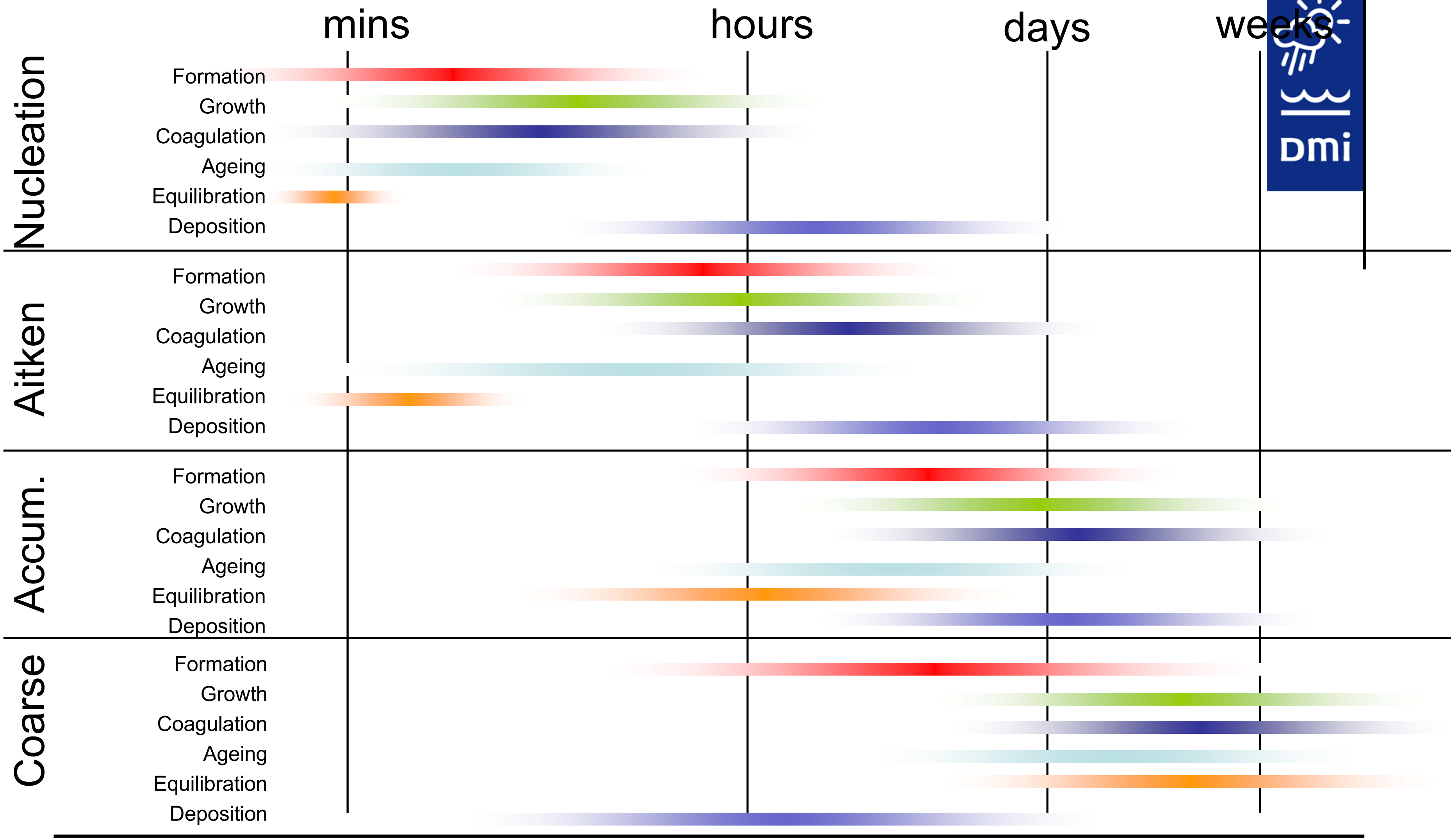
Carslaw, ISSAOS, 2008

Aerosol processes of importance

Other processes:

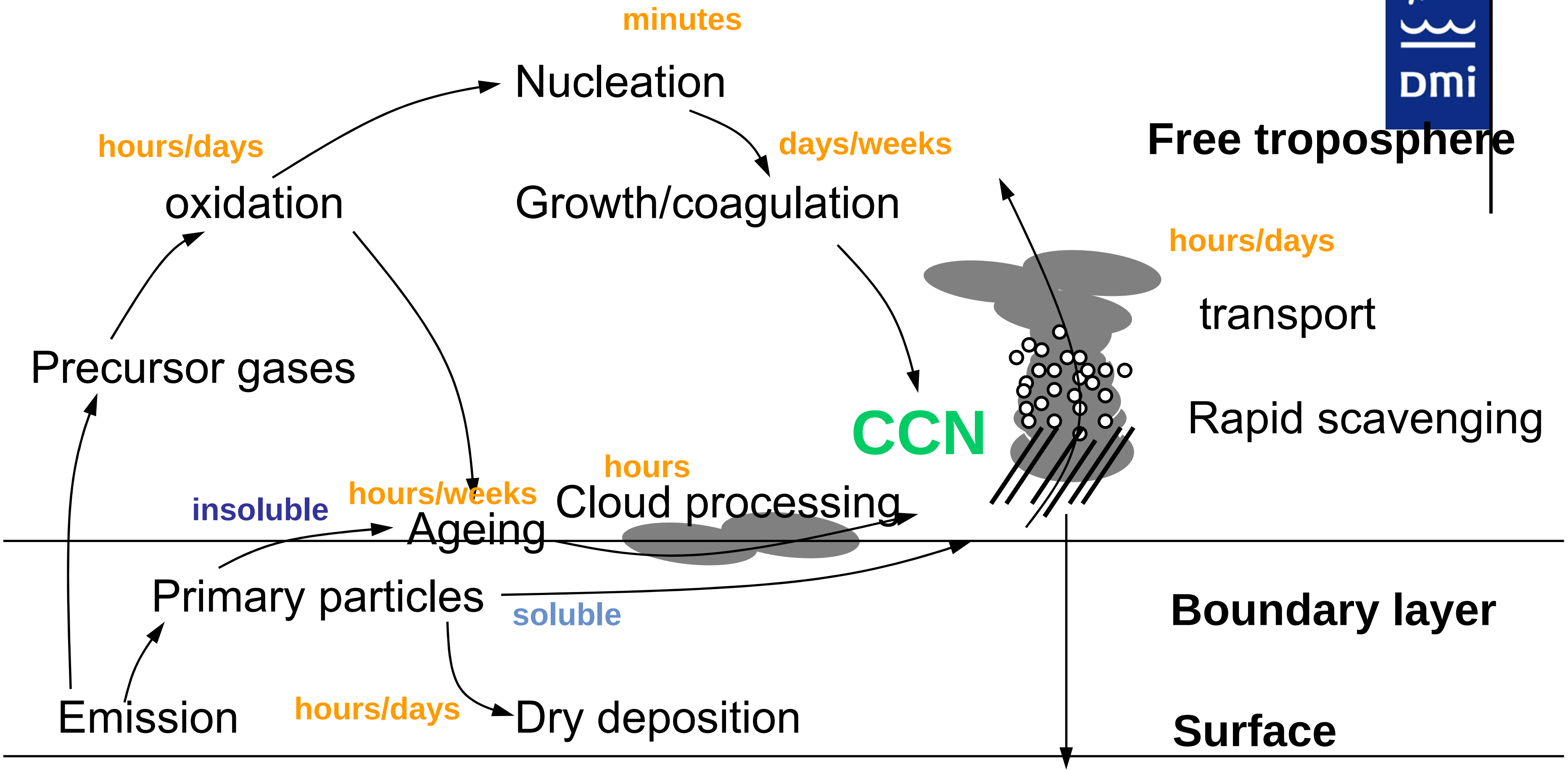
- Coagulation
- Condensation
- Deposition

Aerosol processes of importance



Carslaw, ISSAOS, 2008

Aerosol life cycle - overview



Carslaw, ISSAOS, 2008

Aerosol modeling

How is the evolution of the size distribution accounted for in aerosol models ?

Size resolved aerosol models

Bin models - discrete

Modal models - continous

Aerosol modeling

Bin models

Example

Size bins may be defined according to single particle volume E.g. assuming that the volume ratio between two consecutive bins is constant: $v_j = v_{rat}\, v_{j-1}$; this scheme covers a diameter width of : $\Delta D_j = D_j\, 2^{0.5}\, v_{rat}^{0.3} - 1 / (1+v_{rat})^{0.5}$.

Full stationary structure: Average bin volume is constant; N, V varies during a simulation.

Pro’s: covers large diameter range with few bins
Con’s: loss of initial composition

Other examples: Full-stationary structure, Full-moving structure Quasi-stationary, Hybrid structure, Moving center structure

Aerosol modeling

Currently, the CAC (Chemistry-Aerosol-Cloud) aerosol Model is used in Enviro-HIRLAM

A modal model assumes a shape of the size distribution
In order to close the moment equations

Standard ref. for modal modelling: *Whitby and McMurry, 1997, Aer. Sci and Tech., 27, 673-688*

K'th moment of distribution n: $M_k = \int d^k \, n(\ln d) \, d(\ln d)$
M_0 : number concentration
M_1 :
M_2 : surface concentration prop. to dispersion of n
M_3 : volume concentration prop. to mass concentartion and the geometric mean diameter of the mode

Aerosol modeling

Moment equations

Accumulation mode (j): $\partial M_{kj} / \partial t = G_{kj} - C_{kjj} + C_{kij} + E_{kj}$
Nucleation mode (i) : $\partial M_{ki} / \partial t = M'_{ki} + G_{ki} - C_{kii} - C_{kij} + E_{ki}$

G : condensation, C : intra mode coagulation, E : emisison
M' : nucleation

H_2SO_4-H_2O nucleation follows *Kulmala et al., 1998, JGR, D7, 8301-8307*

Nucleation rate ($cm^{-3}s^{-1}$) dependend on T, q and H_2SO_4 vapor conc.

Aerosol modeling

Coagulation

$$C_{kij} = \iint (d_1{}^3+d_2{}^3)^{k/3} \, \beta \, n_i(d_1)n_j(d_2) \, dd_1dd_2$$
$$- \iint d_2{}^k \, \beta \, n_i(d_1)n_j(d_2) \, dd_1dd_2$$

$$C_{kjj} = 0.5 \iint (d_1{}^3+d_2{}^3)^{k/3} \, \beta \, n_j(d_1)n_j(d_2) \, dd_1dd_2$$
$$- \iint d_1{}^k \, \beta \, n_j(d_1)n_j(d_2) \, dd_1dd_2$$

Brownian coagulator kernal $\beta = 4\pi \, (r_i + r_j)(D_i+D_j)$

Condensation

Parameterization follows *Wilck, 1999*

H_2SO_4-H_2O Aerosol water mole fraction in mode j:

$$X_j = X_{par}/(1+d_{par}/d_{gj})$$

X_{par} and d_{par} depends on q

Aerosol modeling

Specifying the shape of the size distrbution

Examples:
Marshall-Palmer distribution, Modified Gamma distribution,
Log-normal distribution

$$n_j(\ln D) = N_j \; (\; (2\pi)0.5 \ln \sigma_{gj} \;)\text{-}1 \; \exp \; (\text{-}0.5 \; (\ln(D/D_{gj})/\ln \sigma_{gj}))$$

Where n_j is the fraction of N_j with diameter D, N_j is the number concentration in mode j, D_{gj} is the geometric mean diameter of the mode and σ_{gj} is the geometric mean standard deviation

Aerosol modeling

Hence, three parameters are needed to characterize a mode (j): N_j, σ_{gj} and D_{gj}

These parameters may be diagnosed from the lowest order moments of the ditribution function:

$$\ln^2\sigma_g = 1/3\,(2\ln(M_3) - 3\ln(M_0)) - \ln(M_2)$$

$$D^3_g = M^3/(M_0\exp(9/2\,\ln^2\sigma_g\,))$$

In a modal model it is therefore nough to transport and disperse a few low order moments (M_0, M_2, M_3) of each mode

The CAC aerosol model consists of nucleation, accumulation and coarse mode; more can be added if neccessary

Aerosol modeling

Using the log-normal assumption:

$$C_{kij} = N_i N_j F_{kij}$$

$$C_{kjj} = N^2{}_j F_{kjj}$$

where F depends on d_g and σ_g only

Number concentration tendency equations

Accunulation mode: $\partial N_j / \partial t = E_{0j} - N^2{}_j F_{0jj}$

Primary emissions

Intra mode coagulation

Solution: $N_j(t) = \alpha(1-\gamma \exp(2\alpha t))\ (F_{0jj}(1+ \gamma \exp(2\alpha t)))^{-1}$

With $\alpha = (F_{0jj}E_0)^{0.5}$ and $\gamma = (\alpha - F_{0jj}N_j(t_0))\ (\alpha + F_{0jj}N_j(t_0))^{-1}$

Aerosol modeling

Nucleation mode: $\partial N_i / \partial t = E_{0i}{}' - N^2_i F_{0ii} - N_i N_j F_{0ij}$

Intra mode coagulation

Primary and secondary emissions

Inter mode coagulation

Aerosol dynamic mass transfer:

Nucleation mode: $\partial \varphi_i / \partial t = P_i - L \varphi_i$

Accumulation mode: $\partial \varphi_j / \partial t = P_j - L \varphi_j$

Φ: mass concentration

L : $N_i N_j F_{3ij} / M_{3i}$

P_i: emission, nucleation, condensation

P_j: emission, condensation

General solution:

$\Phi = P/L + (\varphi(t_0) - P/L)\exp(-Lt)$

Aerosol modeling

Composition depends on primary species, presence of trace gasses, limitations of the schemes

Non-equilibrium between aerosols and gases:
Equilibrium between trace gases and aerosols not instantaneous

- Calculation of mass transfer
- Formation of gas-aerosol equilibrium - equilibration

Aerosol modeling

Mass transfer calculations

$\partial C_{i,liq} / \partial t = K_{ti} \, (C_{i,gas} - C_{i,surf})$

C : moles per volume of air

K_{ti}: mass transfer coefficient

See *'Jacobson, 1999'* for details

Aerosol modeling

Equilibration: gas-aerosol thermodynamic equilibrium

Processes included in the newest version

$SO_2(g) <-> SO_2(aq)$

$SO_2(aq) + H_2O(aq) <-> HSO^{3-} + H^+$

$HSO^{3-} <-> SO_3^{2-} + H^+$

$H_2SO_4(aq) <-> HSO_4^- + H^+$

$HSO_4^- <-> SO_4^{2-} + H^+$

$NH_3(g) <-> NH_3(aq)$

$NH_3(aq) + H_2O(aq) <-> NH_4^+ + HO^-$

$HNO_3(g) <-> HNO_3(aq)$

$HNO_3(aq) <-> NO_3^- + H^+$

$NH_4NO_3(aq) <-> NH_4^+ + NO_3^-$

$(NH_4)_2SO_4 <-> 2\ NH_4 + SO_4^{2-}$

MSIA(g) <-> MSIA(aq)

MSA(g) <-> MSA(aq)

Aerosol modeling

Equilibration: gas-aerosol thermodynamic equilibrium

Analytical equilibrium iteration method (AEI, *Jacobson, 1999*)

Example:

D(gas) <-> A(aq)

ψ_D, ψ_A : concentrations mol $cm^{-3}{}_{air}$

Assuming equilibrium: $\psi_A / \psi_D = (\psi_{A,0}+\Delta X_{fin})(\psi_{D,0}-\Delta X_{fin})^{-1} = K_r$

Where K_r is an equilibrium constant: $m_A c_w M_w RT/p_D$

m_A : molality of compound A

C_w : aerosol water content

M_w : molecular weight of water

p_D : partial pressure of compound D

Aerosol modeling

Equilibration: gas-aerosol thermodynamic equilibrium

Converged solution obtained by substitution of

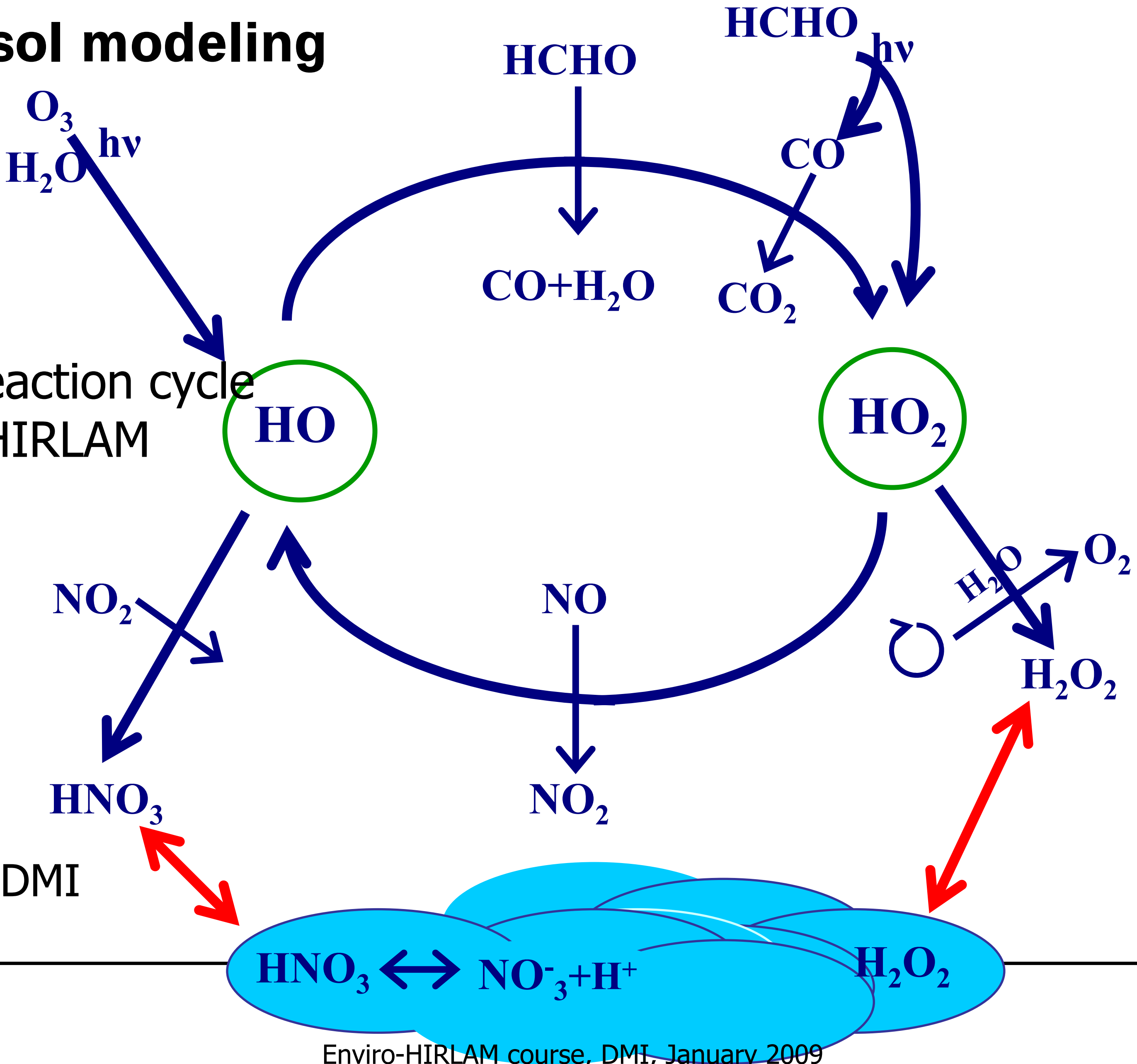
$$\Delta X_{fin} = (\psi_{D,0}K_r - \psi_{A,0})/(1+K_r)$$

Eliminates iterations for individual equilibria,
but not among all the reactions

First equation solved and used as input for the next etc.

Iterations continue untill convergence criteria is fulfilled:
Percentwise change in spcies concentration less than 0.0001 %

Aerosol modeling

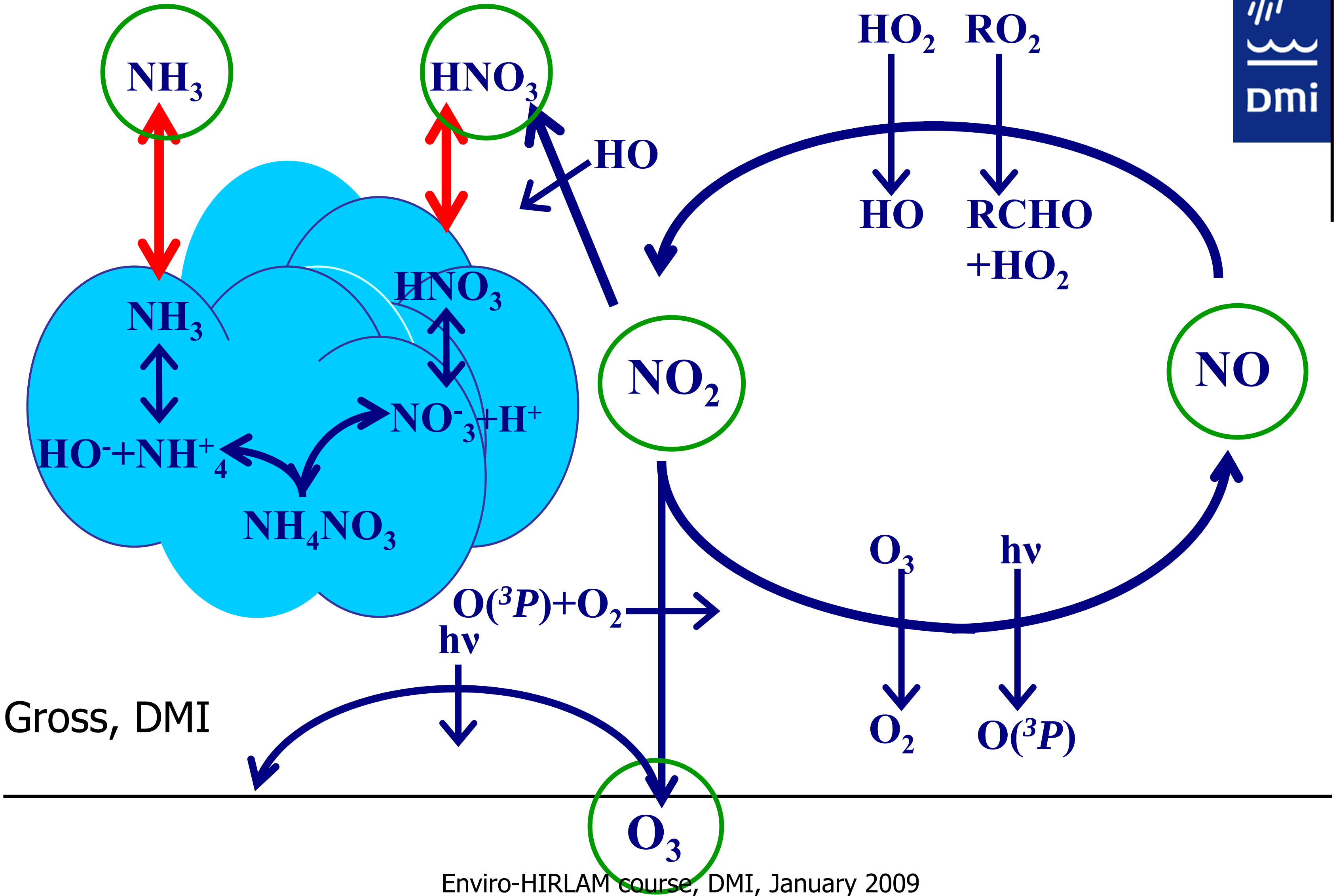


Full HO_x reaction cycle in Enviro-HIRLAM

A. Gross, DMI

Aerosol modeling

Full NO_x reaction cycle in Enviro-HIRLAM

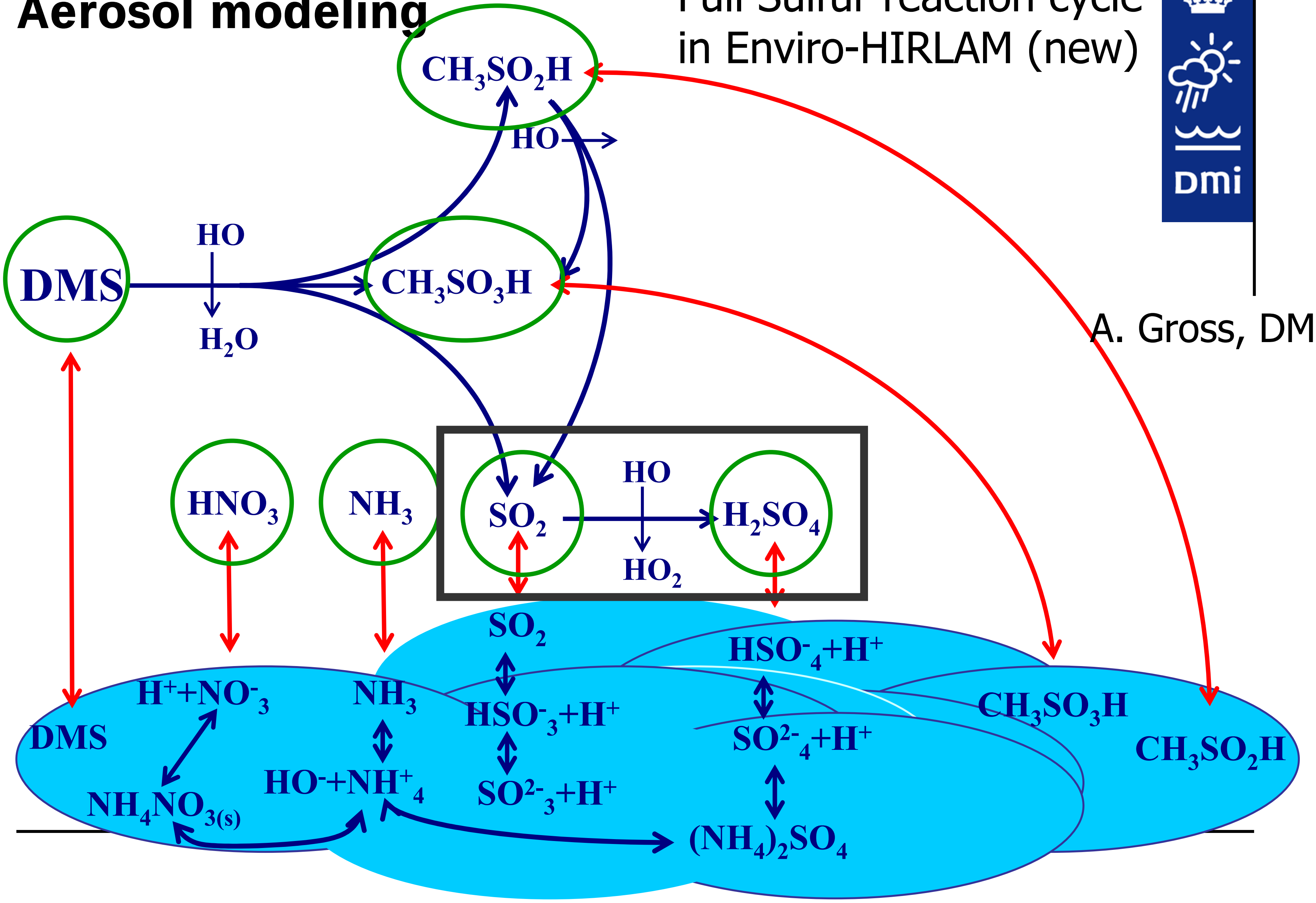


A. Gross, DMI

Aerosol modeling

Full Sulfur reaction cycle in Enviro-HIRLAM (new)

A. Gross, DMI



Aerosol modeling

Testing of the aerosol scheme

- Simulation of sulfate aerosol in Paris
- Comparison with hourly data at five AIRPARIF urban/sub urban stations
- Assuming 15 % SO_4^{2-} in PM2.5 measurements, due to volatilization of aerosol components during measurements
- 00 UTC 29 June 2005 – 00 UTC 01 July 2005; 24 hour spin-up; 0.05 x 0.05 degree resolution; 40 levels; top level at 10 hPa
- GEMS-TNO inventory; no inflow

Aerosol modeling

Testing of the aerosol scheme

Diurnal cycle
Negative bias
Average observation : 1.46 µg m^{-3}
Average REF : 0.48 µg m^{-3}
Average 12IE : 0.58 µg m^{-3}
Average deviation REF : -0.97 µg m^{-3}
Average deviation 12IE: -0.87 µg m^{-3}

Large uncertainty in observations !!!