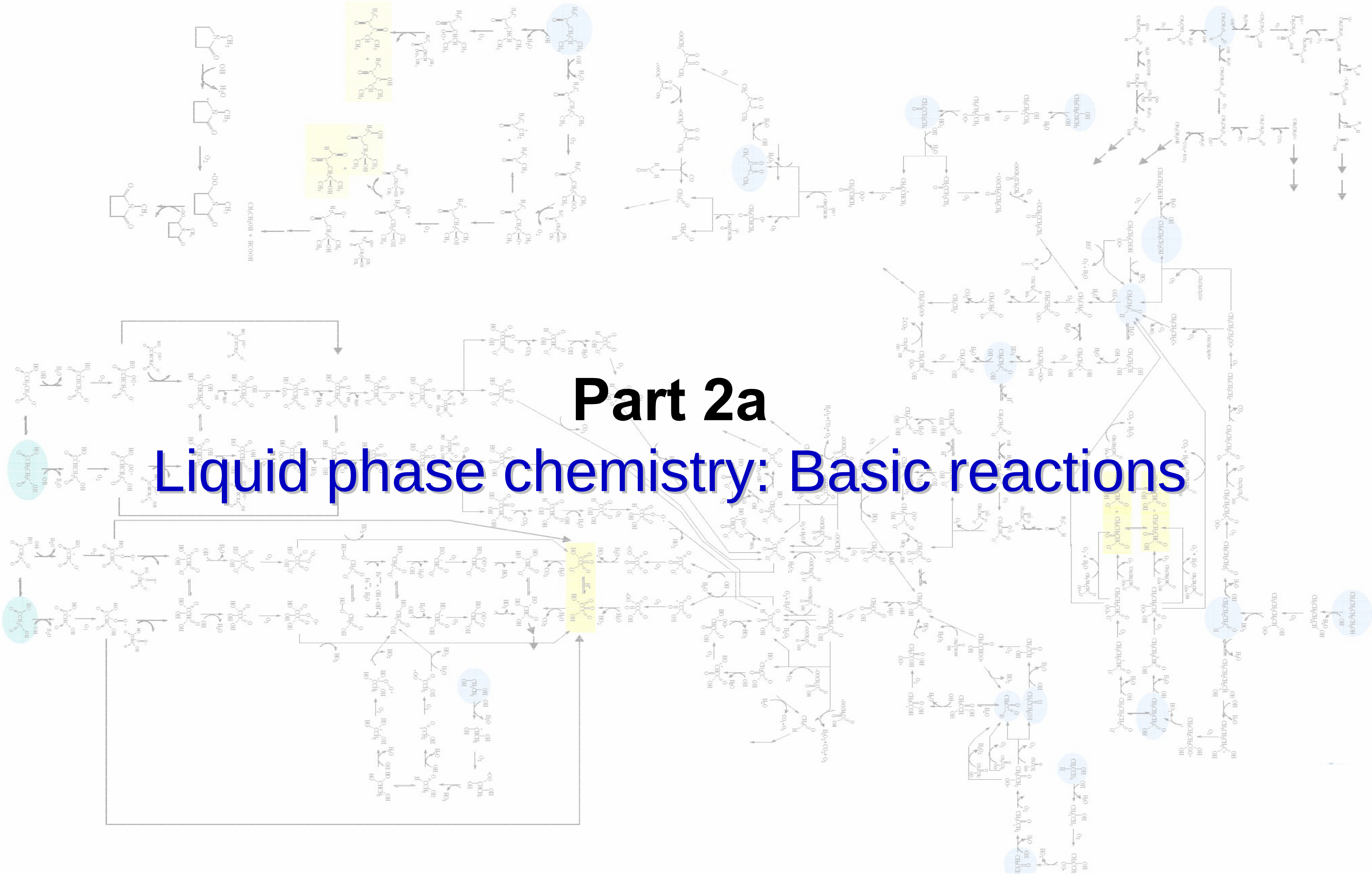


Part 2a

Liquid phase chemistry: Basic reactions

Typical Atmospheric Aerosol Compositions in micro g per m3

- Marine
  - Electrolytes: Na^+ (2.91), K^+ (0.11), NH_4^+ (0.16), Ca^{2+} (0.17), Mg^{2+} (0.40)
    SO_4^{2-} (2.58), NO_3^- (0.05), Cl^- (4.63), Br^- (0.015), I^- (?), MSA (0.12)
  - Mineral compounds: Fe_2o_3 (0.07)
  - Organic compounds: neutral aliphatic (0.16) and aromatic compounds (0.20), organic acids (0.23) and bases (0.03)

- Continental
  - Electrolytes: Na^+ (0.08), K^+ (0.12), NH_4^+ (0.16), Ca^{2+} (0.30), Mg^{2+} (0.25)
    SO_4^{2-} (4.90), NO_3^- (1.35), Cl^- (0.14), Br^- (<0.01)
  - Mineral components: SiO_2 (1.25), Al_2O_3 (0.39), Fe_2O_3 (0.37), CaO (0.18)
  - Organic compounds: neutral aliphatic and aromatic compounds, organic acids and bases

Chemical Composition of Liquid Water in Clouds

- Material from the condensation nuclei.
- Dissolution of gasses from the surrounding air.

Basic chemistry of CH4 oxidation induced by HO radicals

Gas Phase

NO2+*hv* → NO + O(3P)
O(3P) + O2 + M → O3 + M
NO + O3 → NO2 + O2

O3 + *hv* → O(1D) + O2
O(1D) + M → O(3P) + M
O(1D) + H2O → 2HO
HO + O3 → HO2 + O2
HO2 + O3 → HO + 2O2

HO + CH4 → CH3 + H2O
CH3 + O2 → CH3O2
CH3O2 + NO → CH3O + NO2
CH3O + O2 → HCHO + HO2

HCHO + *hv* → CO + H2
HCHO + *hv* → HCO + H
HCO + O2 → CO + HO2

HO + CO → CO2 + H
H + O2 + M → HO2 + M
HO2 + HO2 → H2O2 + O2

Gas-Liquid Exchange

↔ O3

low solubility

↔ HO

↔ HO2

Chemistry mainly driven by

↔ HCHO

high solubility

↔ H2O2

Aqueous Phase

O3 + *hv* → O(1D)
O(1D) + H2O → 2HO

Major HO source

HO2 ↔ H+ + O2-
O2- + O3 → O3- + O2
H+ + O3- → HO + O2

HCHO + H2O → CH2(OH)2
HO + CH2(OH)2 → H2O + CH(OH)2
CH(OH)2 + O2 → HCOOH + HO2
HO + HCOO- → H2O CO2-
CO2- + O2 → CO2 + O2-
HO + HCO3- → H2O + CO3-
O2 + CO3- →HCO3- + O2

H2O2 + HO → H2O + HO2
HO2 + HO2 → H2O2 + O2
HO2 + O2- + H+ → H2O2 + O2
H2O2 + *hv* → 2HO

Nitrogen chemistry

Gas Phase

O(3P) + O2 + M → O3 + M
HONO + *hv* → NO + HO

O3 + NO → NO2 + O2

HO + NO2 → HNO3

HO2 + NO2 ↔ HNO4

O3 + NO2 → NO3 + O2
NO3 + *hv* → NO3 + O2

NO3 + NO2 ↔ N2O5

Gas-Liquid Exchange

↔ HONO
relative low solubility
↔ NO2

↔ HNO3
high solubility
↔ HNO4

↔ NO3
Only important at nighttime
↔ N2O5

Aqueous Phase

HONO ↔ NO2- + H+
NO2- + O3 → NO3- + O2
HONO + *hv* → NO + HO
NO2- + *hv* + H+→ NO + HO
NO2- + HO → HO- + NO2

NO2- + NO2 ↔ N2O4
N2O4 + H2O → HNO2 + NO3- + H+

<u>HNO3</u> → H+ + NO3-
NO3- + *hv* + H+ → NO2 + HO-

<u>HNO4</u> ↔ H+ + NO4-
NO4- → NO2- + O2-
<u>HNO4</u> + HSO3- → NO3- + SO42- + H+

NO3 + Cl- → NO3- + Cl
NO3 + HSO3- → NO3- + SO3- + H+

N2O5 + H2O → 2H+ + 2NO3-

Sulphur chemistry

Gas Phase

$DMS + HO \rightarrow ..... \rightarrow SO_2$

$SO_2 + HO \rightarrow SO_3 + HO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$

Gas-Liquid Exchange

$\leftrightarrow CH_3SO_2H$

$\leftrightarrow CH_3SO_3H$

$\leftrightarrow SO_2$

$\leftrightarrow H_2SO_4$

Aqueous Phase

$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$
$O_3 + HSO_3^- \rightarrow HSO_4^- + O_2$
$O_3 + SO_3^- \rightarrow SO_4^{2-} + O_2$
$O_3 + SO_3^{2-} \rightarrow SO_4^{2-} + O_2$

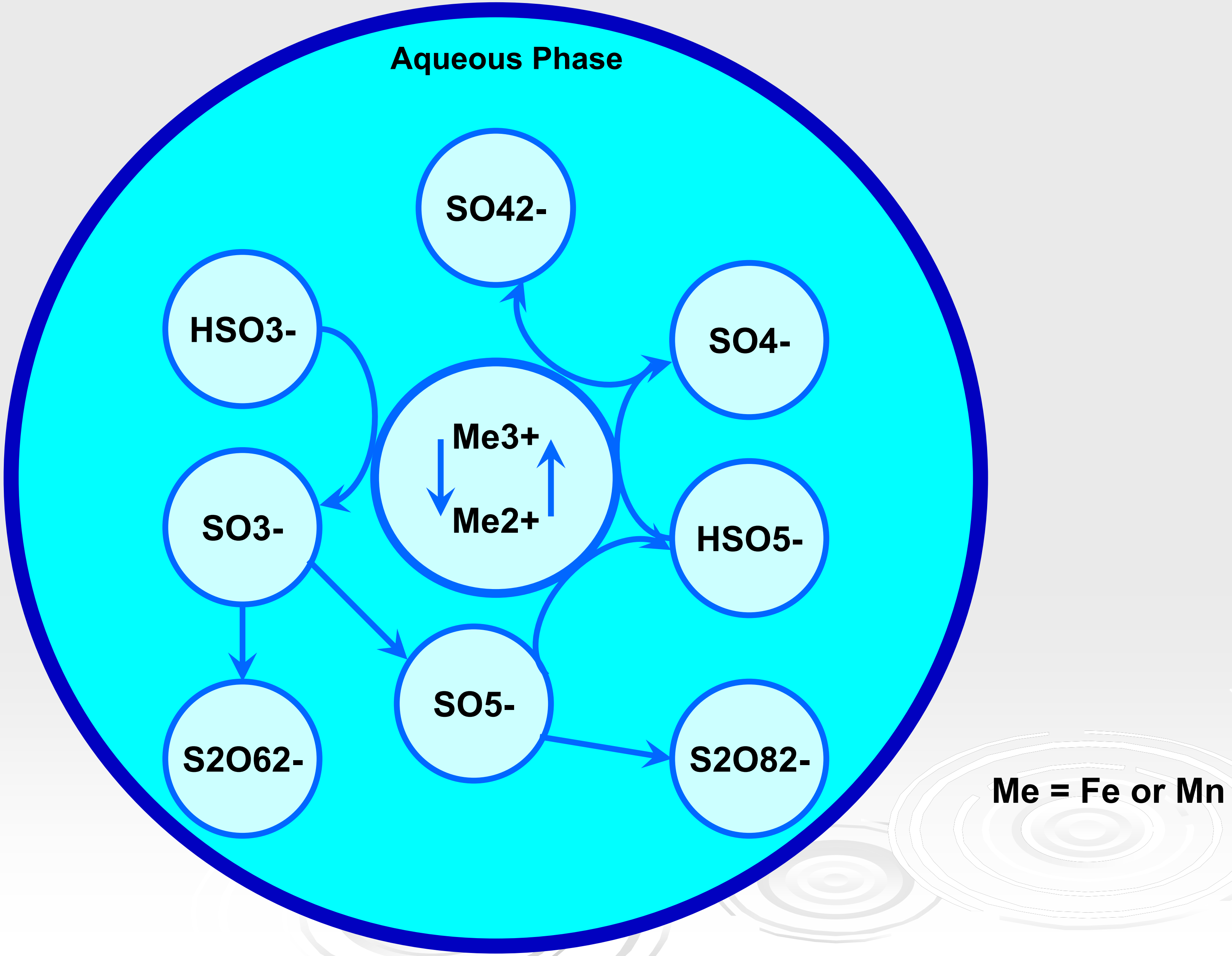
$H_2O_2 + HSO_3^- \rightarrow HSO_4^- + CH_3OH$
$HSO_5^- + HSO_3^- \rightarrow 2HSO_4^-$

$HNO_4 + HSO_3^- \rightarrow HSO_4^- + NO_3^- + H^+$
$HNO_3 + HSO_3^- \rightarrow HSO_4^- + HONO$

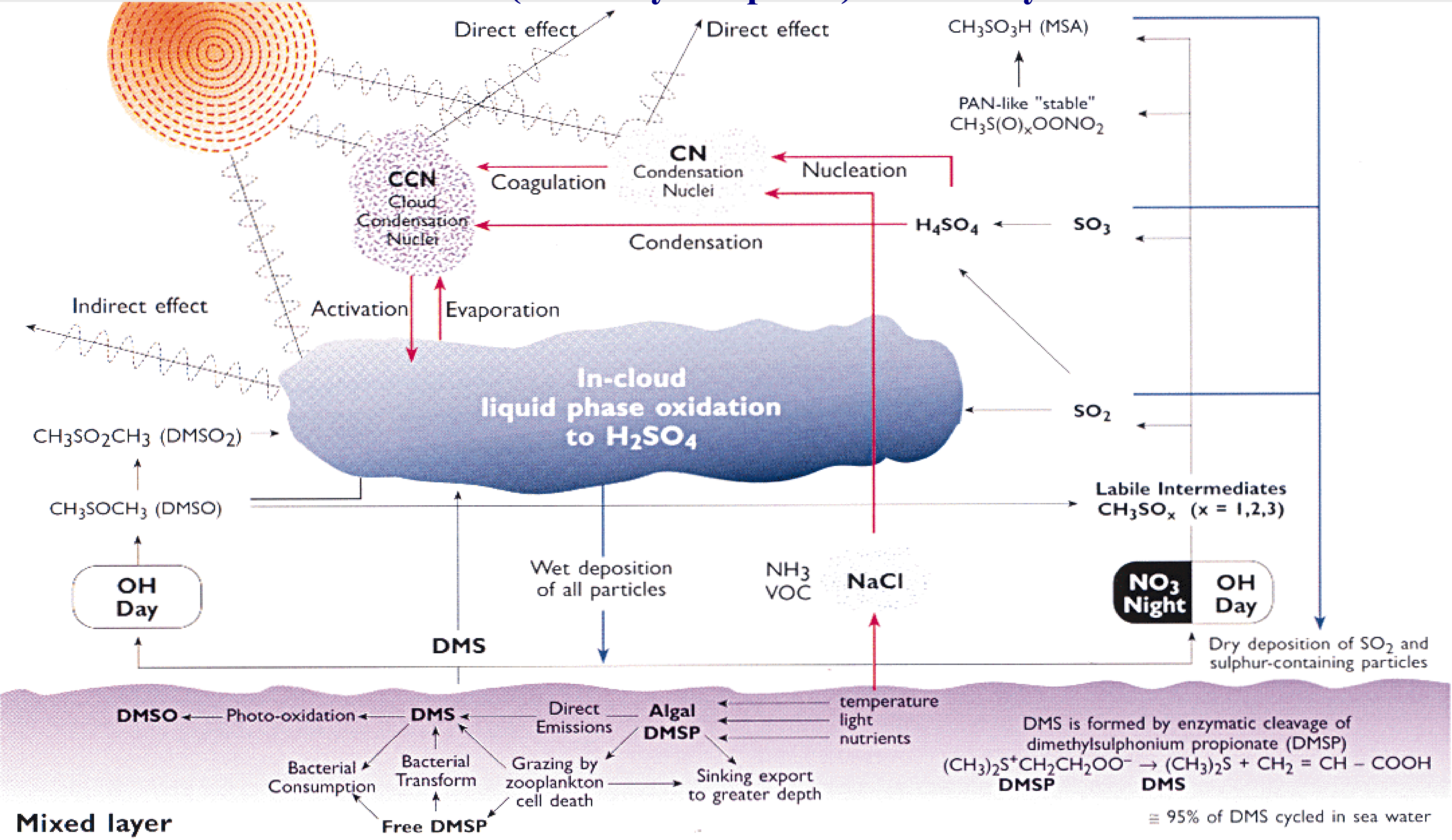
$SO_5^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^-$
$SO_5^- + SO_5^- \rightarrow 2SO_4^- + O_2$

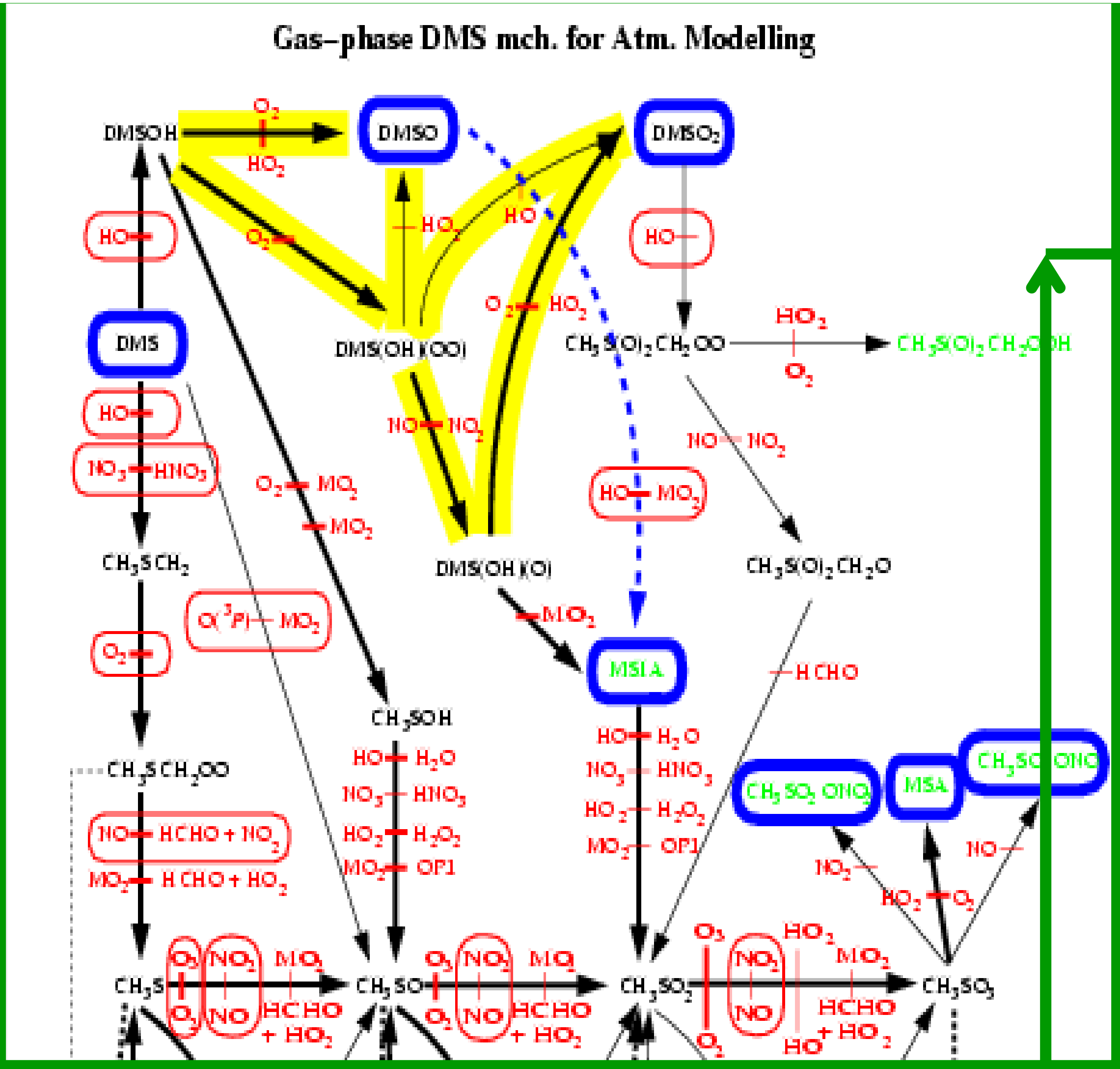
$CH_3SO_2H \leftrightarrow CH_3SO_2^- + H^+$?
$CH_3SO_2H \leftrightarrow CH_3SO_2^- + H^+$?
$H_2SO_4 \rightarrow HSO_4^- + H^+$
$HSO_4^- \leftrightarrow SO_4^{2-} + H^+$

Chemistry of transition metals



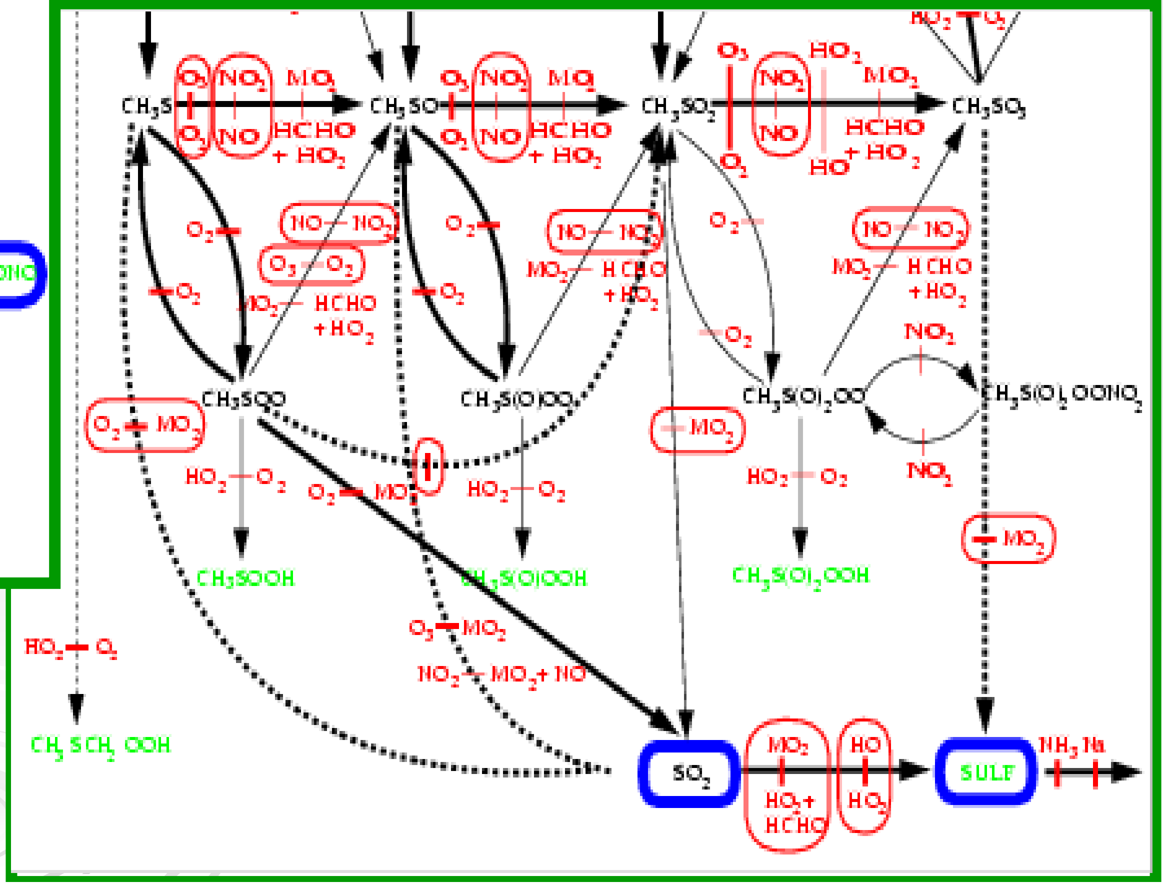
DMS (DiMethyl Sulphide) Chemistry



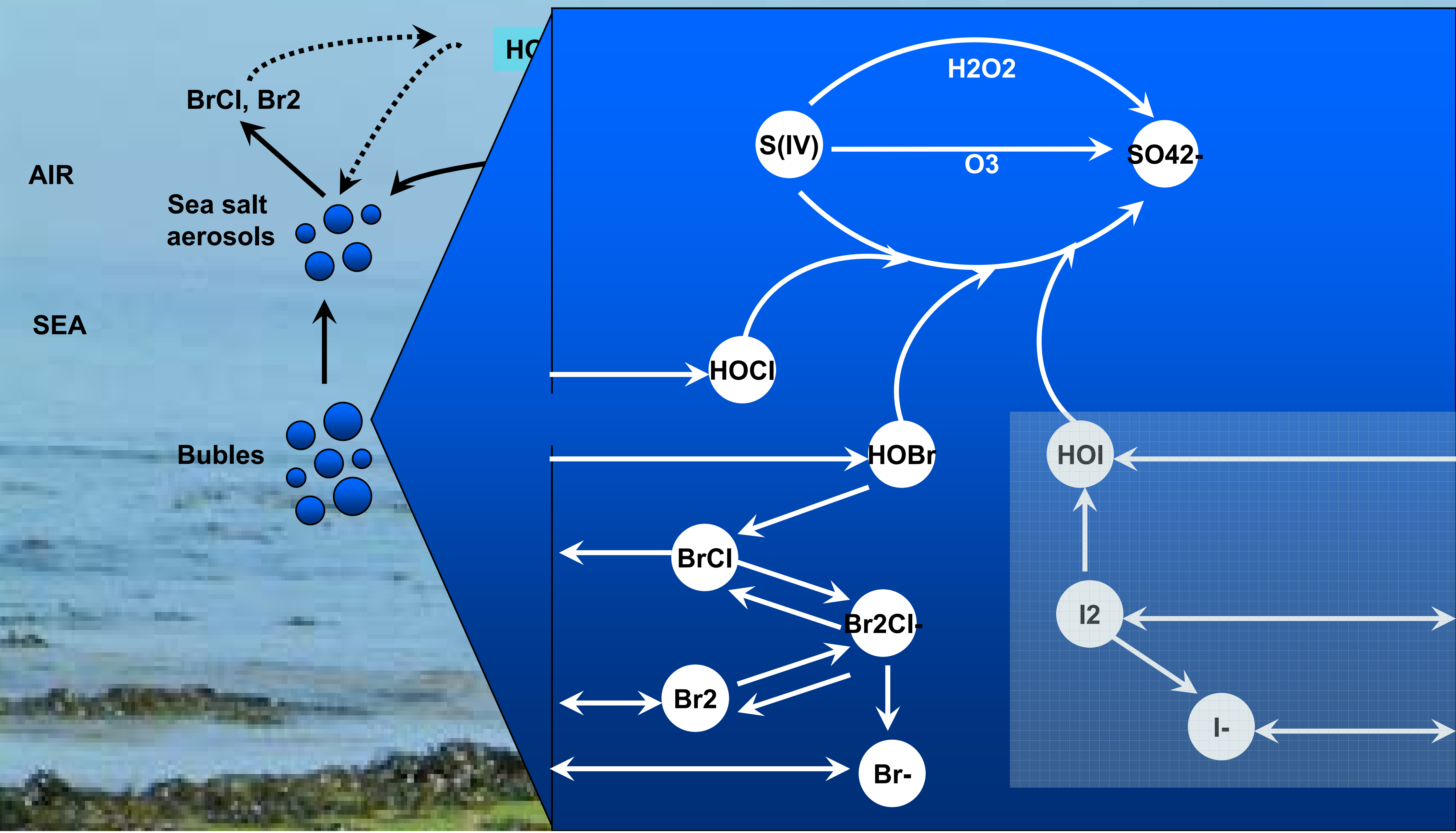


30 (→ 21) sulphur species and 72 (→ 34) reactions [49 (→ 22) guessed & 23 (→ 12) experimental rates].

(→ means reduced to)

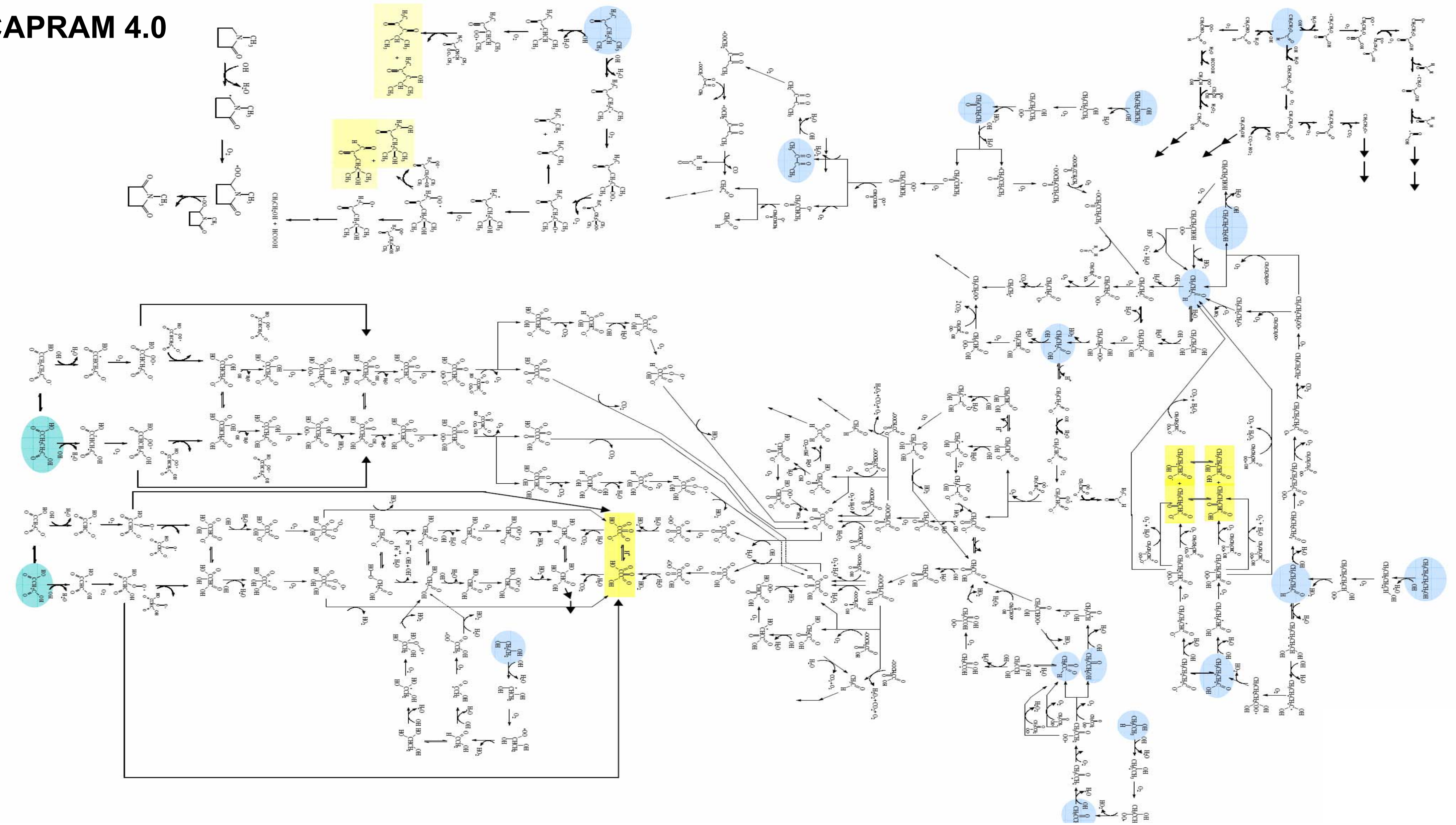


Halogens and sea salt particles



Liquid phase chemistry: Basic reactions.

CAPRAM 4.0



CAPRAM2.3
Highlights

- A **detailed treatment of the oxidation of organic compounds with one and two carbon atoms.**
- **an explicit description of S(IV)-oxidation by radicals and iron(III), as well as by peroxides and ozone.**
- **the reactions of HO, NO3, Cl2-, Br2-, and CO3- radicals, as well as reactions of the transition metal ions iron, manganese and copper.**

CAPRAM2.4 Highlights

- Based on the former version CAPRAM2.3.
- Extended organic and transition metal chemistry.
- Is formulated more explicitly based on a critical review of the literature.

- A condensed version (183 reactions) has also been developed to allow the use of CAPRAM 2.4 in larger scale models.

CAPRAM3.0 Highlights

- Incorporates the former version CAPRAM 2.4.
- A new extended reaction mechanism for atmospherically important hydrocarbons containing more than two and up to six carbon atoms. The chemistry of several organic compounds containing three and four carbon atoms is now described in detail.

Most detailed liquid phase chemical mechanism for cloud and aerosol modelling

- Chemical Aqueous Phase RAdical Mechanism (CAPRAM) Herman et et.
  - CAPRAM2.3:

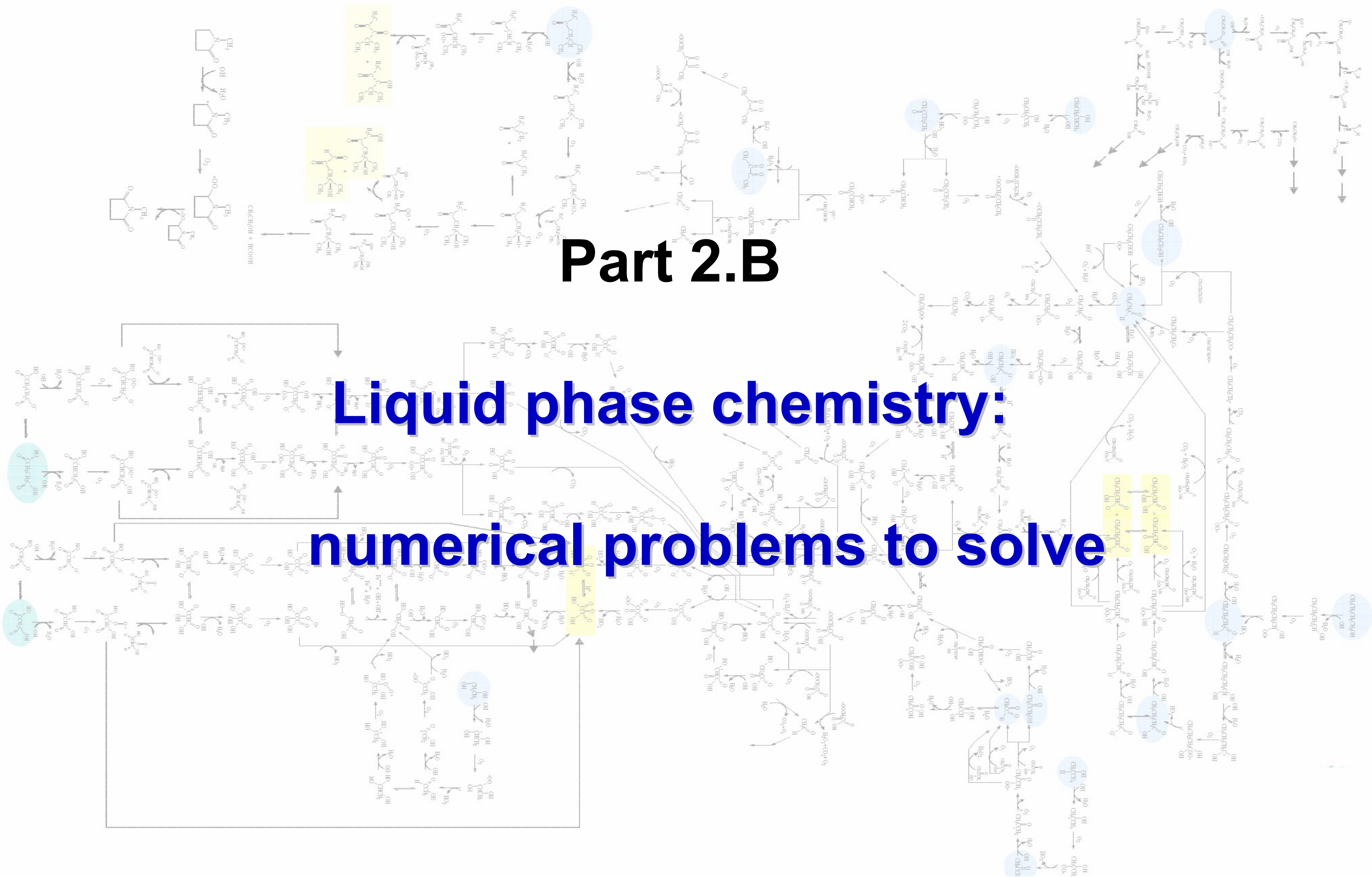
aqueous-phase species	photolysis reactions	aqueous-phase reac.	heterogeneous equili.	aqueous-phase equili.
70	6	199	34	31

  - CAPRAM2.4:

aqueous-phase species	photolysis reactions	aqueous-phase reac.	heterogeneous equili.	aqueous-phase equili.
153	11	324	34	57

  - CAPRAM3.0:

aqueous-phase species	photolysis reactions	aqueous-phase reac.	heterogeneous equili.	aqueous-phase equili.
164	12	686	36	97



Part 2.B

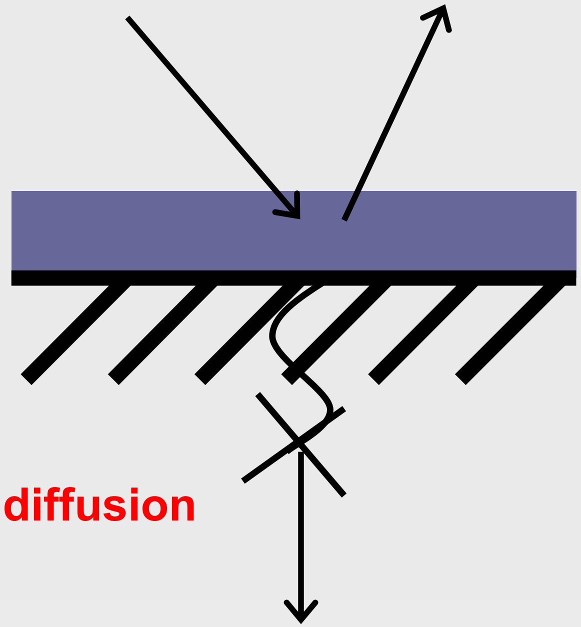
Liquid phase chemistry: numerical problems to solve

Heterogeneous Chemistry

Interaction between gas-phase species and particles involves

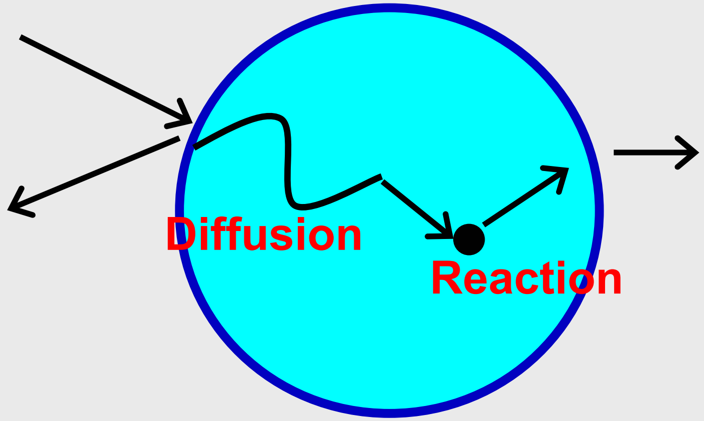
- gas-phase species ⟷ aqueous particles
- gas-phase species ⟷ solid particle
- gas-phase species ⟷ ion-equilibrium
- aqueus species ⟷ ion-equilibrium
- aqueus species ⟷ solid
- ion ⟷ ion-equilibrium
- solid ⟷ ion-equilibrium
- solid ⟷ solid

Solid

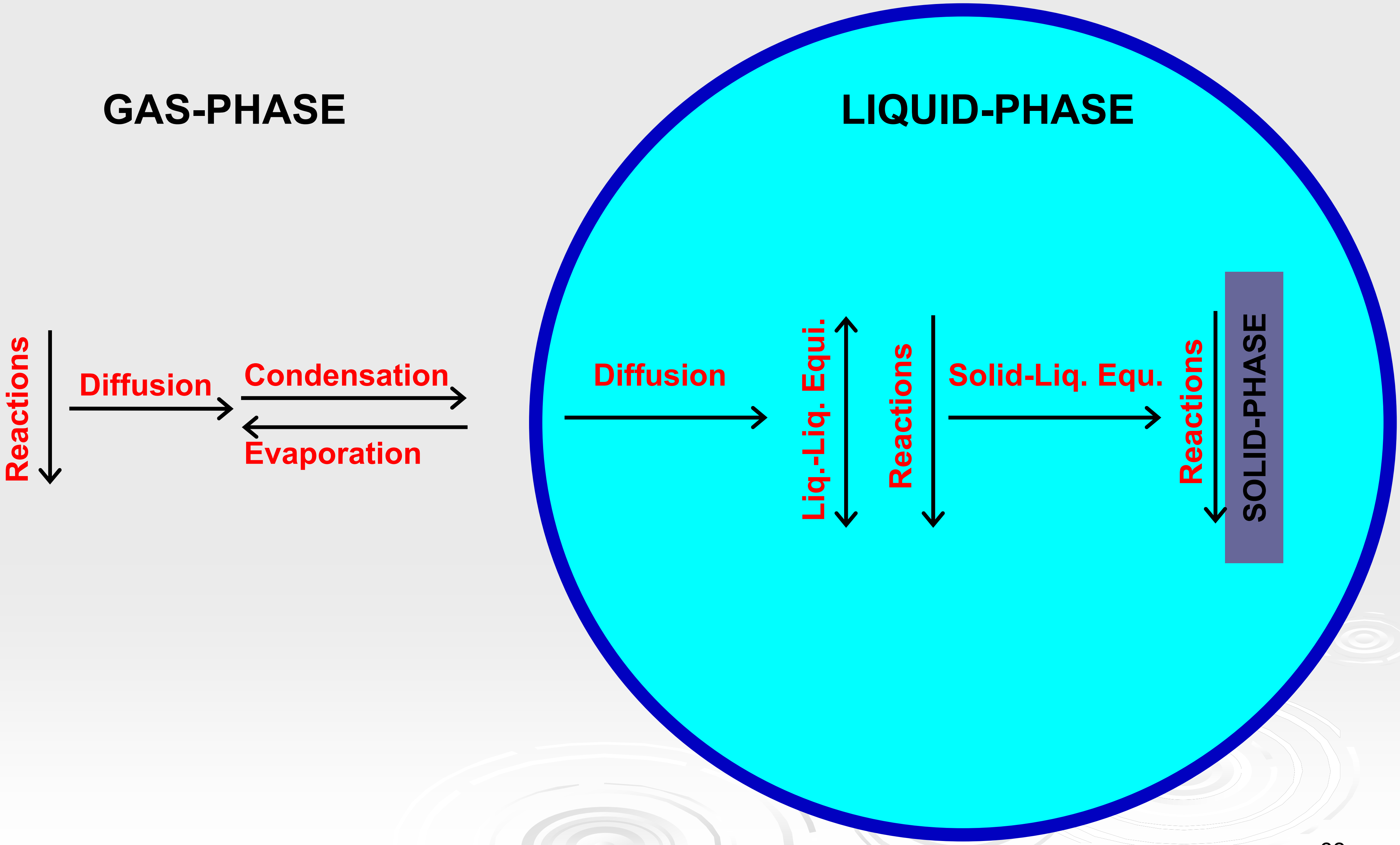


Diffusion into the bulk of the solid is assumed to be too slow to effect the concentration at the surface; thus the reaction is cónfined to the surface.

Liquid



In the liquid, is it assumed that the reaction takes place after the molecule has been incorporated into the bulk of the liquid.


GAS-PHASE
LIQUID-PHASE
Reactions
Diffusion
Condensation
Evaporation
Diffusion
Liq.-Liq. Equi.
Reactions
Solid-Liq. Equ.
Reactions
SOLID-PHASE

Chemical Equilibrium, Example

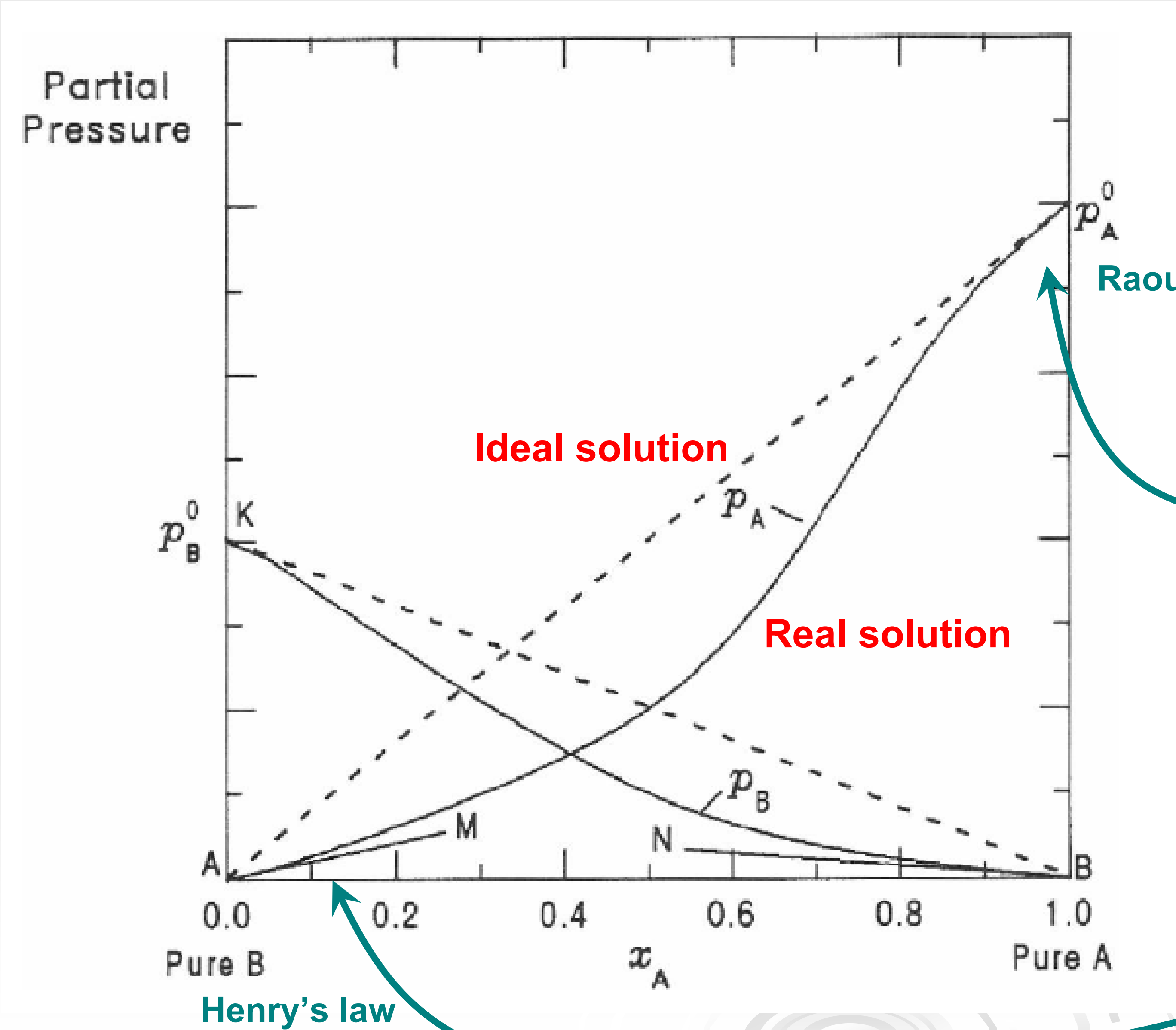
Reac. 1: $HCl_g \rightleftarrows H^+ + Cl^-$

Reac. 2: $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$

Assumption Considered in General:

- Gasses are considered to have ideal behaviour
- Liquids and Solids are considered to have real behaviour

Ideal ↔ Real Mixtures



Raoult's law

Gasses:
$f = \varphi p (/p^o)$
f: fugacity
φ: fugacity coefficient

$$\ln \varphi = \int_0^p (pv/nRT-1)p\, dp$$

$\varphi \to 1$ as $p \to 0$

Mixtures, solvent:
$a = p/p^* \to a = \gamma x$
$\gamma \to 1$ as $x \to 1$

Mixtures, solute:
$a = p/K \to a = \gamma x$
$\gamma \to 1$ as $x \to 0$

$a = p/p^* \to a = \gamma m (/m^o)$
$\gamma \to 1$ as $m \to 0$

Ionic strength and activity in solutions

- calculation of the ionic strength in the solution,
- calculation of the activity coefficients in the solution, different methods

Bromley method : Bromley (AlCh J. 1973, 19, 313) and Saxena and Peterson (J. Colloid Interface Sci. 1981, 79, 496)

Kusik and Meissner method : Kusik and Meissner (AlChE Symp. Ser. 1978, 173, 14)

Pitzer method Pitzer and Kim (J. Am. Chem. Soc. 1974, 96, 5701) and Pitzer (Pure Appl. Chem. 1986, 58, 1599)

Equations to solve – Equilibrium expressions:

$$\frac{\mathsf{m}_{H+,eq}\mathsf{m}_{Cl-eq}\gamma^2_{H+,Cl-,eq}}{p_{HCl,eq}} = K_{eq,1}$$

$$\frac{\mathsf{m}_{H+,eq}\mathsf{m}_{SO_4^{2-},eq}\gamma^3_{2H+,SO_4^{2-},eq}}{\mathsf{m}_{HSO_4^-,eq}\gamma^2_{H+,HSO_4^-,eq}} = K_{eq,2}$$

$\mathsf{m}_{i,eq}$: molality of species i alone in the solution (mole/kg) at equilibrium.

$\gamma_{i^+,j^-,eq}$: mean mixed activity coefficient at equilibrium.

$p_{i,eq}$: saturation vapor pressure of gas i at equilibrium.

$K_{eq,1}$: Henry coefficient for reac. 1.

$K_{eq,2}$: Ion-ion equilibrium coefficient for reac. 2.

Equations to solve – Mass balance constraints:

$$C_{HCl(g),eq} + c_{Cl^-,eq} = C_{HCl(g),t=0} + c_{Cl^-,t=0}$$

$$c_{HSO_4^-(g),eq} + c_{SO_4^{2-},eq} = c_{HSO_4^-(g),t=0} + c_{SO_4^{2-},t=0}$$

Equations to solve – Charge balance equation:

$$c_{Cl^-,eq} + c_{HSO_4^-(g),eq} + 2\,c_{SO_4^{2-},eq} = c_{H^+,eq}$$

$C_{i(g),eq}$: mole concentration of gas i (mole/cm^3) at equilibrium.
$c_{i,eq}$: mole concentration of species i in the liquid (mole/cm^3) at equilibrium.
$C_{i(g),t=0}$: the initial mole concentration of gas i (mole/cm^3).
$c_{i,t=0}$: the initial mole concentration of species i in the liquid (mole/cm^3).

Equations to solve – Charge balance equation:

The solution of the above equations requires not only the aerosol sulphate and aerosol chloride, but also the amount of water in the aerosol phase.

The particle liquid water content ($C_{w,eq}$) is given by:

$$C_{w,eq} = \frac{1000}{m_w}\left(\frac{c_{H^+,Cl^-,m}}{\mathrm{m}_{H^+,Cl^-,a}} + \frac{c_{H^+,HSO^-4,m}}{\mathrm{m}_{H^+,HSO_4^-,a}} + \frac{c_{2H^+,SO_4^{2-},m}}{\mathrm{m}_{2H^+,SO_4^{2-},a}}\right) \tag{34}$$

m_w: mole weight of water

$\mathrm{m}_{i,j,a}$: the molarity of the species alone (determined from empirical functions) $\mathrm{m}_{i,j,a} = \sum_{i=0} y_i \, a_w$

water activity: $a_w = \frac{RH}{100}$

$c_{i,j,m}$: hypothetical mole concentrations of the electrolyte pairs, constrained by

Hypothetical mole concentrations of the electrolyte pair

$$c_{H^+,eq} = c_{H^+,Cl^-,m} + c_{H^+,HSO^-4,m} + c_{2H^+,SO_4^{2-},m}$$

$$c_{Cl^-,eq} = c_{H^+,Cl^-,m}$$

$$c_{HSO^-4,eq} = c_{H^+,HSO^-4,m}$$

$$c_{SO_4^{2-},eq} = c_{2H^+,SO_4^{2-},m}$$

Total number of equations to solve for a problem considered of two equilibriums

two equilibrium equations,

two mass balance equations,

the water equation, and

the activity coefficients.

Non-equilibrium between gas and particle described by Schwartz:

Rate of mass transport for a gas-phase species A:

$$\frac{\mathrm{d}C_{i(g)}}{\mathrm{d}t} = -k_{mt,i}\, C_{i(g)} + \frac{k_{mt}}{m_w c_w R T k_{eq,i}} c_i$$

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = k_{mt,i}\, C_{i(g)} - \frac{k_{mt,i}}{m_w c_w R T k_{eq,i}} c_i + \left(\frac{\mathrm{d}c_i}{\mathrm{d}t}\right)_{eq}$$

The liquid phase equilibrium problem

$C_{i(g)}$: mole concentration of gas i (mole/cm^3).

$k_{mt,i}$: mass transfer rate (s^{-1}).

m_w: mole weight of water.

c_w: liquid water content.

$k_{eq,i}$: Henry's coefficient.

c_i: mole concentration of species i in the liquid (mole/cm^3).

Non-equilibrium between gas and particle the resistance method (Ravishanhara, and Williams and Tolbert)

The uptake coefficient is given by

$$\frac{1}{\gamma} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sol} + \Gamma_{rxn}}$$

The gas transport coefficient

$$\frac{1}{\Gamma_g} = \frac{c\ d}{8\ D_g} - \frac{1}{2}$$

The solubility limited uptake coefficient:

$$\Gamma_{sol} = \frac{4HRT}{\pi^{1/2}c}\left(\frac{D_l}{t}\right)^{1/2}$$

Reactive uptake coefficient:

$$\Gamma_{rxn} = \frac{4HRT}{c}\left(D_l k_{rxn}\right)^{1/2}$$

$\frac{1}{\alpha}$: accommodation coefficient.
c: mean molecular speed.
d: sphere diameter.
D_g: gas phase diffusion coefficient.
D_l: liquid phase diffusion coefficient.
H: Henry's law coefficient.
k_{rxn}: reaction rate of the dissolved gas in the condensed phase

Method for solving equilibrium reactions (Mass-Flux Iteration (MFI) method)

Consider:

$$\nu_{\mathrm{D}}\mathrm{D} + \nu_{\mathrm{E}}\mathrm{E} \rightleftharpoons \nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B}$$

gasses (D, E) **liquids** (A, B)

Iteration loop:

Step 1:

$$Q_d = \min\left(\frac{c_{\mathrm{D},0}}{\nu_{\mathrm{D}}}, \frac{c_{\mathrm{E},0}}{\nu_{\mathrm{E}}}\right) \qquad Q_n = \min\left(\frac{c_{\mathrm{A},0}}{\nu_{\mathrm{A}}}, \frac{c_{\mathrm{B},0}}{\nu_{\mathrm{B}}}\right)$$

Step 2:

$$z_i = 0.5(Q_d + Q_n) \text{ and } \Delta x_1 = Q_d - z_1$$

Method for solving equilibrium reactions (MFI method), cont.

Step 3:

$$c_{\mathrm{A},l+1} = c_{\mathrm{A},l} + \nu_{\mathrm{A}} \Delta x_l \quad c_{\mathrm{B},l+1} = c_{\mathrm{B},l} + \nu_{\mathrm{B}} \Delta x_l$$

$$c_{\mathrm{D},l+1} = c_{\mathrm{D},l} - \nu_{\mathrm{D}} \Delta x_l \quad c_{\mathrm{E},l+1} = c_{\mathrm{E},l} - \nu_{\mathrm{E}} \Delta x_l$$

Step 4:

$$F = \frac{m_{\mathrm{A},l+1}^{\nu_{\mathrm{A}}} m_{\mathrm{B},l+1}^{\nu_{\mathrm{B}}} \gamma_{\mathrm{AB},l+1}^{\nu_{\mathrm{A}}+\nu_{\mathrm{B}}}}{p_{\mathrm{D},l+1}^{\nu_{\mathrm{D}}} p_{\mathrm{E},l+1}^{\nu_{\mathrm{E}}}} \frac{1}{K_{eq}(\mathrm{T})}$$

Analyze:

$$F = \begin{cases} > 1 & \rightarrow \quad \Delta x_{l+1} = -z_{l+1} \\ < 1 & \rightarrow \quad \Delta x_{l+1} = +z_{l+1} \\ = 1 & \rightarrow \quad \text{convergence} \end{cases}$$

go to step step 1

stop

Example NH4HSO4 ↔ NH4+ + HSO4- & HSO4- ↔ H+ + SO42-

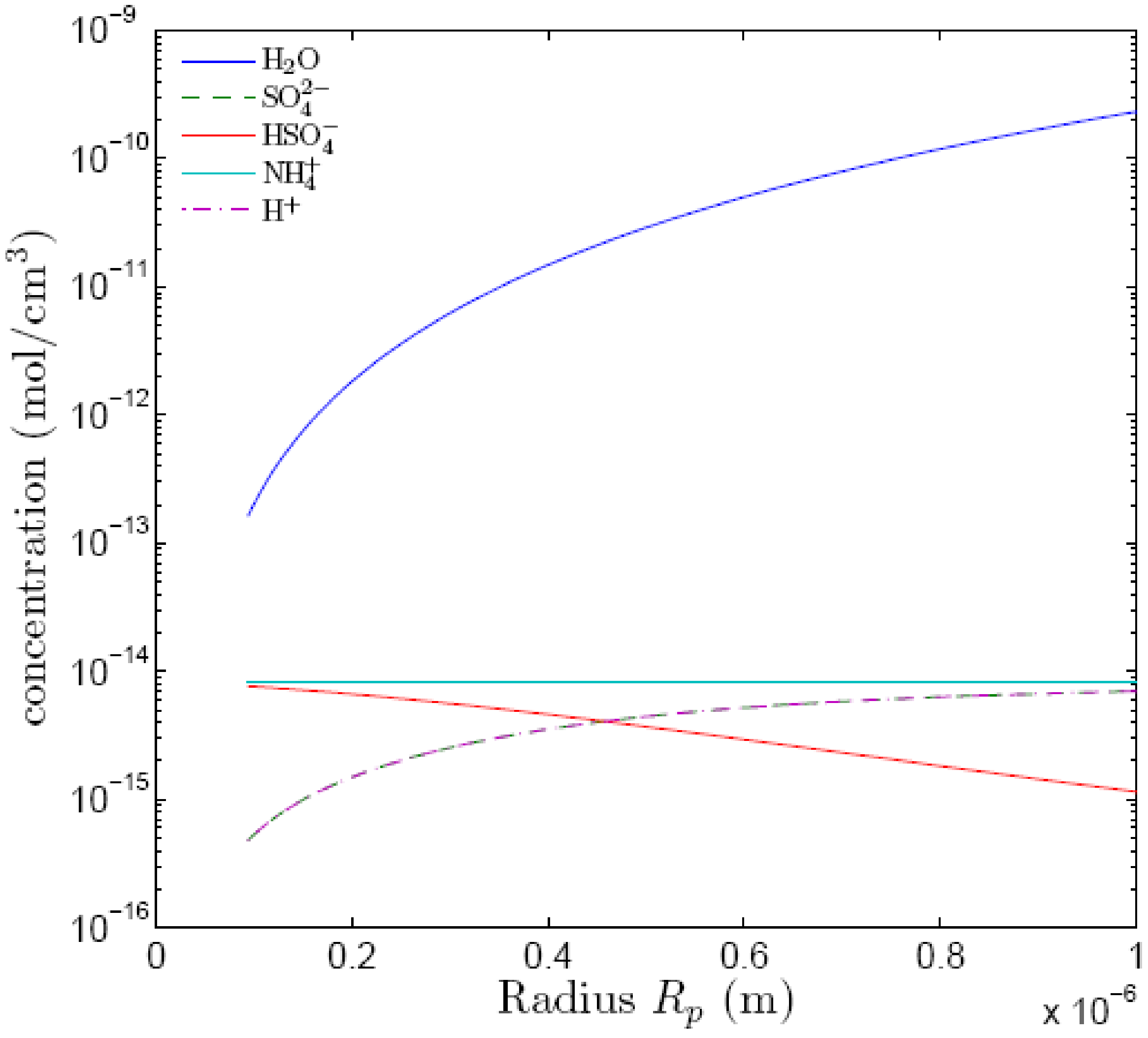


Figure 1: Concentrations as a function of radius

Most detailed liquid phase chemical **database** for cloud and aerosol modelling

- Chemical Aqueous Phase RAdical Mechanism (CAPRAM) Herman et et.
  - CAPRAM2.3:

aqueous-phase species	photolysis reactions	aqueous-phase reac.	heterogeneous equili.	aqueous-phase equili.
70	6	199	34	31

  - CAPRAM2.4:

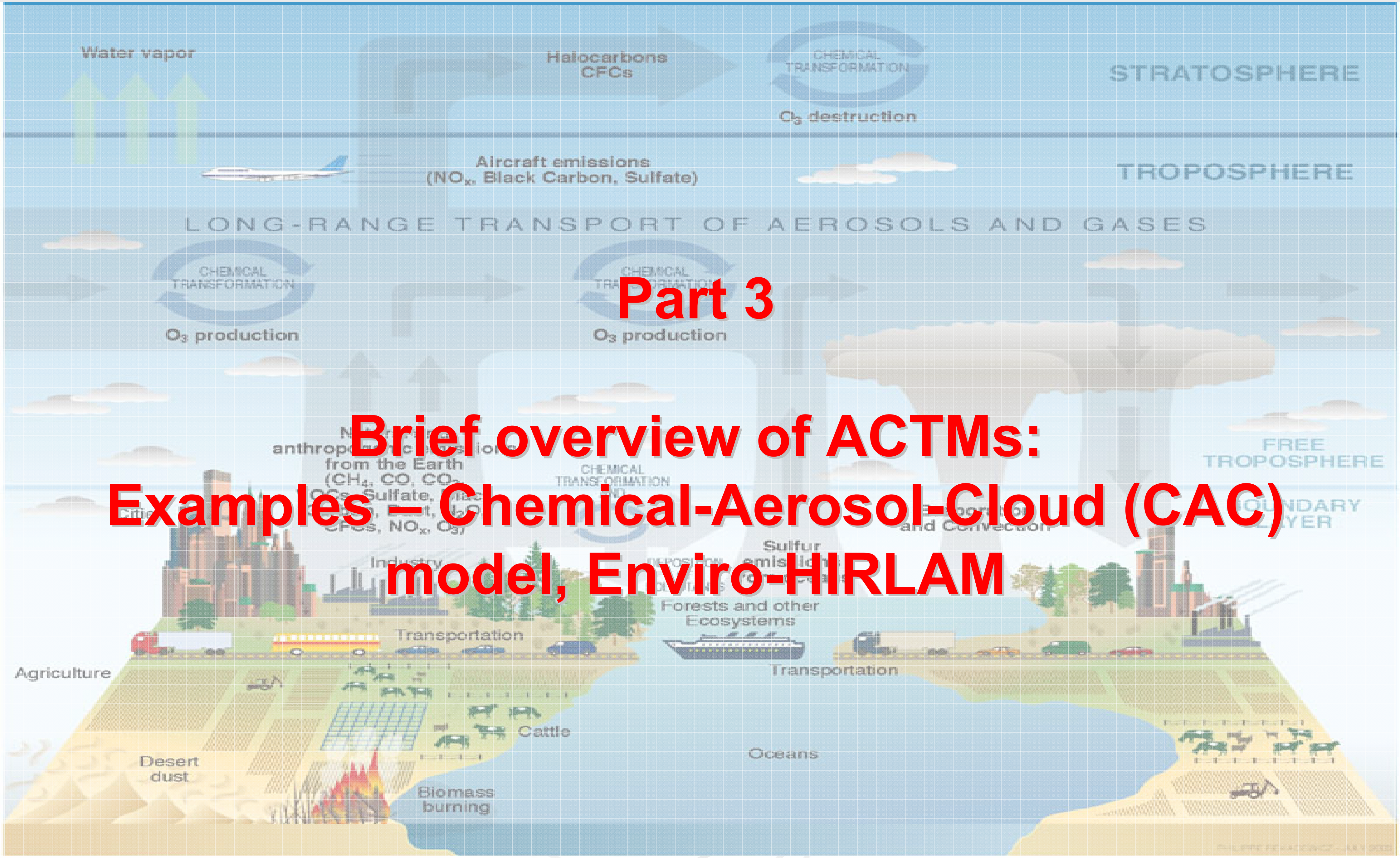
153	11	324	34	57

  - CAPRAM3.0:

164	12	686	36	97

Part 3

Brief overview of ACTMs: Examples – Chemical-Aerosol-Cloud (CAC) model, Enviro-HIRLAM



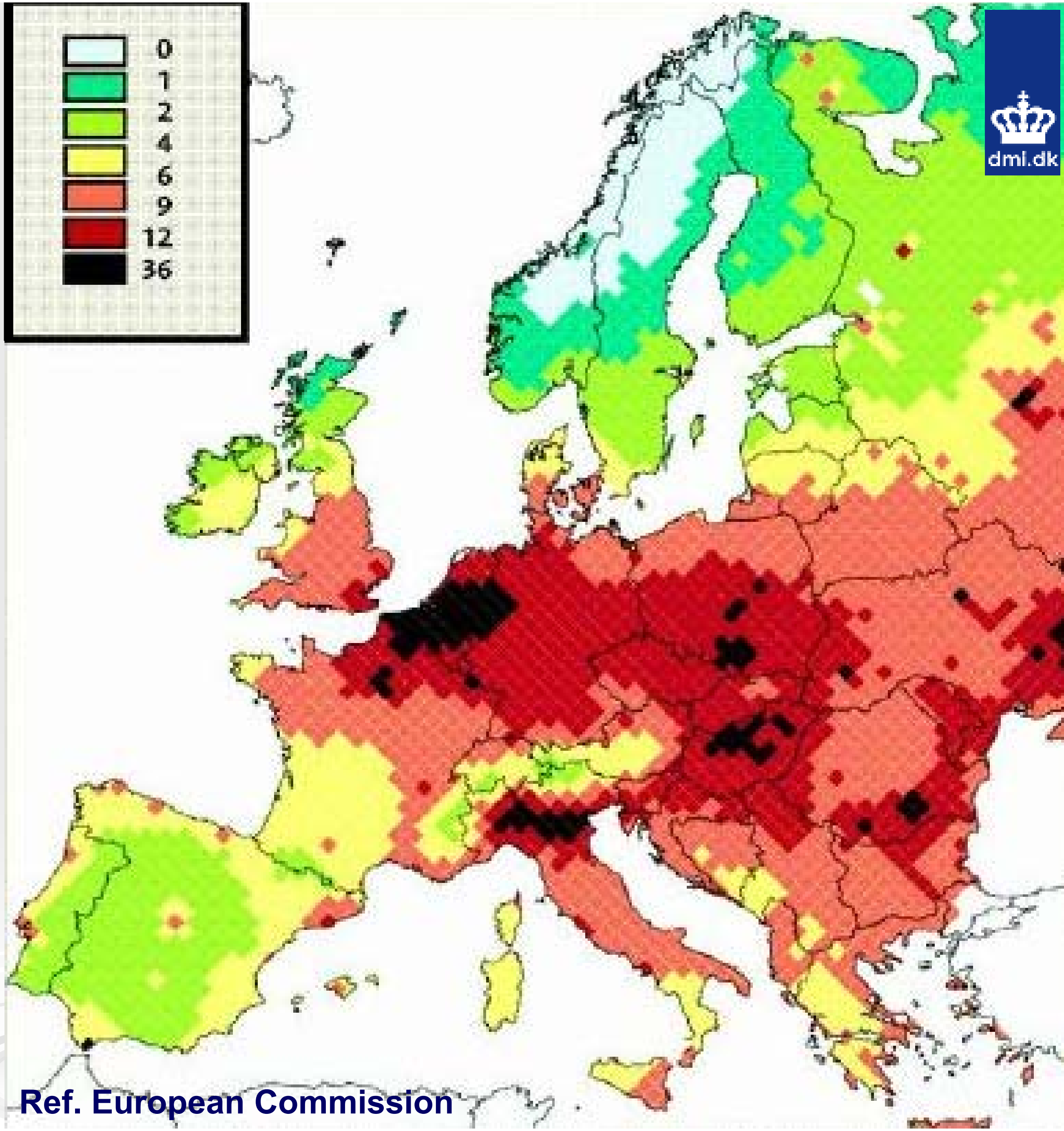
Air Pollutants Thresholds

	Threshold	Av. per.	Effects on humans
O_3 Population information Population warning	 180 µg/m³ 240 µg/m³	 1 h./max. 1 h./max. 3 h.	Forringet lungefunktion, hoste, brystsmerter, åndedrætsbesvær, hovedpine og øjenirritation.
SO_2 Population information	350 µg/m³ 125 µg/m³ 350 µg/m³	1 h./24 times 24 h. 1 h./max.	Forringet lungefunktion, åndedrætsbesvær og i sidste instans forøget dødelighed.
NO_2 Population information	 350 µg/m³	 1 h./max.	Nedsat lungefunktion og åndenød. Øger luftvejenes følsomhed ex. øger infektioner.
CO	10 mg/m³	8 hours	Optages i blodet og hæmmer blodets transport af ilt. Kan derfor have skadelig effekt på hjerne, hjerte, fosters udvikling etc.
Particular Matter: PM10	50 µg/m³ 40 µg/m³	24 hs/35 times yearly	Luftvejslidelser- og hjerte-karsygdomme.
Benzene	5 µg/m³	yearly	Kræftfremkaldende
Pb	0.5 µg/m³	yearly/max.	Nerveskadende stof. Nedsat intelligens, nedsat koncentration og hyperaktivitet.

Red from the Danish Smog and ozoneberedskabet

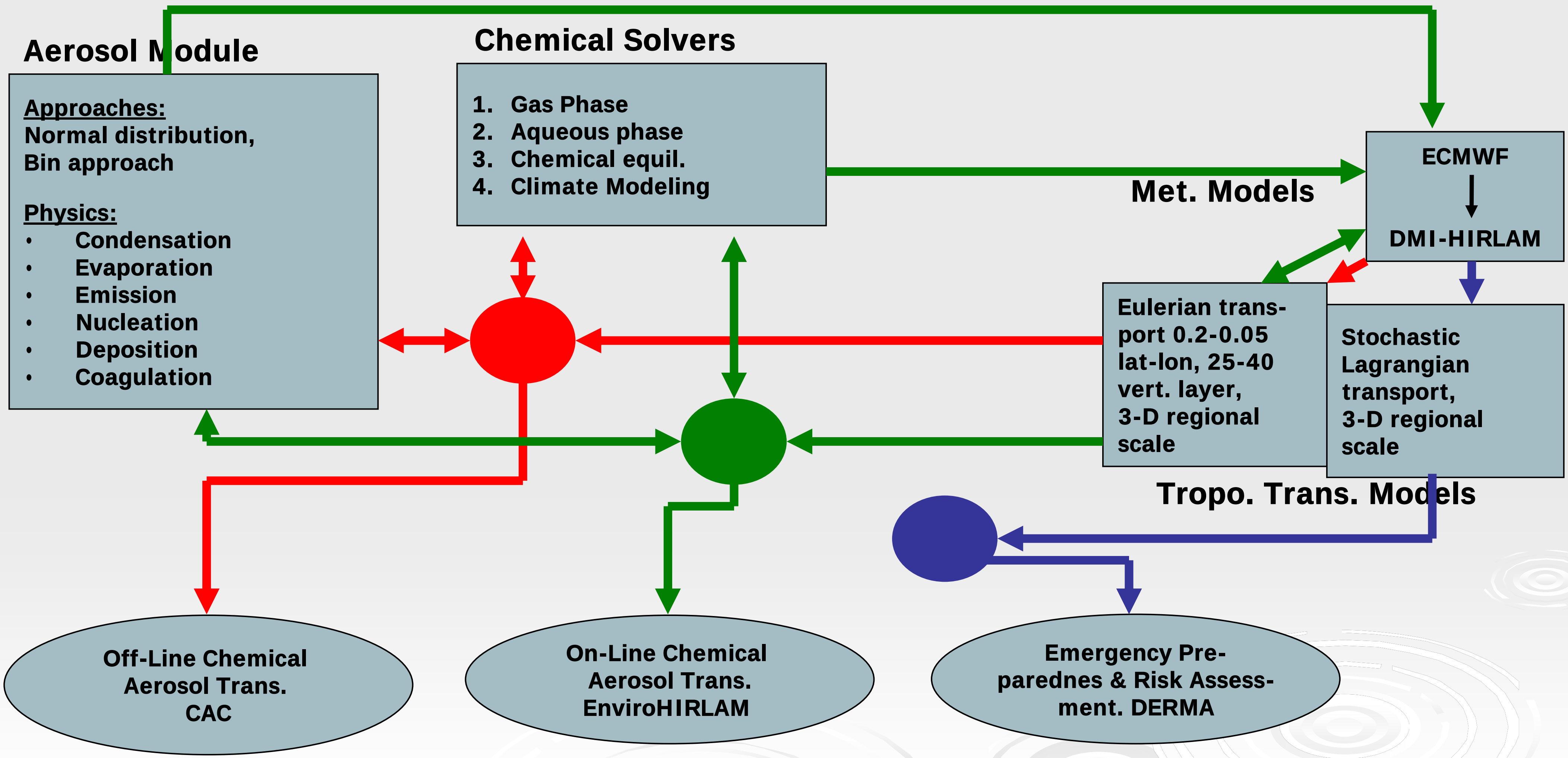
Green from EU

Number of months air pollutants reduce the life of an European on the average →



On the average air pollutants reduce nine months of an European's life.

Air pollution systems at DMI



Regional (European) to city scale air pollution: particles, smog and ozone.

Regional (European) to city scale air pollution: particles, smog and ozone, and pollen.

Nuclear, veterinary and chemical.

Enviro-HIRLAM, Status

Chemistry

- Gas phase chemistry, 17 chemical species, 28 chemical reactions and 1 operator reaction. The mechanism covers:
  - urban plume chemistry (14 reactions)
  - Sulphur/DMS chemistry (4 reactions)
  - Biogenic chemistry (5 reactions)

- Liquid phase chemistry:
  - 4 gas/liquid phase equilibriums
  - 9 liquid/liquid phase equilibriums

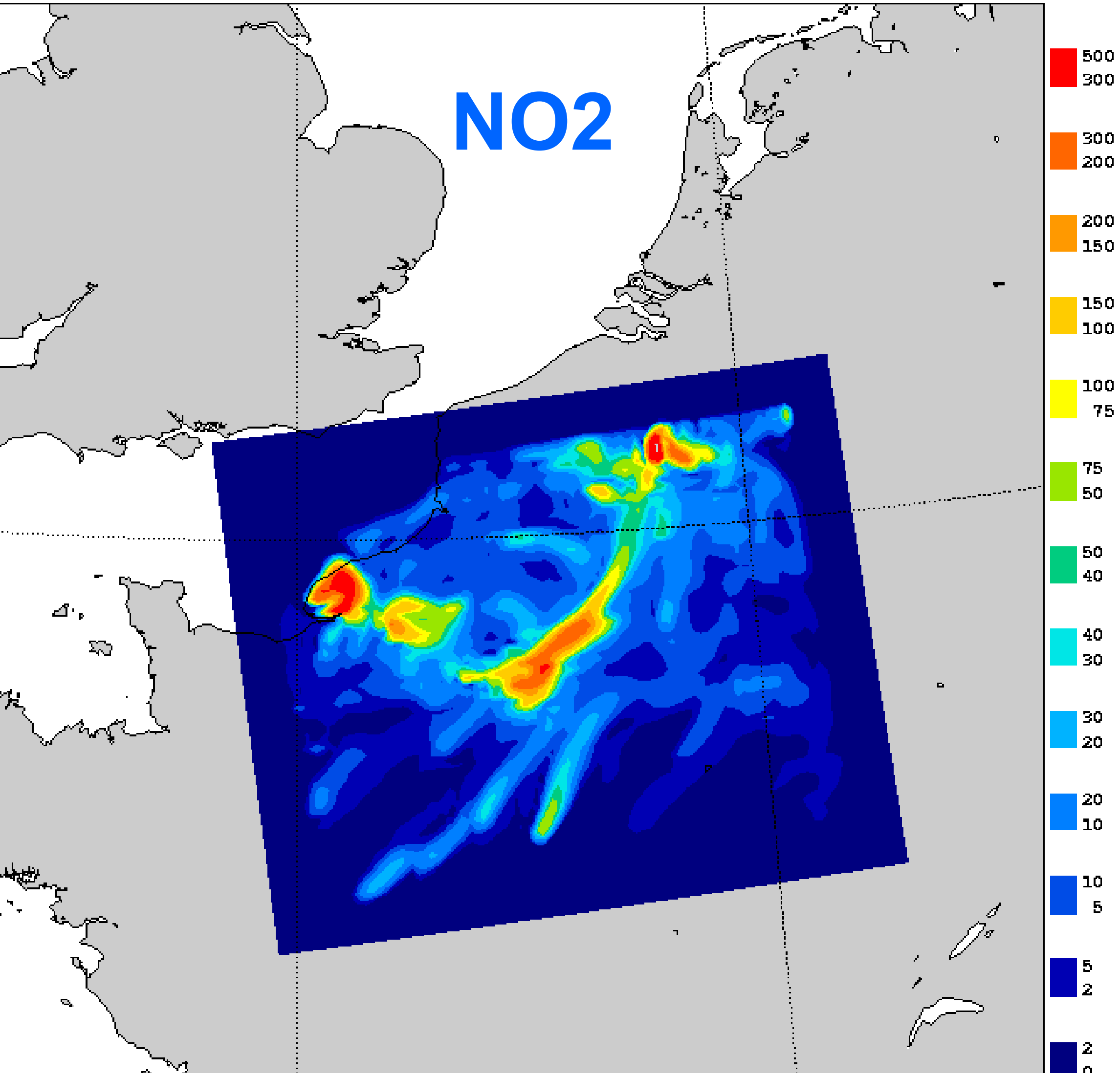
Aerosol physics

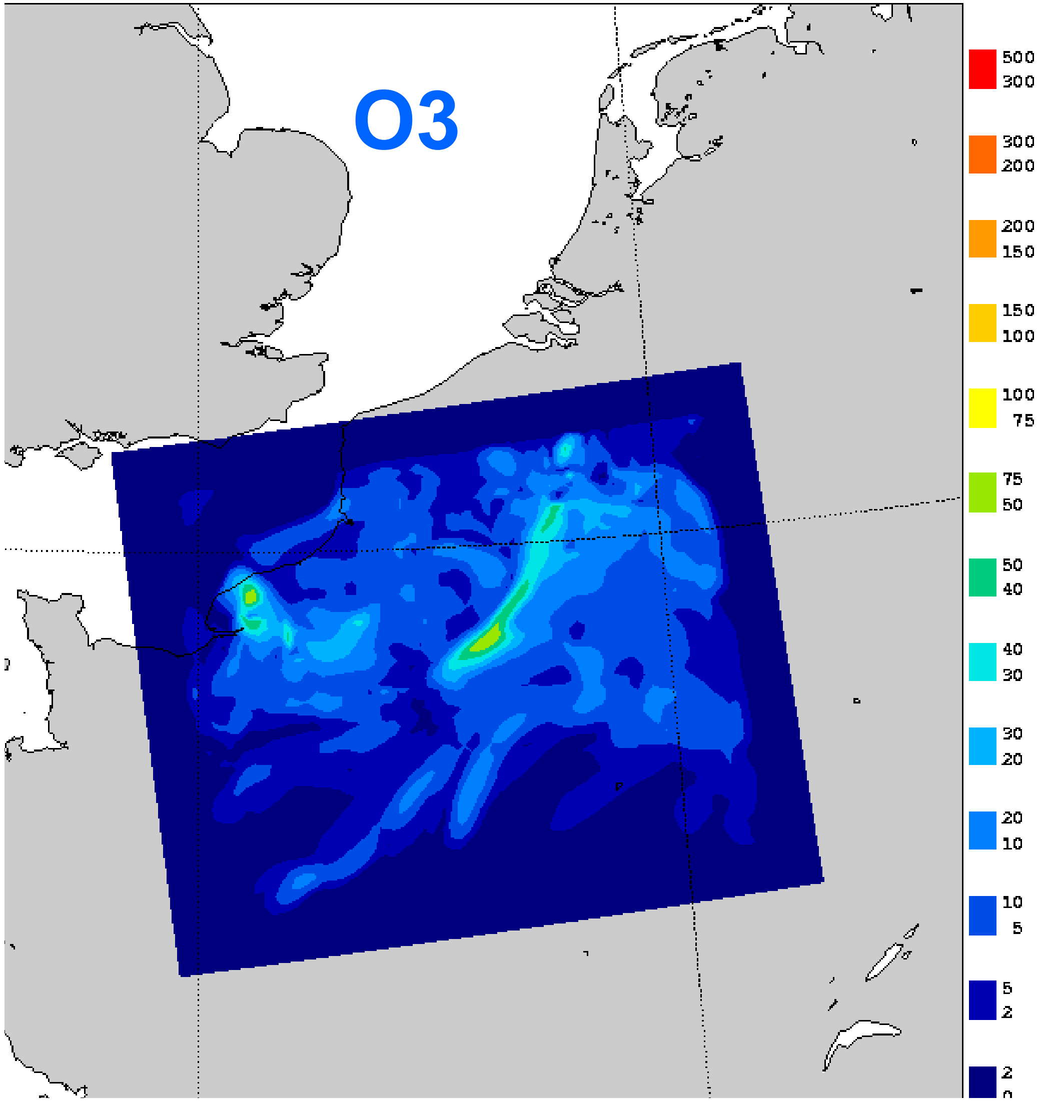
- Modal description (three modes: nucleation, accumulation, coarse):
  - Physics – Condensation, Evaporation, Emission, Nucleation, Deposition and Coagulation

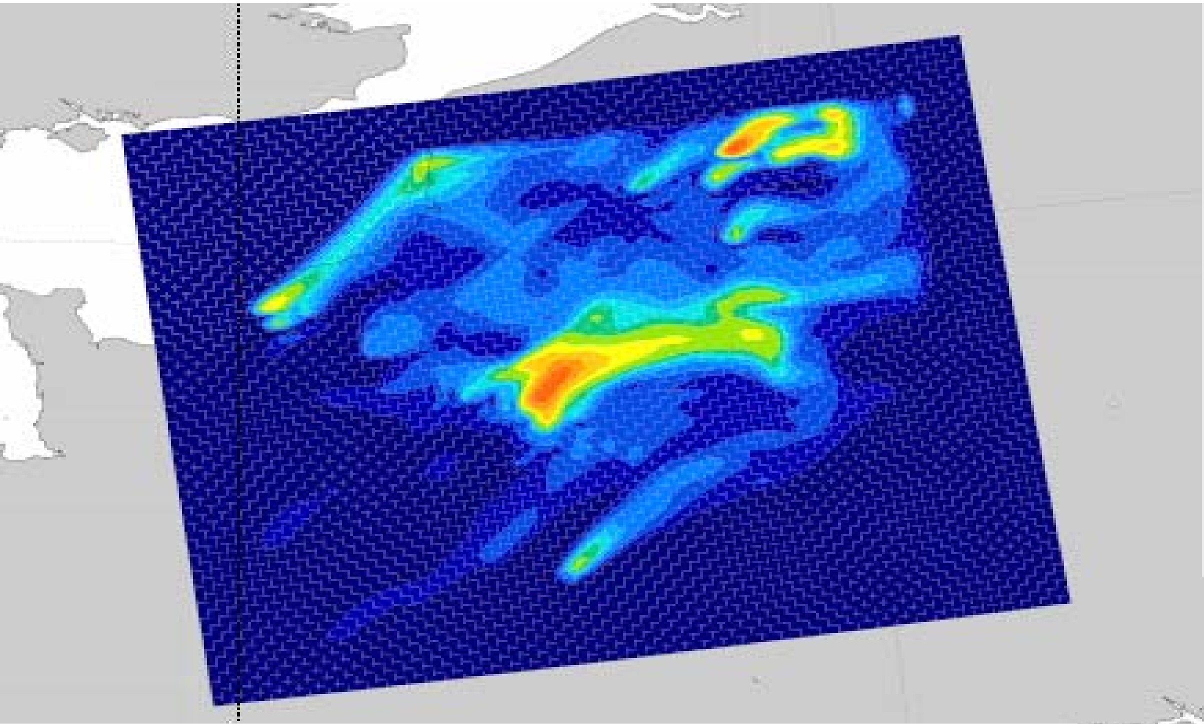
Feedbacks

- First and second indirect effect, and direct effect

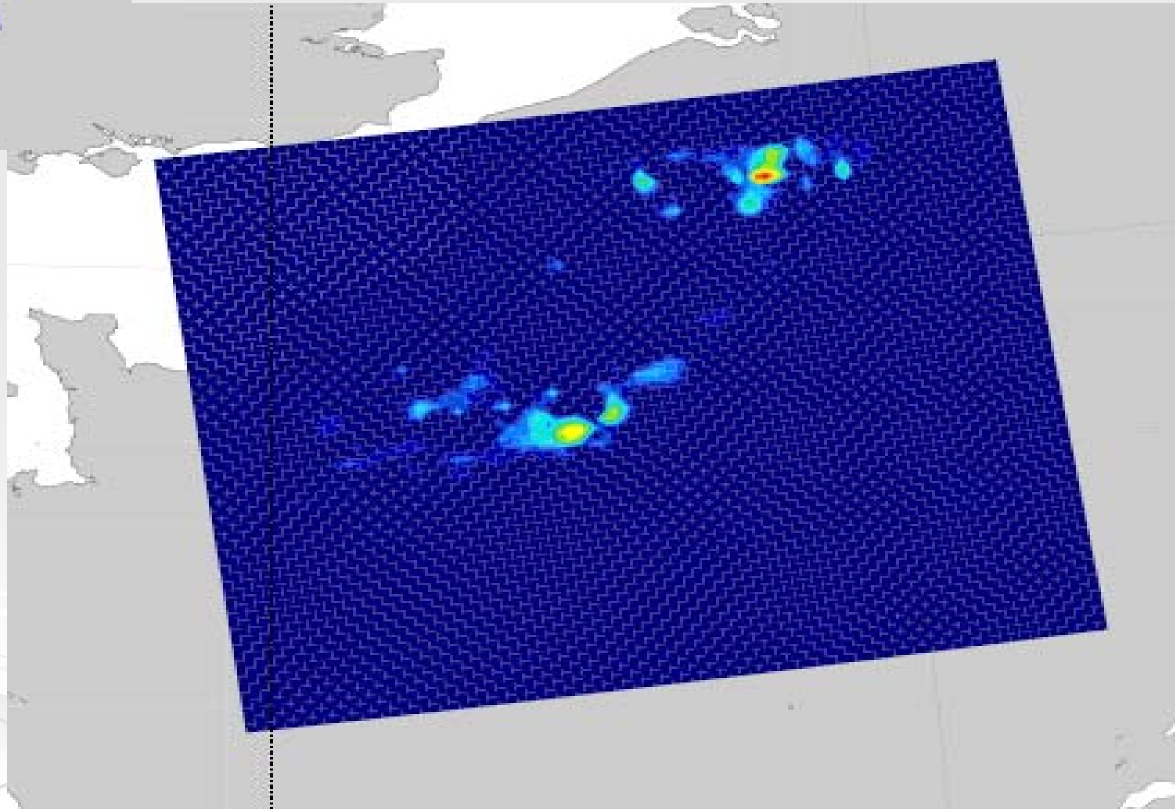
Enviro-HIRLAM, June 29-30 -2005



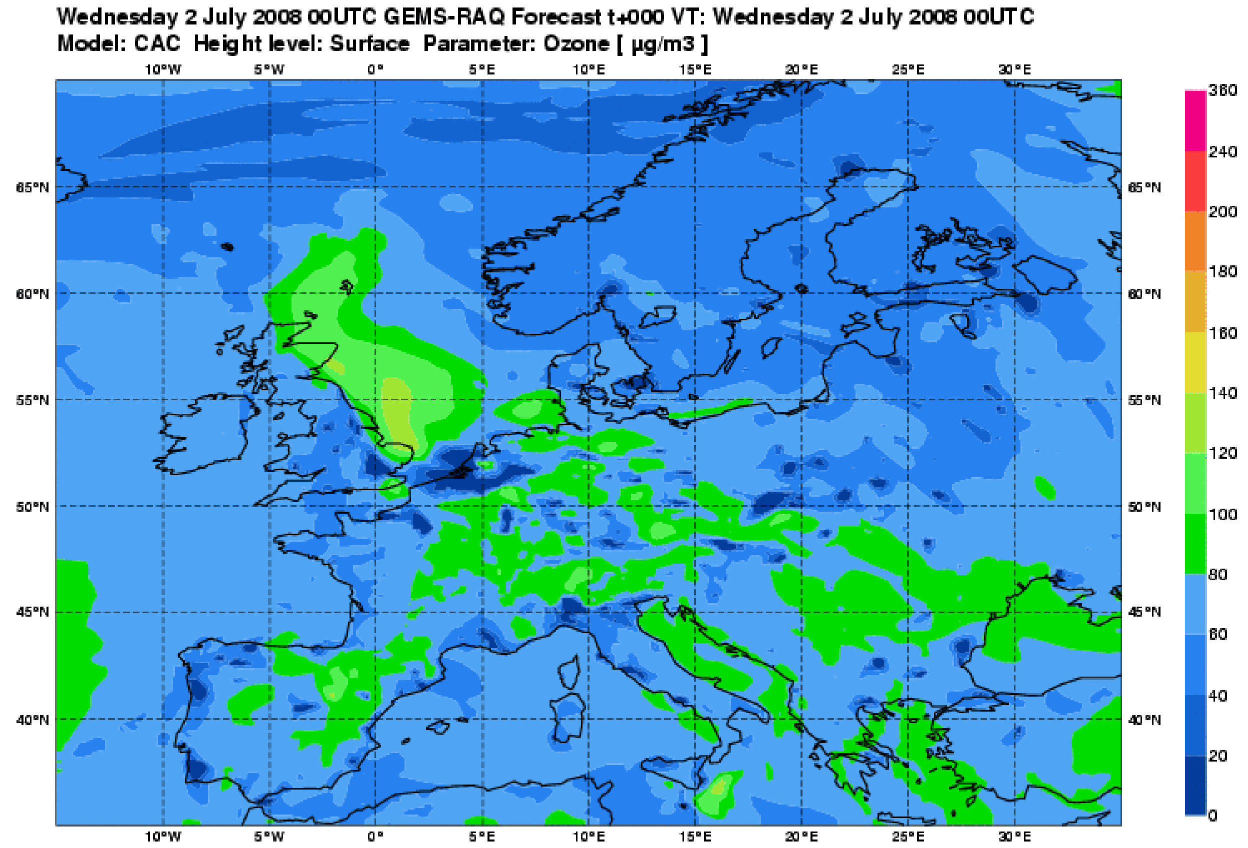




HO after 36 hour
June 30, 2005



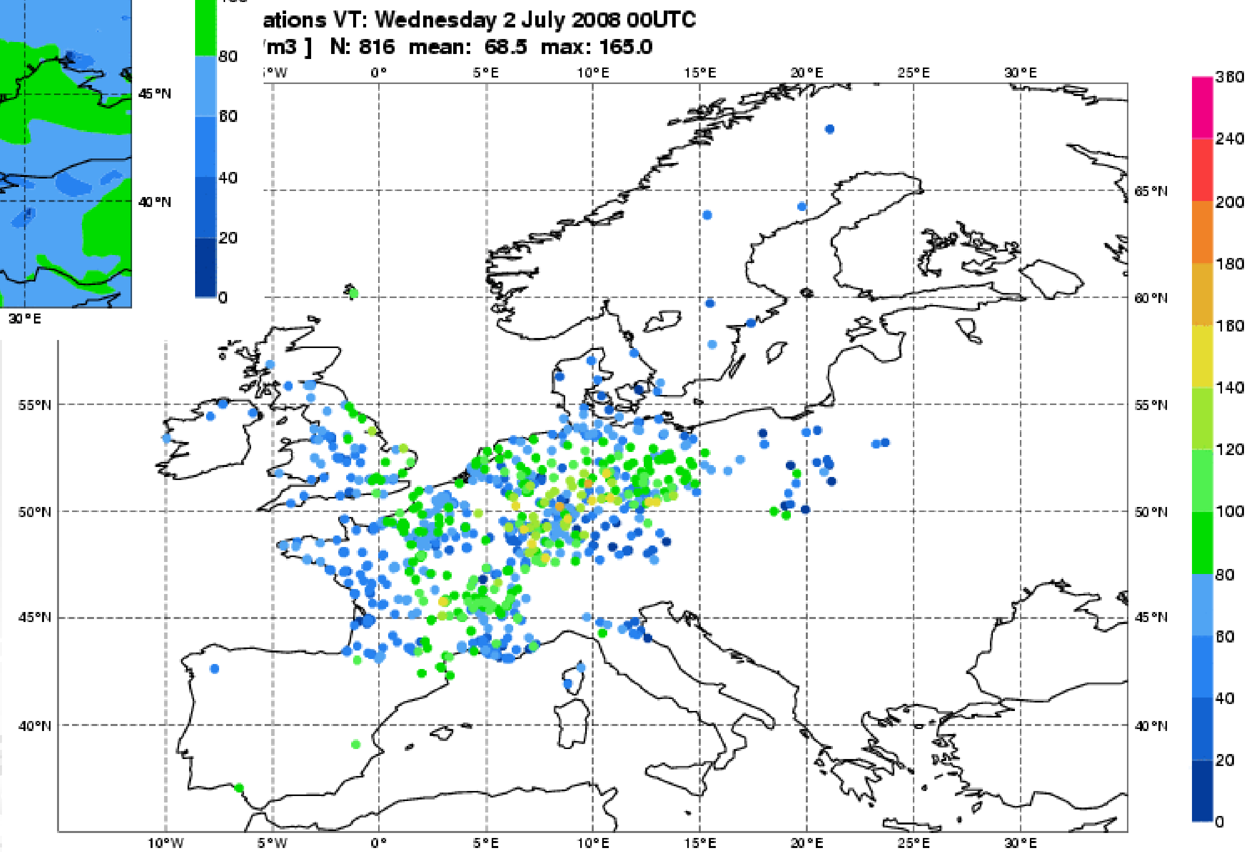
Sulphate aerosols
after 24 hours
June 30, 2005



72 hour ozone forecast

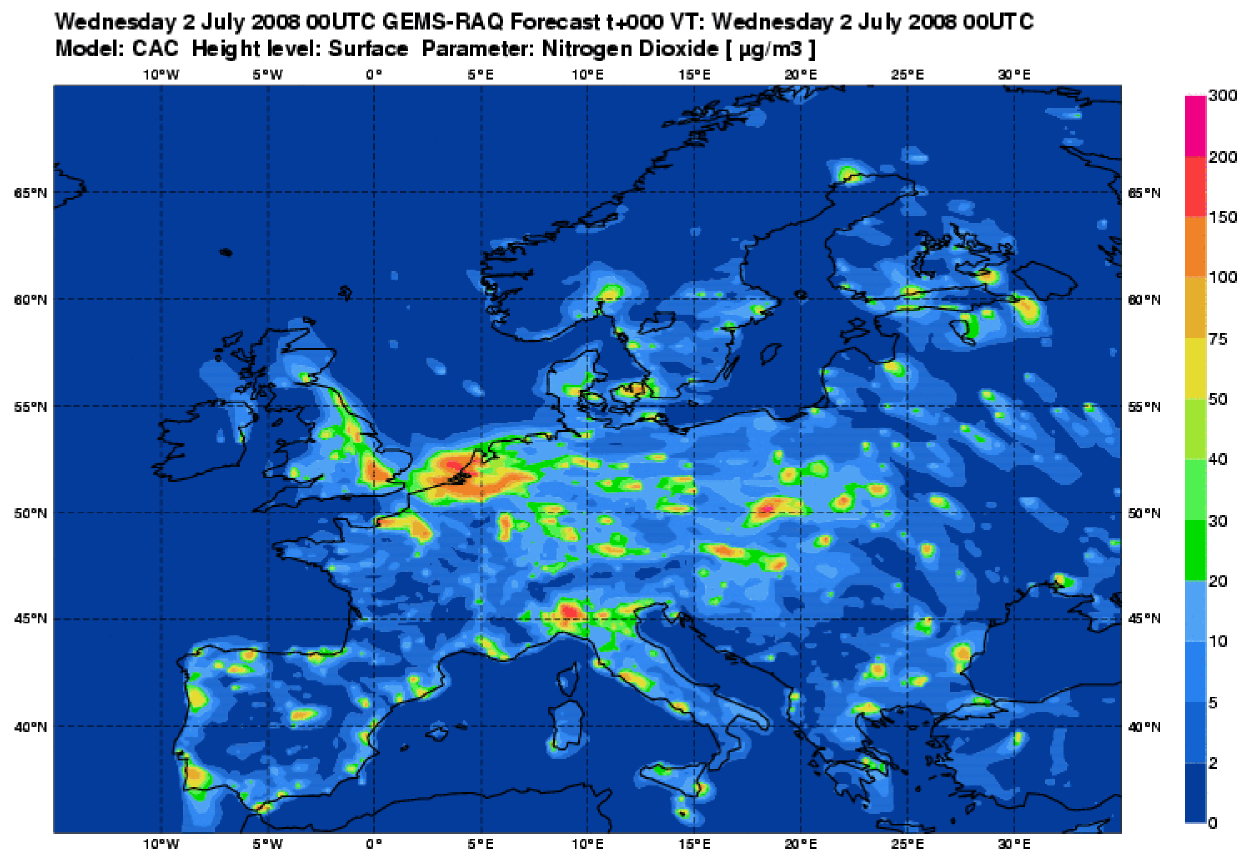
Model: DMI-CAC

June 2 to June 4, 2008



ozone observations

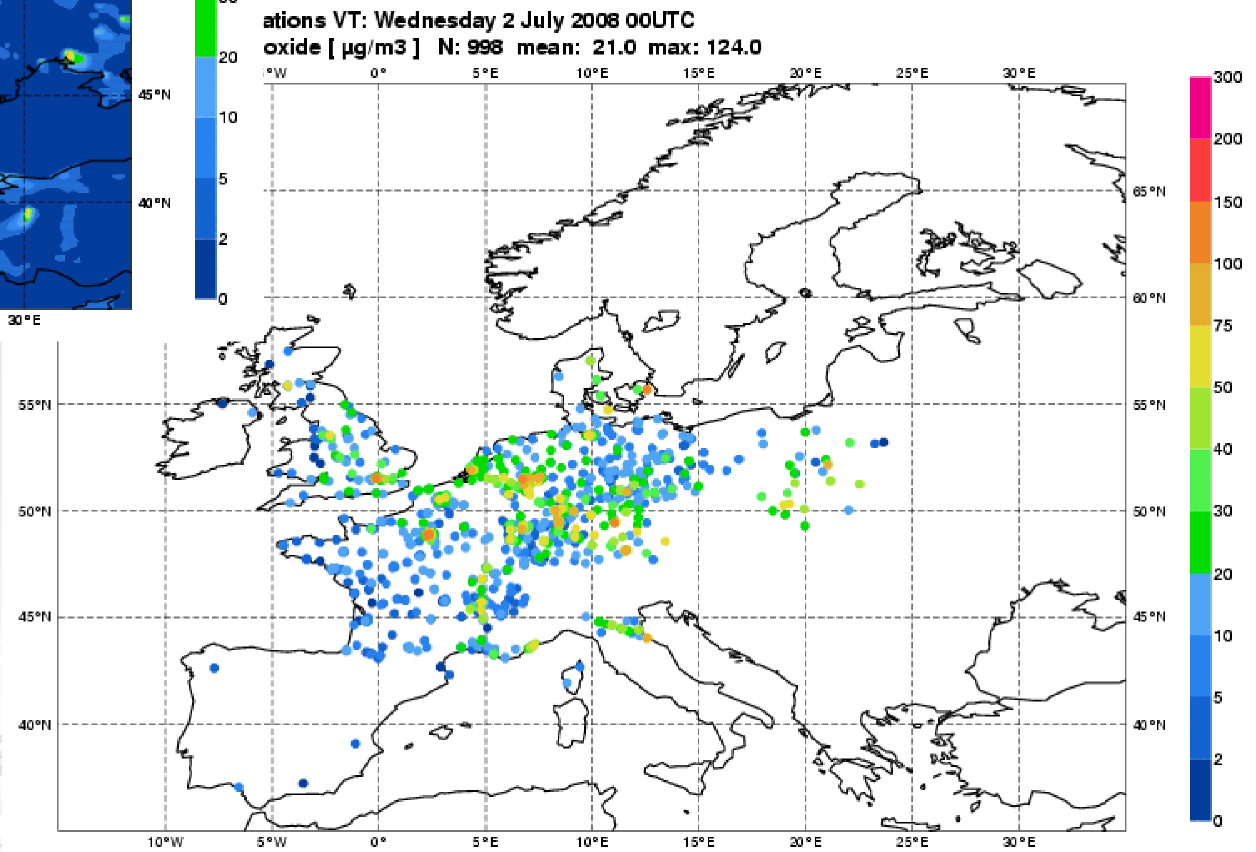
June 2 to June 3, 2008



72 hour NO_2 forecast

Model: DMI-CAC

June 2 to June 4, 2008



NO_2 observations

June 2 to June 3, 2008