Chem-NWP

Contents

- Presentation of NWP-Chem
  - Background of how it is constructed
- Future prospects

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NWP-Chem: Background

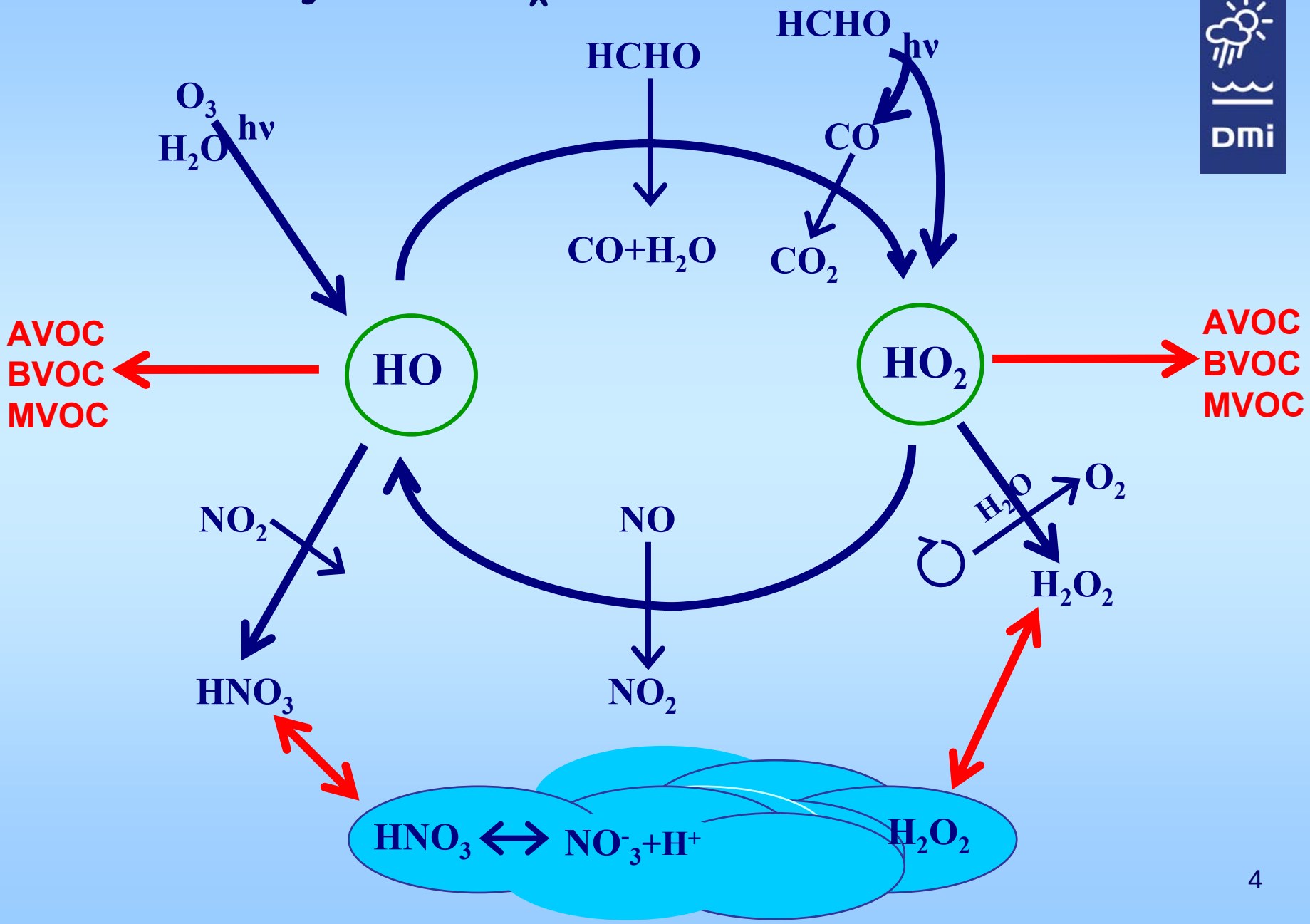
Describe the basics of

- the NO_X cycle
- the HO_X cycle
- the anthropogenic VOC oxidation
- the biogenic VOC oxidation
- the DMS oxidation

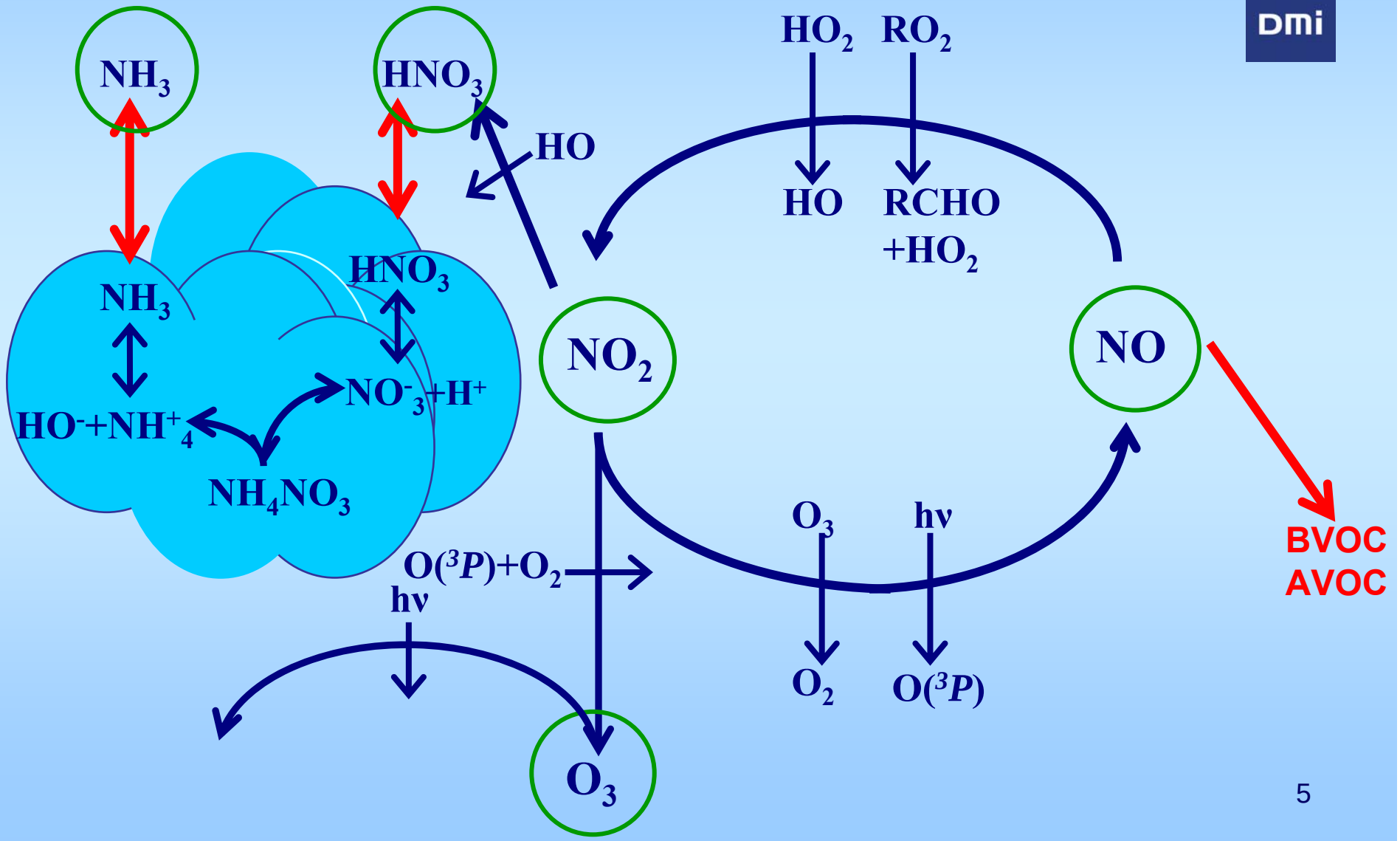
Lumped Atmospheric Chemical Mechanisms

Mechanism Abbreviation	Developed in	Number of Species	Number of Reactions
ADOM-11	USA	47	114
CB-05	USA	52	156
RADM2	USA	63	158
SAPRC-90	USA	60	155
EMEP	Europe	79	141
RACM	USA	77	237
SAPRC-99	USA	74	211
NWP-Chem	Europe	28 (22)	32 (ph = 7) (24)

Reaction Cycle of HO_x



Reaction Cycle of NO_x



Lumped Species in RACM

Alkanes:

CH4 (1.0) methane

ETH (2.0) ethane

HC3 (2.9) alkanes, alcohols, esters and alkynes with HO rate constant (298 K, 1 atm) less than $3.4\times10^{-12}cm^3s^{-1}$

HC5 (4.8) alkanes, alcohols, esters and alkynes with HO rate constant (298 K, 1 atm) between 3.4×10^{-12} cm^3s^{-1} and $6.8\times10^{-12}cm3s^{-1}$

HC8 (7.9) alkanes, alcohols, esters and alkynes with HO rate constant (298 K, 1 atm) greater than $6.8\times10^{-12}cm^3s^{-1}$

Alkenes: ETE (2.0) - OLT (3.8) - OLI (5.0) DIEN (4.0)

Stable Biogenic Alkenes: ISO (5.0) - API (10.0) LIM (10.0)

Aromatics: TOL (7.1) - XYL (8.9) - CSL (6.6)

Carbonyls: HCHO (1.0) - ALD (2.4) - KET (3.5) - GLY (2.0) - MGLY (3.0) - DCB - (4.2) MACR (4.0) - UDD (4.2)- HKET(3.0)

Organic Nitrogen: ONIT (4.0) - PAN (2.0) TPAN (4.0)

Organic Peroxides: OP1 (1.0) - OP2 (2.0) PAA (2.0)

Organic Acids: ORA1 (1.0) - ORA2 (2.0)

Peroxy Radicals From Alkanes:

MO2 (1.0) methyl peroxy radical

ETHP (2.0) peroxy radical formed from ETH

HC3P (2.9) peroxy radical formed from HC3

HC5P (4.8) peroxy radical formed from HC5

HC8P (7.9) peroxy radical formed from HC8

Peroxy Radicals From Alkenes: ETEP (2.0) OLTP (3.8) - OLIP (4.8)

Peroxy Radicals From Biogenic Alkenes: ISOP (5.0) - APIP (10.0) - LIMP (10.0)

Radicals Produced From Aromatics: PHO (6.6) ADDT (7.1) - ADDX (8.9) - ADDC (6.6) TOLP (7.1) - XYLP (8.9) - CSLP (6.6)

Peroxy Radicals With Carbonyl Groups: ACO3 (2.0) - TCO3 (4.0) - KETP (3.9)

Other Peroxy Radicals: OLNN (3.0) - OLND (3.0) - XO2

Lumped Species in RACM and NWP-Chem

Alkanes:
CH4 - ETH - HC3 - HC5 - HC8
HR

Alkenes:
ETE - OLT - OLI - DIEN
HR

Stable Biogenic Alkenes:
ISO - API - LIM
BIO

Aromatics:
TOL - XYL - CSL
HR

Carbonyls:
HCHO - ALD - KET - GLY - MGLY
DCB - MACR - UDD - HKET
RCHO

Organic Nitrogen:
ONIT - PAN - TPAN
HR

Organic Peroxides:
OP1 - OP2 - PAA
RCHO

Organic Acids:
ORA1 - ORA2
ROOH

Peroxy Radicals From Alkanes:
MO2 - ETHP - HC3P - HC5P - HC8P
RO2

Peroxy Radicals From Alkenes:
ETEP - OLTP - OLIP
RO2

Peroxy Radicals From Biogenic Alkenes:
ISOP - APIP - LIMP
BIO2

Radicals Produced From Aromatics:
PHO - ADDT - ADDX – ADDC
TOLP - XYLP - CSLP
RO2

Peroxy Radicals With Carbonyl Groups:
ACO3 - TCO3 - KETP
RO2

Other Peroxy Radicals:
OLNN - OLND - XO2
RO2 - XO2

Organic Sulphur Species:
DMS - MSA - MSIA

Typical AVOC Emission Load in Europe

Lumping Group	Emission in %
ALD – RCHO	0.5
ETE – HR	*6.5*
ETH – HR	3.4
HC3 – HR	*41.8*
HC5 – HR	*10.9*
HC8 – HR	*6.4*
HCHO – RCHO	2.0
KET – RCHO	*7.2*
OLI – HR	2.7
OLT – HR	3.1
TOL – HR	*8.1*
XYL – HR	*7.4*

- **HC3, HC5 and HC8 represents more than 65% of the HR emissions**
- **KET represents more than 74 % of the RCHO emissions**

Emission weighting is used in the development of NWP-Chem.

Numerical solution of the chemistry

- Rates and coefficients in NWP-Chem-gas is estimated based on lumping, optimization procedures and emission weighting.
- Chemical reactions →QSSA.
- Equilibrium systems → Mass-Flux Iteration method.
- NWP-Chem-gas are tested against the RACM+ELCID mch. at different standard marine, rural and plume scenarios.

Plume Case Simulations

July 1, 1985, clear sky

ground albedo 0.10

solar declina. 23º

longitude 45º north

altitude 0.0 km

temperature 288.15 K

pressure 1.01315 bar

H_2O	1.00	%
O_3	50.0	ppbV
NO	0.20	ppbV
NO_2	0.50	ppbV
HNO_3	0.20	ppbV
CO	200.	ppbV
CH_4	1700	ppbV
H_2	500.	ppbV
H_2O_2	2.00	ppbV
HCHO	1.00	ppbV
O_2	20.9	%
N_2	78.1	%

NO	1.1×10^{6} $cm^{-3}s^{-1}$
NO_2	0.0 $cm^{-3}s^{-1}$
SO_2	2.2×10^{5} $cm^{-3}s^{-1}$
CO	2.4×10^{6} $cm^{-3}s^{-1}$
VOC	3.0×10^{6} $cm^{-3}s^{-1}$

Quasi Steady State Approximation (QSSA)

Summary

A method related to the simple exponential is called QSSA.

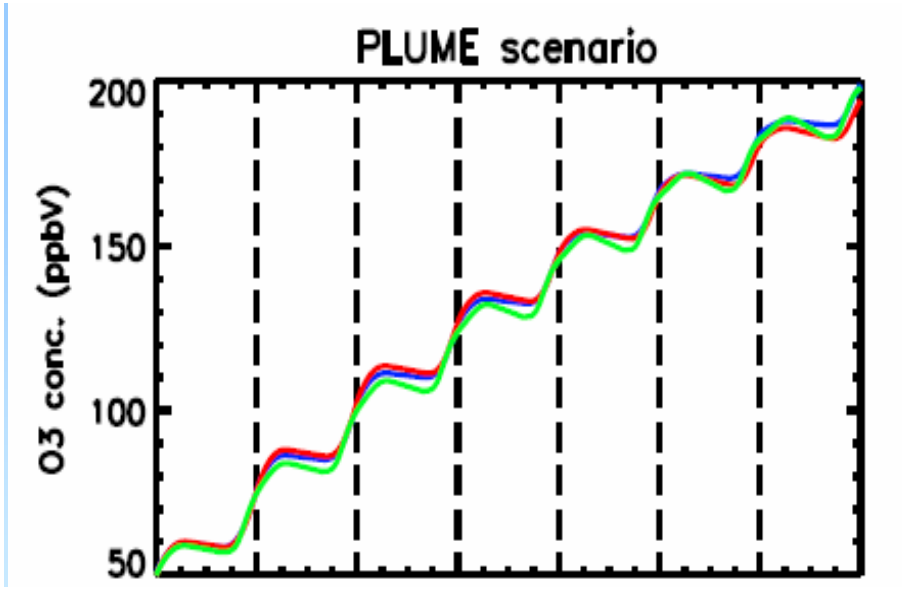
$\delta L_{i,t-\delta}$: used to determined how the lifetime of the species slowed during the time evolution

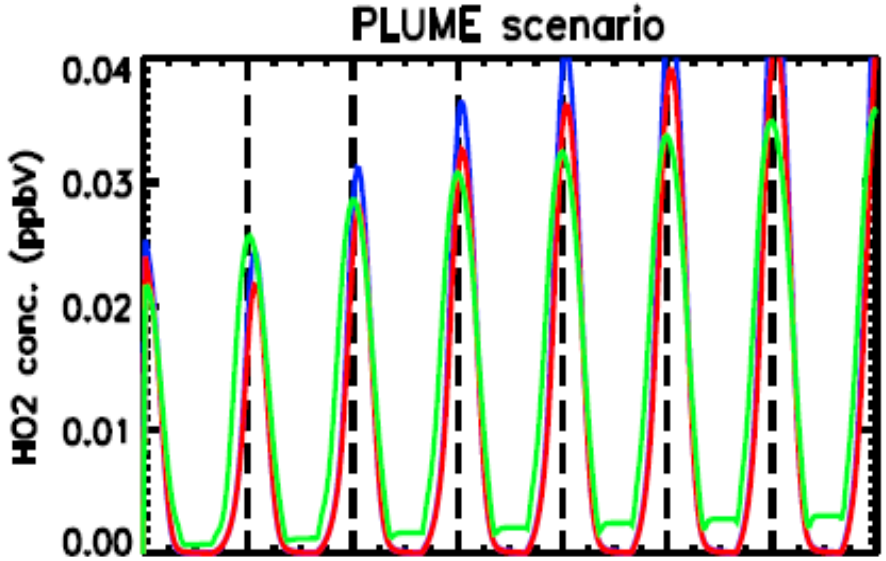
species' lifetime long → forward Eulerian equation

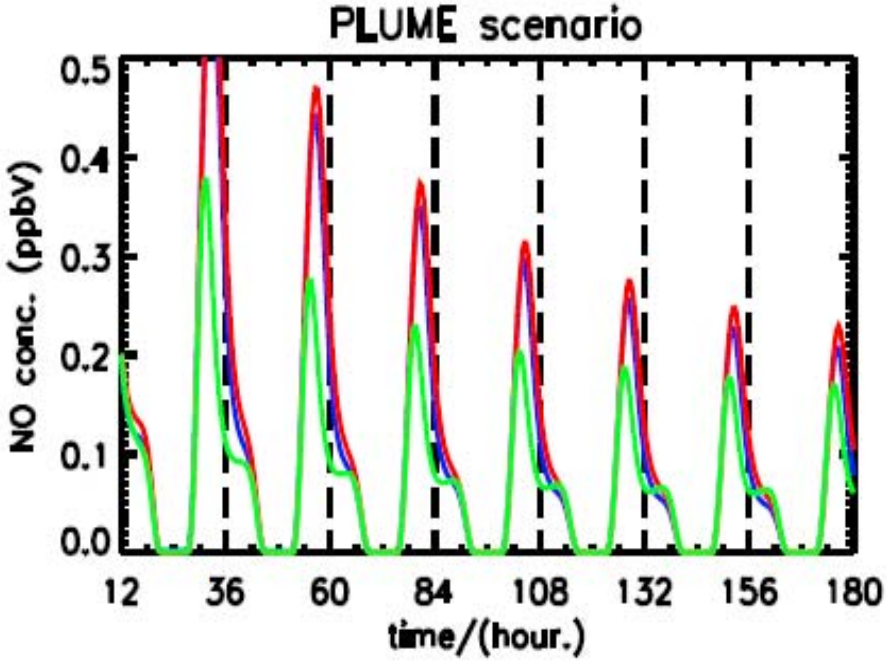
species' lifetime moderate → simple exponential method

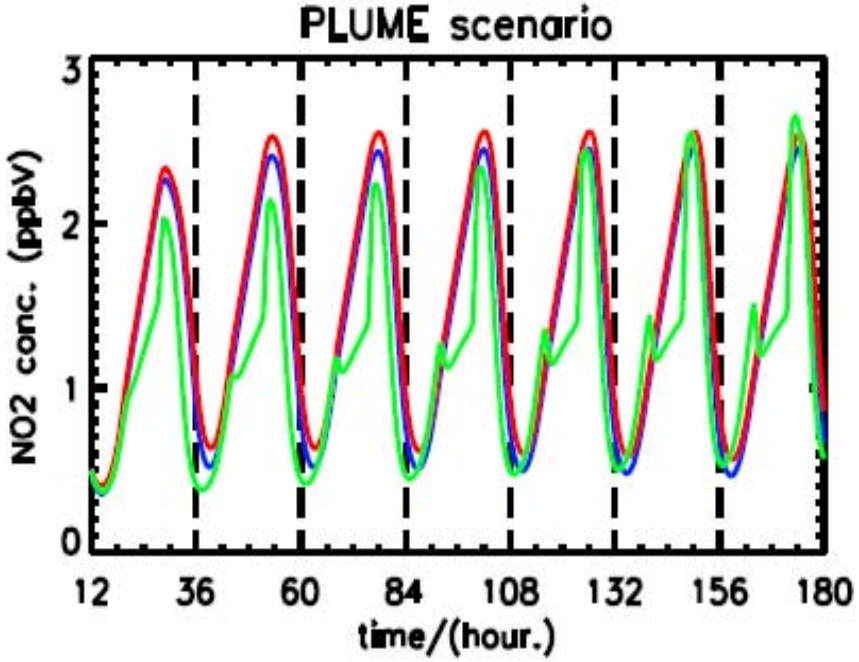
$$N_{i,t} = \begin{cases} N_{i,t-\delta} + \delta\,(P_{i,t-\delta} - L_{i,t-\delta}) & \text{if } \delta L_{i,t-\delta} < 0.001 \\ N_{i,t-\delta}\exp(-\delta P_{i,t-\delta}) + P_{i,t-\delta}/L_{i,t-\delta}(1 - \exp(-\delta L_{i,t-\delta})) & \text{if } 0.001 \le \delta L_{i,t-\delta} \le 10 \\ P_{i,t-\delta}/L_{i,t-\delta} & \text{if } \delta L_{i,t-\delta} > 10 \end{cases}$$

species' lifetime short → steady state equation

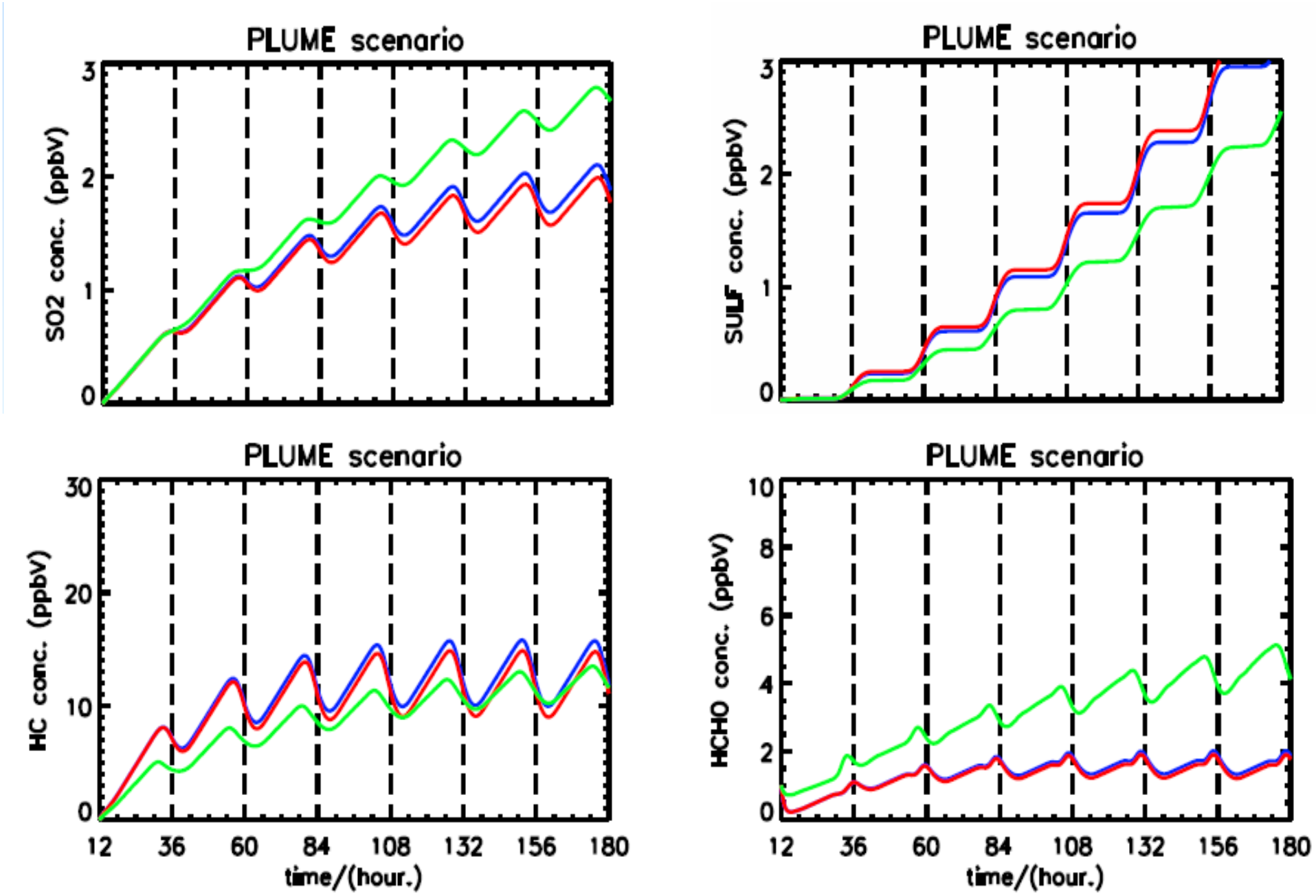








RACM/GEAR NWP-Chem-Gas/GEAR NWP-Chem/QSSA



RACM/GEAR NWP-Chem-Gas/GEAR NWP-Chem/QSSA

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 **liquids**

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: $z_i = 0.5(Q_d + Q_n)$ 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:

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

go to step step 1

stop

Ex. $NH_4HSO_4 \leftrightarrow NH_4^+ + HSO_4^-$ & $HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$

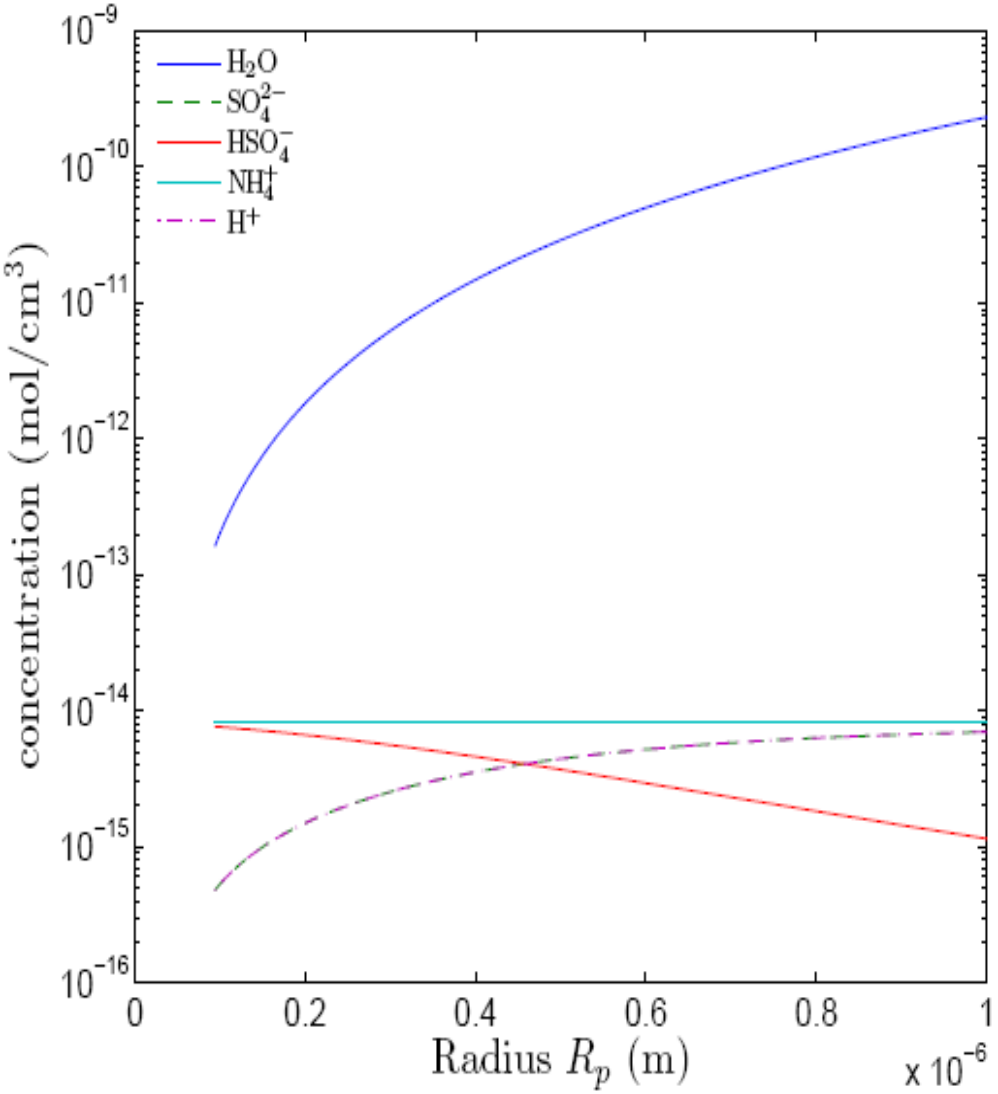


Figure 1: Concentrations as a function of radius

Future developments:

- Implementation of DMS chemistry.
- Improvements and tests of NWP-Chem gas.
- Add aqua phase chemistry and liquid phase equilibrium to NWP-Chem.
- Change the MFI with non-iterative scheme.
- Change QSSA with another fast solver.

- Methods:
  - Development of scenarios,
  - compare NWP-Chem with more detailed atmospheric chemical mechanisms using 0D modelling.

Final Goal with NWP-Chem Implementation in 3D models

NWP-Chem is today used in

- Enviro-HIRLAM (3D regional model) and
- M2UE (street canyon model)

New versions of NWP-Chem will be implemented

- in Enviro-HIRLAM,
- maybe in the climate model EC-EARTH and
- Maybe in the climate model HIRHAM.