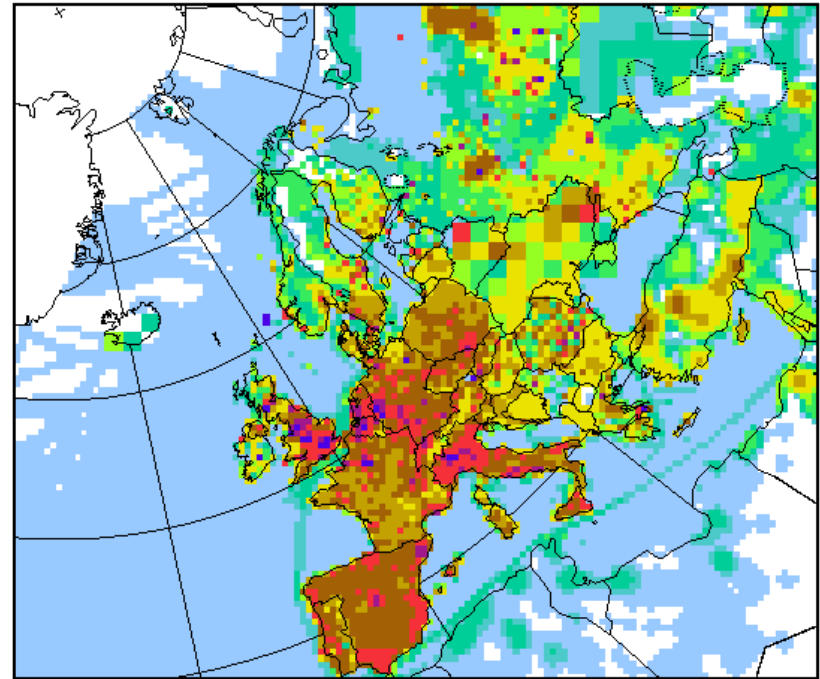
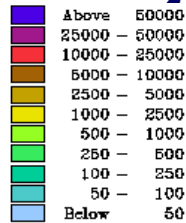


Block 2: Lectures 5 and 6

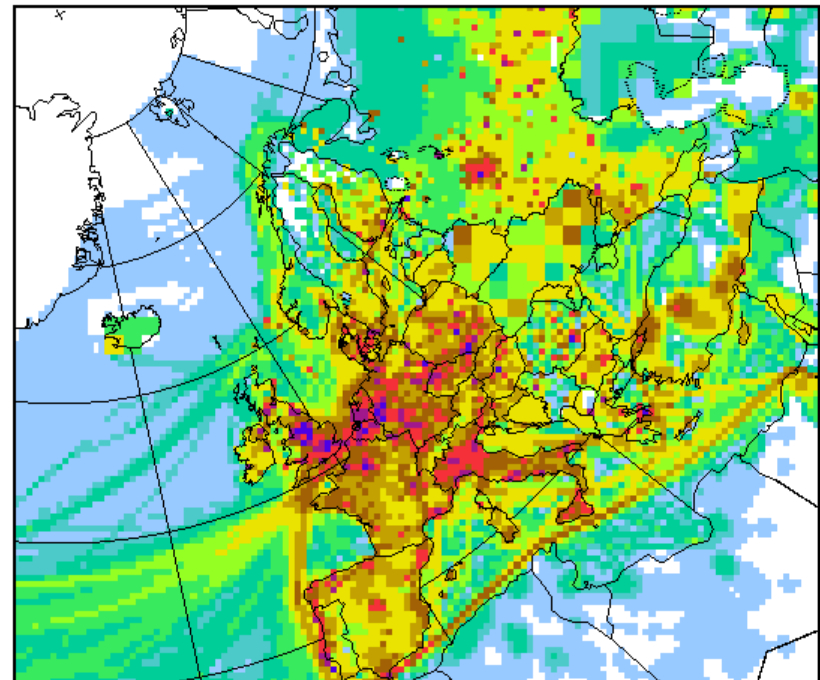
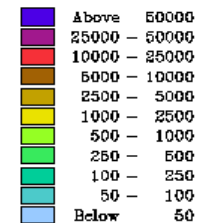
1. Implementation of Chemistry in ACTM:
 - A. Lumping of chemical mechanisms
 - B. How is the ODE for chemical mechanisms solved numerically
2. Liquid phase chemistry:
 - A. Basic reactions
 - B. Numerical problems to solve
3. Brief overview of ACTMs:
 - A. Examples – Chemical-Aerosol-Cloud (CAC) model, Enviro-HIRLAM

**50×50 km²
EMEP
emission
inventories**

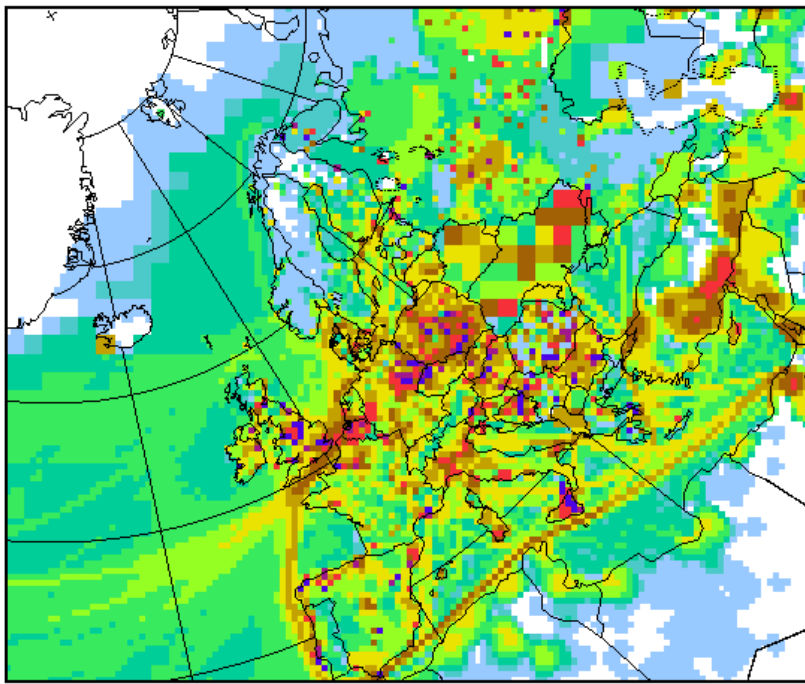
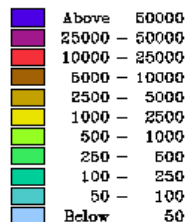
**tonnes
of SO₂**



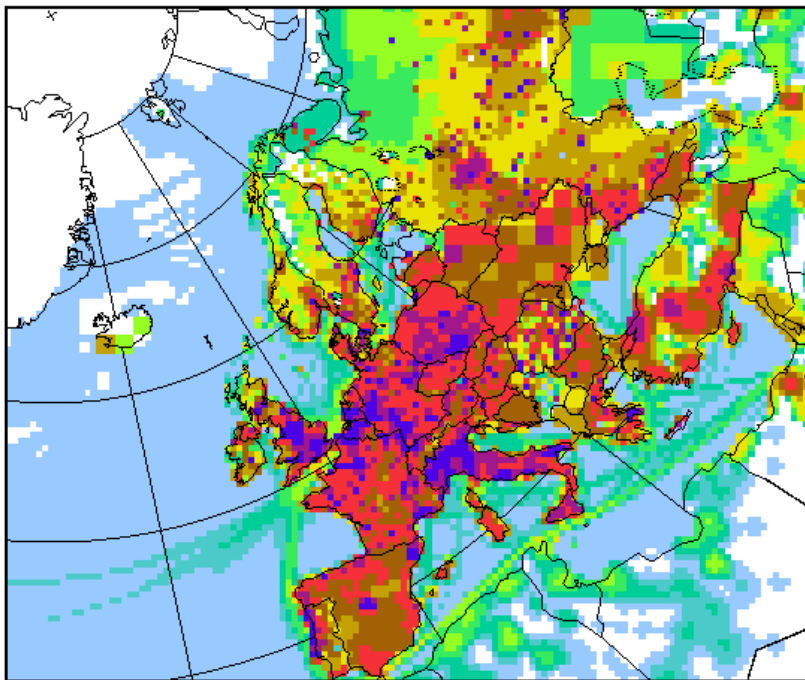
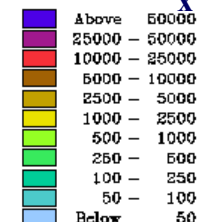
**tonnes of
NMVOC**



**tonnes
of CO**



**tonnes
of NO_x**



Typical VOC emissions in Europe

methane	pent-2-ene	2-methylpentane	m-ethyltoluene
ethane	pent-1-ene	2,2-dimethylbutane	p-ethyltoluene
propane	butylene	2-methylhexane	1,2,3-trimethylbenzene
n-butane	acetylene	methylheptanes	1,2,4-trimethylbenzene
i-butane	benzene	methyloctanes	1,3,5-trimethylbenzene
n-pentane	toluene	2-methylbut-1-ene	formaldehyde
i-pentane	o-xylene	3-methylbut-1-ene	acetaldehyde
n-hexane	m-xylene	2-methylbut-2-ene	propionaldehyde
n-heptane	p-xylene	methylnonanes	butyraldehyde
n-octane	methanol	n-undecane	i-butyraldehyde
n-nonane	ethanol	3-methylpentane	valeraldehyde
n-decane	acetone	2,3-dimethylbutane	benzaldehyde
n-dodecane	methylethylketone	3-methylhexane	n-butyl-acetate
ethylene	methylisobutylketone	ethylbenzene	i-butyl-acetate
propylene	methyl-acetate	n-propylbenzene	methane-chloroform
but-1-ene	ethyl-acetate	i-propylbenzene	methyl-chloroform
but-2-ene	i-propyl-acetate	o-ethyltoluene	tetrachloroethylene



Application of Chemistry in Atmospheric –Chemical Transport Models

Problems:

- A “Complete Mechanism” would require tens of thousands of chemical species and reactions.
- The reaction mechanisms and rates are not known for most of these.
- The ordinary differential equation for chemical mechanisms is very stiff, i.e. numerical standard methods are not applicable **(described in Part 1.B).**

Application of Chemistry in Atmospheric –Chemical Transport Models

Way of solving it:

- Using lumped chemical mechanism (**described in Part 1**).
- Use a fast solver (**described in Part 1.B**).



Part 1.A: Lumping of chemical mechanisms



Lumped Atmospheric Chemical Mechanisms

Mech. Abbreviation	Developed in	Number of	
		Species	Reactions
ADOM-11	USA	47	114
CB-IV	USA	27	63
RADM2	USA	63	158
SAPRC-90	USA	60	155
EMEP	Europe	79	141
RACM	USA	77	237
SAPRC-99	USA	74	211
CB-05	USA	52	156

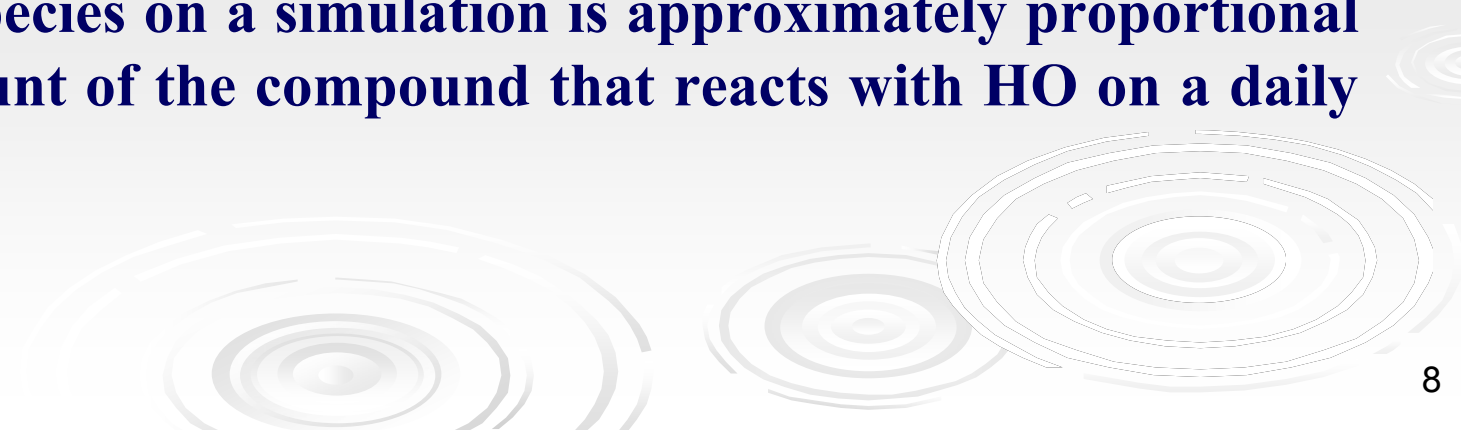
What is a lumped mechanisms?

Reducing comprehensive chemical mechanism into families with same chemistry.

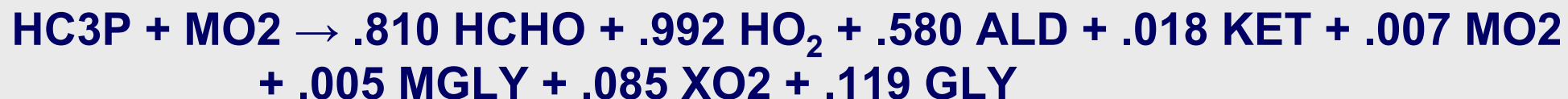
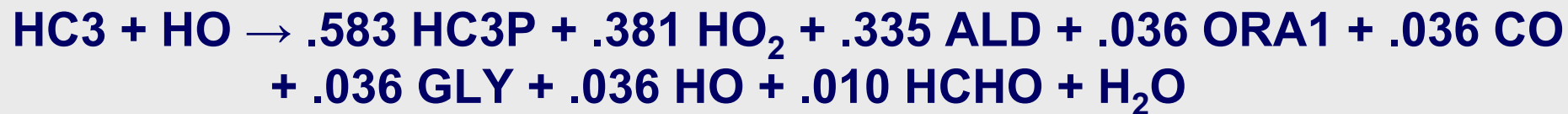
Example RACM developed by W.R. Stockwell:

Reactivity weighting: account for the differences in the reactivity between chemical and model species.

It is based on the assumption that the effect of an emitted chemical species on a simulation is approximately proportional to the amount of the compound that reacts with HO on a daily basis.



Alkane chemistry in RACM

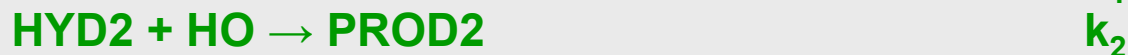


Lumped Species in RACM



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 $3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$				
HC5 (4.8)	alkanes, alcohols, esters and alkynes with HO rate constant (298 K, 1 atm) between $3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $6.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$				
HC8 (7.9)	alkanes, alcohols, esters and alkynes with HO rate constant (298 K, 1 atm) greater than $6.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$				
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) - XYL P (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		

Simple Example of Reactive Weighting



where $[\text{HYDR}] = [\text{HYD1}] + [\text{HYD2}]$, and $[\text{PRODi}]^0 = 0$

The differential eqs. $d[\text{HYDi}] / dt = - d[\text{PRODi}] / dt = - k_i [\text{HYDi}] [\text{HO}]$
 $d[\text{HYDR}] / dt = - k_3 [\text{HYDR}] [\text{HO}]$

The solutions $[\text{PRODi}] = [\text{HYDi}]^0 \{ 1 - \exp (- k_i \int [\text{HO}] dt) \}$

Assumption 1: reaction 1 and 2 are weighted according to reactivity, i.e.

$$a = [\text{PROD1}] / ([\text{PROD1}] + [\text{PROD2}]), \quad b = [\text{PROD2}] / ([\text{PROD1}] + [\text{PROD2}])$$

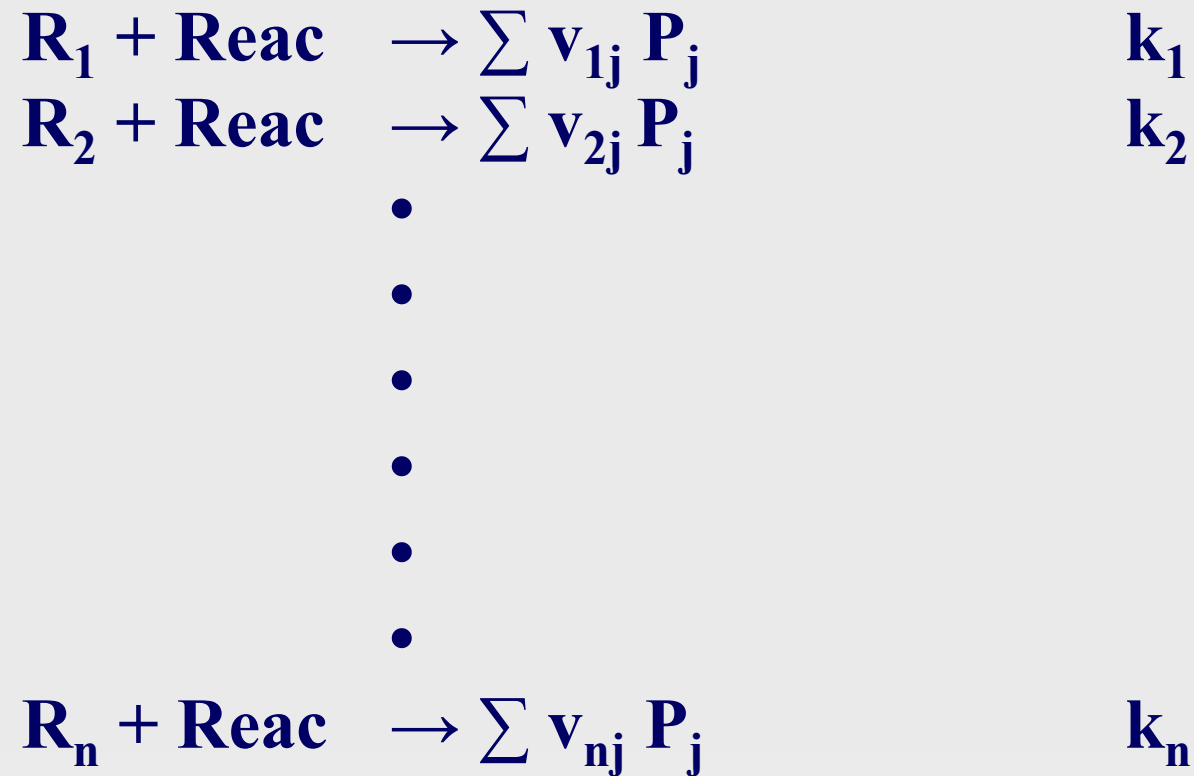
Assumption 2: the loss rate of the lumped compound, HYDR, is the same as that of the unlumped compounds, HYD1 and HYD2, i.e.

$$k_3 = a k_1 + b k_2$$

$$a = \frac{[\text{HYD1}]^0 \{ 1 - \exp(- k_1 \int [\text{HO}] dt) \}}{([\text{HYD1}]^0 \times \{ 1 - \exp(- k_1 \int [\text{HO}] dt) \} + [\text{HYD2}]^0 \{ 1 - \exp(- k_2 \int [\text{HO}] dt) \})}$$

$$b = 1 - a$$

General Example:



Become:



where

$$[\mathbf{R}_{\text{agg}}] = \sum \text{agg}_i [\mathbf{R}_i]$$

New rates:

$$k_{\text{agg}} = \frac{\sum \int \text{agg}_i [\text{R}_i] [\text{Reac}] dt}{\int [\text{R}_{\text{agg}}] [\text{Reac}] dt}$$

New products yields:

$$v_{\text{agg},j} = \frac{\sum \int v_{i,j} k_i [\text{R}_i] [\text{Reac}] dt}{\sum \int \text{agg}_i k_i [\text{R}_i] [\text{Reac}] dt}$$

Aggregation of Organic Compounds

- the similarity of chemical reactivity within the organic functional groups, and the reactivity of the organic compounds with HO.

$$\text{agg}_i = \{ 1 - \exp(-k_{i,\text{HO}} \int [\text{HO}] dt) \} / \{ 1 - \exp(-k_{m,\text{HO}} \int [\text{HO}] dt) \}$$

where

$$k_{m,\text{HO}} = \{ \sum_{\text{cat} \in m} E_{\text{cat}} k_{\text{cat},\text{HO}} \} / \{ \sum_{\text{cat} \in m} E_{\text{cat}} \}$$

$$E_{\text{cat}} = \sum_{\text{cat} \in m} E_i$$

$$k_{\text{cat},\text{HO}} = \{ \sum_{i \in \text{cat}} E_i k_{i,\text{HO}} \} / \{ \sum_{i \in \text{cat}} E_i \}$$

E_i : emission rate of specie i

$k_{i,\text{HO}}$: rate constant of specie i with HO

Plume Case Simulations

July 1, 1985, clear sky

ground albedo 0.10

solar declina. 23°

longitude 45° north

altitude 0.0 km

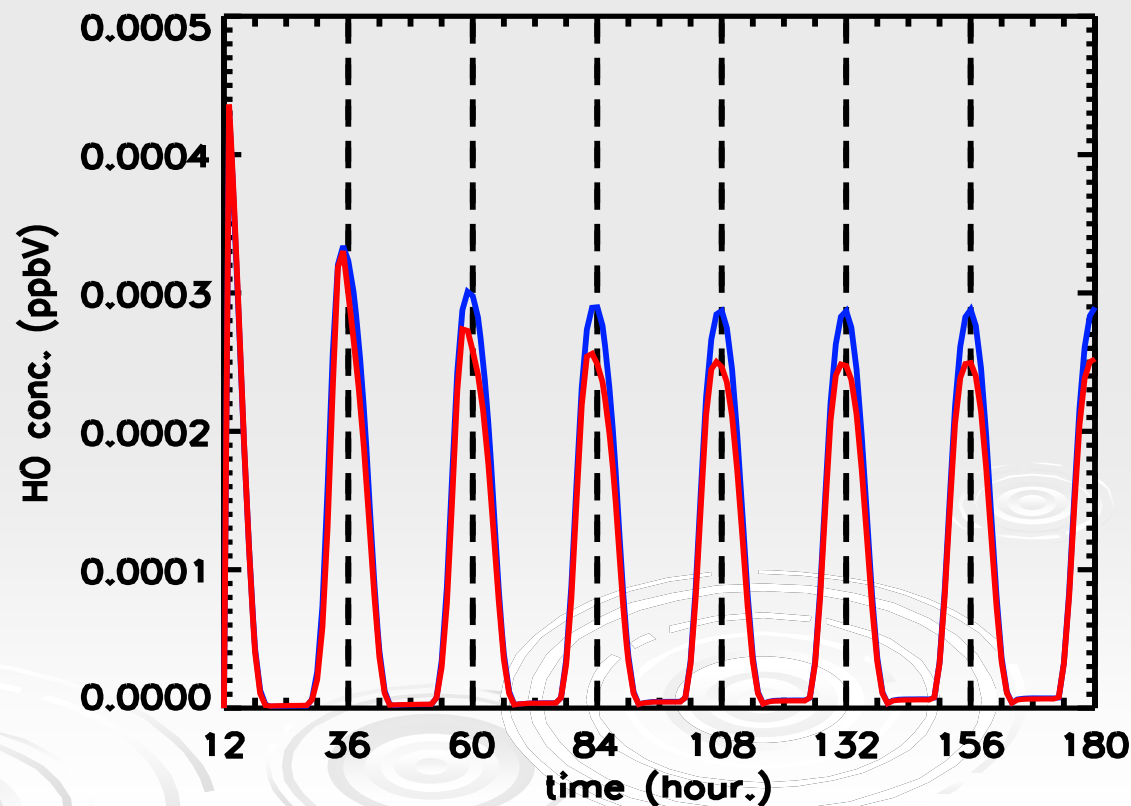
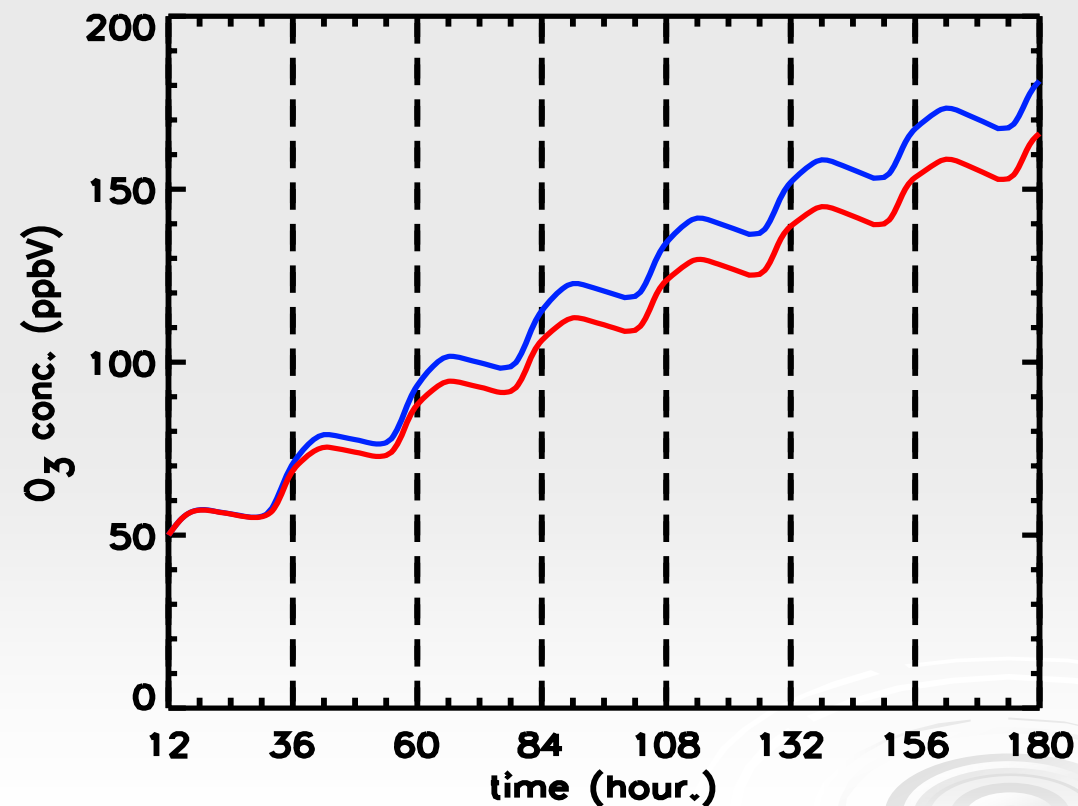
temperature 288.15 K

pressure 1.01315 bar

H ₂ O	1.00 %	NO	$1.1 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$
O ₃	50.0 ppbV	NO ₂	0.0 cm ⁻³ s ⁻¹
NO	0.20 ppbV	SO ₂	$2.2 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$
NO ₂	0.50 ppbV	CO	$2.4 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$
HNO ₃	0.20 ppbV	VOC	$3.0 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$
CO	200. ppbV		
CH ₄	1700 ppbV		
H ₂	500. ppbV		
H ₂ O ₂	2.00 ppbV		
HCHO	1.00 ppbV		
O ₂	20.9 %		
N ₂	78.1 %		

Comparison:

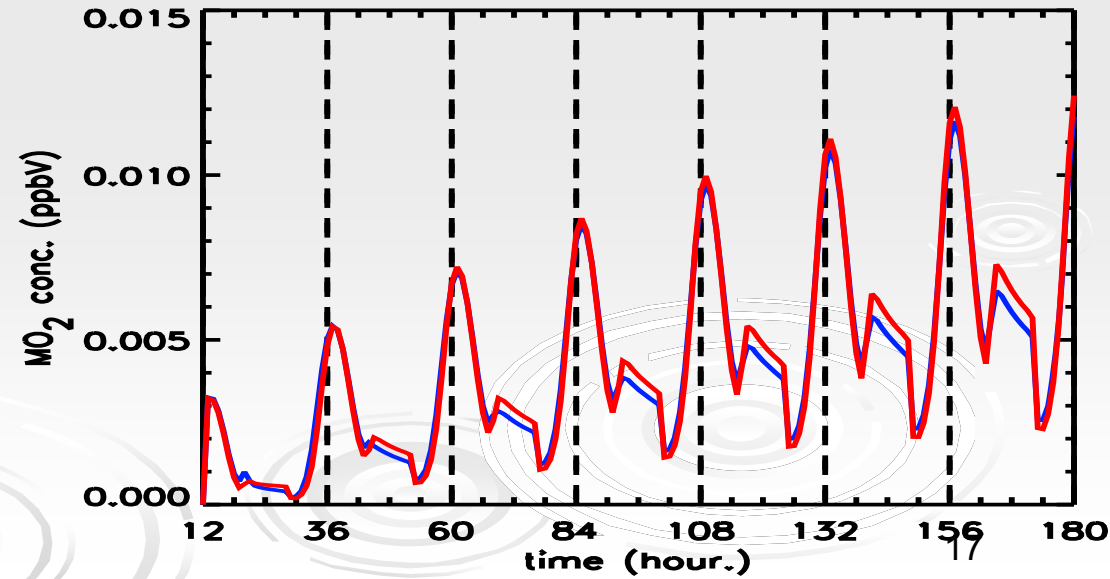
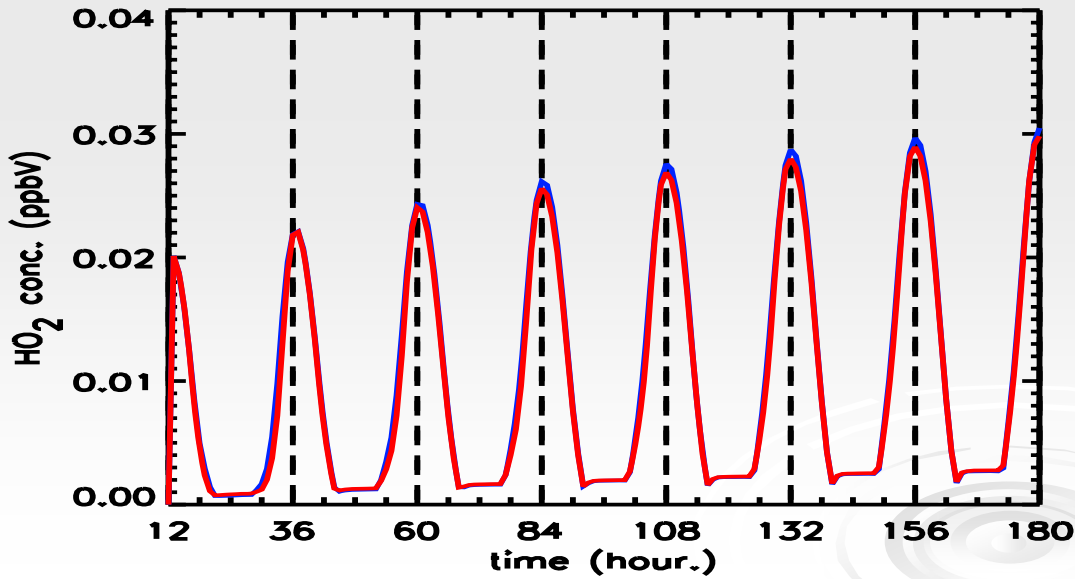
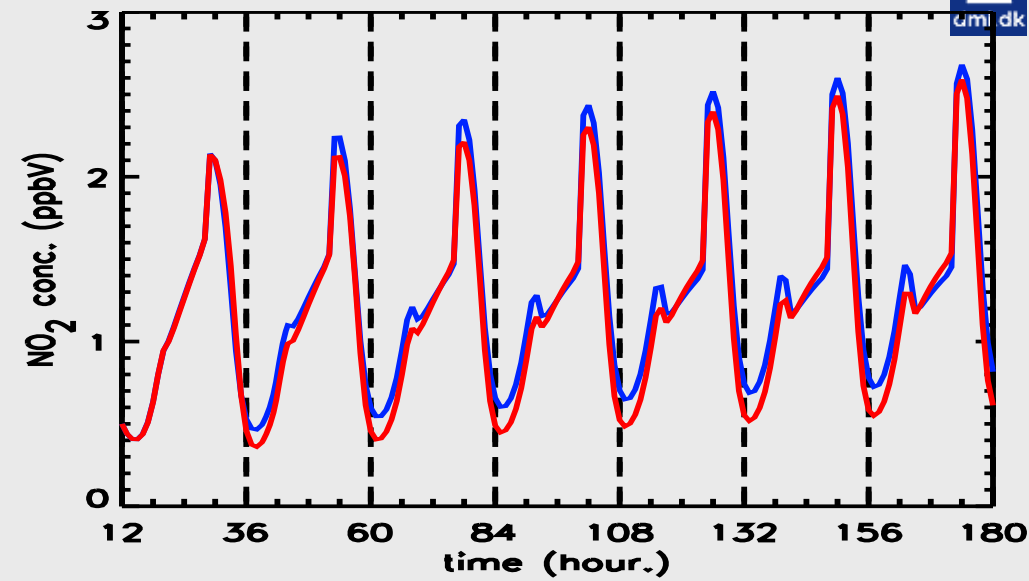
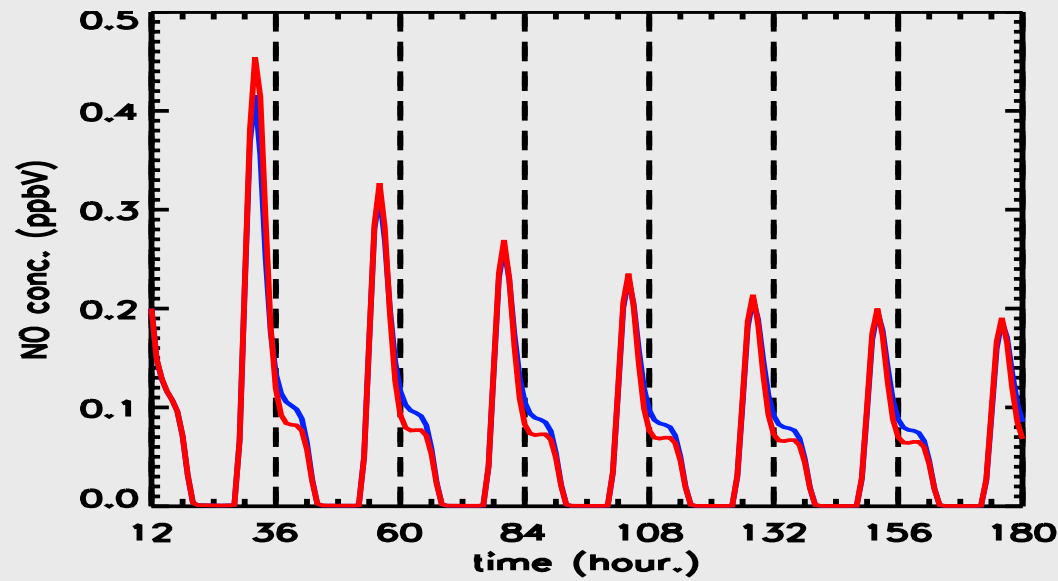
- Regional Atmospheric Chemical Mechanism (RACM)
- new lumped mechanism reduction of RACM (redRACM)



Comparison: redRACM ↔ RACM



um.dk



Part 1.B

How is the ODE for chemical mechanisms solved numerically



Implementation of Chemistry in ACTM – ODE



$$\frac{\partial c_i}{\partial t} = P_i(\vec{c}, t, \vec{k}) - L_i(\vec{c}, t, \vec{k}) \times c_i$$

$$\begin{aligned} & + \left. \frac{\partial c_i}{\partial t} \right|_{\text{Advection}} & + \left. \frac{\partial c_i}{\partial t} \right|_{\text{Diffusion}} \\ & + \left. \frac{\partial c_i}{\partial t} \right|_{\text{Aerosols}} & + \left. \frac{\partial c_i}{\partial t} \right|_{\text{Clouds}} & + \left. \frac{\partial c_i}{\partial t} \right|_{\text{Emission}} & + \left. \frac{\partial c_i}{\partial t} \right|_{\text{Deposition}} \end{aligned}$$

P_i = production of c_i
 c_i = concentration of i^{th} species

L_i = loss of c_i
 k_i = i^{th} rate constant

Solving the chemical reactions' set of ODE:

The big difficulty:

- **The set of ODE is 'stiff', i.e.:**
the chemical lifetimes cover a very large range of time scales
 - **stiff systems are more difficult to solve than non-stiff systems.**
 - **Stiff systems require very small time steps.**
- ⇒ **Time step necessary to resolve all the chemical reactions?**

Lifetime of species A:

$$I_A = \frac{1}{I_{A1}^{-1} + I_{A2}^{-1} + I_{A3}^{-1} + \dots + I_{An}^{-1}}$$

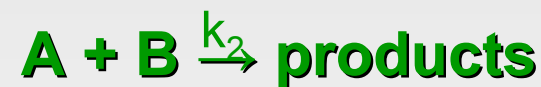
Lifetime of A due to unimolecular reactions:



gives

$$I_{A1} = k_1^{-1}$$

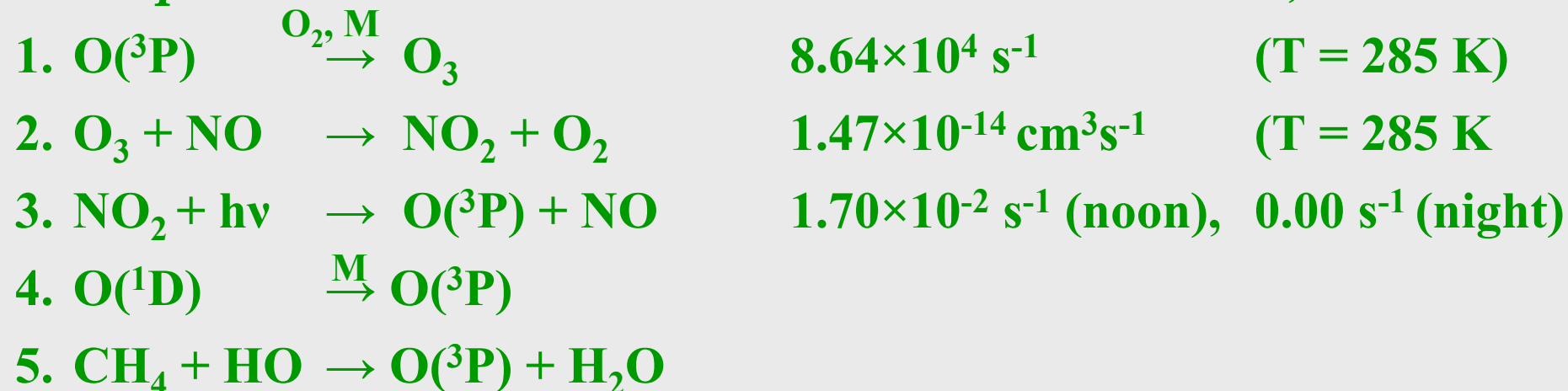
Lifetime of A due to bimolecular reactions:



gives

$$I_{A2} = (k_2 \times [B]_0)^{-1}$$

Example



$$l_{\text{O}({}^3\text{P})} = 1.16 \times 10^{-5} \text{ s}$$

$$l_{\text{O}_3} = 6.80 \times 10^{13} \text{ cm}^{-3} \text{ s} [\text{NO}]^{-1}$$

$$l_{\text{NO}} = 6.80 \times 10^{13} \text{ cm}^{-3} \text{ s} [\text{O}_3]^{-1}$$

$$l_{\text{NO}_2} = 58.8 \text{ s (noon)}, = \infty \text{ (night)}$$

$$l_{\text{CH}_4} = 10.2 \text{ years}$$

$$l_{\text{O}({}^1\text{D})} = 2 \times 10^{-9} \text{ s}$$

I.e. even such a simple system can be rather stiff



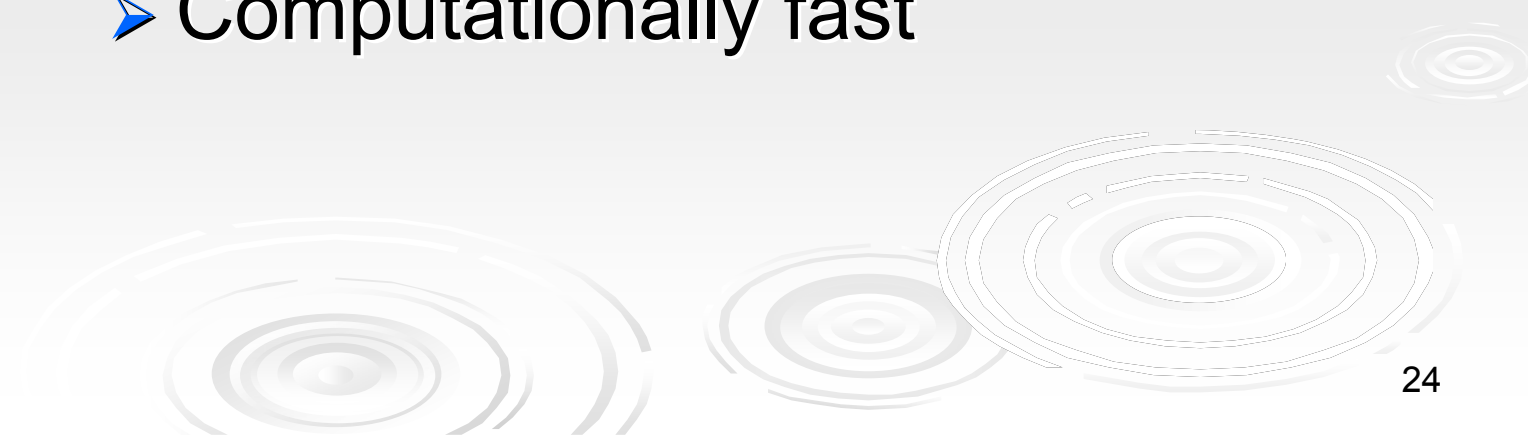
Several methods exists to solve chemical ODEs

Examples:

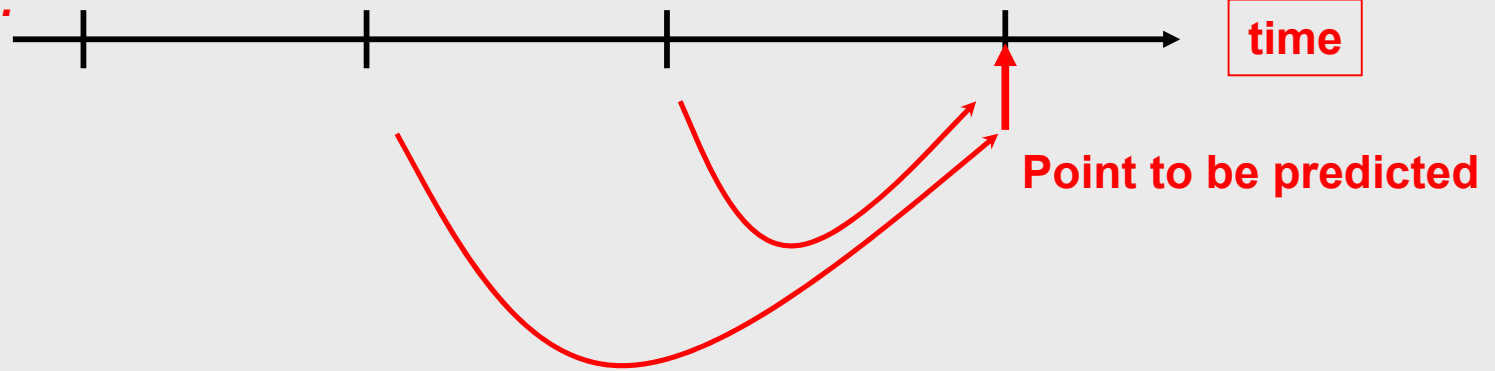
- Taylor series
- Forward Euler
- Backward Euler
- Simple exponential
- Quasi-steady-state
- Multistep implicit-explicit
- Backward differentiation (GEAR)
- Hybrid predictor-corrector methods
- Parameterization methods
- Runge-Kutta-Rosenbrock schemes
- Iterative backward Euler methods
- Hybrid Newton Raphson iterative schemes

Selection of method depend on

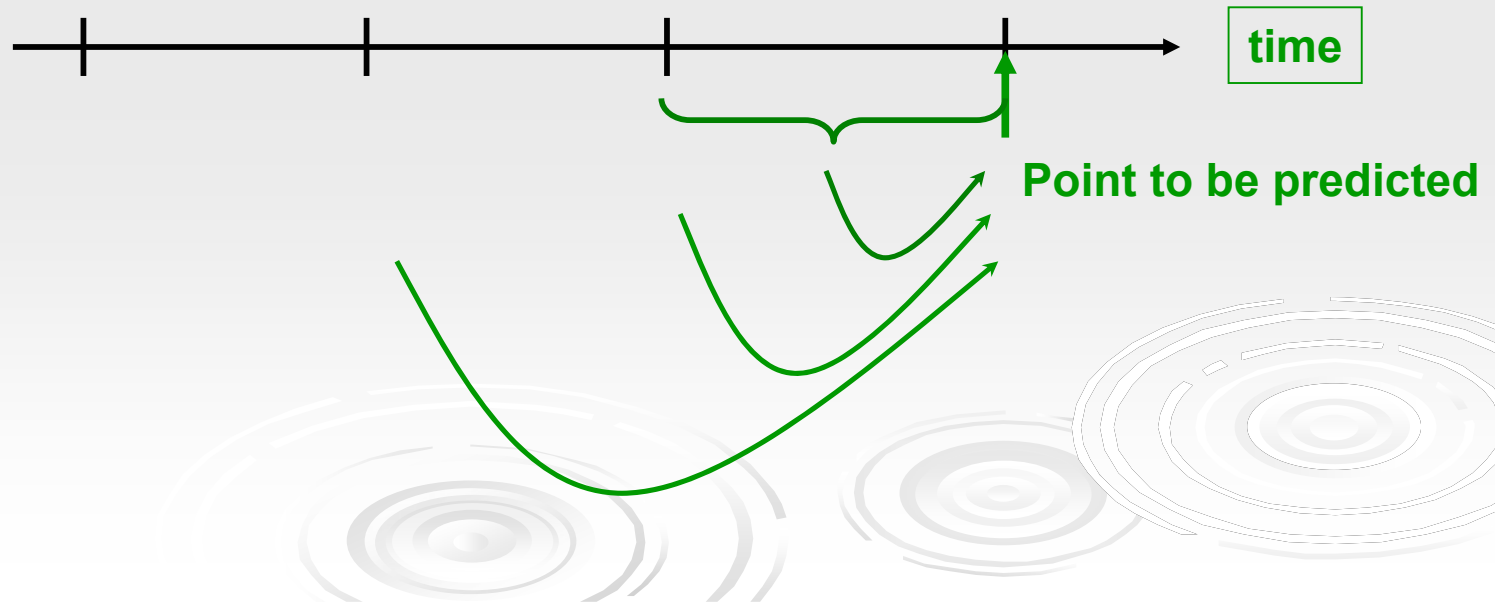
- Stable
- Accurate
- Mass conserving
- Positive definite
- Computationally fast



Explicit solvers:



"Semi"-implicit solvers:



Methods for solving chemical ODEs

1. Eulerian forward
2. Eulerian backward
3. QSSA
4. The GEAR solver
5. Family approach



Simplest methods for solving chemical ODEs



1) The simplest (explicit) solver: Forward Euler (1st order Taylor

$$\begin{aligned}c_i(t) &= c_i(t-\Delta t) + \Delta t \times dc_i(t-\Delta t) / dt \\ &= c_i(t-\Delta t) + \Delta t (P_i(\vec{c}, t-\Delta t, \vec{k}) - L_i(\vec{c}, t-\Delta t, \vec{k}) \times c_i(t-\Delta t))\end{aligned}$$

2) The simplest (“semi”-implicit) solver : Backward Euler

$$\begin{aligned}c_i(t) &= c_i(t-\Delta t) + \Delta t \times dc_i(t, t-\Delta t) / dt \\ &= c_i(t-\Delta t) + \Delta t (P_i(\vec{c}, t-\Delta t, \vec{k}) - L_i(\vec{c}, t-\Delta t, \vec{k}) \times c_i(t)) \\ &= (c_i(t-\Delta t) + \Delta t (P_i(\vec{c}, t-\Delta t, \vec{k}))) / (1 - L_i(\vec{c}, t-\Delta t, \vec{k}) \times \Delta t)\end{aligned}$$

Example

$$\frac{dc_i}{dt} = P_i(\underline{c}, t, \underline{k}) - L_i(\underline{c}, t, \underline{k}) \times c_i$$

Example



Rate constant

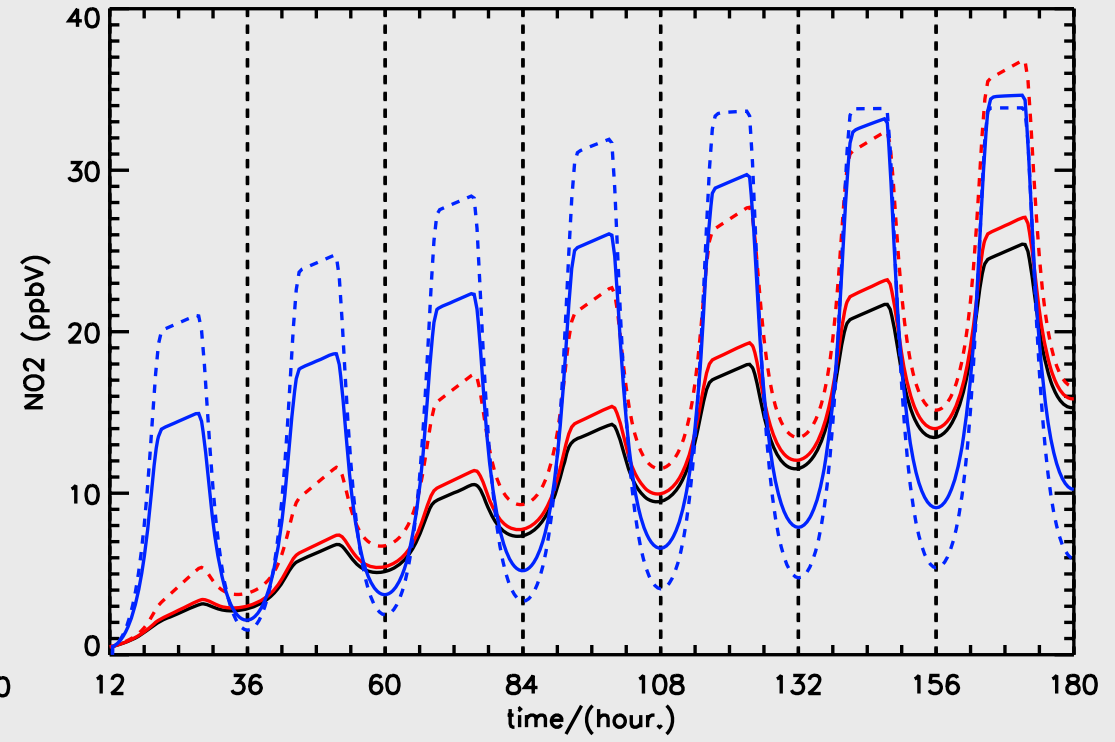
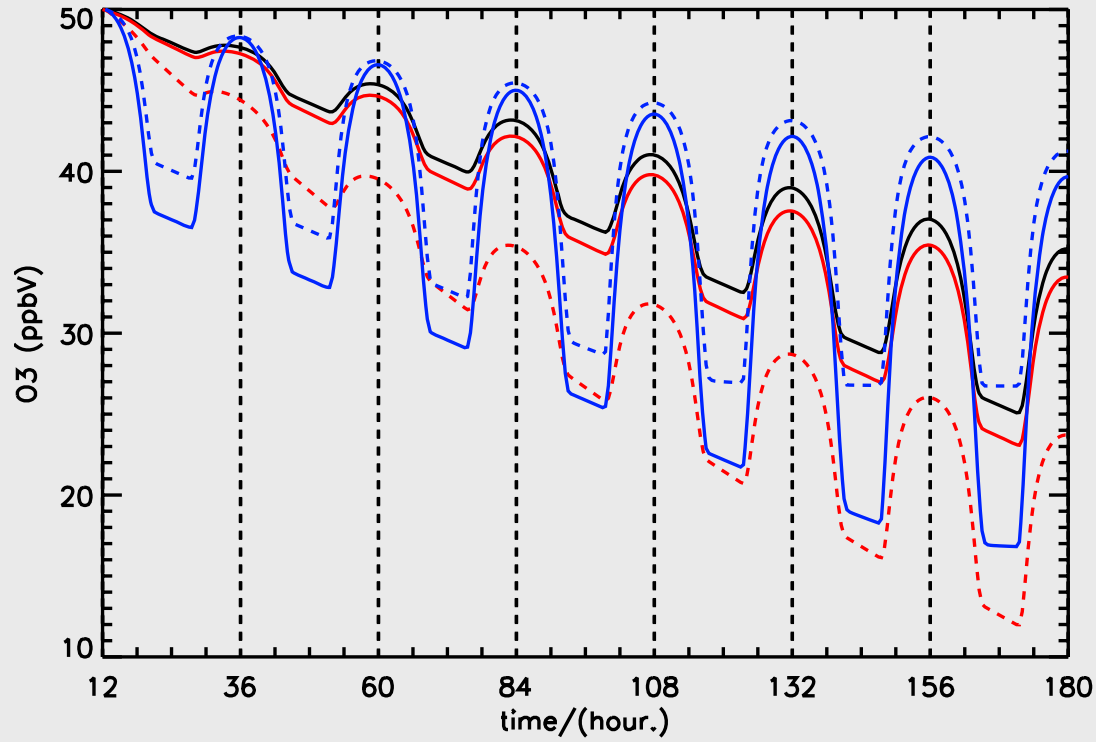
$1.4 \times 10^3 \exp(1175/T) \quad (s^{-1})$



$1.8 \times 10^{-12} \exp(-1370/T) \quad (cm^3s^{-1})$



$2.5 \times 10^{-2} \exp(-.39/\cos \theta) \quad (s^{-1})$



Δt

Gear

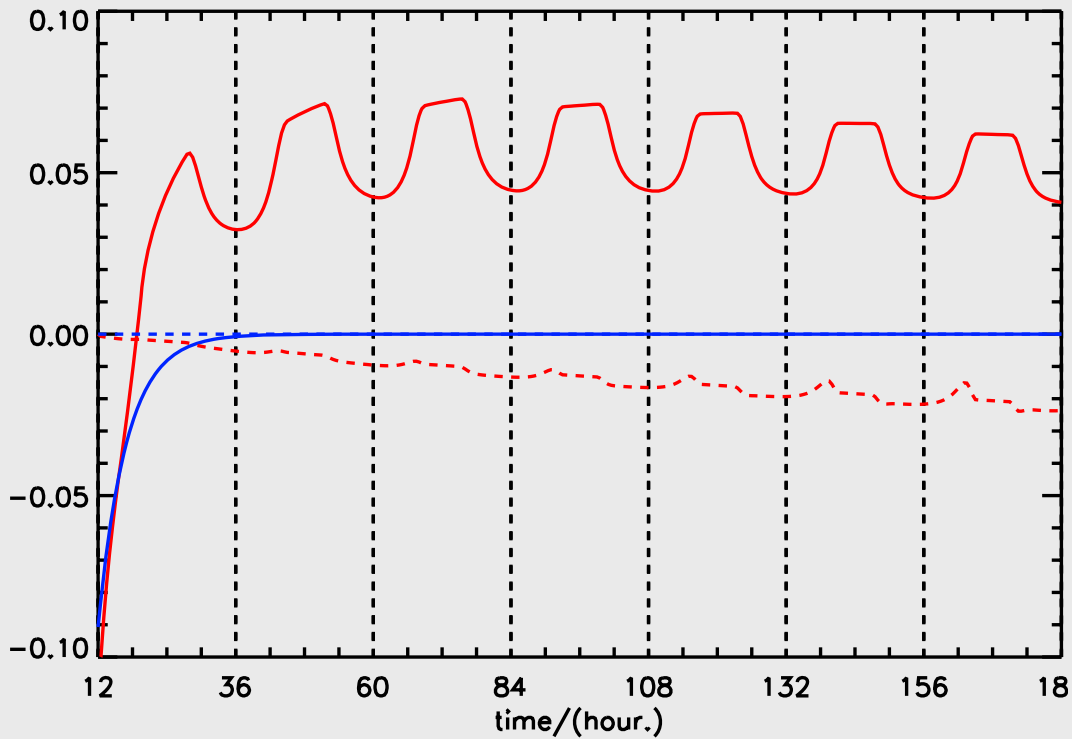
Eulerian backward

Eulerian forward

60 sec.

240 sec.





Conservation of mass

Relative mass change of N

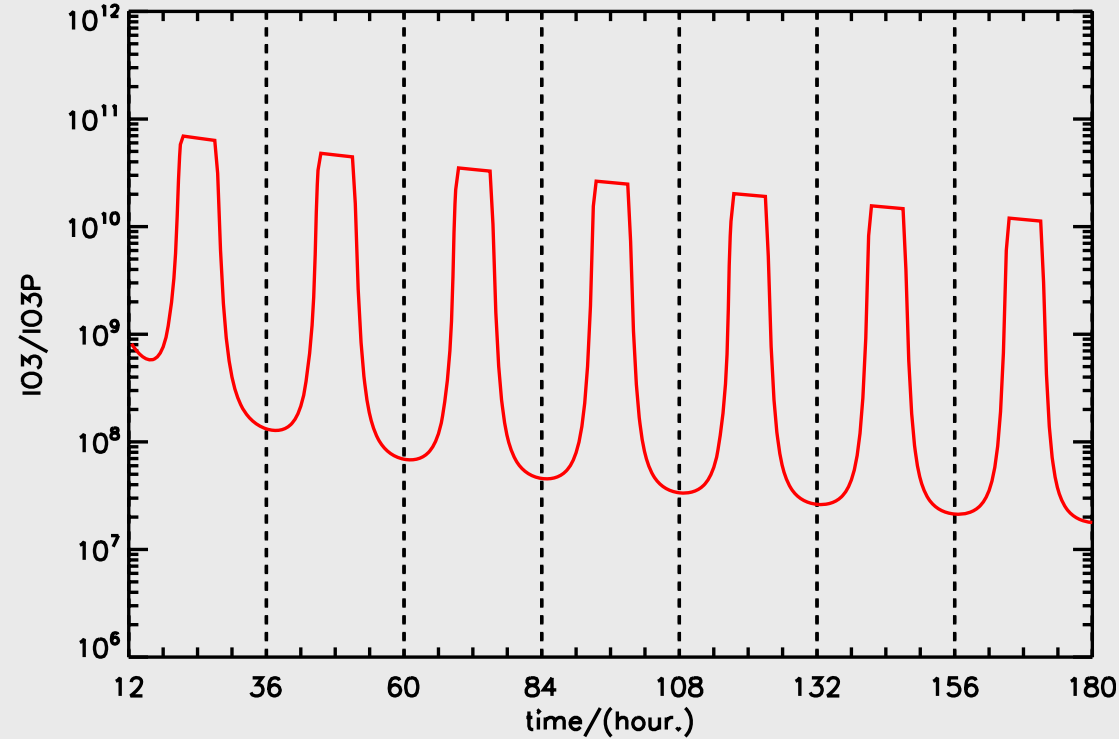
Relative mass change of O

$\Delta t = 60 \text{ sec}$

Gear

Eulerian backward

Eulerian forward



Stiffness of system

Lifetime of O3 relative to O(3P)

Explicit versus implicit methods, In general



	Explicit	(Semi-)implicit
Stable	For too stiff ODEs become unstable. Small time steps required.	+
Accurate	Small time steps required.	+
Mass conserving	+	-
Positive definite	+	+
Computational fast	-	(+)

Quasi Steady State Approximation (QSSA)

$$\frac{dc_i}{dt} = P_i(\vec{c}, t, \vec{k}) - L_i(\vec{c}, t, \vec{k}) \times c_i$$

For moderate lifetime of C_i is used

$$\frac{dc_{i,t}}{dt} = P_i(\vec{c}, t-\Delta, \vec{k}) - L_i(\vec{c}, t-\Delta, \vec{k}) \times c_{i,t}$$

$$C_{i,t} = C_{i,t-\Delta} \exp(-\delta P_{i,t-\Delta}) + P_{i,t-\Delta} / L_{i,t-\Delta} (1 - \exp(-\Delta L_{i,t-\Delta}))$$

Quasi Steady State Approximation (QSSA)

If the lifetime of C_i is short (i.e. radicals), $dC_i/dt \approx 0$:

$$C_{i,t} = P_{i,t-\Delta} / L_{i,t-\Delta}$$

For long lifetime of C_i Eulerian forward is used

$$C_{i,t} = C_{i,t-\Delta} + \Delta (P_{i,t-\Delta} - L_{i,t-\Delta} C_{i,t-\Delta})$$

Quasi Steady State Approximation (QSSA)

Summary

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

species' lifetime long \rightarrow
forward Eulerian equation

species' lifetime moderate \rightarrow
simple exponential method

if $\delta L_{i,t-\delta} < 0.001$

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

if $\delta L_{i,t-\delta} > 10$

species' lifetime short \rightarrow
steady state equation

NWP-Chem-Gas

Photolysis reactions

1. $\text{NO}_2 + h\nu \rightarrow \text{O}(3P) + \text{NO}$
2. $\text{O}_3 + h\nu \rightarrow \text{O}(3P) + \text{NO}$
3. $\text{HCHO} + h\nu \rightarrow \text{O}(1D) + \text{O}_2$
4. $\text{HCHO} + h\nu \rightarrow 2 \text{HO}_2 + \text{CO}$

Inorganic chemistry

1. $\text{O}(3P) + \text{O}_2 \rightarrow \text{O}_3$
2. $\text{O}(1D) + \text{N}_2 \rightarrow \text{O}(3P) + \text{N}_2$
3. $\text{O}(1D) + \text{O}_2 \rightarrow \text{O}(3P) \text{ O}_2$
4. $\text{O}(1D) + \text{H}_2\text{O} \rightarrow \text{HO} + \text{HO}$
5. $\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}$
6. $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$
7. $\text{CO} + \text{HO} \rightarrow \text{HO}_2 + \text{CO}_2$
8. $\text{HO} + \text{NO}_2 \rightarrow \text{HNO}_3$
9. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
10. $\text{HO}_2 + \text{HO}_2 \text{ H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O} + \text{O}_2$

NWP-Chem-Gas

Organic chemistry

1. $\text{HC} + \text{HO} \rightarrow \text{RO}_2 + \text{H}_2\text{O}$
2. $\text{RO}_2 + \text{NO} \rightarrow \text{HCHO} + \text{HO}_2 + \text{NO}_2$
3. $\text{HCHO} + \text{HO} \rightarrow \text{HO}_2 + \text{CO} + \text{H}_2\text{O}$
4. $\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2$
5. $\text{RO}_2 + \text{RO}_2 \rightarrow x \text{HCHO} + y \text{HO}_2$

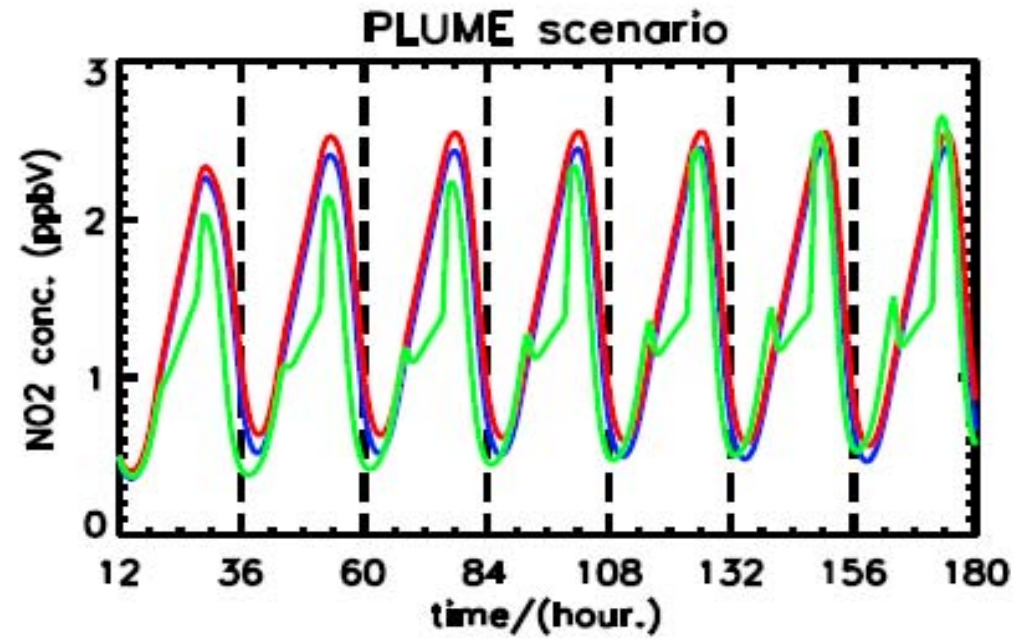
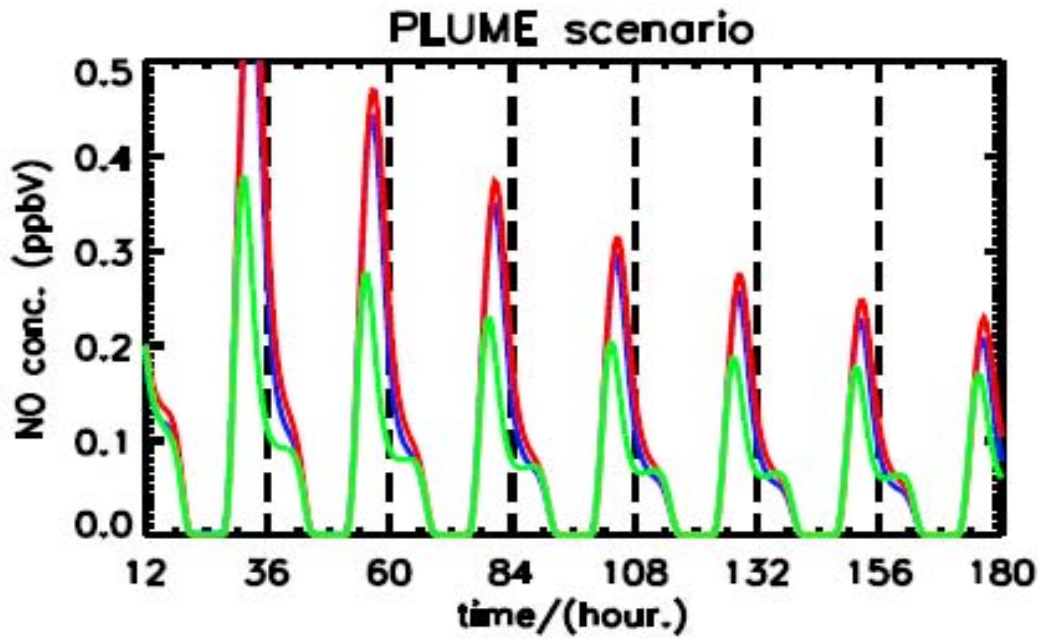
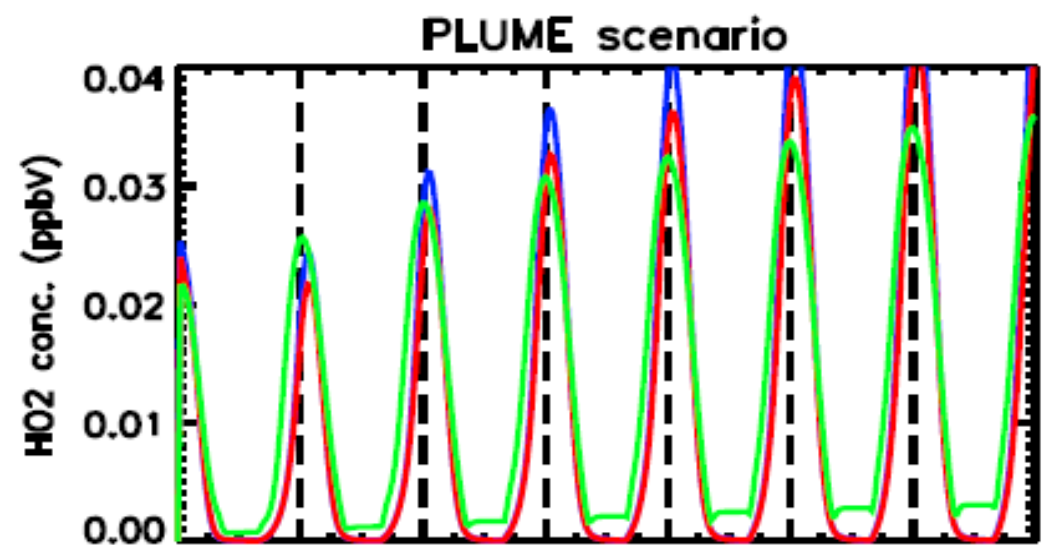
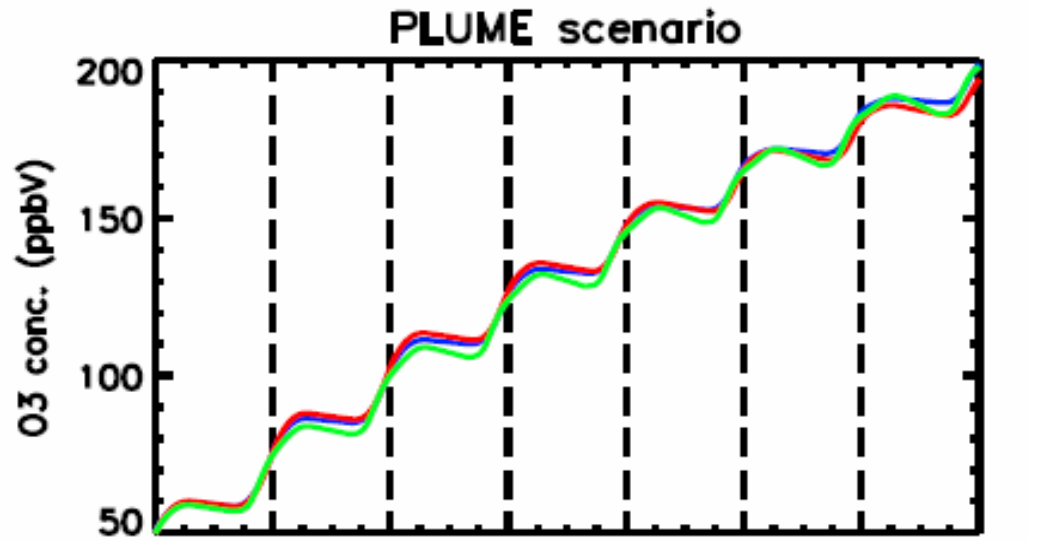
Sulphur chemistry

1. $\text{HO} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{HO}_2$
2. $\text{DMS} + \text{HO} \rightarrow 0.85 \text{SO}_2 + 0.15 \text{MSA}$
3. $\text{DMS} + \text{HO} \rightarrow \text{MSIA}$
4. $\text{MSIA} + \text{HO} \rightarrow 0.85 \text{SO}_2 + 0.15 \text{MSA}$

Biogenic chemistry

1. $\text{BIO} + \text{HO} \rightarrow \text{BIOO}_2$
2. $\text{BIO} + \text{O}_3 \rightarrow 1.23 \text{HCHO} + 0.14 \text{CO} + 0.28 \text{ROOH} + 0.25 \text{HO}_2 + 0.18 \text{RO}_2 + 0.09 \text{H}_2\text{O}_2$
3. $\text{BIOO}_2 + \text{NO} \rightarrow 2.0 \text{HCHO} + \text{HO}_2 + \text{NO}_2$
4. $\text{BIOO}_2 + \text{HO}_2 \rightarrow \text{RO}_2$
5. $\text{BIOO}_2 + \text{BIOO}_2 \rightarrow 2.0 \text{HCHO} + \text{HO}_2$

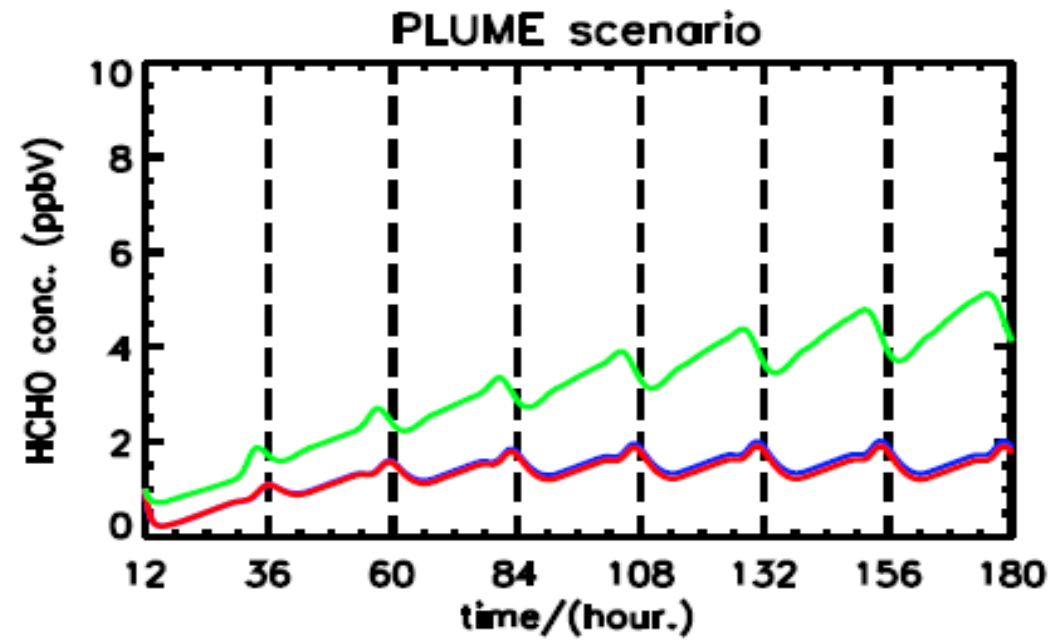
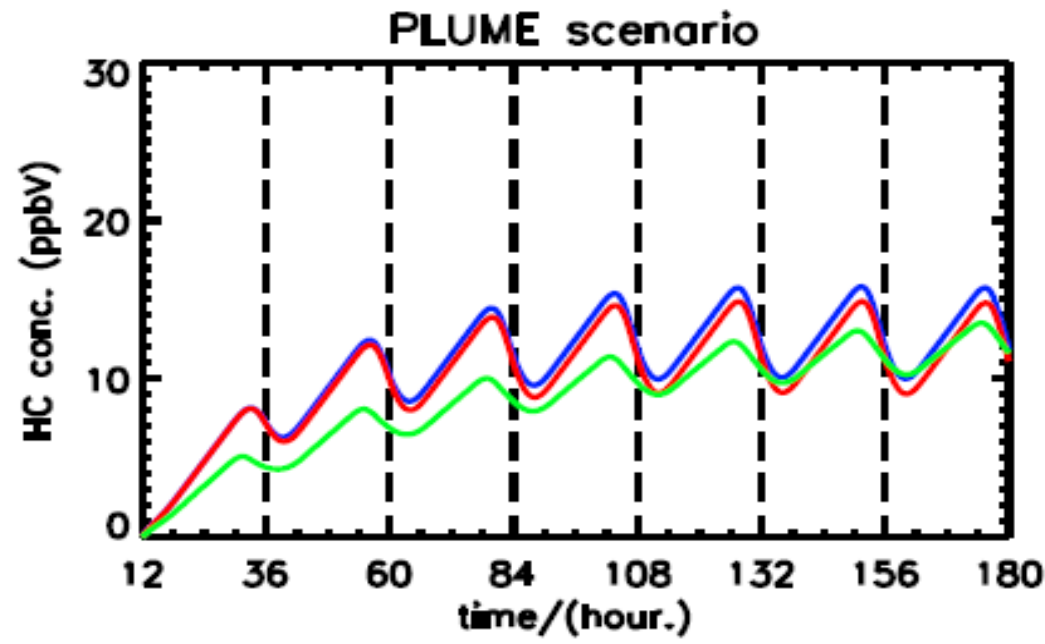
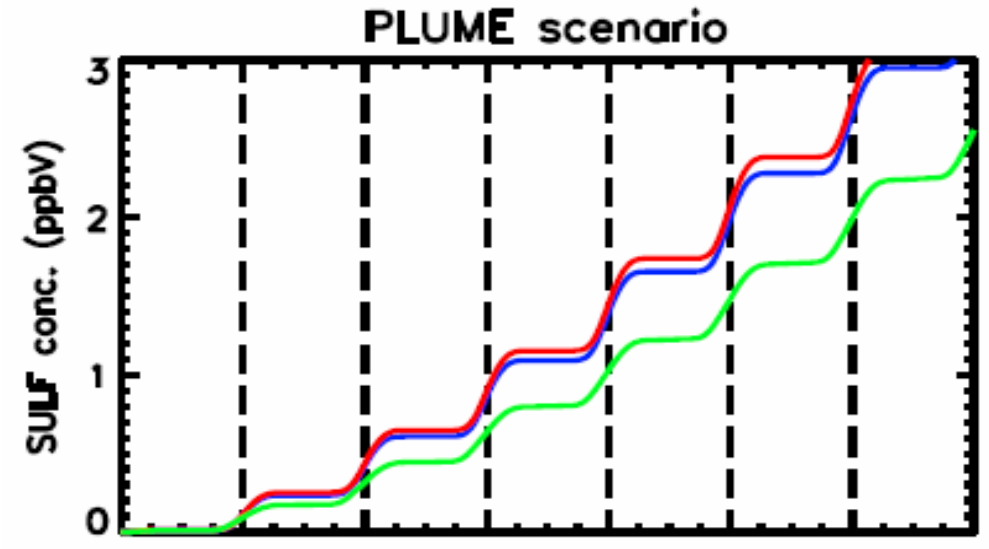
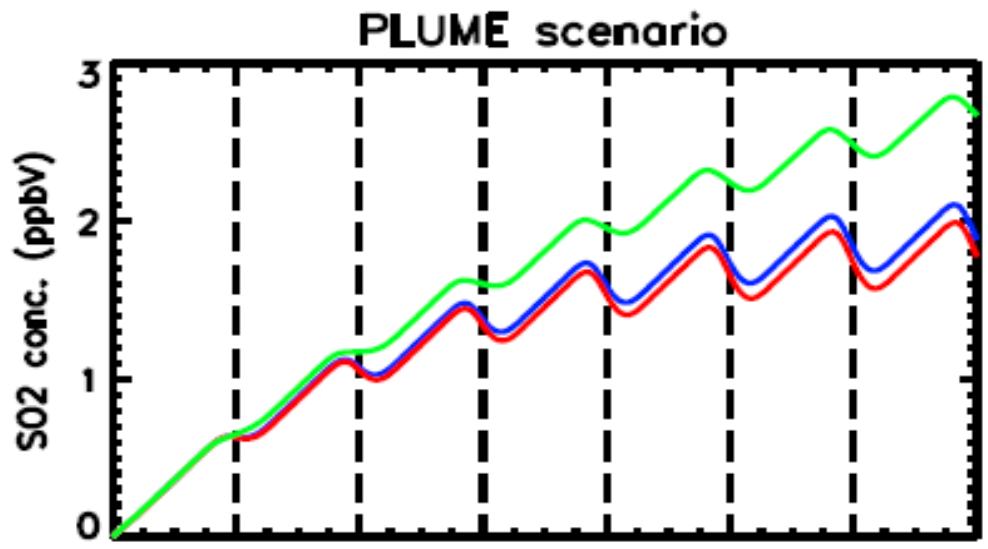
+ 1 operator reaction



RACM/GEAR

NWP-Chem-Gas/GEAR

NWP-Chem-Gas/QSSA



RACM/GEAR

NWP-Chem-Gas/GEAR

NWP-Chem-Gas/QSSA

3) The GEAR solver:

hybrid explicit/implicit predictor-corrector method in which an explicit equation is used to predict the solution in the next time step.

This solution is then corrected using an explicit method.

advantages:

- the order and time steps are chosen by an adaptive method that ensure high accuracy for a minimum of computer time,

disadvantages:

- computational very expensive.

considered as a benchmark solver



4) The Family approach:

1. Production / Loss is calculated for each species
2. Concentrations within a family are summed over
3. The family concentration is advanced in time (e.g. with a forward Euler scheme)
4. Individual species are re-partitioned

Example families:

- Odd oxygen: $[O_T] = [O(^3P)] + [O(^1D)] + [O_3] + [NO_2]$
- Odd hydrogen: $[HO_T] = [HO] + [HO_2] + [HO_2] + [H_2O_2]$
- Odd nitrogen: $[NO_T] = [NO] + [NO_2] + [NO_3]$

Advantages:

- Computational fast
- Accurate for moderate- to low-stiffness systems

Disadvantages:

- Need to be carefully set up and validated for each set of chemistry
 - Accuracy decreases with increasing stiffness
1. The forward Euler scheme often become unstable \Rightarrow time step must be reduced

Summary

In a chemistry model used to solve 3D atmospheric chemistry, it is not possible to have too small time steps. An iterative method can also be computational expensive.

⇒ Need integration schemes that are non-iterative and stable when time steps are larger than the smallest chemical lifetime.

It is more important for a scheme to be accurate than exactly mass conserving.

Best methods to use are mixed explicit implicit methods.