Numerical modelling of atmospheric chemistry

Glenn Carver : Numerical Aspects
Glenn.Carver@ecmwf.int

With thanks to:
Johannes Flemming : Atmospheric Composition
Lecture content

- Introduction – why is atmospheric chemistry important for ECMWF?
- Atmospheric chemistry characteristics
- Brief look at chemistry kinetics
- Numerical integrators
- Some issues when adding chemistry to a numerical model
- Coding practices and comments
Atmospheric composition

Composition is: Chemistry and Aerosols.

Why is ECMWF interested in composition?

- New Atmospheric Composition Division.
- Composition impacts on radiation (e.g. aerosols, ozone, methane)
- Air quality forecasting e.g. heatwaves, fires
- Reanalysis of past composition
  
  http://www.gmes-atmosphere.eu

- Forecasts of composition.
- Aerosol and global reactive gas models in IFS.
- Data assimilation of aerosol optical-depth and trace gas retrievals.
MACC Daily (NRT) Service Provision

Air quality

Global Pollution

Aerosol

UV index

Fires

Numerical Modelling of Atmospheric Chemistry
Numerical Modelling of Atmospheric Chemistry

MACC Service Provision (retrospective)

Flux Inversions

Ozone records

Reanalysis 2003-2012

J. Flemming

Numerical Modelling of Atmospheric Chemistry
Impact of Aerosol Climatology on NWP

Motivation.
Changes in aerosol can impact on NWP.

Surface Sensible heat flux differences

20 W m\(^{-2}\) ~ 20-30%

Boundary layer height increases >1km

J. Flemming
Integration of chemistry & aerosol modules in ECMWF’s integrated forecast system (IFS)

C-IFS
On-line Integration of Chemistry in IFS
Developed in MACC
10 x more efficient than Coupled System

Coupled System
IFS- MOZART3 / TM5
Developed in GEMS
Used in MACC

Integrated System
Feedback: fast
Flexibility: low

Coupled System
Feedback: slow
Flexibility: high

Flemming et al. 2009
The Ozone Hole – a 3D problem

NASA/Goddard Space Flight Center
Scientific Visualization Studio
Atmospheric Composition – global averages

- Small concentrations matter: chemical conversion is non-linear & can be v. fast
Atmospheric chemistry modelling

- Components of an atmospheric chemistry model are:
  - Chemistry scheme: set of reactions & reaction rate data.
  - Photolysis scheme: computes reaction rates due to light, including effects of clouds and aerosols.
  - Dry and wet deposition scheme: loss of chemical species to surfaces.
  - Heterogeneous chemistry: aqueous or solid surfaces e.g. polar stratospheric clouds.
  - Emissions: source of chemical species.
  - Numerical solver: integrates reaction scheme.
Types of atmospheric chemistry models

- Types of models:
  - Box models: Eulerian & Lagrangian; good for very complex chemistry mechanisms.
  - 2D models: early stratospheric chemistry models based.
  - 3D models: several types.
    - Chemical Transport Models: use observed met fields.
    - C-GCM models: allow feedbacks & prediction.
    - Lagrangian models: Good for dispersion studies and source attribution.

- Typically:
  - 3D models include 50-100 species and more than 250 reactions.
  - In IFS chemistry/aerosol increases runtime by factors of 2-10.
  - Efficient solvers and computer code are essential.
Numerical solution of atmospheric chemistry

- In general, a operator-splitting approach is used.

- Note each operator has different characteristics, time and spatial scales and solved using different numerical techniques.

\[
\frac{\partial c_i}{\partial t} = \left( \frac{\partial c_i}{\partial t} \right)_{adv} + \left( \frac{\partial c_i}{\partial t} \right)_{diff} + \left( \frac{\partial c_i}{\partial t} \right)_{aerosol} + \left( \frac{\partial c_i}{\partial t} \right)_{dep} + R_i + E_i
\]

Where:
- \(c_i\) is the concentration of chemical species \(i\)
- \(R_i\) is the net production from chemical reactions for species \(i\)
- \(E_i\) is the emission rate for species \(i\)

And \(adv, diff, aerosol\) and \(dep\) are the operators for advection, diffusion, aerosol processes and wet/dry deposition respectively.
Chemical production and loss

- $R_i$ is the net change due to gas phase chemical reactions which we can express in terms of production rate $P$ and loss rate $L$:

$$R_i = \frac{\partial c_i}{\partial t} = P_i - L_i = P_i - l_i c_i$$

- This is a non-linear system of coupled equations where $P_i$ and $L_i$ are functions of $c_i$. We will consider ways of solving this set of equations.

- Considering loss only and solving analytically then:

$$c = c_0 e^{-t/\tau}$$

Where: $\tau$ is the ‘lifetime’ of the species ($1/l$ in this simple case).

- As lifetimes of chemical species in the atmosphere vary over several orders of magnitude, this system of equations is numerically ‘stiff’.
Chemical lifetime v. spatial scales

- Stratospheric source
- Inter-hemispheric mixing time
- Intra-hemispheric mixing time
- Boundary layer mixing time

Temporal Scale
- 100yr
- 10yr
- 1yr
- 1mon
- 1d
- 1h
- 1min
- 1s

Spatial Scale
- 1m
- 10m
- 100m
- 1km
- 10km
- 100km
- 1000km
- 10000km

Long-lived Species
- CFCs
- N$_2$O
- CH$_4$
- CH$_3$CCl$_3$
- CH$_3$Br

Moderately long-lived Species
- CO
- Aerosol O$_3$ (trop.)
- NO$_x$
- SO$_2$
- H$_2$O$_2$
- C$_3$H$_6$
- DMS
- C$_5$H$_8$

Short-lived Species
- CH$_3$O$_2$
- NO$_3$
- HO$_2$
- OH

After Seinfeld and Pandis [1998]
Carbon monoxide animation showing source regions.
Nitrogen dioxide (NO$_2$) near tropopause
Chemical kinetics - 1

To understand how \( P & L \) are computed we take a brief look at kinetics.

Reaction types:
- **Unimolecular**: e.g. \( NO_2 +hv \rightarrow NO + O : J \)
- **Bimolecular**: e.g. \( OH + HO_2 NO_2 \rightarrow H_2O + O_2 + NO_2 : k_1 \)
  \( \rightarrow H_2O_2 + NO_3 \)
- **Termolecular**: e.g. \( O + O_2 + M \rightarrow O_3 + M : k_2 \)

Reaction rates, \( k, J \) are determined by laboratory experiments and fitted to ‘Arrhenius’ expressions.
- Rates are not always well known beyond two significant figures
- Many reactions have a temperature and pressure dependence.
- Some reaction rates are computed from theoretical calculations.

Kinetic rates available in several online databases (e.g. IUPAC, JPL)
Chemical kinetics - 2

- Example: ozone formation:
  \[ \text{O}_2 + hv \rightarrow \text{O} + \text{O} : J_1 \]
  \[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} : k_2 \]
  \[ \text{O}_3 + hv \rightarrow \text{O}_2 + \text{O} : J_3 \]
  \[ \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 : k_4 \]

  (Chapman reactions)

- Compute reaction rates:
  \[ R_1 = J_1 [\text{O}_2]; \ldots; R_4 = k_4 [\text{O}_3][\text{O}] \]

- Compute production, loss tendency for ozone and atomic oxygen:
  \[ P_{\text{O}_3} = R_2 \]
  \[ P_{\text{O}} = 2R_1 + R_3 \]
  \[ L_{\text{O}_3} = R_3 + R_4 \]
  \[ L_{\text{O}} = R_2 + R_4 \]
  \[ \frac{d[\text{O}]}{dt} = P_{\text{O}} - L_{\text{O}} \]
  \[ \frac{d[\text{O}_3]}{dt} = P_{\text{O}_3} - L_{\text{O}_3} \]

- The computer code for this can be written efficiently for both vector and cache based processors because use of CPU functional units can be chained and reuse of terms gives memory locality.
Ozone layer – Chapman theory

- Chapman reproduces vertical profile well but not magnitude.
- Observed magnitude is less because:
  - Lower stratosphere, transport important as ozone has longer lifetime.
  - In upper stratosphere, catalytic cycles are important.
Chemistry mechanisms

Formaldehyde (HCHO) reaction pathways. Taken from: Master Chemical Mechanism. Mat Evans, Andrew Rickard, Uni York


Properties of solvers

Desirable properties of a ODE solver for atmospheric chemistry are:

- Accurate and stable. A good solver will test convergence using absolute and relative errors.

- Mass conserving. Iterative methods and (semi-)implicit methods may not conserve. Chemical scheme may not conserve mass! Accuracy is more important than mass conservation.

- Positive definite. Negative concentrations are unrealistic.

- Computationally fast. Solve stiff equations with long timesteps whilst maintaining accuracy and efficiency. Chemistry is highly parallel.
Types of solvers

- Explicit methods (e.g. Euler forward):
  - Cheap, first order, but requires small timestep for stability.
    \[ c_{i}^{n+1} = c_{i}^{n} + (P_{i}^{n} - L_{i}^{n}) \Delta t \]

- Implicit / semi-implicit methods: (e.g. linearized Euler backward)
  - Stable for long timesteps but more expensive.
    \[ c_{i}^{n+1} = c_{i}^{n} + f(c_{i}^{n+1}, c_{j}^{n}) \Delta t \quad \text{where} \quad f = P-L \]

- Hybrid / asymptotic methods:
  - For example, linearize to get first guess
    \[ \frac{c_{n+1}^{(0)} - c_{n}}{\Delta t} = f(c_{i}^{n}) + \left( \frac{\partial f}{\partial c} \right)_{n} (c_{n+1}^{(0)} - c_{n}) \]
    - Then iterate to convergence, or use estimates in Euler forward step.
    - There are many hybrid methods in the literature!
Stiff solvers

- There is considerable literature on solving chemical stiff ODEs and many standard and hybrid methods exist.

- Formally, stiffness is defined as:

\[
\max \left| \text{Re}(\lambda_i) \right| \gg 1
\]

for a general non-linear system

\[
\frac{dc}{dt} = f(c)
\]

where \( \lambda_i \) are the eigenvalues of the Jacobian matrix

\[
J = \frac{\partial f}{\partial c}
\]

- Why is stiffness important?
  - Determines choice of solver and computational cost.
  - Much of the cost is associated with requirement to invert the Jacobian matrix in the solver.

- Good reviews by Sandu et al (1997a,b), Atm. Env.
Off-the-shelf solvers

- Many good solvers exist for free!

- VODE – Variable coefficient ODE solver based on implicit Backward Differentiation Formula (BDF). Successor to LSODE (Livermore solver).
  - From ODEPACK in LAPACK library (see [www.netlib.org](http://www.netlib.org))
  - Too expensive for use in 3D models but good for comparison with cheaper, faster solvers.

- RODAS, RODAS3, ROS3, ROS4 – Runge-Kutta-Rosenbrook methods.

- TWOSTEP, CHEMEQ – explicit solvers.

- In all cases, it is important to test several solvers as performance and accuracy depends on the chemical mechanism.
Reducing complexity

- Various methods are used to reduce the computational cost: focus on reducing the complexity and stiffness of the system.

- Reduction of mechanism
  - Pseudo chemical reactions
    e.g. $A + B \rightarrow C^* + D$ where $(C + M \rightarrow C^*)$.

- Reduce stiffness of ODE system by:
  - Use of steady state relationship.
    Suitable for short lived species.
  - Family or lumped methods.
    Several related species are treated as one.

- Reduce computation cost by:
  - Customize numerical method for chemistry.
  - Efficient programming for computer hardware.
Steady state

- For species with short lifetimes (high reactivity), where $\tau$ is much less than the dynamical timescale being considered, we can assume a ‘steady state’ approximation:

$$\frac{\partial c_i}{\partial t} = P_i - l_i c_i = 0 \quad \text{with} \quad c_i = \frac{P_i}{l_i}$$

so that $c$ is in steady state with species that give rise to $P_i$ and $l_i$. Note this does not mean that $c_i$ is constant.

- Steady state is a useful approximation to reduce the number and the stiffness of equations.
  - Note it still requires the computation of production and loss terms.

- The QSSA (quasi-steady-state approximation; Hesstvedt et al) uses the lifetime to determine $c^{n+1}$ by either: Euler forward, exponential or SS.
Chemical families - 1

In the family method, groups of chemistry species are treated as a single species.

- This works as some gases cycle quickly with each other.
- The loss or gain by the chemical family is much slower than the cycling reactions of the family itself.

Advantages:
- Reduces stiffness in the equations.
- Longer timesteps.
- Less variables to transport.
- Smoother fields

Disadvantages:
- Accuracy.
- Emissions difficult.

Typical chemical families are:

\[
[\text{Ox}] = [O] + [O(1D)] + [O_3] + \text{[NO}_2\text{]} \\
[\text{HOx}] = [\text{OH}] + [\text{HO}_2] + [\text{H}_2\text{O}_2] \\
[\text{NOx}] = [\text{NO}] + [\text{NO}_2] + [\text{NO}_3] \\
[\text{Clx}] = [\text{Cl}] + [\text{ClO}] + [\text{2Cl}_2\text{O}_2]
\]
Chemical families - 2

- We consider the Ox family: 
  \[ [Ox]_{n+1} = [Ox]_n + \Delta t \frac{d[Ox]_n}{dt} \]

- The individual concentrations are computed by ratios assuming a major member (usually with the longer lifetime): 
  \[ [Ox] = [O] + [O(1D)] + [O_3] = [O_3](1 + \frac{[O]}{[O_3]} + \frac{[O(1D)]}{[O_3]}) \]

  with 
  \[ R_O = \frac{[O]}{[O_3]} \]
  \[ R_{O(1D)} = \frac{[O(1D)]}{[O_3]} \]
  \[ R_{O_3} = \frac{[Ox]}{1 + R_O + R_{O(1D)}} \]

- The unknown ratios are typically solved by assuming steady state, often using a few iterations to improve accuracy.
  - Using Chapman reactions: 
    \[ \frac{[O]}{[O_3]} = \frac{J_3}{k_2 \cdot [O_2]} \]

- Families provide significant reduction in stiffness and allow approximate Jacobian to be used.
Solvers – Gear’s method

- Gear’s method – solves the Backward Differentiation Formula.
  \[
  \frac{dc^n_i}{dt} = \left( \frac{1}{\beta_s \Delta t} \right) \left( c^n_i - \sum_{j=1}^{s} \alpha_{s,j} c_{i-j}^{n-1} \right)
  \]
e.g. if \( s = 1 \), then
  \[
  \frac{dc^n_i}{dt} = \frac{c^n_i - c^{n-1}_i}{\Delta t}
  \]
  where coefficients \( \alpha \) and \( \beta \) are tabulated and \( s \) is the order of the method.

- From this a predictor matrix, \( P \), is constructed. \( P = I - \Delta t \beta_s J(c^{n,m}) \)

- Solution requires matrix decomposition and backsubstitution with convergence checks after each iteration, where:
  \( m \) is the iteration count. \( J = \begin{bmatrix} \frac{\partial f_m}{\partial c_m} \end{bmatrix} \)

- \( J \) is sparse as not all species react with each other.
  - Reorder matrix so species with more reactions are near bottom.

- Multiple \( J \) result from day/night/gas-phase/heterogeneous chemistry (SMVGEOAR1&II: Jacobson)

- Gear only suitable for 3D with sparse matrix techniques, complexity reduction and efficient coding.
Solvers – Rosenbrock methods

- An s-stage Rosenbrock method is given by (Hairer & Wanner, Sandu):
  \[ c^{n+1} = c^n + \sum_{i=1}^{s} b_i k_i \]
  \[ k_i = \Delta t \cdot f(c_i^*) + \Delta t \cdot J \sum_{j=1}^{i} \gamma_{ij} k_j \]
  \[ c_i^* = c^n + \sum_{j=1}^{i-1} \alpha_{ij} k_j, \quad 1 \leq i \leq s \]

- These are popular solvers following the work of Sandu et al.
  - Choice of methods based on accuracy and order.
  - Relatively easy to code because they do not require an iteration procedure like true implicit methods.
  - One step nature is useful for operator-split type restarts.
  - Like other general purpose ODE solvers, a variable step-size based on error estimates.

- For use in 3D models, as before, sparse matrix techniques to compute \( J^{-1} \) must be used.
  - Constant \( J \) or partial \( J \) can also be used but loses conservation.
Model aspects – advection requirements

- Desirable properties of advection method.
  - Mass conservation is very important.
  - Mass fixers should NOT be global!
  - Maintain sharp gradients.
  - Computationally cheap to transport many extra variables (e.g. SL)
  - Should not disrupt chemical ratios or tracer-tracer correlations (e.g. non-linear mass fixers) (see Lauritzen & Thuburn 2012)

- High order advection methods e.g. 2nd order moments (Prather 1987).
  - Defines shape in gridbox.
  - Preserves gradients better than SL.
  - Conservative.
  - Suffers from reducing timestep at higher resolution.
Model aspects – subgrid scale

- Chemistry assumes well mixed grid box.
- Subgrid scale effects are not considered:
  \[
  \overline{[A]} = \overline{[A]} + \overline{[A']} \\
  -\frac{d\overline{[A]}}{dt} = k_1\overline{[A][B]} + k_1\overline{[A'][B']} 
  \]
- Effect is resolution dependent and chemical lifetime dependent.
- Methods that define ‘shape’ in the box could be used but in practice the computational & storage overhead is prohibitive.
- Parametrization of ‘mix-down’ by Thuburn & Tan (1997) worked by slowing the reaction rate so low resolution matched high resolution.
Computational aspects

- Atmospheric chemistry suits the use of automation:
  - Black-box solvers e.g. FACSIMILE (http://www.mcpa-software.com)
  - Code-writers (e.g. KPP; Damian et al. 2002)

  in which the chemistry mechanism is input as series of tables
  (e.g. SMVGGEAR I&II, ASAD).

- KPP (Kinetics Pre-processor) is very popular and:
  - includes a variety of solvers optimized for sparse Jacobians
    typically found in atmospheric chemistry.
  - can write code for the forward model, tangent-linear & adjoint.

- Advantages of such tools are:
  - Coding errors are avoided.
  - Maintenance of kinetic rates is easier.
  - Output code can be targeted at specific hardware.
Further reading

- Introduction to Atmospheric Chemistry (free online book)
    http://acmg.seas.harvard.edu/people/faculty/djj/book/

- Fundamentals of Atmospheric Modelling
  - M. Jacobson, Cambridge University Press
    (highly recommended; includes dynamics, physics & chemistry)

- Atmospheric Chemistry and Physics
  - Seinfeld and Pandis, Wiley and Sons
    (old now but good introductory text)

- Chemistry of Atmospheres
    (excellent for covering many aspects of atmospheric chemistry)

- Solving Ordinary Differential Equations I & II
  - E. Hairer and G. Wanner, Springer.
Thank you for listening!