Modelling of Chemistry and Transport in the Troposphere

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Outline

Why modelling?

- Numerical models comprise and couples our theoretical knowledge of engaged and featured physical and chemical processes
- balance equations
  - numerical approaches for chemical transformation and transport of trace compounds in the troposphere
  - models with different spatial resolution (examples)
  - Reynold’s average and the K-approach
  - numerical aspects
Supernational modelling initiatives “Earth Observation”

“Earth Observation“ comprises global scientific and environmental activities, targeting at:

- environmental impact on health
- climate research
- mitigating natural hazards.

Global: "Group on Earth Observations" (GEO) and "Global Earth Observing System of Systems“ (GEOSS)  
European: Global Monitoring for Environment and Security (GMES)  
Projekte MACC, PASODOBLE,"
Use and users of modelling results

“Upgrade data to information”

Forecast of the “atmospheric reactor”

Emission inventories

Meteo data

Landuse data

Health information

Legislation

Municipal information

Farming support

Aviation control

Science
Scope of Simulations: Example Chemistry-Transport model EURAD-IM
(Reaction-Advection-Diffusion equation) and further simulated processes

Chemistry mechanisms,
60 Gas phase constituents

Aqueous phase chemistry

Aerosols
- anorganic
- secondary organic
- mineral dust
- sea salt
- biomass burning
- vulcanic emissions

Mexico City
Mount Etna
Processes in a complex chemistry-transport model

Weather Research and Forecast model WRF
radiative transfer, winds, temperature, aqueous processes, cloud physics

condensation
evaporation
wet deposition
sublimation

aerosols
chemistry
dynamics
• nucleation
• coagulation
• sedimentation
• deliquescence
• ....

transport
diffusion

chemical transformations
Gas phase
aqueous phase

anthropogenic
+ biogenic
emissions

dry deposition
Transport-diffusion-reaction equation

Tendency Equations

direct chemistry transport equation

\[
\frac{dc_i}{dt} + \nabla \cdot (vc_i) - \nabla \cdot (\rho K \nabla \frac{c_i}{\rho}) - \sum_{r=1}^{R} \left( k(r) \left( s_i(r_+) - s_i(r_-) \right) \prod_{j=1}^{U} c_j^{s_i^{(r_-)}} \right) = E_i + D_i
\]

- \( c_i \): concentration of species \( i \)
- \( v \): wind velocity
- \( k(r) \): reaction rate of reaction \( r \)
- \( U \): number of species in the mechanism
- \( E_i \): emission rate of species \( i \) (source)
- \( D_i \): deposition rate of species \( i \) (sink)

- \( c_i^* \): adjoint of concentration of species \( i \)
- \( s \): stoichiometric coefficient
- \( K \): diffusion coefficient
- \( R \): number of reactions in the mechanism

Chemistry processes extremely diverse:
- gas phase reactions (ODEs as given above)
- aqueous phase (well mixed solution in droplets)
- aerosols (surface reactions)
Chemistry and transport models (CTM)

- off-line models
  - First determine the meteorological fields solving the equations of motion (Navier[1827]-Stokes[1845]-equations),...
  - then solve the balance equations for trace compounds
  - no feedback of the chemistry on transport

- full coupling: simultaneous determination of the meteorological fields and the trace gas budgets
  - feedback of the chemistry on the dynamics (meteorology) via the physical properties of trace compounds [important for climate modelling]
Models in atmospheric chemistry

Based on a quantitative understanding of the physical and chemical processes, equations are developed that can be used to calculate the temporal evolution and the spatial distributions of trace gases.

– theory: equations of motion and the continuity equations from fluid dynamics and state equation of gases,...

– phenomenological models: for instance dry deposition in analogy to electric circuits
Balance equations I

Relation between the state of a system and the change of the state. Examples:

- Radioactive decay

\[ \frac{dN(t)}{dt} = -\frac{1}{\tau} N(t) \]

- Newton’s equation of motion

\[ m \frac{d^2 x(t)}{dt^2} = K(x(t)) \]

- response $X$ of the immune system on an attack by pathogenic agents $P(r)$

\[ \frac{dX(t)}{dt} = +\kappa \int_{\text{body}} P(r)dr \]
Additivity

Consider the first order decay of X via processes 1 and 2

\[
\begin{align*}
\left( \frac{d[X]}{dt} \right)_1 &= -k_1[X] \\
\left( \frac{d[X]}{dt} \right)_2 &= -k_2[X] \\
[X]_1 &= [X(0)] \exp(-k_1 t) \\
[X]_2 &= [X(0)] \exp(-k_2 t)
\end{align*}
\]

Additivity of the balance equations

\[
\left( \frac{d[X]}{dt} \right) = \left( \frac{d[X]}{dt} \right)_1 + \left( \frac{d[X]}{dt} \right)_2
\]

\[
[X(t)] = [X(0)] \exp(-(k_1 + k_2)t) \neq [X(t)]_1 + [X(t)]_2
\]
Balance equation II

Coupled partial differential equations in space and time
rate of chemical production $P_i$ and the
frequency of destruction $D_i$
are in general non linear functions of concentrations

$$C = (C_1(r, t), ..., C_n(r, t))$$

$$\frac{\partial C_i(r, t)}{\partial t} = P_i(C) - D_i(C)C_i + T(C_i)$$
The chemical balance equations (nonlinear ordinary 1. order differential equations) are **stiff** because of the large variability of relaxation times (life times) between nano seconds (O(1D)) and many years (CH4).

Standard numerical integration requires time steps which are much smaller than the smallest relaxation time.

Gear’s solver (often used as reference)

option: applying the quasi-stationary state approximation (QSSA) to reduce stiffness. The balance (differential) equations for short lived compounds are replaced by algebraic equations \( C_{QSSi} \approx P_i(C)/D_i(C) \)
Solve
\[
\begin{align*}
\frac{dx}{dt} &= -1000x + 999y + 2 \\
\frac{dy}{dt} &= +999x - 1001y + 2
\end{align*}
\]
with initial conditions \( x(0) = 3 \) and \( y(0) = 1 \).

For this linear problem an exact solution is available:
\[
\begin{align*}
x(t) &= 1 + \exp(-2t) + \exp(-2000t) \\
y(t) &= 1 + \exp(-2t) - \exp(-2000t)
\end{align*}
\]
The solution \( x(t) \) and \( y(t) \) relax within 1/2000 sec to \( x \approx 2 \) and \( y \approx 2 \). Then \( x \) and \( y \) vary slowly with a characteristic time of 0.5 sec.

In order to integrate the differential equations numerically with standard algorithms
\[
\begin{align*}
x(t + t) &= x(t) + f(t) \\
y(t + t) &= y(t) - f(t)
\end{align*}
\]
one would need time steps \( t \ll 1/2000\text{sec} \).
Numerical solution methods of chemical ODEs

Gas phase chemical reactions are
• first-order
• homogeneous
• stiff

The numerical solver needs to be
• stable
• “accurate” (more precisely: consistent + stable $\rightarrow$ convergent)
• mass-conserving (for each chemical element)
• positive definite
• computationally efficient
A look into numerical stability

Explicit Euler error scheme

Explicit Euler and Adams-Moulton displaying instability on a stiff equation
Box -model
(= 0-dimensional model)

Assumption: Vertical mixing is so fast, that trace gases are spatially homogeneously mixed in a box of height H

\[
T(C_i) = -\nabla (v \cdot C_i) = 0
\]

\[
\frac{dC_i}{dt} = P_i(C) - D_i(C)C_i + \frac{F_i}{H} - \frac{v^d_i}{H} C_i
\]

$F_i$: emission strength [cm$^{-2}$s$^{-1}$]
$v^d_i$: velocity of dry deposition [cm s$^{-1}$]
**Numerical solution (1) an analytical example**

Only very simple reactions can be solved analytically: e.g. photo-dissociation of nitrogen dioxide

<table>
<thead>
<tr>
<th>Chemical equation</th>
<th>[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear ODE</td>
<td>[ \frac{d}{dt} [\text{NO}<em>2] = -J</em>{\text{NO}_2} [\text{NO}_2] ]</td>
</tr>
<tr>
<td>Exact solution</td>
<td>[ [\text{NO}<em>2](t + \Delta t) = <a href="t">\text{NO}_2</a> \exp(-J</em>{\text{NO}_2} \Delta t) ]</td>
</tr>
</tbody>
</table>
Numerical solution (2)  
simple approach: forward Euler

A small 4-constituent NOx cycle, destructing ozone

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O}
\end{align*}
\]

Production and Loss terms of NO\textsubscript{2} forward Euler scheme

\[
\frac{d[\text{NO}_2]}{dt} = k_1 [\text{NO}] [\text{O}_3] - k_2 [\text{NO}_2] [\text{O}_3] - J [\text{NO}_2]
\]

\[
[\text{NO}_2](t + \Delta t) = [\text{NO}_2](t) + \Delta t \left( P_{\text{NO}_2}(t) - L_{\text{NO}_2}(t) \right)
\]

Performance: needs extremely small \( \Delta t \) to be stable: \( \rightarrow \) inefficient
Numerical solution (3)
implicit approach: backward Euler

Each target species is expressed for next time step explicit after rearrangement

\[
\begin{align*}
[\text{NO}_2](t + \Delta t) &= [\text{NO}_2](t) + \Delta t \left( P_{[\text{NO}_2]}(t) - L_{[\text{NO}_2]}(t + \Delta t, t) \right) \\
\bar{L}_{[\text{NO}_2]}(t) &= \frac{L_{[\text{NO}_2]}(t + \Delta t, t)}{[\text{NO}_2](t + \Delta t)} := \frac{k_2 [\text{NO}_2(t + \Delta t)] [\text{O}_3(t)] + J [\text{NO}_2(t + \Delta t)]}{[\text{NO}_2(t + \Delta t]}
\end{align*}
\]

\[
[\text{NO}_2](t + \Delta t) = \frac{[\text{NO}_2](t) + \Delta t P_{[\text{NO}_2]}(t)}{1 + \Delta t \bar{L}_{[\text{NO}_2]}(t)}
\]

\[
c_i(t + \Delta t) = \frac{c_i(t) + \Delta t P_{c_i}(t)}{1 + \Delta t \bar{L}_{c_i}(t)}
\]

Performance: positive definite, but no mass conservation
Numerical solution (4)
Quasi Steady State Approximation (QSSA)

Example again

general solution for inhomogen. ODE

\[
\frac{d [NO_2]}{dt} = k_1 [NO][O_3] - (k_2 [O_3] + J) [NO_2]
\]

\[
c_i(t + \Delta t) = c_i(t) \exp(-\Delta t L) + \frac{P_c(t)}{L_c(t)} \left(1 - \exp(-\Delta t L_{c_i}(t))\right)
\]

\[
c_i(t+\Delta t) = \begin{cases} 
  c_i(t) + \Delta t(P_{c_i(t)} - L_{c_i(t)}) & \Delta t L_{c_i(t)} < 0.01 \\
  c_i(t) \exp(-\Delta t L) + \frac{P_c(t)}{L_c(t)} \left(1 - \exp(-\Delta t L_{c_i}(t))\right) & 0.01 \leq \Delta t L_{c_i(t)} \leq 10 \\
  P_{c_i(t)}/L_{c_i(t)} & \Delta t L_{c_i(t)} > 10 
\end{cases}
\]

Performance: nearly stable, but not mass conserving
Numerical solution (5)
backward differentiation formula, Gear

backward differentiation formula (BDF)

\[
\frac{dc(t)}{dt} = \frac{1}{\Delta t \beta_s} \left( c(t) - \sum_{j=1}^{s} \alpha_{s,j} c(t - j\Delta t) \right)
\]

\(\alpha, \beta\) order dependent factors, \(m^{th}\) iteration

iterative solution to BDF

\[
P_t(c_m(t + \Delta t) - c_m(t)) = -c_m(t) + \sum_{j=1}^{s} \alpha_{s,j} c(t - j\Delta t) + \Delta t \beta_s \frac{dc_m(t)}{dt}
\]

\(P_t \approx I - \Delta t \beta_s J_t\)

with Jacobian matrix \(J_t = \left( \frac{\partial^2 c_i,m(t)}{\partial c_j,m(t)\partial t} \right)\)

Performance:
stable and efficient for stiff systems,
if applied with sparse matrix techniques
Numerical solution (6a)
Family solution

Example family:
Reaction cycle of “odd oxygen”

odd oxygen

\[
\begin{align*}
O_3 + h\nu &\rightarrow O_2 + O(^{1}D) \\
O_2 + h\nu &\rightarrow O + O \\
O(^{1}D) + M &\rightarrow O + M \\
O + O_2 + M &\rightarrow O_3 + M
\end{align*}
\]

other amenable fast reaction cycles (families)

\[
\begin{align*}
[O_F] &= [O] + [O(^{1}D)] + [O_3] + [NO_2] \\
[HO_F] &= [HO] + [HO_2] + [H_2O_2] \\
[NO_F] &= [NO] + [NO_2] + [NO_3] \\
[Cl_F] &= [Cl] + [ClO] + [ClO_2]
\end{align*}
\]
Numerical solution (6b)
Family solution

\[
\begin{align*}
\frac{d[A]}{dt} &= -k_a [A] \\
\frac{d[C]}{dt} &= k_b [B] - k_c [C] = 0 \\
\frac{d[B]}{dt} &= k_a [A] - k_b [B] = 0 \\
\frac{d[D]}{dt} &= k_c [C]
\end{align*}
\]

\[
\frac{d[F_1]}{dt} = \frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[C]}{dt} = -k_c [C]
\]

\[
\frac{d[F_2]}{dt} = \frac{d[D]}{dt} = k_c [C]
\]

\[
\begin{align*}
\frac{[B]}{[A]} &= \frac{k_a}{k_b} \\
\frac{[C]}{[A]} &= \frac{k_a}{k_c}
\end{align*}
\]

\[
[A] = \frac{[\text{Fam}_1]}{1 + \frac{k_a}{k_b} + \frac{k_a}{k_c}}
\]

Performance: fast, but not mass conserving.
Families must be set up with care.
KPP  The Kinetic PreProcessor
a very well validated comfortable chemical solver environment
for chemical mechanisms

- translates a specification of the chemical mechanism into Fortran77, Fortran90, C, or Matlab,
- implements the concentration time derivative function, its Jacobian, and it Hessian, with a suitable numerical integration scheme,
- exploits sparsity in Jacobian/Hessian for computational efficiency,
- incorporates a library with several widely used atmospheric chemistry mechanisms;
- accepts user defined chemical mechanisms to the library,
- includes a comprehensive suite of stiff numerical integrators.


http://people.cs.vt.edu/~asandu/Software/Kpp/
KPP solvers
For details consult Hairer and Wanner (1991)

- **Rosenbrock methods**: Ros-1 and Ros-2 (Verwer et al., 1999), Ros-3 (Sandu et al., 1997), Rodas-3 (Sandu et al., 1997), Ros-4 (Hairer and Wanner, 1991), and Rodas-4 (Hairer and Wanner, 1991).

- **Radau5**: Runge Kutta method of order 5 based on Radau-IIA quadrature (Hairer and Wanner, 1991) is relatively expensive (when compared to the Rosenbrock methods), it is more robust and is useful to obtain accurate reference solutions.


- **SEULEX**: variable order stiff extrapolation code, follows the one in Hairer and Wanner (1991),

- **LSODE, LSODES**: Livermore ODE solver (Radhakrishnan and Hindmarsh, 1993) backward differentiation formula (BDF). LSODES (Radhakrishnan and Hindmarsh, 1993),

- **VODE**: BDF (Brown et al., 1989)

- **ODESSA**: BDF-based direct-decoupled sensitivity integrator (Leis and Kramer, 1986)
Transport I

Transport caused by *divergence* of the flux (more precisely: current density)

\[ T(C_i) = - \nabla \cdot (\mathbf{v}C_i) \]

in cartesian coordinates

\[ \mathbf{v} = (u, v, w) \quad \mathbf{r} = (x, y, z) \]

\[ T(C_i) = - \frac{\partial (uC_i)}{\partial x} - \frac{\partial (vC_i)}{\partial y} - \frac{\partial (wC_i)}{\partial z} \]

The transport \( T(C_i) \) is a linear operator.
Purpose of box-models

study of chemistry and identification of key compounds and processes
• chemical life time
• estimation of the influence of transport
• validation of chemical reaction mechanisms
  (observationally constrained modelling)
chamber experiments
Balance equations III

Goal: Calculate $\text{Ci}(r, t)$

- the wind field $v(r, t)$ and other meteorological fields have to be determined prior to the CTM simulation (for example with a weather prediction model)
- input data (Initial conditions at $t = 0$ and boundary conditions for the whole simulation period $t = ...T$ are required):
  - measured data, from other model calculations, back ground data, ...
  - Influence depends on the scale of the model.
- Information on emission strengths and non chemical losses are required.

Only numerical solution possible (Quite a job! )
London smog (winter smog)

The London smog episode in winter 1952 was the severest winter smog period that is scientifically documented.

- Inversion heights of about 100 m and slow exchange with clean air from aloft
- Low wind velocities and consequently slow horizontal exchange
- Fog
- $[\text{SO}_2] \approx 1000 \text{ ppb and more (nowadays in western Europe typically less than } 1 \text{ ppb and maximum } 50 \text{ ppb)}$
- Particle burden $4.5\text{mg/m}^3$ (typ. several $\mu\text{g/m}^3$)
- Additional 4000 casualties in London during that period
Two-Box-model of the planetary boundary layer

Well mixed layer 0 ... h(t) with daytime dependent height h(t) (concentrations C_i(t)):

$$\frac{dC_i}{dt} = P_i(C) - D_i(C)C_i + \frac{F_i}{h(t)} - \frac{v_i^d}{h(t)}C_i - w(t)(C_i - c_i)$$

$$w(t) = \frac{1}{h(t)} \frac{dh(t)}{dt}$$

reservoir layer (h(t) ... H) (concentrations c_i(t)):

$$\frac{dc_i}{dt} = p_i(c) - d_i(c)c_i$$

F_i emission strength [cm^{-2}s^{-1}] \quad v_i^d \text{ velocity of dry deposition [cm}s^{-1}]
Jülich 1993

$O_3 (\text{ppb})$

2.8.  4.8.  6.8.  8.8.  10.8.  12.8.
Jülich 1993

HCHO(ppb)

2.8.  4.8.  6.8.  8.8.  10.8.  12.8.
1-dimensional model

- Dependence of concentrations on height $z$
- assumption: horizontally well mixed

\[
\frac{\partial C_i(z, t)}{\partial t} = P_i(C) - D_i(C)C_i - \frac{\partial (wC_i)}{\partial z}
\]

To be solved under initial conditions $C(z, t = 0)$ and boundary conditions for concentrations and fluxes (sources and sinks) at the upper and lower boundary of the model.
3-D models
Example KAMM/DRAIS
KIT IMK (Karlsruhe)
Discretisation of the 1-D advection equation (1)

The advection equation is a special case of quasi-linear partial differential equation of 1. order

$$\frac{\partial u(t, \mathbf{r})}{\partial t} + \mathbf{v}(t, \mathbf{r}) \cdot \nabla u(t, \mathbf{r}) = g(t, \mathbf{r})$$

It describes transport of
- a material property $u(t, \mathbf{r})$
- advected by speed $\mathbf{v}$
- with generation and destruction, collectively termed $g(t, \mathbf{r})$
- in spatio-temporal dependency $(t, \mathbf{r})$. 
Discretisation of the 1-D advection equation (2) \textit{spatial}

One possible discretisation of the spatial derivative are “centred differences”

\[ \frac{\partial u}{\partial x} =: u_x \]

\[ u_x|_{x_j} = \frac{u_{j+1} - u_{j-1}}{2h} + \frac{h^3}{12} \left( u_{xxx}|_{\xi_+} + u_{xxx}|_{\xi_-} \right) \]

with \( \xi_+ \in (x_j, x_{j+1}) \) and \( \xi_- \in (x_{j-1}, x_j) \), as following Taylor

\[ u_{j\pm 1} = u_j \pm h u_x|_{x_j} + \frac{h^2}{2} u_{xx}|_{x_j} \pm \frac{h^3}{6} u_{xxx}|_{\xi_\pm} \]

approximation is of quadratic order \( O(h^2) \).
Discretisation of the 1-D advection equation (3)
spatial

Another option is “upstream discretisation because the 2nd node is selected in windward direction (more predictive skill what to expect at node $u_j$.)

$$u_x \big|_{x_j} = \frac{u_j - u_{j-1}}{h} + \frac{h}{2} u_{xx} \big|_{\xi}, \quad \xi \in (x_{j-1}, x_j)$$

Error is of linear order only!
Discretisation of the 1-D advection equation (3) 
temporal

The temporal discretisation like “upwind scheme”.


denn

\[
\left. u_t \right|_{t_n} = \frac{u_j^{n+1} - u_j^n}{\Delta t} - \frac{\Delta t}{2} u_{tt} \big|_{\eta}, \quad \eta \in (t_n, t_{n+1}).
\]

linear order $O(\Delta t)$. 
Discretisation of the 1-D advection equation (3) spatial

Alltogether, the 1-dim. discretized form of equation

$$\frac{\partial u(t, r)}{\partial t} + \mathbf{v}(t, r) \cdot \nabla u(t, r) = g(t, r)$$

then reads

$$\frac{u_j^{n+1} - u_j^n}{\Delta t} + \frac{c}{2h} (u_{j+1}^n - u_{j-1}^n) = \tau_j^n,$$

with local truncation error $\tau_j^n$ of order $O(\Delta t) + O(h^2)$.

Not that what we can need!!
Leapfrog method for time integration

\[ \lambda = \frac{c \cdot \Delta t}{\Delta x} \leq 1 \] is the Courant number.

\[ U_j^{n+1} = U_j^{n-1} - \lambda (U_{j+1}^n - U_{j-1}^n) \]

Figure 1: Scheme of Leapfrog method.
Numerical diffusion

**FIGURE 23.14** Solution of the square-wave problem using $\Delta x = 0.1 \text{ m}$, $\Delta t = 0.02 \text{ s}$, at $u = 1 \text{ m s}^{-1}$ with the explicit finite difference scheme. Numerical results and true solution for $t = 1 \text{ s}$ (50 steps).

**FIGURE 23.15** Solution of the square-wave problem using $\Delta x = 0.1 \text{ m}$, $\Delta t = 0.02 \text{ s}$, and $u = 1 \text{ m s}^{-1}$ with the finite difference scheme of (23.132). Numerical results and true solution for $t = 1 \text{ s}$ (100 steps) and $t = 5 \text{ s}$ (500 steps).
The impact of PM\(_x\) (Particulate Matter) on human health is strong. CAFE (Clean Air For Europe, 2005) final report states:

- Estimated reduction of lifetime expectancy due to PM\(_{2.5}\) is large
- Modelling of TPM is not yet satisfying
  - Too few measurements
  - Too large model uncertainties

How to get to a more reliable estimation of aerosol load and exposure?
- react on sudden emission changes?
- deal with heterogeneous data?

→ inverse modelling

Estimated PM\(_{2.5}\) caused reduction of lifetime expectancy in months (Emissions 2000)[CAFE]
Aerosol Chemistry in MADE
Modal Aerosol Dynamics for EURAD/Europe
(Ackerman et al., 1998, Schell, 2000)

Aerosol dynamics (included)
Coagulation, nucleation, condensation-evaporation
Cloud-aerosol interaction
Diffusion, advection
Dry deposition, sedimentation

\[ \frac{dM_i^k}{dt} = nuk_i^k + coag_{ii}^k + coag_{ij}^k + cond_i^k + sink_i^k + emi_i^k \]

\[ M_i^k := k^{th} \text{ Moment of } i^{th} \text{ Mode} \]
Example: chemical complexity:
The EURAD Secondary ORGanic Aerosol Model (SORGAM)
Mesoscale EURAD 4D-var data assimilation system

- meteorological driver: WRF
- EURAD emission model: EEM
- emission 1. guess
- Initial values
- emission rates
- direct CTM
- forecast
Symmetric operator split procedure

time direction


Chemie
Reynolds average

For practical reasons only averaged quantities are experimentally available. All quantities $q$ are considered as a sum of an average $q$ (scale quantity) and a fluctuation $q'$ (subscale quantity) mit $q' = 0$.

$$C_i = \overline{C_i} + C_i'$$

$$w = \overline{w} + w'$$

For the transport term of the 1d model (similar for 3d models)

$$\frac{\partial wC_i}{\partial Z} = \frac{\partial \overline{wC_i}}{\partial Z} + \frac{\partial w'C_i}{\partial Z} + \frac{\partial \overline{wC_i'}}{\partial Z} + \frac{\partial w'C_i'}{\partial Z}$$

$$\frac{\partial \overline{wC_i}}{\partial Z} = \frac{\partial \overline{wC_i}}{\partial Z} + \frac{\partial w'C_i'}{\partial Z}$$
Reynolds average for a 1-dim model

Using the continuity equation and averaging yield

\[
\frac{\partial \bar{C}_i(z, t)}{\partial t} = P_i(C') - D_i(C')C_i - \frac{\partial (\bar{wC}_i)}{\partial z} - \frac{\partial (\bar{w'C}_i)}{\partial z}
\]

The set of e

\[
\frac{\partial \bar{C}_i(z, t)}{\partial t} \approx P_i(C') - D_i(C')C_i - \frac{\partial (\bar{wC}_i)}{\partial z} - \frac{\partial (\bar{w'C}_i)}{\partial z}
\]
Closure with the (approximate) K-Ansatz

We adopt an ad-hoc ansatz that relates the subscale terms and the scale terms

\[ \overline{w' C'_i} = -K \frac{\partial C_i(z, t)}{\partial z} \]

\[ \frac{\partial \overline{C_i(z, t)}}{\partial t} \approx P_i(\overline{C}) - D_i(\overline{C}) \overline{C_i} - \frac{\partial (\overline{w C_i})}{\partial z} + \frac{\partial}{\partial z} \left( K \frac{\partial \overline{C_i(z, t)}}{\partial z} \right) \]
Analogy with molecular diffusion I

For a constant $K(z) = k$ we get

$$\frac{\partial}{\partial z} \left( K(z) \frac{\partial C}{\partial z} \right) = \frac{\partial}{\partial z} \left( k \frac{\partial C}{\partial z} \right) = k \frac{\partial^2 C}{\partial z^2}$$

The subscale transport term for a chemically inert tracer looks like a (molecular) diffusion term. The physical picture is that of a multi scale turbulent diffusion.
Analogy with molecular diffusion II

Important differences between molecular and turbulent diffusion or Eddy-diffusion
– molecular diffusion changes with the mass of the diffusing molecules. For air
  \[ \text{kmol} \approx 5 \times 10^{-2} \text{cm}^2\text{s}^{-1}. \]
– the turbulent diffusion coefficient does not depend on mass \[!\]
– turbulent diffusion depends on the scale i.e. the definition of the average process
– in general \( \text{kmol} \ll \text{kturb} \)

vertical Eddy-diffusion:
stable boundary layer \( \text{kturb} \approx 5 \times 10^3...5 \times 10^4 \text{cm}^2\text{s}^{-1} \)
unstable boundary layer \( \text{kturb} \approx 10^6 \text{cm}^2\text{s}^{-1} \)
– time scale of diffusion over length \( l \) is \( \tau \) with \( k = l^2/\tau \)
Numerical aspects II (Transport)

Operator splitting

\[
\left( \frac{\partial C_i(z, t)}{\partial t} \right)_{\text{total}} = \left( \frac{\partial C_i(z, t)}{\partial t} \right)_{\text{adv}} + \left( \frac{\partial C_i(z, t)}{\partial t} \right)_{\text{turb}} + \left( \frac{\partial C_i(z, t)}{\partial t} \right)_{\text{chem}}
\]

The set of partial differential equations (PDE) are discretized in space yielding only time dependent ordinary differential equations (ODE). These ODEs are more diffusive than the PDEs.

problem: numerical diffusion
Treatment of the inverse problem for emission rate inference

**Treatment of Emissions**

- Emission inventory: EMEP
- Emitted species: NO\(_2\), NO, SO\(_2\), H\(_2\)SO\(_4\), CO, NH\(_3\), C\(_2\)H\(_6\), HC3, HC5, HC8, C\(_2\)H\(_4\), C\(_3\)H\(_6\), C\(_4\)H\(_8\), C\(_5\)H\(_8\), CH\(_3\)CH\(_2\)H\(_5\), (CH\(_3\))\(_2\)C\(_6\)H\(_4\), HCHO, R-CHO, KET

- Height level emissions (industrial) held constant in time
- Surface level emissions (traffic, domestic) diurnal variation
Normalised diurnal cycle of anthropogenic surface emissions $f(t)$

$\text{emission}(t) = f(t; \text{location, species, day}) \times v(\text{location, species})$

day in \{working day, Saturday, Sunday\}   \quad v \text{ optimization parameter}
Overview on existing models

<table>
<thead>
<tr>
<th>type</th>
<th>scale*</th>
</tr>
</thead>
<tbody>
<tr>
<td>global models</td>
<td>1000km × 1000km</td>
</tr>
<tr>
<td>regional models</td>
<td>100km × 100km</td>
</tr>
<tr>
<td>mesoscale models</td>
<td>&lt;&lt; 100km</td>
</tr>
<tr>
<td>microscale models</td>
<td></td>
</tr>
</tbody>
</table>
Some regional CTMs

CMAQ (US)
http://www.cmaq-model.org/index.cfm

CAMx (US)
http://www.camx.com/

NAME (UK Met Office) Lagrangian
http://www.metoffice.gov.uk/environment/name_iii.html

WRF Chem (US)
http://ruc.noaa.gov/wrf/WG11/

CHIMERE (France)
http://www.lmd.polytechnique.fr/chimere/

Polyphemus (FRANCE)
http://cerea.enpc.fr/polyphemus/

LOTOS-EUROS (Netherlands)
http://www.lotos-euros.nl/

MOCAGE (FRANCE)

EURAD-IM (Germany)
http://www.riu.uni-koeln.de (presently under modification)
What needs to be done?

– Reducing of uncertainties of CTM
  * emissions
  * atmospheric transport
  * microphysics of multiphase processes (involving the aerosol and liquid phase)
  * chemistry of the homogeneous phases
– Coupling to climate models
  * earth system modeling