COMPONENTS OF ATMOSPHERIC CHEMISTRY MODELS

DYNAMICAL EQUATIONS
- Mass Continuity Equation
- Momentum Equations
- Thermodynamic Equation

CHEMICAL CONTINUITY EQUATIONS
\[ \frac{\partial [i]}{\partial t} = P_i - L_i - \nabla \cdot ([i] \mathbf{v}) \]

RADIATION EQUATIONS
- Winds, eddy diffusion coefficients
- Temperature
- Rates for Heating
- Concentrations (O_3 etc.)
- UV Fluxes
- For photodissociation rates
- Rates for Chemistry

Figure by MIT OCW.
To solve the model equations, we divide the atmosphere into a finite number of boxes (grid cells).

Assume that each variable has the same value throughout the box.

Write a budget for each box, defining the changes within the box, and the flows between the boxes.
Combining Chemistry and Transport: The Continuity Equation

Physical picture:
(Eulerian)

Notation:

Inputs = $I_x^i dydz + I_y^i dzdx + I_z^i dxdy$

Outputs = $O_x^i dydz + O_y^i dzdx + O_z^i dxdy$

$$\begin{bmatrix} I_x^i & I_y^i & I_z^i \end{bmatrix}$$

$$dx \begin{bmatrix} u \\ v \\ w \end{bmatrix}$$ (input fluxes)

$$du/dt, dv/dt, dw/dt$$ (wind velocities)

$P_i, L_i =$ rates of chemical production, loss

$[i]$ = concentration of i

Local rate of change of $[i]$ given by:

$$\frac{\partial [i]}{\partial t} = \frac{\text{Inputs} - \text{Outputs} + \text{Internal net production}}{\text{dxdydz}}$$

$$= P_i - L_i - \frac{\partial}{\partial x} ([i] u) - \frac{\partial}{\partial y} ([i] v) - \frac{\partial}{\partial z} ([i] w)$$

$$= P_i - L_i - \nabla \cdot ([i] \vec{V})$$ (1)

Continuity equation for i

For total molecular concentration $[M]$, $P_M - L_M = 0$ so:

$$\frac{\partial [M]}{\partial t} = -\nabla \cdot ([M] \vec{V})$$ (2)
Continuity equation for $M$

Defining mixing ratio $[i]/[M] = X_i$:

$$\frac{\partial X_i}{\partial t} = \frac{\partial}{\partial t} \left( \frac{[i]}{[M]} \right) = \frac{\partial [i]}{\partial t} \frac{[M]}{[M]^2} - \frac{\partial [M]}{\partial t} \frac{[i]}{[M]^2}$$

$$= \frac{\left( P_i - L_i - \nabla \cdot \left( X_i [M] \bar{V} \right) \right) [M] + \nabla \cdot \left( [M] \bar{V} \right) X_i [M]}{[M]^2}$$

(Using equations (1) and (2))

$$= \frac{\left( P_i - L_i - [M] \bar{V} \cdot \nabla X_i \right) [M]}{[M]^2}$$

$$= \frac{P_i - L_i}{[M]} - \bar{V} \cdot \nabla X_i$$

(3)

Continuity Equation for $i$ (mixing ratio form)

Theorem: If there is no gradient in the mixing ratio of $i$ ($\nabla X_i = 0$) then there can be no local changes in $i$ due to transport.

Rate of change of $X_i$ traveling with the air given by (Lagrangian view):

(a)

$$\frac{dX_i}{dt} = \frac{d}{dt} \left[ X_i \left( x, y, z, t \right) \right]$$

$$= \frac{\partial X_i}{\partial x} \frac{dx}{dt} + \frac{\partial X_i}{\partial y} \frac{dy}{dt} + \frac{\partial X_i}{\partial z} \frac{dz}{dt} + \frac{\partial X_i}{\partial t}$$

(chain rule)

$$= \frac{\partial X_i}{\partial x} \bar{u} + \frac{\partial X_i}{\partial y} \bar{v} + \frac{\partial X_i}{\partial z} \bar{w} + \frac{\partial X_i}{\partial t}$$

$$= \bar{V} \cdot \nabla X_i + \frac{P_i - L_i}{[M]} \bar{V} \cdot \nabla X_i$$

(using equation (3))

$$= \frac{P_i - L_i}{[M]}$$

(4)

Theorem: If there is no “net chemical production” ($P_i - L_i = 0$), then the mixing ratio of $i$ is conserved moving with the air.
Theorem: The change in mixing ratio in an air mass from its initial value is a line integral of the “net chemical production” over the trajectory of the air mass.

A steady state exists when the local rate of change is zero:

\[
\frac{\partial [i]}{\partial t} = 0 \quad \text{i.e.} \quad P_i - L_i = \nabla \cdot ([i] \bar{V}) \quad (6)
\]

\[
\frac{\partial [M]}{\partial t} = 0 \quad \text{i.e.} \quad \nabla \cdot ([M] \bar{V}) = 0 \quad (6)
\]

\[
\frac{\partial X_i}{\partial t} = 0 \quad \text{i.e.} \quad \frac{P_i - L_i}{[M]} = \bar{V} \cdot \nabla X_i \quad (7)
\]

One-Dimensional (Horizontal) Model

Source Region | Downwind Region
---|---
[Constant \(X_i\)] | [Constant wind speed \(u\), \(P_i = 0\), \(L_i = \frac{[i]}{\tau_i} = \frac{[M]X_i}{\tau_i}\)]

Equation (7) with \(v = w = 0\) gives:

\[
P_i - L_i = 0 - \frac{[M]X_i}{\tau_i}
\]

\[
= \frac{[M]u}{\tau_i} \frac{dX_i}{dx}
\]

i.e. \(\frac{d\ln X_i}{dx} = -\frac{1}{u\tau_i}\)

i.e. \(X_i(x) = X_i(0)\exp\left(-\frac{x}{u\tau_i}\right)\) (8)
[chemical (e-folding) distance, \( h = u \tau_i \)]
[advection time = \( x/u \)]

i.e.

(a) Inert Case
\[
\frac{x}{h}, \quad \tau_i \gg \frac{x}{u}
\]

(b) Reactive Case
\[
\frac{x}{h}, \quad \tau_i < \frac{x}{u}
\]

Figure by MIT OCW.