One-Dimensional (Vertical) Chemistry-Transport Model

Take horizontal average of equation (5) and denote horizontal average with overbar and deviation from horizontal average with a prime:

$$\overline{P_i - L_i} = \overline{\nabla\cdot\left([i]\vec{V}\right)} = \overline{\frac{d}{dz}\left([i]w\right)} = \overline{\frac{d}{dz}\left(X_i[M]w\right)}$$

$$= \frac{d}{dz}\left(\overline{X_i'[M]w} + \overline{\bar{X}_i[M]w}\right)$$

$$= \frac{d}{dz}\left(\overline{X_i'[M]'w'} + \overline{[M]}\,\overline{X_i'w'} + \bar{w}\,\overline{X_i'[M]'} + \overline{X_i'}\,\overline{[M]}\bar{w}\right) \qquad \text{(net vertical flux of air } \overline{[M]w} = 0\text{)}$$

$$= \frac{d}{dz}\left(\overline{X_i'[M]'w'} + \overline{[M]}\,\overline{X_i'w'}\right) \qquad (\overline{X_i'} = 0 \text{ and } \bar{w} = 0)$$

$$\simeq \frac{d}{dz}\left(\overline{[M]}\,\overline{X_i'w'}\right) \qquad \left([M]' \ll \overline{[M]}\right)$$

$$\simeq -\frac{d}{dz}\left(\overline{[M]}\frac{d\overline{X_i}}{dz}|\delta z||w'|\right) \qquad \text{(\underline{eddy diffusion approximation}*)}$$

$$= -\frac{d}{dz}\left(\overline{[M]}\frac{d\overline{X_i}}{dz}K_z\right) \qquad (9)\ \ (K_z = \text{eddy diffusion coefficient} = |\delta_z||w'|)$$

*<u>eddy diffusion approximation</u>:

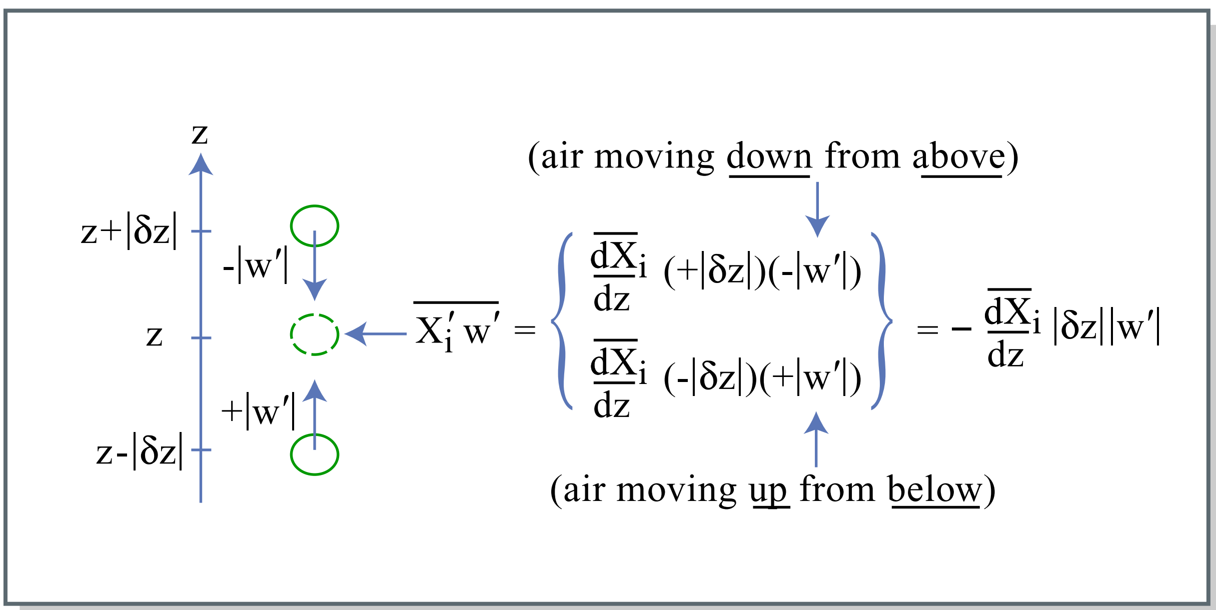


Figure by MIT OCW.

Consider case when loss only:

$$\overline{P_i - L_i} = -\overline{L_i} = -\frac{\overline{[i]}}{\tau} \qquad (\tau = \text{chemical lifetime of i})$$

$$= -\frac{\left(\overline{[M]'X_i'} + \overline{[M]}\,\overline{X_i}\right)}{\tau} \qquad (\overline{X_i'} = 0 \text{ and } \overline{[M]'} = 0)$$

$$\simeq -\frac{\overline{[M]}\,\overline{X_i}}{\tau} \qquad \left(\overline{[M]'X_i'} \ll \overline{[M]}\,\overline{X_i}\right)$$

For brevity drop subscripts i and overbars and assume $K_z = K$ is independent of altitude and temperature is constant:

$$\frac{X[M]}{\tau} = K\frac{d}{dz}\left([M]\frac{dX}{dz}\right)$$

$$= K\left(\frac{d[M]}{dz}\frac{dX}{dz} + [M]\frac{d^2X}{dz^2}\right)$$

$$= K\left(-\frac{[M]}{H}\frac{dX}{dz} + [M]\frac{d^2X}{dz^2}\right)$$

(In hydrostatic equilibrium: $\frac{d[M]}{dz} = -\frac{[M]}{H}$ for constant temperature)

Rearranging:

$$\frac{d^2X}{dz^2} - \frac{1}{H}\frac{dX}{dz} - \frac{X}{K\tau} = 0 \qquad (10)$$

General solution is:

$$X = A\exp\left(\frac{z}{h_+}\right) + B\exp\left(\frac{z}{h_-}\right)$$

$$\frac{1}{h_\pm} = \frac{1}{2H} \pm \left(\frac{1}{4H^2} + \frac{1}{K\tau}\right)^{\frac{1}{2}}$$

(Note that $h_+ > 0$ and $h_- < 0$)

Determine A and B from boundary conditions. Say X → 0 as z → ∞, then $A = 0$ and $X = X(0)$ at z = 0 is given so $B = X(0)$. Thus specific solution is:

$$X = X(0)\exp\left[z\left(\frac{1}{2H} - \left(\frac{1}{4H^2} + \frac{1}{K\tau}\right)^{\frac{1}{2}}\right)\right] \qquad (11)$$

Consider two cases:

(a) $\frac{4H^2}{K} \gg \tau$ denoted <u>REACTIVE SPECIES</u> case,

i.e. (vertical transport time) $\gg$ (chemical lifetime)

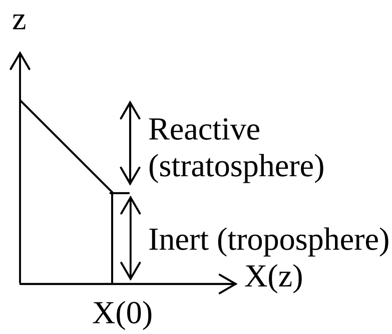
Then $X \simeq X(0)\exp\left(-\frac{z}{\sqrt{K\tau}}\right)$ <u>{rapid decreases in mixing ratio with z}</u>

(b) $\frac{4H^2}{K} \ll \tau$ denoted <u>INERT SPECIES</u> case

Then $X \simeq X(0)\exp\left(-z\left(\frac{1}{2H}-\frac{1}{2H}\right)\right)$ <u>{mixing ratio constant with z}</u>

$= X(0)$

(i.e. $h_{-} \gg H$)



<u>Example</u>: surface source and stratospheric sink (such as N_2O, $CFCl_3$, CF_2Cl_2, etc.)

Coupled Chemistry-Transport 3D Models

1. <u>Basic Equations</u>

Want to solve the 3D Eulerian continuity equation as an initial value problem:

$$\frac{\partial[i]}{\partial t} = P_i - L_1 - \nabla\cdot\left(\vec{V}[i]\right) \qquad \text{(“concentration” form)}$$

$$\frac{\partial X_i}{\partial t} = \frac{P_i - L_i}{[M]} - \vec{V}\cdot\nabla X_i \qquad \text{(“mixing ratio” or “mole fraction” form)}$$

subject to upper and lower boundary conditions. But do not know $\vec{V}$ as continuous function of space and time. Thus express the flux as the sum of “mean advective” and “eddy diffusive” parts:

$$\left\langle \vec{V}[i]\right\rangle = \left\langle \vec{V}\right\rangle\left\langle [i]\right\rangle + \left\langle \vec{V}'[i]'\right\rangle$$

$$\simeq \left\langle \vec{V}\right\rangle\left\langle [i]\right\rangle - \mathbf{K}\nabla\left\langle [i]\right\rangle$$

where $\langle\ \rangle$ denotes time and/or space average, $(\ )'$ denotes deviation from $\langle\ \rangle$, and $\mathbf{K}$ is a 3x3 matrix containing “eddy diffusion” (or “turbulent exchange”) coefficients. The average winds $\langle\vec{V}\rangle$ can be obtained in principle from general circulation models (gcm’s), observations, or gcm’s “corrected” through assimilation of observations (“forecast” or “analyzed observed” winds). In this case $\langle\vec{V}\rangle$ are Eulerian averages appropriate to the grid spacing and time step in the g.c.m. and $\mathbf{K}$ refers to unresolved “sub-grid-scale” winds. **K** may be determined by empirical (e.g. fitting observed $[i]$), semi-empirical, or theoretical approaches. The latter two approaches involve so-called "parameterizations."

2. <u>Prognostic and diagnostic continuity equations</u>

It is not usually necessary to consider transport of <u>all</u> chemical species. Consider the <u>prognostic</u> (time dependent) continuity equation in mixing ratio form:

$$\frac{P_i}{[M]} = \frac{L_i}{[M]} + \vec{V}\cdot\nabla X_i + \frac{\partial X_i}{\partial t}$$

$$= \left(\frac{1}{\tau_i} + \vec{V}\cdot\nabla + \frac{\partial}{\partial t}\right)X_i \qquad \text{(using } [M] = \frac{[i]}{X_i} \text{ and } \tau_i = \frac{[i]}{L_i}\text{)}$$

$$\simeq \left(\frac{1}{\tau_i} + \frac{u}{\Delta x} + \frac{v}{\Delta y} + \frac{w}{\Delta z} + \frac{1}{\Delta t}\right)X_i \qquad \text{(assuming } \Delta u \simeq u,\ \Delta v \simeq v,\ \Delta w \simeq w\text{)}$$

$$\simeq \frac{X_i}{\tau_i} \ \underline{\text{if}}\ \frac{u}{\Delta x}, \frac{v}{\Delta y}, \frac{w}{\Delta z}, \frac{1}{\Delta t} \ll \frac{1}{\tau_i}$$

$$= \frac{L_i}{[M]} \qquad \text{[chemical steady state; \underline{diagnostic equation}]} \qquad (8)$$

where $\tau_i = \text{chemical time scale} = \dfrac{[i]}{L_i}$

$\dfrac{\Delta x}{u}, \dfrac{\Delta y}{v}, \dfrac{\Delta z}{w} = \text{transport (advection) time scales}$

$\Delta t = \text{integration time scale}$

The diagnostic equation is much faster to solve.

<u>Chemical families</u>:

$\tau_i \ll$ transport time (for loss by conversion of one family member to another)

$\tau_i \geq$ transport time (for loss of overall family)

$[O_x] = [O] + [O_3] =$ odd oxygen

$[HO_x] = [H] + [OH] + [HO_2] =$ odd hydrogen

$[NO_x] = [NO] + [NO_2] =$ odd nitrogen

$[Cl_x] = [Cl] + [ClO] =$ odd (reactive) chlorine

Without chemical families and diagnostic equations, atmospheric chemical models are invariably <u>"stiff"</u> systems. Specifically if $\vec{X}$ is a vector of chemical mixing ratios X_i and $\dfrac{\partial \vec{X}}{\partial t} = \vec{R}(\vec{X}, t)$ then the ratio of the largest and smallest eigenvalues λ_i of the Jacobian matrix $\frac{\partial\vec{R}}{\partial\vec{X}}$ is typically $\gg 1$ (equivalently the ratios of the largest to smallest "lifetimes" $\lambda_i^{-1} \gg 1$)

3. <u>Spatial representations</u>
   a. <u>Finite difference</u> schemes (truncated Taylor expansion at J grid-points)
   b. <u>Spectral</u> techniques (express variables using truncated series of N orthogonal harmonic functions and solve for N coefficients of expansion;) see
   c. <u>Interpolation</u> schemes (interpolates between grid points e.g. using a polynomial)
   d. <u>Finite element</u> schemes (minimizes error between actual and approximate solutions using a "basis function", good for irregular geometries, c.f. (b) above which is good for regular geometries)

4. <u>Explicit and Implicit time stepping</u>

<u>Explicit</u>: $\left(\ \right)_x^{t+\Delta t} = f\left[\ldots.,\left(\ \right)_{x*}^{t},\ldots\right]$

<u>Implicit</u>: $\left(\ \right)_x^{t+\Delta t} = f\left[\ldots,\left(\ \right)_{x*}^{t},\left(\ \right)_{x*}^{t+\Delta t},\ldots.\right]$

(Implicit methods more stable (but often less accurate) than explicit methods for longer time steps)