Lecture 2

ENVIRONMENTAL TRANSPORT AND FATE MODELING
Principles, Methods and Limitations
ENVIROMENTAL TRANSPORT AND FATE MODELS

- Typically consist of two components
  - a flow model (from energy, momentum and total mass balance considerations)
  - a transport/transformation model (based on species mass balance)

- and of
  - preprocessors for inputs
  - post-processors for outputs

- Flow and transport transformation models are based on
  - balance equations (employing the principles of thermodynamics, chemical kinetics and transport phenomena)
  - constitutive equations (that determine the values of physico-chemical parameters and are often derived from molecular statistical mechanics considerations)
The Bulk Flow ("Advection") Component of Environmental Models

Example: Atmospheric Flow

• Empirical Interpolation Procedures
  – Simple Interpolation
  – Variational Interpolation
  – "Optimal" Interpolation

• Objective Analysis Procedures (Mass-Consistent Wind Field Generation Routines)
  – Direct Application of a Physical Constraint such as mass continuity
  – Variational Application of a Divergence Minimization Constraint

• Primitive Equation (Prognostic, or Numerical Boundary Layer) Models
  – solve numerically the coupled, turbulent, conservation equations of mass, momenttum, energy and water substance together with the appropriate state equations. Existing formulations employ either first or higher order turbulence closure schemes

• Simplified Physics Models.
Example I: The Prognostic Regional Atmospheric Modeling System (RAMS) (Tripoli and Cotton, 1982)

The equations used in RAMS to determine meteorological fields are:

- The compressible continuity equation in the terrain following coordinate

\[
\frac{A}{\partial t} \frac{\partial \rho}{\partial t} + \frac{B}{a} (ab^{ij} \rho_0 u_j) = 0
\]

where,

- \( A \) Local rate of change of density,
- \( B \) Flux divergence of density.

- the Grid volume averaged Navier–Stokes equations to describe compressible motion

\[
\frac{A}{\partial t} (\rho_0 u_i) + \frac{1}{a} \left( \frac{\partial ab^{ij} \rho \overline{p}}{\partial x_j} \right) + \rho' g \delta_{i3} =
\]

\[
- \frac{1}{a} \frac{\partial}{\partial x_k} (ab^{jk} \rho_0 u_i u_j) + \frac{1}{a} \frac{\partial}{\partial x_k} (ab^{jk} \rho_0 u_j) - \frac{\rho_0}{a} \frac{\partial}{\partial x_k} \left[ ab^{jk} (u''_i u''_j) \right] - \frac{\partial}{\partial x_k} \left[ ab^{jk} (u''_i u''_j) \right] - \rho' g \delta_{i3} + \varepsilon_{ijk} f_j u_k
\]
**Example I (Continued): Regional Atmospheric Modeling System**

where \(i, j, k=1, 2, 3\) and \(a \ b\) are coordinate transformation coefficients inherent in the use of terrain following coordinate system. Here, \(\rho_0\) is reference state density, \(\bar{u}_i\) is the mean velocity, \(p\) is pressure, \(x\) is the terrain following coordinate, \(\rho\) is the density of dry air, \(g\) is gravity, \(\delta_{ij}\) is the Kronecker delta function, \(u''\) is the sub-grid scale velocity, \(r_T\) is the total water mixing ratio, \(\varepsilon_{ijk}\) is the permutation symbol or alternating tensor, and \(f\) is the Coriolis acceleration.

\(\text{A) local time rate of change of momentum,}\)

\(\text{B) pressure gradient term,}\)

\(\text{C) gravitational acceleration of dry air,}\)

\(\text{D) flux divergence part of the advection of momentum,}\)

\(\text{E) momentum divergence part of the advection of momentum,}\)

\(\text{F) turbulent momentum flux contribution,}\)

\(\text{G) gravitational acceleration due to the density of suspended total water,}\)

\(\text{H) the Coriolis acceleration.}\)
Example I (Continued): Regional Atmospheric Modeling System

- The energy equation:

\[
\frac{\partial \theta_{il}}{\partial t} = -\frac{1}{\rho_0 a} \frac{\partial}{\partial x_k} (ab^{jk} \rho_0 u_j \theta_{il}) + \frac{1}{\rho_0 a} \frac{\partial}{\partial x_k} (ab^{jk} \rho_0 \bar{u}_j) - \frac{1}{a} \frac{\partial}{\partial x_k} [ab^{jk} (\theta_{il}'' u_j'')]
\]

\[= -\nabla \cdot \nabla^{ab^{jk} \rho_0 u_j \theta_{il}} + \frac{1}{\rho_0 a} \theta_{il} \frac{\partial}{\partial x_k} (ab^{jk} \rho_0 \bar{u}_j) - \frac{1}{a} \frac{\partial}{\partial x_k} [ab^{jk} (\theta_{il}'' u_j'')]
\]

\[= -\nabla \cdot \nabla^{ab^{jk} \rho_0 u_j \theta_{il}} + \frac{1}{\rho_0 a} \theta_{il} \frac{\partial}{\partial x_k} (ab^{jk} \rho_0 \bar{u}_j) - \frac{1}{a} \frac{\partial}{\partial x_k} [ab^{jk} (\theta_{il}'' u_j'')]
\]

\[= -\nabla \cdot \nabla^{ab^{jk} \rho_0 u_j \theta_{il}} + \frac{1}{\rho_0 a} \theta_{il} \frac{\partial}{\partial x_k} (ab^{jk} \rho_0 \bar{u}_j) - \frac{1}{a} \frac{\partial}{\partial x_k} [ab^{jk} (\theta_{il}'' u_j'')]
\]

where $\theta$ is potential temperature, $\theta_{il}$ is the ice–liquid water potential temperature, $T$ is temperature, $C_p$ is the heat capacity of dry air, $L_{lv}$ and $L_{iv}$ are the latent heats of vaporization and sublimations, respectively, and $Pr_r$, $Pr_i$, and $Pr_g$ are the precipitation tendencies of rain-water, ice and graupel.

- $A)$ the local time rate of change of potential temperature,
- $B)$ flux divergence part of the advection of potential temperature,
- $C)$ momentum divergence part of the advection of potential temperature,
- $D)$ turbulent heat flux contribution for subgrid scale, and
- $E)$ source or sink term during phase changes of water.
Transport/Transformation Environmental Models

- Typically systems of parabolic partial differential equations derived through either
  - the Eulerian or continuum approach, resulting in Advection/Dispersion/Reaction equations (ADRE) for the concentration of the species of concern, or
  - the Lagrangian or fluid particle approach, resulting in master equations such as the Fokker-Planck equation (similar in form to the ADRE) for the probability density of location in space-time for a fluid particle (directly reflecting concentration).
    (Note: actually both Eulerian and Langrangian approaches are due to Euler)

- The balance equations alone do not provide complete systems; they need appropriate constitutive relations for “closure”
  - in environmental models, due to the randomness inherent in the geophysical medium (atmosphere, hydrosphere, lithosphere) closure approximations have also to be made in a macroscopic context, through an averaging (ensemble or space) process. The parabolic character of macroscopic transport/transformation environmental models is actually due to the “local” character of common closure approximation.
THE ATMOSPHERIC DIFFUSION EQUATION (ADE)

\[
\frac{\partial c_i}{\partial t} + \frac{\partial (uc_i)}{\partial x} + \frac{\partial (vc_i)}{\partial y} + \frac{\partial (wc_i)}{\partial z} = \frac{\partial}{\partial x} \left( K_H \frac{\partial c_i}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_H \frac{\partial c_i}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_V \frac{\partial c_i}{\partial z} \right) + R_i + S + L_i
\]

where,

- \( c_i \) = the concentration of pollutant \( i \) and is a function of location \((x, y, z)\) and time \((t)\),
- \( u, v, w(x, y, z, t) \) = the horizontal and vertical wind speed components, functions of location and time,
- \( K_H, K_V(x, y, z, t) \) = the horizontal and vertical turbulent dispersion coefficients, functions of location and time,
- \( R_i \) = the net rate of production of pollutant \( i \) by chemical reactions, function of the concentrations of all chemical species comprising the photochemical system \( R_i(c_1, c_2, ... c_i, ... c_N) \),
- \( S \) = emission rates of all precursors \( S_j(x, y, z, t; E_1, E_2, ... E_j, ... E_N) \), where \( E_j \) is the precursor, and
- \( L_i(x, y, z, t) \) = net rate of removal of pollutant \( i \) by surface uptake processes, function of location and time.
Example II: Industrial Source Complex Short Term (ISCST) version 3

- A typical Gaussian atmospheric dispersion model (formally derived through Lagrangian considerations)

- Steady-State Gaussian Plume Equation:

\[
\chi = \frac{QK}{2\pi u_s} \int x \frac{VD}{\sigma_y \sigma_z} \int y \exp \left[ 0.5 \left( \frac{y}{\sigma_y} \right)^2 \right] dy \, dx,
\]

where,
\[
\begin{align*}
\chi & = \text{concentration at a receptor located a distance } x \text{ upwind, and } y \text{ crosswind of all or a portion of a source (mass per unit volume)} \\
Q & = \text{pollutant emission rate (mass per unit time)} \\
K & = \text{concentration unit conversion coefficient} \\
V & = \text{vertical term} \\
D & = \text{decay term} \\
\sigma_y, \sigma_z & = \text{standard deviation of lateral } (y) \text{ and vertical } (z) \text{ concentration distribution} \\
u_s & = \text{mean wind speed (m/s)}
\end{align*}
\]
Example III: Green’s Function Methods for Atmospheric Dispersion

- When the mean concentration of a pollutant is known at the location \((x', y', z', t')\) the mean concentration at any other point can be evaluated using the following expression:

\[
\bar{c}(x, y, z, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{0}^{t} \bar{c}(x', y', z', t') G_{xy}(x, y, t | x', y', t') G_{z}(x, z, t | x', z', t') dt' dx' dy' dz'
\]

where \(G_{xy}\) and \(G_{z}\) are the Green's functions.

- Under assumptions of locally homogeneous and stationary turbulence:

\[
G_{xy}(x, y, t | x', y', t') = \frac{1}{2\pi \sigma_x \sigma_y} \exp \left[ -\frac{(x-x' - \hat{u}(t-t'))^2}{2\sigma_x^2} - \frac{(y-y' - \hat{v}(t-t'))^2}{2\sigma_y^2} \right]
\]

\[
G_{z}(x, z, t | x', z', t') = \frac{1}{\sqrt{2\pi \sigma_z}} \left[ \exp \left( -\frac{(z-z')^2}{2\sigma_z^2} \right) + \exp \left( -\frac{(z+z')^2}{2\sigma_z^2} \right) \right]
\]

where \(\hat{u}, \hat{v}\) are the \(x\) and \(y\) components of the wind velocity. For a simple “concentration wall” model, where the concentration of the pollutant from an area source is assumed to form a uniform, cross-wind “wall” of height proportional to the along-wind dimension of the source and width proportional to the linear dimension \(b\) of the source.

- The solution based on the above assumptions can be written as:

\[
\bar{c}(x, y, 0) = \bar{c}_m(x_0) \frac{1}{2} \left[ \text{erf} \left( \frac{b/2 + x \cos \theta - y \sin \theta}{\sqrt{2\sigma_\theta(-x \sin \theta - y \cos \theta)}} \right) + \text{erf} \left( \frac{b/2 - x \cos \theta + y \sin \theta}{\sqrt{2\sigma_\theta(-x \sin \theta - y \cos \theta)}} \right) \right] \times \text{erf} \left[ \frac{1 + \sqrt{2}}{2\sqrt{2}} \left( \frac{b}{-x \sin \theta - y \cos \theta} \right) \right]
\]

where, \(\theta\) is the angle of the wind direction (standard NWS) and a North-South system of coordinates is adopted.
**Example IV: The Fugitive Dust Transport Model (FDM)**

- EPA’s FDM (Fugitive Dust Model) model is a Gaussian plume model for fugitive dust sources. It incorporates transport, dispersion and deposition of pollutants in the atmosphere, using input data for particulate matter (particle radius, density, etc.) and air flow (mean velocity, wind direction) characteristics.

- Both concentrations and deposition rates are calculated.

- Assumptions for solution of the atmospheric dispersion equation in FDM:
  - The pollutant is composed of different classes of uniformly-sized particles and the diffusion in $x$ direction is small compared to the advection in that direction by the wind.
  - Eddy diffusivities are assumed constant.
Example IV (Continued): The Fugitive Dust Transport Model

- The equation which governs pollutant advection and dispersion in FDM can be written as:

\[
 u \frac{\partial c}{\partial x} = K_{yy} \frac{\partial^2 c}{\partial y^2} + K_{zz} \frac{\partial^2 c}{\partial z^2} + v_g \frac{\partial c}{\partial z}
\]

where, \( c \) is the concentration \((g/cm^3)\), \( K_{yy} \) and \( K_{zz} \) the eddy diffusivities in the \( y \) and \( z \) directions \((m^2/sec)\), \( u \) is the wind speed \((m/sec)\) and \( v_g \) is the gravitational settling velocity \((m/sec)\).

- The \( x \) direction is chosen parallel to the wind direction. The eddy diffusivity in all directions is parameterized by a value \( K \) which is assumed constant in space and time. The solution to the above equation is then:

\[
 c = \frac{Q}{2\pi \sigma_y \sigma_z u} \exp \left[ -\frac{v_g (z-h) \sqrt{2} \beta}{\sigma_z} - \frac{v_g^2 \beta^2}{\sigma_z^2} \right] \left[ \exp \left( -\frac{(z+h)^2}{2\sigma_z^2} \right) + \exp \left( -\frac{(z-h)^2}{2\sigma_z^2} \right) - 4\sqrt{\pi} v_1 \beta \exp \left( -\frac{(z+h)^2}{2\sigma_z^2} \right) e^{-\gamma^2} \text{erfc}(\gamma) \right]
\]

where the following substitutions were used:

\[
 \gamma = \frac{v_1 \sqrt{2} x}{\sigma_z u} + \frac{z + h}{\sqrt{2} \sigma_z}, \quad \beta = \frac{x}{\sqrt{2} \sigma_z u}
\]

\[
 v_1 = v_d - \frac{v_g}{2}, \text{ where } v_d \text{ is the deposition velocity (m/sec), and } h \text{ is the plume centerline height (m)}.
\]

The dispersion parameter \( \sigma_z \) in the solution above can be written as:

\[
 \sigma_z^2 = \frac{2Kx}{u}
\]
Example V: HYPACT, a numerical Lagrangian Dispersion Model

- HYPACT uses the 3-D meteorological fields calculated by RAMS. The location of fluid particles is calculated by the equation:

\[
x_i(t + \Delta t) = x_i(t) + [u_i(t) + u_i''(t)] \Delta t
\]

\[
u_i''(t + \Delta t) = u_i''(t) R_i \Delta t + u_i''(t)
\]

- **A** Location of a particle at next time level,
- **B** Location of a particle at current time level,
- **C** Advection of a particle by the corresponding component of the wind,
- **D** Advection of a particle by the corresponding turbulent part of the wind,
- **E** Turbulent part of corresponding component of the wind at next time level,
- **F** Turbulent part of corresponding component of the wind at the current time level weighted by a random contribution,
- **G** Turbulent part of corresponding component of the wind at the current time level.

- The concentration of a contaminant is estimated from the number of particles present in a grid cell.
Example VI: Grid-based Photochemical Air Quality Simulation Models (PAQSMs)

- Based on a formulation of the Atmospheric Diffusion Equation (ADE)
  - parameterization of the species-continuity equation, with first order closure scheme for turbulent transport
  - used for numerical solution on grids at resolution between 2 × 2 and 40 × 40 km² horizontally
  - vertical resolution varies spatially and temporally

- Incorporate emissions of precursors, and their transport, diffusion, chemical reactions, and removal processes

- Sequence of 4 steps
  - solve advection/diffusion in the x-direction,
  - solve advection/diffusion in the y-direction,
  - inject emissions and solve vertical advection/diffusion, and
  - perform chemical transformations of the pollutants

- Finite difference / finite element numerical techniques used to solve system of ADEs

- Method of ‘operator-splitting’ or ‘fractional step’ used for each integration time step

- e.g. Urban Airshed Model (UAM-IV), Variable grid UAM (UAM-V), Regional Oxidant Model (ROM), SARMAP Air Quality Model (SAQM), Comprehensive Air Quality Model (CAM-X), CALGRID, MODELS-3
Example VI (Continued): INPUT DATA TO PAQSMs

- meteorological
  - daytime mixing height, nighttime inversion height,
  - wind speeds, surface temperature, atmospheric pressure,
  - temperature gradient (above and below diffusion break),

- emissions estimates
  - anthropogenic (point, area, on-road and off-road mobile) sources
  - biogenic sources

- initial and boundary conditions

- lumped atmospheric chemical mechanisms, e.g., Carbon Bond IV (CB-IV)
  - differential equations comprise ‘stiff’ system
  - quasi-steady state assumptions (QSSA) for low-mass fast-reacting species
  - special algorithms for remaining state species
Example VII: The Reactive Plume Model (RPM-IV)

Movement of a plume from an Industrial Stack

- The Reactive Plume Model (RPM-IV) is a regulatory photochemical trajectory plume model for studying the effects of emissions from industrial stacks on ambient pollutant concentrations.

- This model simulates the evolution of a plume by following a puff emitted from the stack and by solving the transport and transformation equations within the puff.
Example VII: Formulation of the RPM-IV

- An instantaneous puff from a stack is assumed to consist of cells containing equal mass of pollutants
- the cells are assumed to expand in a way such that the amount of an inert species within each cell remains constant throughout the course of the simulation
- At each time step, the transport equations and then the chemical transformations equations are solved for each cell

Governing equations for the RPM-IV model

\[
\frac{dc_i}{dt} = \left( \frac{dc_j}{dt} \right)_{\text{chem}} - \left( \frac{1}{w_j} \cdot \frac{dw_j}{ds} \right) uc_j^i - \left( \frac{1}{w_j} \cdot \frac{dw_j}{ds} \right) uc_j^i + F_j^i
\]

\[
E_j^i = \frac{1}{y_j - y_{j-1}} \left\{ \left( \frac{dy_j}{dt} \right) c_j^{i+1} - \left( \frac{dy_{j-1}}{dt} \right) c_j^i \right\}
\]

\[
D_j^i = \frac{\partial}{\partial y} \left( K \frac{\partial c}{\partial y} \right) = \frac{2}{y_j - y_{j-1}} \left\{ K_j \left( \frac{c_{j+1}^i - c_j^i}{y_{j+1} - y_{j-1}} \right) - K_{j-1} \left( \frac{c_j^i - c_{j-1}^i}{y_j - y_{j-2}} \right) \right\}
\]

where \( t \) is the time, \( y \) represents the position of the cell with respect to the plume centerline, \( c_j^i \) is the concentration of the \( i \)th species in cell \( j \), \( w_j \) is the width of cell \( j \), and \( s \) denotes the downwind distance of the puff from the source.

The \( K_j \)'s are calculated by using the condition that there is no net transfer of an inert species from any cell, meaning that \( E_j^{\text{Inert}} - D_j^{\text{Inert}} = 0 \), and that there is no transfer of any species across the plume centerline.
Example VII (Continued): Formulation of the RPM-IV

- The width of a cell is calculated by assuming the Gaussian plume evolution condition, as follows:

\[
W(s) = f_x \sigma_x(s) \quad \text{and} \quad H(s) = f_y \sigma_z(s)
\]

\[
\frac{2}{M} = \text{erf} \left( \frac{w_j}{\sqrt{2} \sigma_y} \right) - \text{erf} \left( \frac{w_{j-1}}{\sqrt{2} \sigma_y} \right)
\]

- inputs to RPM-IV include of meteorological variables, emission estimates, initial concentrations in the plume and ambient concentrations

- model outputs

- the chemistry is described by the Carbon Bond-IV mechanism

- the equations are solved using the GEAR solver for stiff differential equations
AND A LOOK AT GROUNDWATER MODELS

Example VIII: The EPACMTP Groundwater Model

- EPACMTP consists of two modules: an unsaturated zone module called Finite Element and semi-analytical Contaminant Transport in the Unsaturated Zone (FECTUZ), and a saturated zone module called Combined Analytical-Numerical Saturated Zone in 3-Dimensions (CansaZ-3D).
  - FECTUZ is a one-dimensional model that simulates vertically downward steady-state flow and contaminant transport through the unsaturated zone above an unconfined aquifer.
  - CansaZ-3D simulates 3-D steady-state groundwater flow and transient or steady state contaminant transport. EPACMTP currently uses a simplified 2-D version of the CansaZ-3D, and the modules are optimized for computational efficiency.
Example VIII (Continued): Formulation of the FECTUZ module

Flow Module:

\[-K_s k_{rw} \left[ \frac{d\psi}{dz} - 1 \right] = I ; \quad \psi_l = 0\]

\[k_{rw} = S_e^{1/2} \left[ 1 - \left( 1 - S_e^{1/\gamma} \right) \right]^2 \]

\[S_e = \left[ 1 + \left( -\alpha \psi \right)^\beta \right]^{-\gamma}, \psi < 0 \quad ; \quad S_e = 1, \psi \geq 0\]

where \(\psi\) pressure head (L), \(k_{rw}\) relative permeability, \(K_s\) sat. conductivity (L/T), \(I\) infiltration rate (L/T), \(l\) unsat. zone thickness (L).
\(\alpha, \beta\) and \(\gamma\) are soil specific shape parameters.

Transport Module:

\[\frac{\partial}{\partial z} \left[ D \frac{\partial c_i}{\partial z} \right] - V \frac{\partial c_i}{\partial z} = \theta R_i \frac{\partial c_i}{\partial t} + \theta Q_i \lambda_i C_i - \sum_{m=1}^{M} \theta \xi_{im} Q_m \lambda_m c_m \]

\[D = \alpha L V + \theta D^* \quad ; \quad R = 1 + \frac{\rho_b}{\theta} k_1 \eta c_\eta^{-1} \quad ; \quad Q = 1 + \frac{\rho_b}{\theta} k_1 c_\eta^{-1} \]

I.C.'s and B.C.'s:

\[c_i(z, 0) = c_i^{in} \quad ; \quad -D \frac{\partial c_i}{\partial z}(0, t) = v(c_i^0(t) - c_i) \quad ; \quad c_i(0, t) = c_i^0(t) \quad ; \quad \frac{\partial c_i}{\partial t}(l, t) = 0\]

where \(c_i^{in}\) initial conc. of \(i\)th species (M/L^3), \(c_i^0(t)\) leachate conc. (M/L^3), \(l\) depth of water table (L), \(D\) apparent dispersion coefficient (L^2/T), \(V\) Darcy velocity (L/T), \(\lambda_i\) first order decay const. (1/T).
Example VIII (Continued): Formulation of the CANSAZ-3D module

Flow Module:

\[ K_x \frac{\partial^2 H}{\partial^2 x} + K_y \frac{\partial^2 H}{\partial^2 y} + K_z \frac{\partial^2 H}{\partial^2 z} = 0 \]

I.C.'s and B.C.'s:

\[ H(0, y, z) = H_1, \quad H(x_L, y, z) = H_2 \]

\[ \frac{\partial H}{\partial y}(x, 0, z) = 0; \quad \frac{\partial H}{\partial y}(x, \pm \frac{y_L}{2}, z) = 0; \quad \frac{\partial H}{\partial z}(x, y, 0) = 0 \]

\[ -K_z \frac{\partial H}{\partial z}(x, y, B) = I \quad \text{if} \quad x_u \leq x \leq x_d, \quad -\frac{y_D}{2} \leq y \leq \frac{y_D}{2}; \quad -K_z \frac{\partial H}{\partial z}(x, y, B) = I_r, \quad \text{elsewhere} \]

where \( H \) is the hydraulic head (L), \( K_x, K_y, \) and \( K_z \) are hydraulic conductivities (L/T), \( x_L, y_L \) and \( B \) are length, width and thickness of the aquifer system, \( x_d, x_u \) and \( y_D \) are the upstream and downstream coordinates and the width of the source, \( I \) is the infiltration rate, and \( I_r \) is the recharge rate.

Transport Module:

\[ \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial c_p}{\partial x_j} \right) - V_i \frac{\partial c_p}{\partial x_i} = \phi Q_p \lambda_p c_p + \phi R_p \frac{\partial c_p}{\partial t} - \phi \sum_{m=1}^{M} \xi_{pm} Q_m \lambda_m c_m \quad ; \quad p = 1, n_c; i, j = 1, 2, 3 \]

\[ D_{ii} = \alpha_L \frac{V_i^2}{|V|} + \alpha_T \frac{V_i^2}{|V|} + \alpha_v \frac{V_k^2}{|V|} + \phi D^* \quad ; \quad D_{ij} = (\alpha_L - \alpha_T) V_i V_j / |V| \]

I.C.'s and B.C.'s:

\[ c_i(z, 0) = c_i^{in} \quad ; \quad -D \frac{\partial c_i}{\partial z}(0, t) = v(c_i^0(t) - c_i) \quad ; \quad c_i(0, t) = c_i^0(t) \quad ; \quad \frac{\partial c_i}{\partial t}(l, t) = 0 \]

where \( c_p \) (M/L\(^3\)) is the concentration of the \( p \)th component species in the \( n_c \) member decay chain, \( \lambda_p \) (1/T) and \( R_p \) are the first order decay and retardation coefficients, \( Q_p \) and \( Q_m \) are correction factors to account for sorbed phase decay of species \( p \) and parent \( m \), respectively, and \( \phi \) is the aquifer effective porosity. The initial and boundary conditions are needed at all the edges of the aquifer (detailed analysis is presented in Sudicky, 1989).
Example IX: The ModflowT Groundwater Model

The Flow Component:

\[
\frac{\partial}{\partial x_i} \left( K_{ij} \frac{\partial h}{\partial x_j} \right) = S_s \frac{\partial h}{\partial t} + W^* 
\]

where,

- \( x_i \) = Cartesian coordinates (m), \( i,j=1,2,3 \)
- \( K_{ij} \) = hydraulic conductivity tensor (m/sec)
- \( h \) = hydraulic head (m)
- \( W^* \) = volumetric flux per unit volume, (positive for outflow)
- water sources and/or sinks \( W^* = W^*(x,y,z,t) \) (sec\(^{-1}\))
- \( S_s \) = specific storage of porous material (m\(^{-1}\))
- \( t \) = time (sec)
Example IX (Continued): The ModflowT Groundwater Model

The Solute Transport/Transformation Component:

\[ \varepsilon \frac{\partial C}{\partial t} + \frac{\partial}{\partial x_i} (\varepsilon CV_i) - \frac{\partial}{\partial x_i} \left( \varepsilon D_{ij} \frac{\partial C}{\partial x_j} \right) + C' W^* = \text{CHEM} \]

\[
\text{CHEM} = \begin{cases} 
-\rho_b \frac{\partial \bar{C}}{\partial t} & \text{for linear equilibrium controlled ion exchange reactions} \\
\sum_{k=1}^3 R_k & \text{for chemical rate controlled reactions} \\
-\lambda \left( \varepsilon C + \rho_b \bar{C} \right) & \text{for decay}
\end{cases}
\]

- \( C \) = concentration of the solute in groundwater
- \( V_i \) = seepage velocity in the direction \( x_i \)
  \[ V_i = -K_{ij} \frac{\partial h}{\partial x_j}, \quad \text{where } i, j = 1, 2, 3, \text{ from Darcy’s law} \]
- \( D_{ij} \) = coefficient of hydrodynamic dispersion, (second order tensor)
- \( C' \) = concentration of the solute in the source or sink fluid
- \( \rho_b \) = bulk density of the solid
- \( \varepsilon \) = effective porosity
- \( \bar{C} \) = concentration of the species adsorbed on the solid
  (mass of solute/mass of sediment)
- \( R_k \) = rate of production of solute in reaction \( k \)
- \( \lambda \) = first order decay constant
A SECOND LOOK: THE ADE REVISITED

Starting Point for the Derivation of the ADE

- Eulerian Transport Equations

Assumptions

- Species transport dynamics are uncoupled from the simultaneously occurring momentum and energy transport:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (uc_i) = \nabla \cdot (D_i \nabla c_i) + r_i + s_i
\]

More Assumptions

- Reynolds type decompositions are valid for both the \textit{a priori} known velocity field: \( u_k = \bar{u}_k + u^\prime_k \) and the unknown concentration field: \( c_i = \langle c_i \rangle + \bar{c}_i^\prime \)

- Molecular transport is negligible in comparison to turbulent transport:

\[
\langle u_k^\prime c_i^\prime \rangle \gg k \cdot (\nabla \cdot (D_i \nabla c_i))
\]

\[
\frac{\partial \langle c_i \rangle}{\partial t} + \nabla \cdot (\bar{u} \langle c_i \rangle) = -\nabla \cdot (u_i^\prime \bar{c}_i^\prime) + \langle r_i \rangle + s_i
\]
Derivation of the ADE (Continued)

And More Assumptions
- First order scheme for turbulent transport closure (this imposes limitations on spatial and temporal resolution):
  \[ \langle u'c_i' \rangle = -K \cdot \nabla \langle c_i \rangle, \quad K = K(x, y, z) \]

- Chemical Closure (i.e. the effect of turbulence on the chemical kinetics is assumed negligible):
  \[ \langle r_i \rangle \simeq r_i(\langle c_1 \rangle, ..., \langle c_p \rangle T; h\nu) \]

To finally derive the Atmospheric Diffusion Equation

\[ \frac{\partial \langle c_i \rangle}{\partial t} + \nabla \cdot (\bar{u} \langle c_i \rangle) = \nabla \cdot (K \cdot \nabla \langle c_i \rangle) + r_i(\langle c_1 \rangle, ..., \langle c_p \rangle T; h\nu) + s_i \]

Approximations that lead to working models
- \( K \) is a diagonal tensor
- \( \bar{u} \) is estimated from approximate interpolation schemes
- Values of parameters and both dependent and independent variables are averaged over the volume of some computation cell.
A THIRD, MORE ADVANCED LOOK: NONLOCAL CLOSURE

ADE (or any ADRE) transport closure assumption: \( \langle u_j' c' \rangle = -K_{ij} \frac{\partial \langle c \rangle}{\partial x_i} \)

with \( K_{ij} \) constant

Georgopoulos and Seinfeld showed that an exact relationship is

\[
\langle u_j' c' \rangle = \int_{t_0}^{t} dt' \int dx' \langle u_i' (x', t') \ u_j (x, t) \ \psi (x, t|x', t') \rangle \ \frac{\partial \langle c (x', t') \rangle}{\partial x_i'} \\
+ \int_{t_0}^{t} dt' \int dx' \langle u_j' (x, t) \ \psi (x, t|x', t') \rangle \\
\times \left[ \frac{\partial \langle c (x', t') \rangle}{\partial t'} + \langle u_i (x', t') \rangle \ \frac{\partial \langle c (x', t') \rangle}{\partial x_i'} - S (x', t') \right]
\]

where \( \psi \) is a functional defined as \( \psi (x, t|x_0, t_0) \equiv \psi^{(k)} (x, t) \equiv \delta [x - y (x_0, t)] \)

subject to the initial condition \( \psi (x, t_0|x_0, t_0) = \delta (x - x_0) \)

This quantity can be identified with the stochastic Green’s function. Further,

\[
\overline{\psi} (x, t) = \int \int \psi (x, t|x_0, t_0) \ S (x_0, t_0) \ dx_0dt_0
\]

can be identified with the random fluid particle concentration. \( S (x, t) \) is the distribution of sources.
NONLOCAL CLOSURE (Continued)

Closure of the General Equations

The deterministic transition function $G$, giving the probability that a fluid particle, starting from $x_0$ at time $t_0$ will be at $x$ at time $t$:

$$G(x, t|x_0, t_0) = \langle \psi(x, t|x_0, t_0) \rangle$$

An exact integrodifferential equation for $G$ is given as:

$$\frac{\partial G(x, t|x_0, t_0)}{\partial t} = \int_{t_0}^{t} dt' \int dx' \left\langle u_i'(x', t') u_j'(x, t) \frac{\partial}{\partial x_j} \psi(x, t|x', t') \right\rangle \frac{\partial G(x', t'|x_0, t_0)}{\partial x_i'} +$$

$$- \int_{t_0}^{t} dt' \int dx' \left\langle u_j'(x, t) \frac{\partial}{\partial x_j} \psi(x, t|x', t') \right\rangle \left\langle u_i'(x', t') \frac{\partial}{\partial x_i} \psi(x', t'|x_0, t_0) \right\rangle$$

To obtain closure for the above equation, the mixed correlation of $\psi(x, t|x_0, t_0)$ with the random velocity field,

$$Q_{ij}(x, t|x_0, t_0) \equiv \left\langle u_i(x, t) u_j(x_0, t_0) \psi(x, t|x_0, t) \right\rangle$$

has to be approximated.
From Nonlocal Closure to Alternatives to the ADE

When Corrsin’s Independence Hypothesis is used:

\[ Q_{ij} = \langle u_i (x, t) \, u_j (x_0, t_0) \rangle \psi (x, t|x_0, t_0) \approx \langle u_i (x, t) \, u_j (x_0, t_0) \rangle \langle \psi (x, t|x_0, t_0) \rangle \]

the equations of Roberts (1961) and Jiang (1984) are then derived:

\[ \frac{\partial}{\partial t} G (x, t) = \frac{\partial^2}{\partial x_i \partial x_j} \int_0^t dt' \int dx' R_{ij}^E (x', t') \, G (x', t') \, G (x - x', t - t') \]

or equivalently,

\[ \frac{\partial}{\partial t} G (x, t) = \frac{\partial^2}{\partial x_i \partial x_j} \int_0^t dt' \int dx' Q_{ij} (x - x', t - t') \, G (x', t') \]
Systematic Derivation of Simpler Models

Gradient Transport I: The Local K-Model

Assuming $Q_{ij} = K_{ij} \delta (x - x') \delta (t - t')$
the general equation reduces to the conventional “eddy diffusivity” or “K-theory model”

$$\frac{\partial G(x, t)}{\partial t} = K_{ij} \frac{\partial^2 G(x, t)}{\partial x_i \partial x_j}$$

Gradient Transport II: The Nonlocal K-Model

Assuming $Q_{ij} (x - x', t - t') = \delta (x - x') R_{ij}^* (t - t')$
the general equation reduces to the pseudo-spectral model of Berkowicz and Prahm (1979, 1980)

$$\frac{\partial G(x, t)}{\partial t} = \frac{\partial}{\partial x_i} \int R_{ij}^* (x - x') \frac{\partial G(x', t)}{\partial x'_j} dx'$$

The Hyperbolic Telegrapher’s Equation:

In a one-dimensional case, assuming exponential correlation only in time

$$Q = \delta (x - x') R^L (t - t') = \delta (x - x') \sigma_v^2 \exp \left( -\frac{t - t'}{T^L} \right)$$

the well known telegrapher’s equation or hyperbolic diffusion equation is obtained

$$\frac{\partial^2 G}{\partial t^2} = -\frac{1}{T^L} \frac{\partial G}{\partial t} + \sigma_v^2 \frac{\partial^2 G}{\partial x^2}$$
ADDENDUM

Chemical Transformation in Photochemical Air Quality Simulation Models

Example: The Carbon Bond IV (CB-IV) Mechanism

- Developed for urban smog and regional atmospheric modeling
- Mechanism is hybrid of explicit chemistry, surrogate approximations, and lumped chemistry
- 34 chemical species, including 9 groups of primary organic species
- 82 chemical reactions, with 11 photolytic reactions
- Photolytic reaction rates vary with solar zenith angle
- Extensively studied and tested against smog chamber data
### Example: The Carbon Bond IV Mechanism (Continued)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>NO₂</td>
<td>Nitrogen-di-Oxide</td>
</tr>
<tr>
<td>NO</td>
<td>Nitrogen Oxide</td>
</tr>
<tr>
<td>O₃</td>
<td>Ozone</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>ETH</td>
<td>Ethene</td>
</tr>
<tr>
<td>OLE</td>
<td>Olefinic carbon bond</td>
</tr>
<tr>
<td>ALD2</td>
<td>Aldehydes, higher</td>
</tr>
<tr>
<td>FORM</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>TOL</td>
<td>Toluene</td>
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<tr>
<td>XYL</td>
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<tr>
<td>PAR</td>
<td>Paraffins</td>
</tr>
<tr>
<td>ISOP</td>
<td>Isoprene</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl Nitrate</td>
</tr>
<tr>
<td>HO₂</td>
<td>Hydroperoxy radical</td>
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<tr>
<td>O</td>
<td>Oxygen atom (triplet)</td>
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<tr>
<td>N₂O₅</td>
<td>Dinitrogen pentoxide</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>HNO₂</td>
<td>Nitrous acid</td>
</tr>
<tr>
<td>O¹D</td>
<td>Oxygen atom (singlet)</td>
</tr>
<tr>
<td>PNA</td>
<td>Peroxynitric acid</td>
</tr>
<tr>
<td>C₂O₃</td>
<td>Peroxyacetyl radical</td>
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<td>ROR</td>
<td>Secondary organic oxy radical</td>
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<td>NO₃</td>
<td>Nitrate radical</td>
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<tr>
<td>HNO₃</td>
<td>Nitric acid</td>
</tr>
<tr>
<td>TO2</td>
<td>Toluene-Hydroxyl radical adduct</td>
</tr>
<tr>
<td>CRES</td>
<td>Cresol and higher phenols</td>
</tr>
<tr>
<td>OPEN</td>
<td>Aromatic ring fragment acid</td>
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<tr>
<td>MGLY</td>
<td>Methyl glyoxal</td>
</tr>
<tr>
<td>XO2</td>
<td>NO-to-NO₂ operation</td>
</tr>
<tr>
<td>XO2N</td>
<td>NO-to-Nitrate operation</td>
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<tr>
<td>CRO</td>
<td>Methylphenoxy radical</td>
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<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>Reaction No.</td>
<td>CBM-IV</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
</tr>
<tr>
<td>1</td>
<td>NO₂ + hν →</td>
</tr>
<tr>
<td>2</td>
<td>O      →</td>
</tr>
<tr>
<td>3</td>
<td>O₃ + NO →</td>
</tr>
<tr>
<td>4</td>
<td>O + NO₂ →</td>
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<td>5</td>
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<tr>
<td>7</td>
<td>NO₂ + O₃ →</td>
</tr>
<tr>
<td>8</td>
<td>O₃ + hν →</td>
</tr>
<tr>
<td>9</td>
<td>O₃ + hν →</td>
</tr>
<tr>
<td>10</td>
<td>O¹D     →</td>
</tr>
<tr>
<td>11</td>
<td>O¹D + H₂O →</td>
</tr>
<tr>
<td>12</td>
<td>O₃ + OH →</td>
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<tr>
<td>13</td>
<td>O₃ + HO₂ →</td>
</tr>
<tr>
<td>14</td>
<td>NO₃ + hν →</td>
</tr>
<tr>
<td>15</td>
<td>NO₃ + NO →</td>
</tr>
<tr>
<td>16</td>
<td>NO₃ + NO₂ →</td>
</tr>
<tr>
<td>17</td>
<td>NO₃ + NO₂ →</td>
</tr>
<tr>
<td>18</td>
<td>N₂O₅ + H₂O →</td>
</tr>
<tr>
<td>19</td>
<td>N₂O₅     →</td>
</tr>
<tr>
<td>20</td>
<td>NO + NO →</td>
</tr>
<tr>
<td>21</td>
<td>NO + NO₂ H₂O →</td>
</tr>
<tr>
<td>22</td>
<td>NO + OH →</td>
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<tr>
<td>23</td>
<td>HNO₂ + hν →</td>
</tr>
<tr>
<td>24</td>
<td>OH + HNO₂ →</td>
</tr>
<tr>
<td>25</td>
<td>HNO₂ + HNO₂ →</td>
</tr>
<tr>
<td>26</td>
<td>NO₂ + OH →</td>
</tr>
<tr>
<td>27</td>
<td>OH + HNO₃ →</td>
</tr>
<tr>
<td>28</td>
<td>HO₂ + NO →</td>
</tr>
<tr>
<td>Reaction No.</td>
<td>CBM-IV</td>
</tr>
<tr>
<td>-------------</td>
<td>--------</td>
</tr>
<tr>
<td>29</td>
<td>$\text{HO}_2 + \text{NO}_2 \xrightarrow{M} \text{PNA}$</td>
</tr>
<tr>
<td>30</td>
<td>$\text{PNA} \xrightarrow{M} \text{HO}_2 + \text{NO}_2$</td>
</tr>
<tr>
<td>31</td>
<td>$\text{OH} + \text{PNA} \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>32</td>
<td>$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$</td>
</tr>
<tr>
<td>33</td>
<td>$\text{HO}_2 + \text{HO}_2 \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2$</td>
</tr>
<tr>
<td>34</td>
<td>$\text{H}_2\text{O}<em>2 + \text{h}</em>\nu \rightarrow 2 \text{OH}$</td>
</tr>
<tr>
<td>35</td>
<td>$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2$</td>
</tr>
<tr>
<td>36</td>
<td>$\text{OH} + \text{CO} \xrightarrow{O_2} \text{HO}_2$</td>
</tr>
<tr>
<td>37</td>
<td>$\text{FORM} + \text{OH} \xrightarrow{O_2} \text{HO}_2 + \text{CO}$</td>
</tr>
<tr>
<td>38</td>
<td>$\text{FORM} + \text{h}_\nu \xrightarrow{2O_2} 2 \text{HO}_2 + \text{CO}$</td>
</tr>
<tr>
<td>39</td>
<td>$\text{FORM} + \text{h}_\nu \rightarrow \text{CO}$</td>
</tr>
<tr>
<td>40</td>
<td>$\text{FORM} + \text{O} \rightarrow \text{OH} + \text{HO}_2 + \text{CO}$</td>
</tr>
<tr>
<td>41</td>
<td>$\text{FORM} + \text{NO}_3 \xrightarrow{O_2} \text{HNO}_3 + \text{HO}_2 + \text{CO}$</td>
</tr>
<tr>
<td>42</td>
<td>$\text{ALD}_2 + \text{O} \xrightarrow{O_2} \text{C}_2\text{O}_3 + \text{OH}$</td>
</tr>
<tr>
<td>43</td>
<td>$\text{ALD}_2 + \text{OH} \rightarrow \text{C}_2\text{O}_3$</td>
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<tr>
<td>44</td>
<td>$\text{ALD}_2 + \text{NO}_3 \xrightarrow{O_2} \text{C}_2\text{O}_3 + \text{HNO}_3$</td>
</tr>
<tr>
<td>45</td>
<td>$\text{ALD}<em>2 + \text{h}</em>\nu \rightarrow \text{FORM} + 2 \text{HO}_2 + \text{CO} + \text{XO}_2$</td>
</tr>
<tr>
<td>46</td>
<td>$\text{C}_2\text{O}_3 + \text{NO} \xrightarrow{O_2} \text{FORM} + \text{NO}_2 + \text{HO}_2 + \text{XO}_2$</td>
</tr>
<tr>
<td>47</td>
<td>$\text{C}_2\text{O}_3 + \text{NO}_2 \rightarrow \text{PAN}$</td>
</tr>
<tr>
<td>48</td>
<td>$\text{PAN} \rightarrow \text{C}_2\text{O}_3 + \text{NO}_2$</td>
</tr>
<tr>
<td>49</td>
<td>$\text{C}_2\text{O}_3 + \text{C}_2\text{O}_3 \rightarrow 2 \text{FORM} + 2 \text{XO}_2 + 2 \text{HO}_2$</td>
</tr>
<tr>
<td>50</td>
<td>$\text{C}_2\text{O}_3 + \text{HO}_2 \rightarrow 0.79 \text{FORM} + 0.79 \text{XO}_2 + 0.79 \text{HO}_2 + 0.79 \text{OH}$</td>
</tr>
<tr>
<td>51</td>
<td>$\text{OH} \rightarrow \text{FORM} + \text{XO}_2 + \text{HO}_2$</td>
</tr>
<tr>
<td>52</td>
<td>$\text{PAR} + \text{OH} \rightarrow 0.87 \text{XO}_2 + 0.13 \text{XO}_2\text{N} + 0.11 \text{HO}_2 + 0.11 \text{ALD}_2 + 0.76 \text{ROR} - 0.11 \text{PAR}$</td>
</tr>
<tr>
<td>53</td>
<td>$\text{ROR} \rightarrow 0.96 \text{XO}_2 + 1.1 \text{ALD}_2 + 0.94 \text{HO}_2 + 0.04 \text{XO}_2\text{N} + 0.02 \text{ROR} - 2.1 \text{PAR}$</td>
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<tr>
<td>54</td>
<td>$\text{ROR} \rightarrow \text{HO}_2$</td>
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<td>Reaction No.</td>
<td>CBM-IV</td>
</tr>
<tr>
<td>-------------</td>
<td>--------</td>
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<tr>
<td>55</td>
<td>ROR + NO$_2$ →</td>
</tr>
<tr>
<td>56</td>
<td>O + OLE →</td>
</tr>
<tr>
<td>57</td>
<td>OH + OLE →</td>
</tr>
<tr>
<td>58</td>
<td>O$_3$ + OLE →</td>
</tr>
<tr>
<td>60</td>
<td>O + ETH →</td>
</tr>
<tr>
<td>61</td>
<td>OH + ETH →</td>
</tr>
<tr>
<td>62</td>
<td>O$_3$ + ETH →</td>
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<tr>
<td>63</td>
<td>TOL + OH →</td>
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<td>TO2 + NO →</td>
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<tr>
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<td>TO2 →</td>
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<td>66</td>
<td>OH + CRES →</td>
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<tr>
<td>67</td>
<td>CRES + NO$_3$ →</td>
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<td>68</td>
<td>CRO + NO$_2$ →</td>
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<td>69</td>
<td>OH + XYL →</td>
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<tr>
<td>70</td>
<td>OPEN + OH →</td>
</tr>
<tr>
<td>71</td>
<td>OPEN + $h\nu$ →</td>
</tr>
<tr>
<td>72</td>
<td>OPEN + O$_3$ →</td>
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<tr>
<td>73</td>
<td>OH + MGLY →</td>
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<tr>
<td>74</td>
<td>MGLY + $h\nu$ →</td>
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<tr>
<td>75</td>
<td>O + ISOP →</td>
</tr>
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<td>Reaction No.</td>
<td>CBM-IV</td>
</tr>
<tr>
<td>-------------</td>
<td>------------</td>
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<tr>
<td>77</td>
<td>$\text{O}_3 + \text{ISOP}$</td>
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<tr>
<td>78</td>
<td>$\text{NO}_3 + \text{ISOP}$</td>
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<tr>
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<td>$\text{XO}_2 + \text{NO}$</td>
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<td>$\text{XO}_2 + \text{XO}_2$</td>
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<tr>
<td>81</td>
<td>$\text{XO}_2\text{N} + \text{NO}$</td>
</tr>
<tr>
<td>82</td>
<td>$\text{XO}_2 + \text{HO}_2$</td>
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