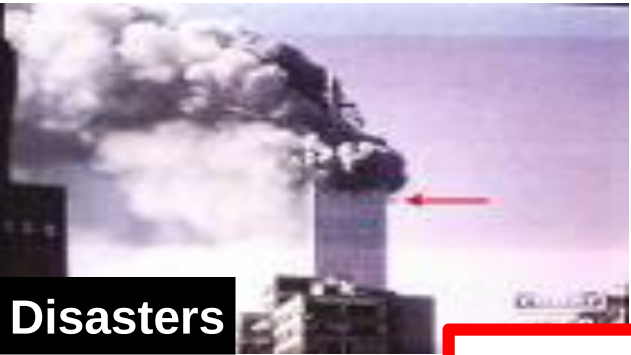
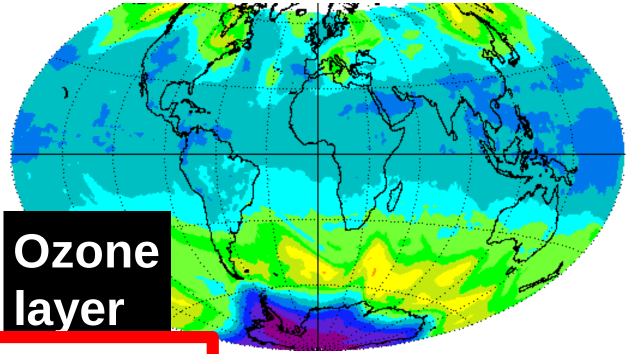
Chemical transport models

Daniel J. Jacob

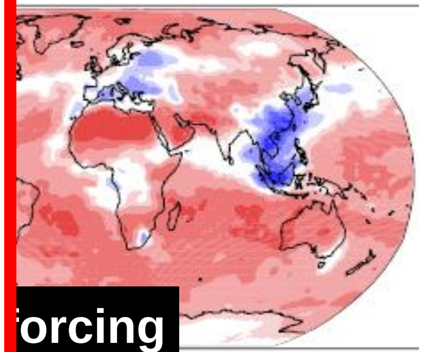
Atmospheric chemists are interested in a wide range of issues

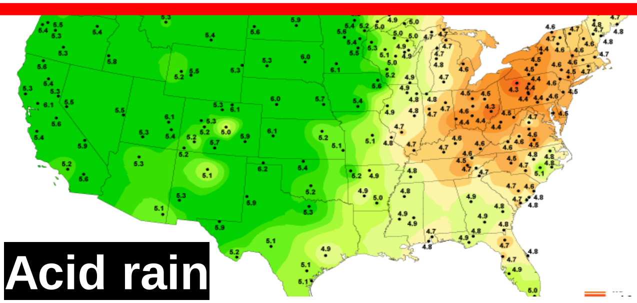




We need chemical transport models (CTMs) to:

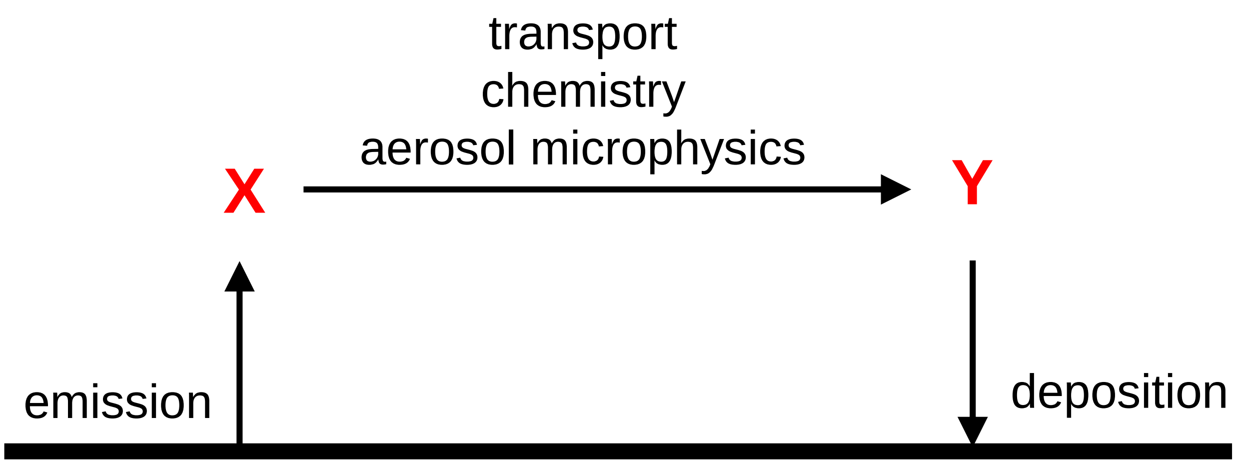
- Understand processes
- Interpret observations
- Make forecasts and projections





LOCAL	REGIONAL	GLOBAL
< 100 km	100-1000 km	> 1000 km

The chemical transport modeling problem



Solve continuity equation for species *i*:

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot (n_i \mathbf{U}) + P_i - L_i$$

local trend in concentration

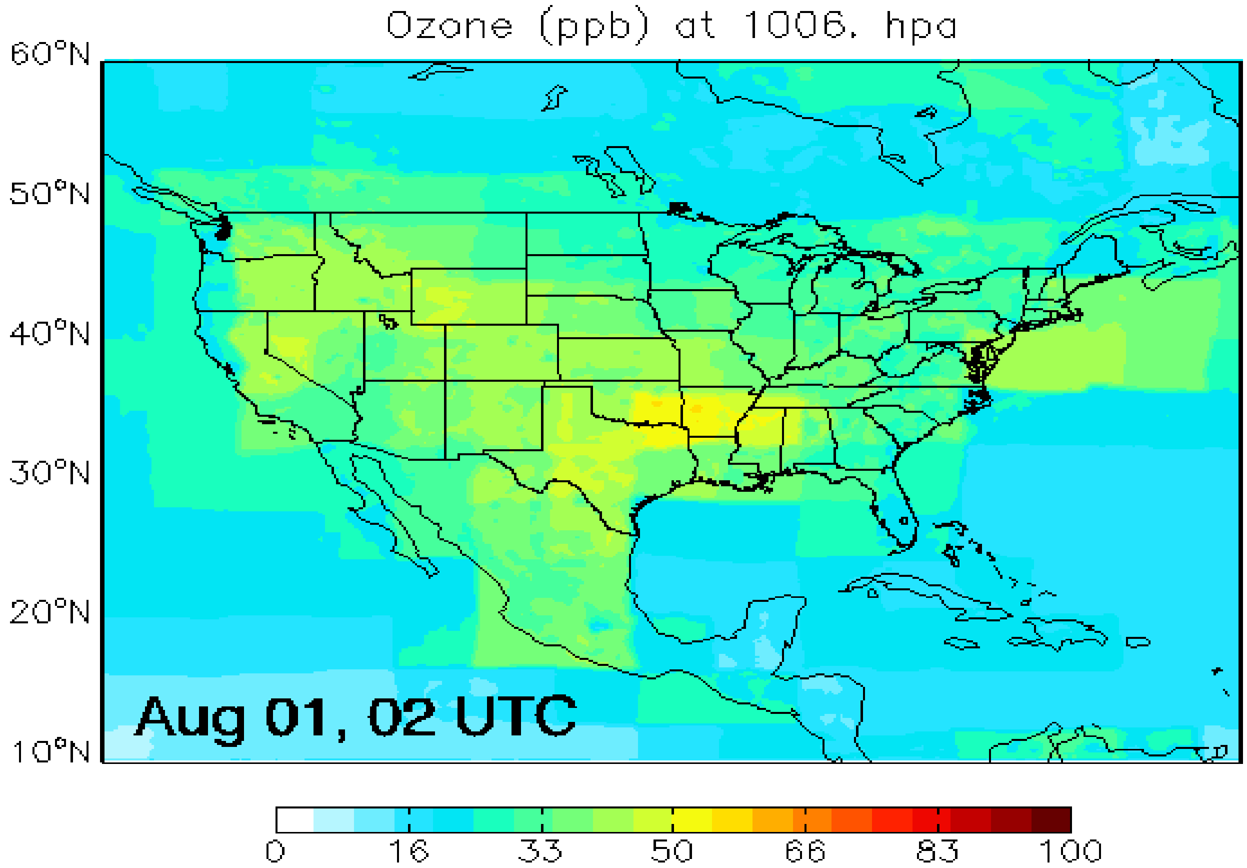
transport (flux divergence)

emissions, deposition, chemical and aerosol processes

Challenges:

- Chemical coupling between large numbers of species
- Coupling between transport and chemistry on all scales

Example: GEOS-Chem CTM simulation of US ozone air quality (Aug-Sep 2013)

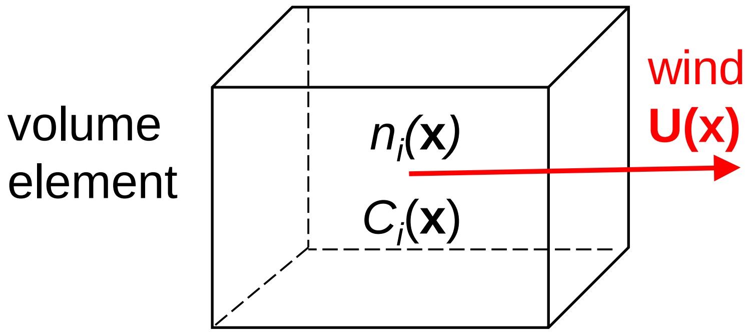


- GEOS-Chem off-line CTM driven by NASA-GEOS assimilated meteorological data
- 0.25°x0.3125° horizontal resolution, 72 vertical levels, 5-minute time steps
- Coupled system of 200 chemical species to describe ozone-aerosol chemistry
- Evaluated with aircraft/sonde/surface observations (aircraft data as circles)

Yu et al. [2016]

The chemical continuity equation

Represent 3-D fields of concentrations of K chemicals coupled by chemistry;
number densities [cm^{-3}] $\mathbf{n} = (n_1,\ldots n_K)^T$ or mixing ratios [mol per mol of air] $\mathbf{C} = (C_1,\ldots C_K)^T$



Flux $\mathbf{F} = n_i\mathbf{U} = C_i n_a \mathbf{U}$

where n_a is air number density

Within volume element: local production P_i and loss L_i
(emission, deposition, chemistry, aerosol processes)

Eulerian forms of continuity equation (fixed frame of reference):

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot (n_i \mathbf{U}) + P_i(\mathbf{n}) - L_i(\mathbf{n}) \qquad \frac{\partial C_i}{\partial t} = -\mathbf{U} \cdot \nabla C_i + P_i(\mathbf{C}) - L_i(\mathbf{C})$$

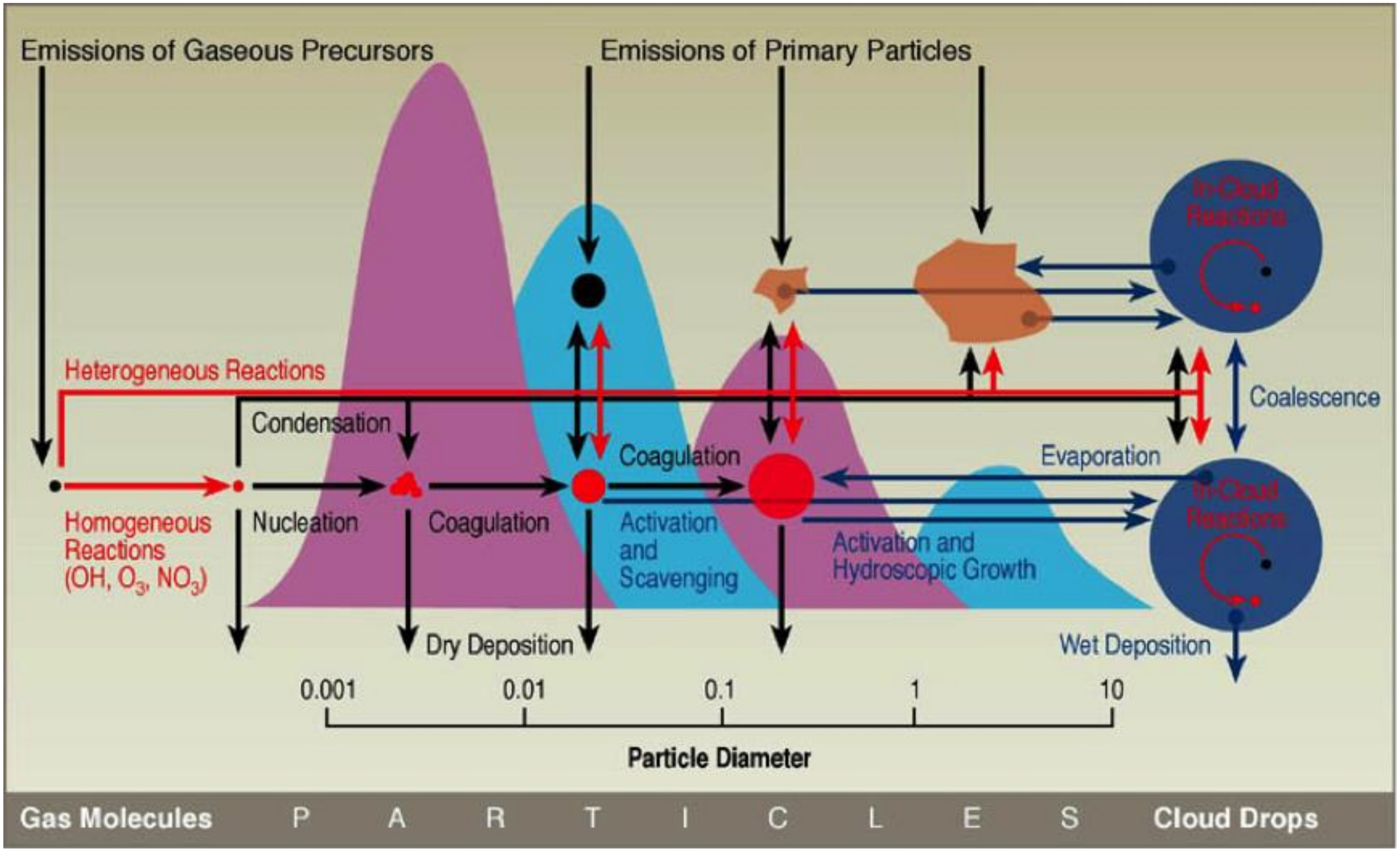
Lagrangian form (moving frame of reference):

$$\frac{dC_i}{dt} = P_i(\mathbf{C}) - L_i(\mathbf{C})$$

Aerosol microphysics included in local terms P_i and L_i

$\mathbf{n} = (n_1, \ldots n_k)^T$ describe concentrations in different size bins or modes

Nucleation, condensation, coagulation are source/sink terms for the different bins



Break down dimensionality of continuity equation by operator splitting

Solve for transport and chemistry separately over time steps Δt

$$\frac{\partial C_i}{\partial t} = -\mathbf{U} \cdot \nabla C_i + P_i(\mathbf{C}) - L_i(\mathbf{C})$$

Advection:

$$\frac{\partial C_i}{\partial t} = -\mathbf{U} \cdot \nabla C_i \quad \text{(Eulerian)}$$

$$\frac{d\mathbf{x}}{dt} = \mathbf{U}(\mathbf{x}, t) \quad \text{(Lagrangian)}$$

Chemistry (local processes):

$$\frac{dC_i}{dt} = P_i(\mathbf{C}) - L_i(\mathbf{C})$$

$$\mathbf{C}(t) \xrightarrow{\Delta t} \mathbf{C^*} \xrightarrow{\Delta t} \mathbf{C}(t+\Delta t)$$

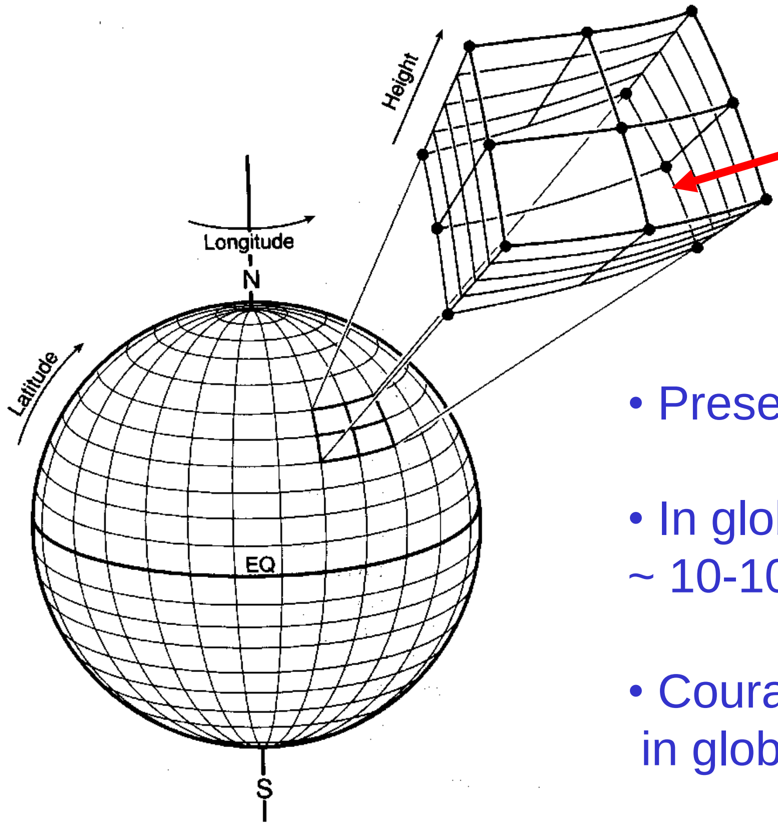
Advection equations:
no chemical coupling

Chemical equations:
K-dimensional ODE system

Operator splitting induces error by ignoring couplings between transport and chemistry over Δt

Eulerian models partition atmospheric domain into gridboxes

This discretizes the continuity equation in space



Solve continuity equation for individual gridboxes

- Present computational limit ~ 10^8 gridboxes

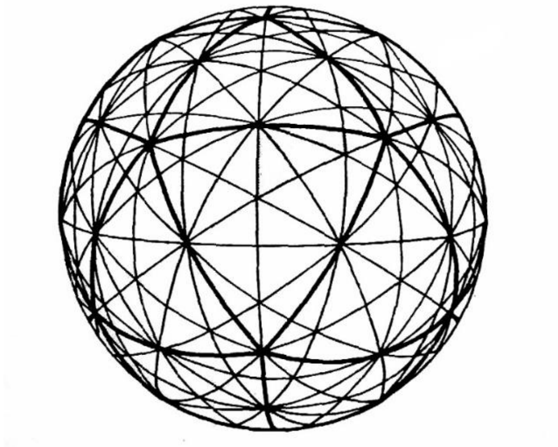
- In global models, this implies a grid resolution Δx of ~ 10-100 km in horizontal and 0.1-1 km in vertical

- Courant number limitation $u \Delta t / \Delta x \leq 1$; in global models, Δt ~10^2-10^3 s

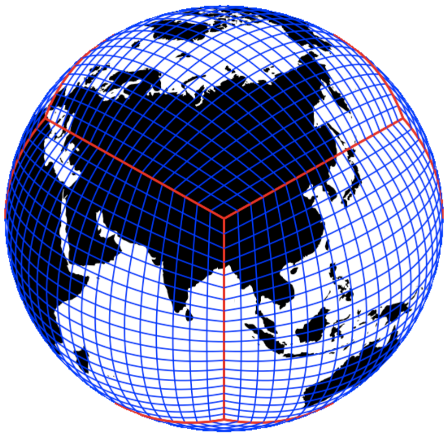
Eulerian models often use equal-area or zoomed grids

Equal-area grids: avoid singularities at poles

icosahedral triangular



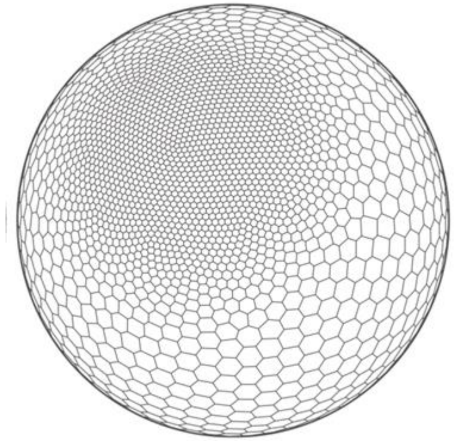
cubed-sphere



Zoomed grids: increase resolution where you need it (or when, in an *adaptive* grid)

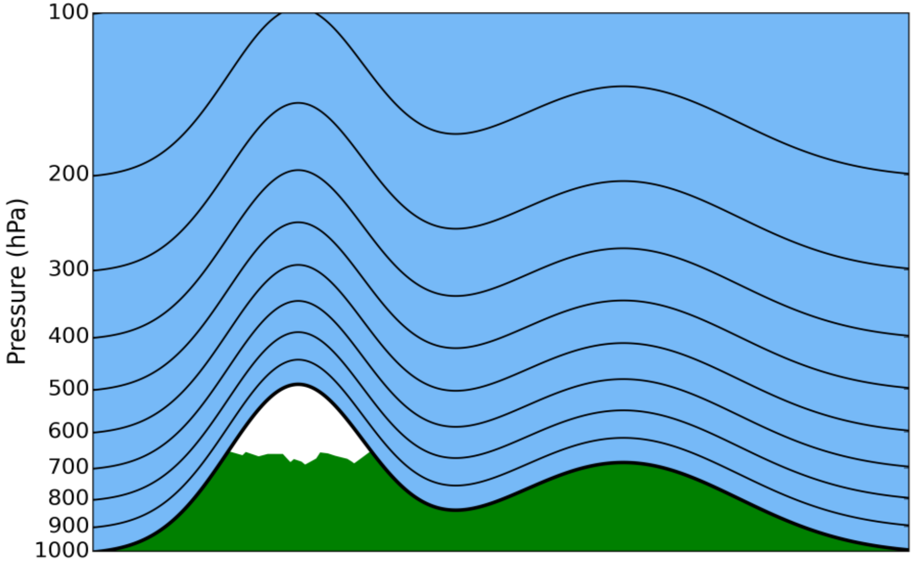
nested

stretched



Vertical coordinate systems

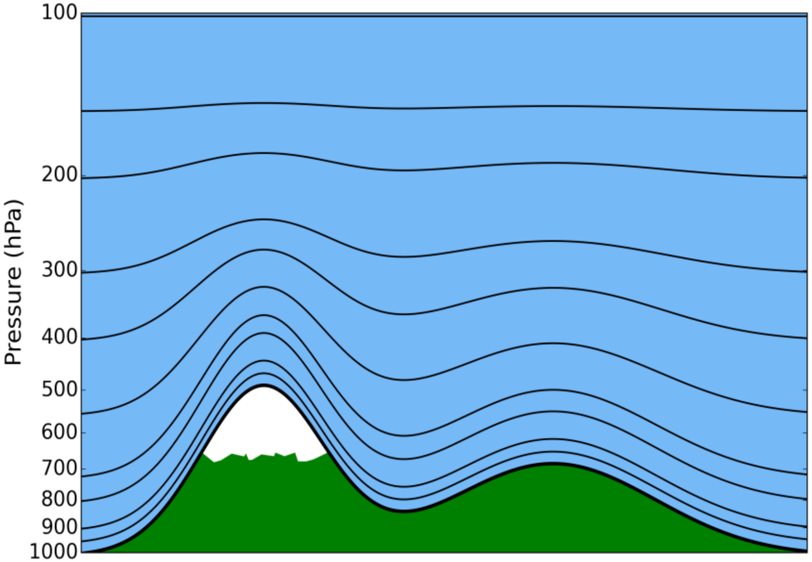
Terrain-following
sigma coordinate system



$$\sigma_k = \frac{p_k - p_T}{p_s - p_T}$$

p_k = pressure at level k
p_s = surface pressure
p_T = pressure at model top
p_o = pressure at sea level

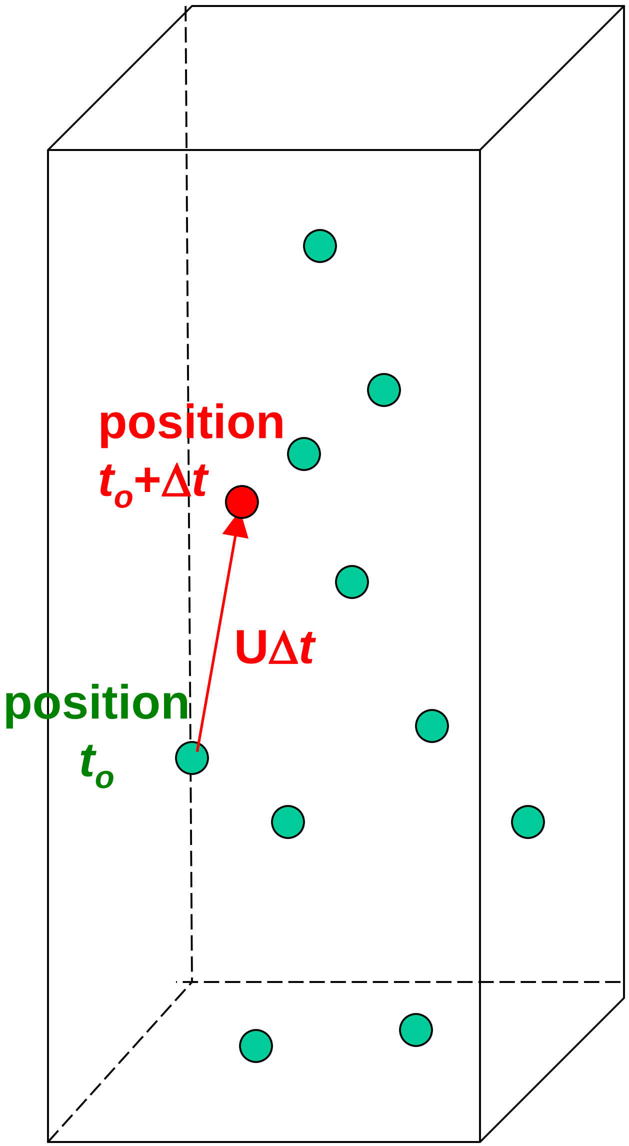
Hybrid sigma-pressure
coordinate system



$$p_k = A_k p_0 + B_k p_s$$

σ_k = sigma coordinate
A_k, B_k = coefficients

Lagrangian models track points in model domain (no grid)



- Transport large number of points with trajectories from input meteorological data base (**U**) over time steps Δt

- Points have mixing ratio or mass but no volume

- Determine local concentrations in a given volume by the statistics of points within that volume or by interpolation

PROS over Eulerian models:

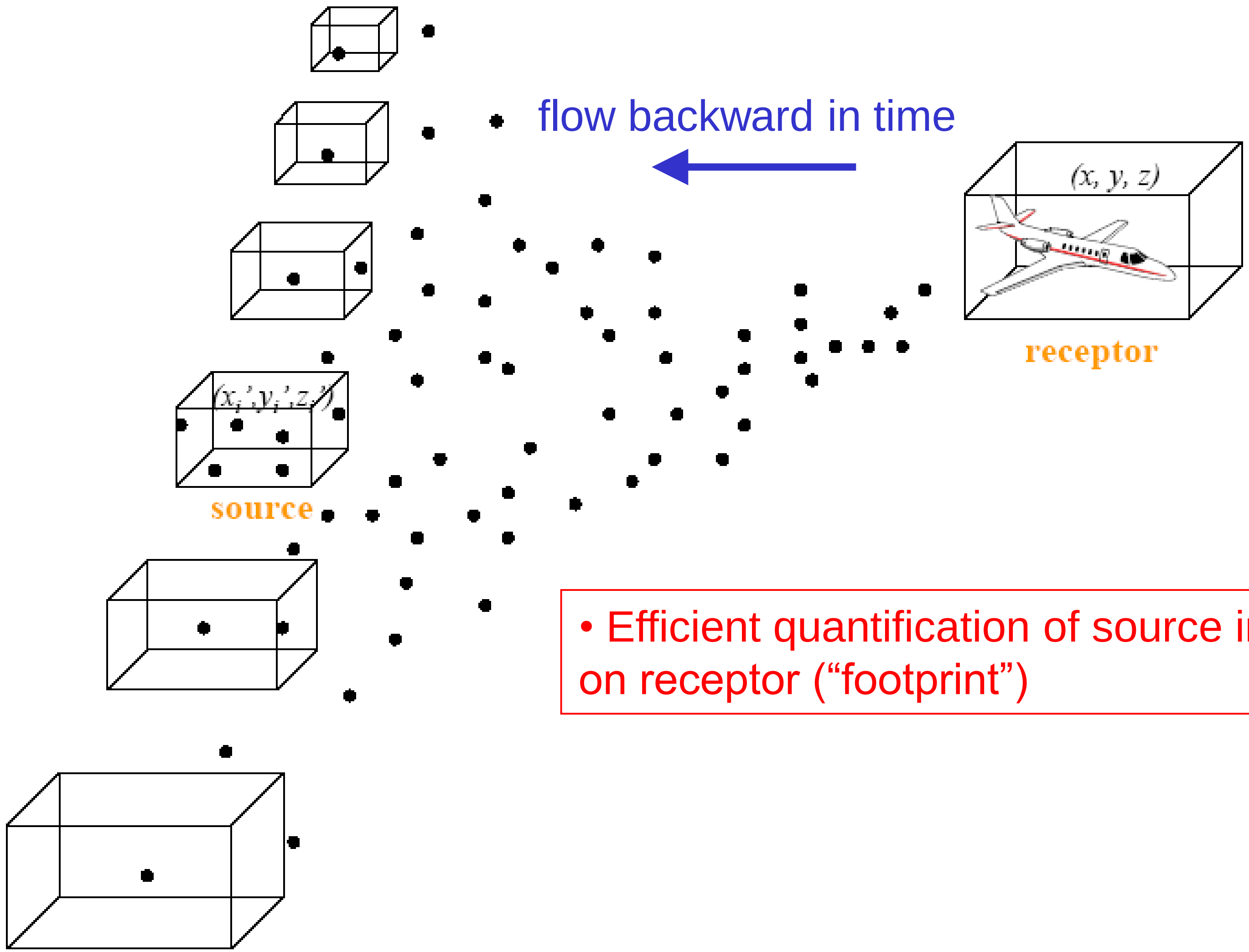
- stable for any wind speed
- no error from spatial averaging
- easy to parallelize
- easily track air parcel histories
- efficient for receptor-oriented problems

CONS:

- need very large # points for statistics
- inhomogeneous representation of domain
- individual trajectories do not mix
- cannot do nonlinear chemistry
- cannot be conducted on-line with meteorology

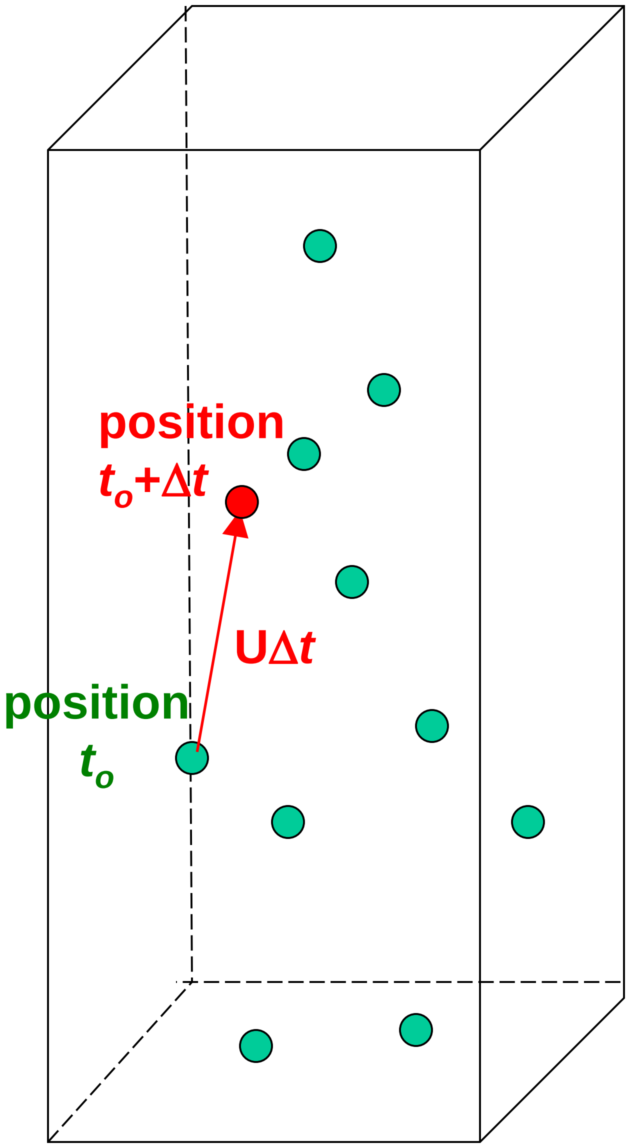
Lagrangian receptor-oriented modeling

Run Lagrangian model backward from receptor location,
with points released at receptor location only



• Efficient quantification of source influence distribution on receptor ("footprint")

Lagrangian models track points in model domain (no grid)



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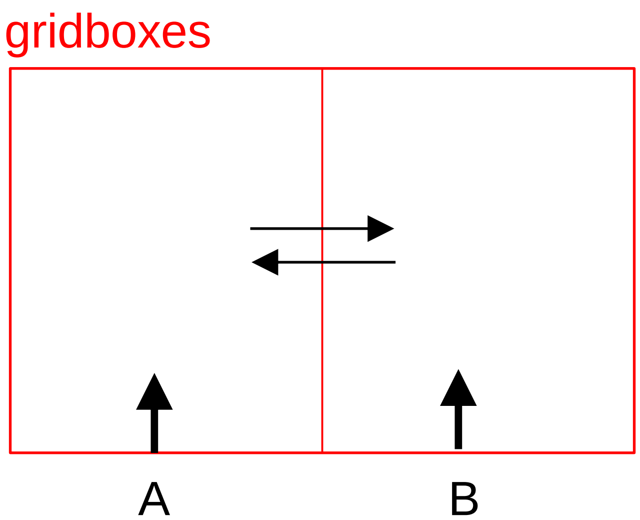
Representing non-linear chemistry

Consider two chemicals A and B emitted in different locations, and reacting by

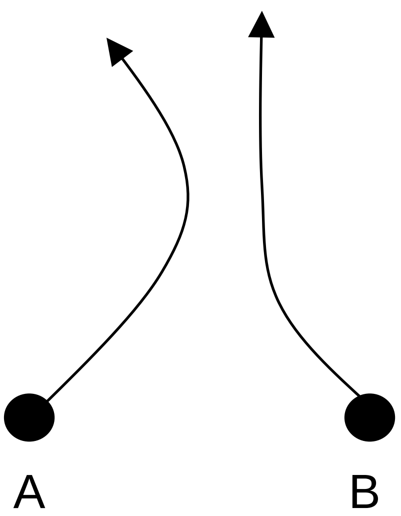
$$A + B \rightarrow \text{products}$$

Eulerian model



A and B react following
the mixing of gridboxes

Lagrangian model



A and B never react

On-line and off-line approaches to chemical modeling

On-line: coupled to dynamics

GCM conservation equations:
air mass: $\partial\rho_a/\partial t = \ldots$
momentum: $\partial\mathbf{u}/\partial t = \ldots$
heat: $\partial\theta/\partial t = \ldots$
water: $\partial q/\partial t = \ldots$
chemicals: $\partial C_i/\partial t = \ldots$

PROs of off-line vs on-line approach:
- computational cost
- simplicity
- stability (no chaos)
- compute sensitivities back in time

CONs:
- no fast chemical-dynamics coupling
- need for meteorological archive
- transport errors

Off-line: decoupled from dynamics

GCM conservation equations:
air mass: $\partial\rho_a/\partial t = \ldots$
momentum: $\partial\mathbf{u}/\partial t = \ldots$
heat: $\partial\theta/\partial t = \ldots$
water: $\partial q/\partial t = \ldots$

↓

meteorological archive
(averaging time ~ hours)

↓

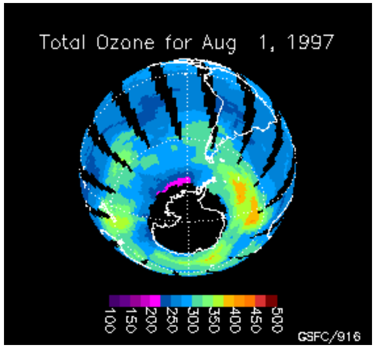
Chemical transport model:
$\partial C_i/\partial t = \ldots$

Chemical data assimilation, forecasts best done on-line ↔ **Chemical sensitivity studies may best be done off-line**

Improving meteorological forecasts through chemical information

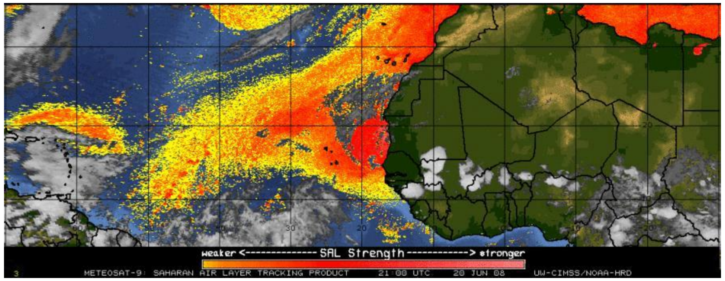
Ozone for stratospheric dynamics

Ozone columns, profiles



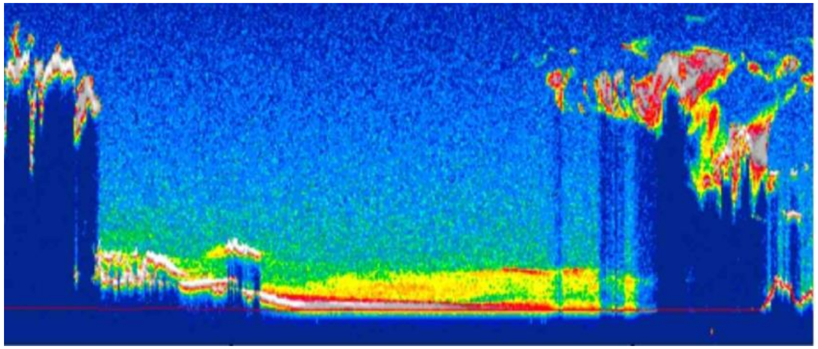
Aerosols for radiation/precipitation

GOES aerosol optical depth



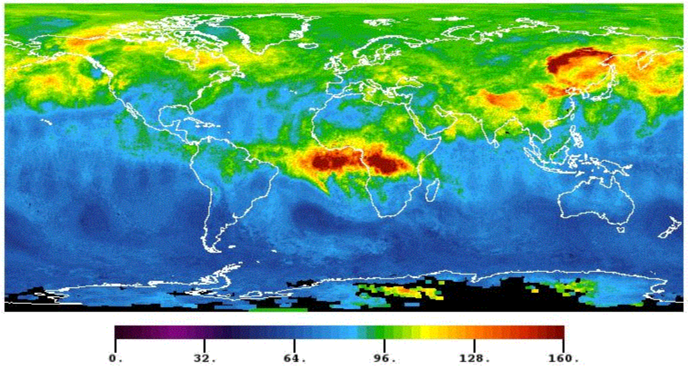
PBL heights

CALIOP lidar aerosol profiles



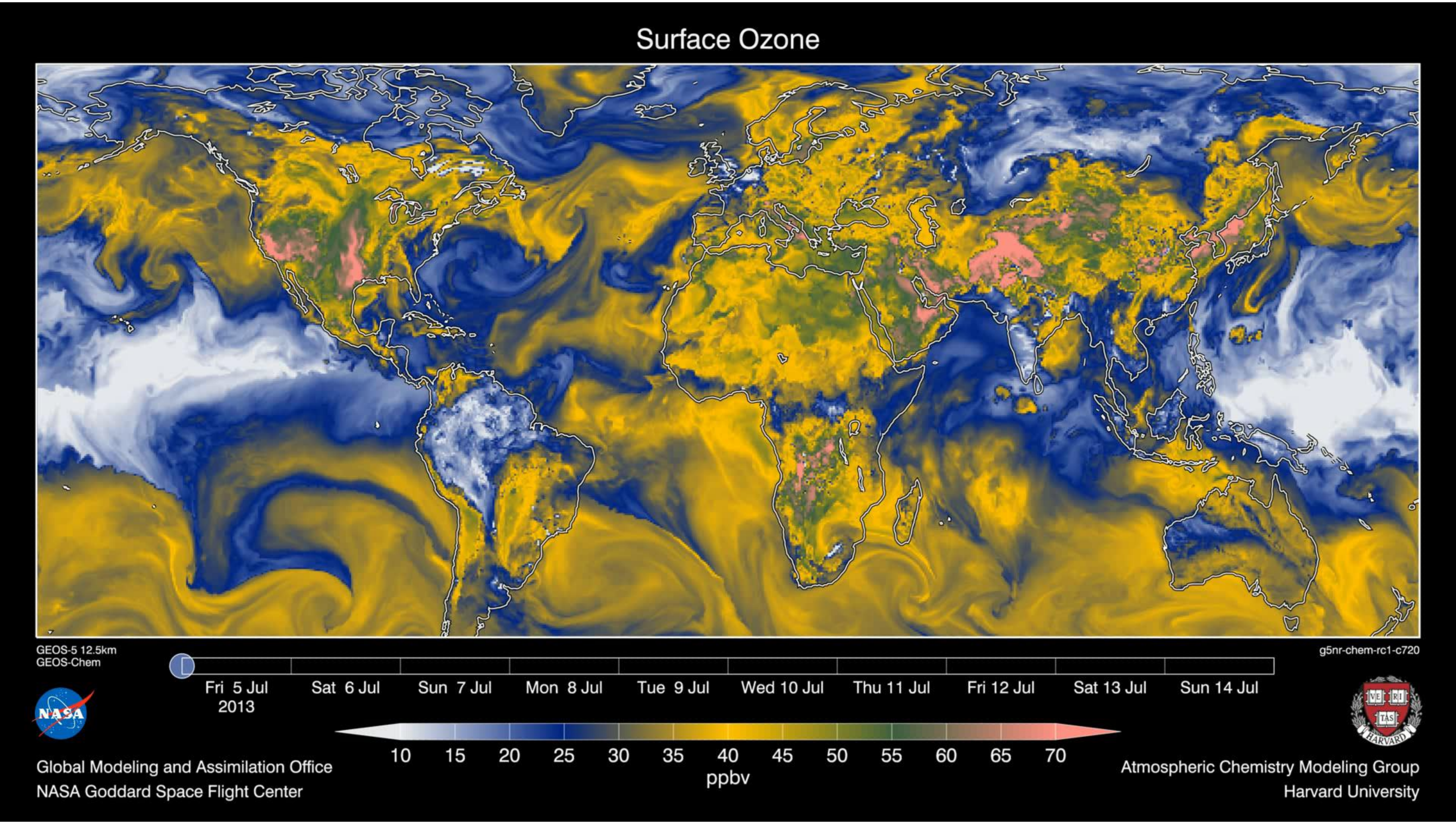
Chemical tracers of winds

Free tropospheric carbon monoxide (CO)



On-line applications may benefit from large computational resources

Full-year simulation of GEOS-Chem chemistry in c720 (12 km) GEOS-5 GCM



Michael Long (Harvard), Christoph Keller (NASA)

Solving the chemical and advection equations

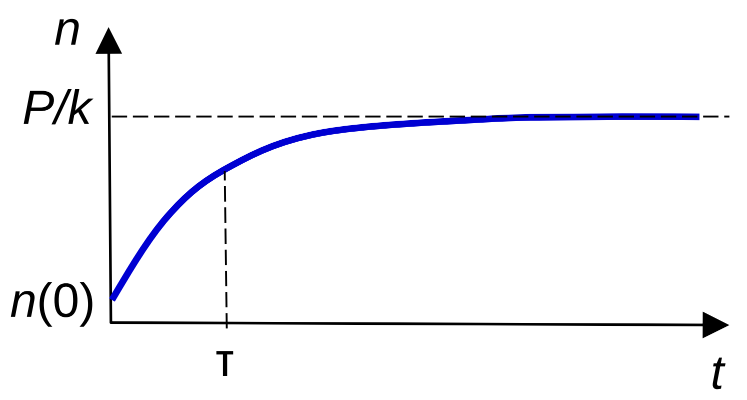
Stability and time scales in chemical equations

Loss term in chemical equations is generally first-order:

$$\frac{dn_i}{dt} = P_i(\mathbf{n}) - L_i(\mathbf{n}) = P_i(\mathbf{n}) - k_i(\mathbf{n})n_i$$ where k_i [s^{-1}] is an effective loss rate constant

For a single species, solution is exponential relaxation to steady state:

$$n(t) = n(0)\exp[-kt] + \frac{P}{k}(1-\exp[-kt])$$



with relaxation time scale τ = 1/k

For general case of K coupled species, the system of chemical equations

$$\frac{d\mathbf{n}}{dt} = \mathbf{s(n)}$$ with elements $s_i = P_i(\mathbf{n}) - L_i(\mathbf{n})$

has K relaxation time scales $\tau_i = -1/\lambda_i$ where λ_i is i^{th} eigenvalue of Jacobian $\mathbf{J} = \frac{\partial \mathbf{s}}{\partial \mathbf{n}}$

One finds that all eigenvalues are negative and real: system is stable against perturbations

Solving the system of chemical equations

For single species: $$\frac{dn}{dt} = P - L = s(n)$$

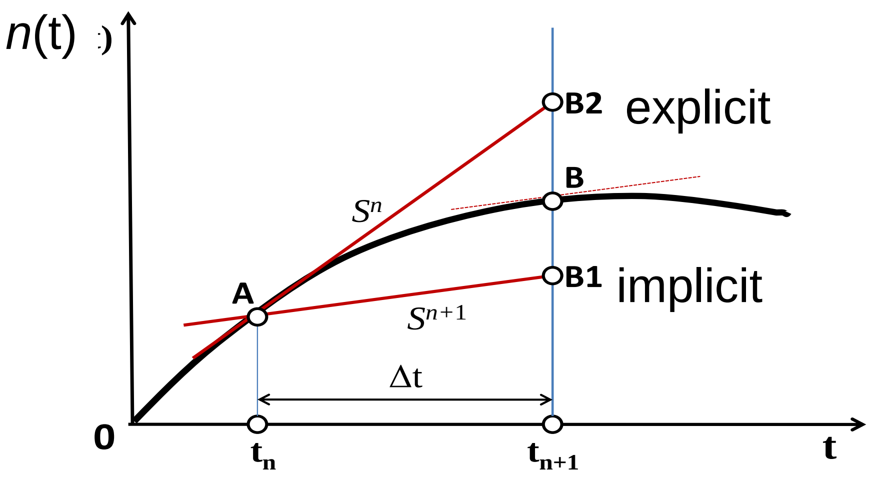
For K coupled species: $\mathbf{n} = (n_1, n_2, \ldots n_K)^T$ $$\frac{d\mathbf{n}}{dt} = \mathbf{s}(\mathbf{n})$$ system of ODEs

First-order explicit solution: $$\mathbf{n}(t + \Delta t) = \mathbf{n}(t) + \mathbf{s}(\mathbf{n}(t))\Delta t$$

requires time steps Δt smaller than lifetime of shortest species

First-order implicit solution: $$\mathbf{n}(t + \Delta t) = \mathbf{n}(t) + \mathbf{s}(\mathbf{n}(t + \Delta t))\Delta t$$

is stable for any time step but requires solving system of algebraic equations for $\mathbf{n}(t+\Delta t)$



- Atmospheric chemistry mechanisms require implicit solvers because of *stiffness* of system (time scales varying over many orders of magnitude)
- Higher-order methods feature more accurate calculation of **s** over time step
- Multistep methods use information from previous time steps

Stability and positivity in explicit and implicit solvers

Consider single species with first-order decay: $dn/dt = -kn$

Exact solution over time step Δt : $n(\Delta t) = n(0)\exp[-\Delta t]$

Stability requirement : $\left| n(\Delta t)/n(0) \right| < 1$

First-order explicit solution

$$\frac{n(\Delta t) - n(0)}{\Delta t} = -kn(0)$$

$$\Rightarrow n(\Delta t) = n(0)(1 - k\Delta t)$$

Stable only if $\Delta t < 2/k$

Positive only if $\Delta t < 1/k$

First-order implicit solution

$$\frac{n(\Delta t) - n(0)}{\Delta t} = -kn(\Delta t)$$

$$\Rightarrow n(\Delta t) = \frac{n(0)}{1 + k\Delta t}$$

- Stable and positive for all values of Δt
- Correct asymptotic behavior $n \rightarrow 0$ as $\Delta t \rightarrow \infty$
- Not any more accurate than explicit

Numerical solution of the Eulerian advection equation

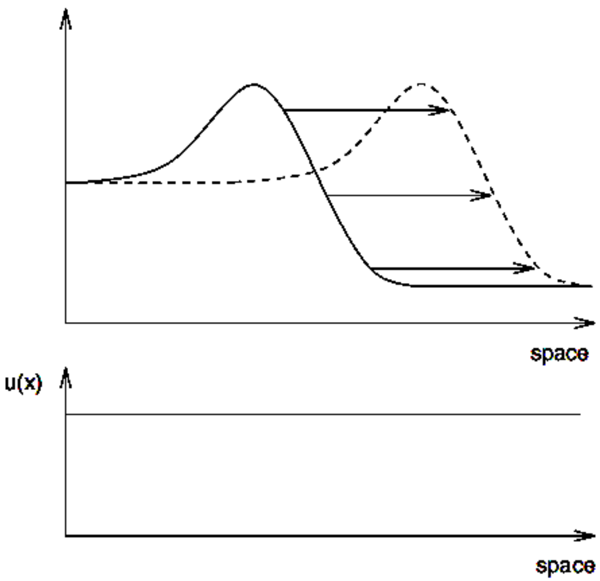
Reduce to 1-D by operator splitting over the three directions (*x*, *y*, *z*):

$$\frac{\partial n}{\partial t} = -\nabla \cdot n\mathbf{U} \quad \text{becomes} \quad \frac{\partial n}{\partial t} = -\frac{\partial nu}{\partial x} \quad \text{or} \quad \frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x}$$

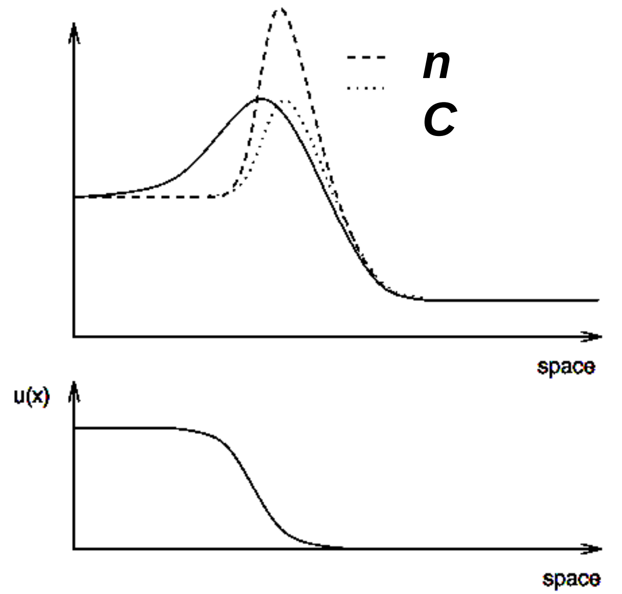
General idea: finite differencing of the derivatives.

Challenge: equation is conservative:

n* or *C



Steady flow



Convergent flow

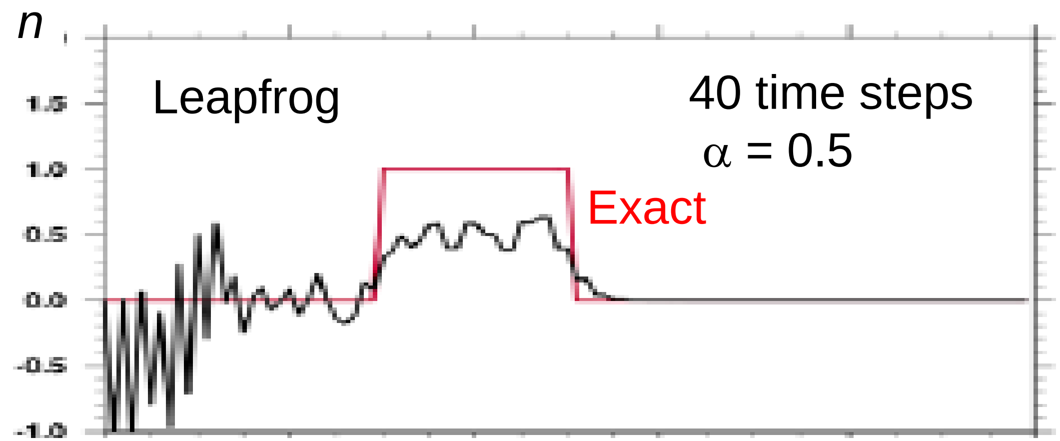
Steady flow conserves number density and mixing ratio,
convergent flow conserves mixing ratio

Numerical advection schemes can be diffusive and/or dispersive

Advection of a square wave in steady flow with Courant number $\alpha = u\Delta t/\Delta x = 0.5$

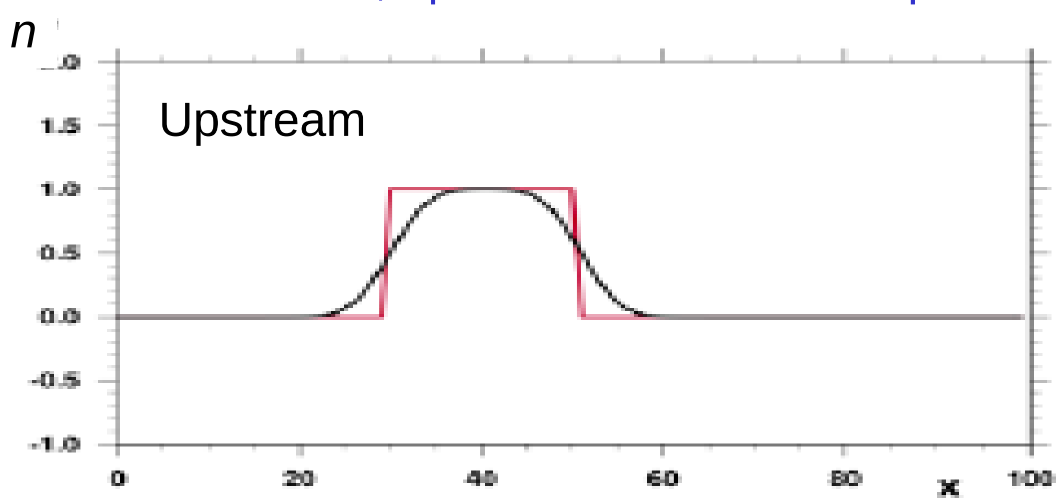
Leapfrog scheme: centered derivatives in time and space

Highly dispersive, negative values

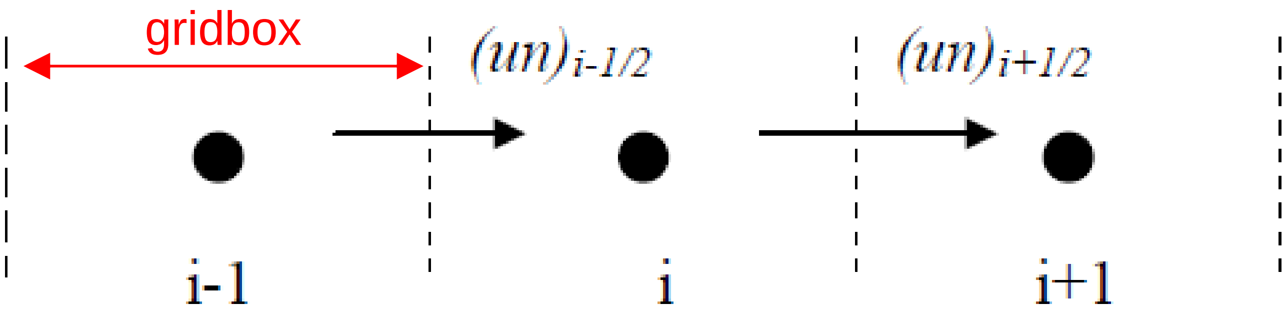


Linear upstream scheme: forward derivative in time, upstream derivative in space

Highly diffusive

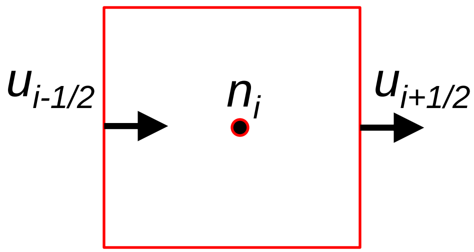


Finite-volume upstream schemes

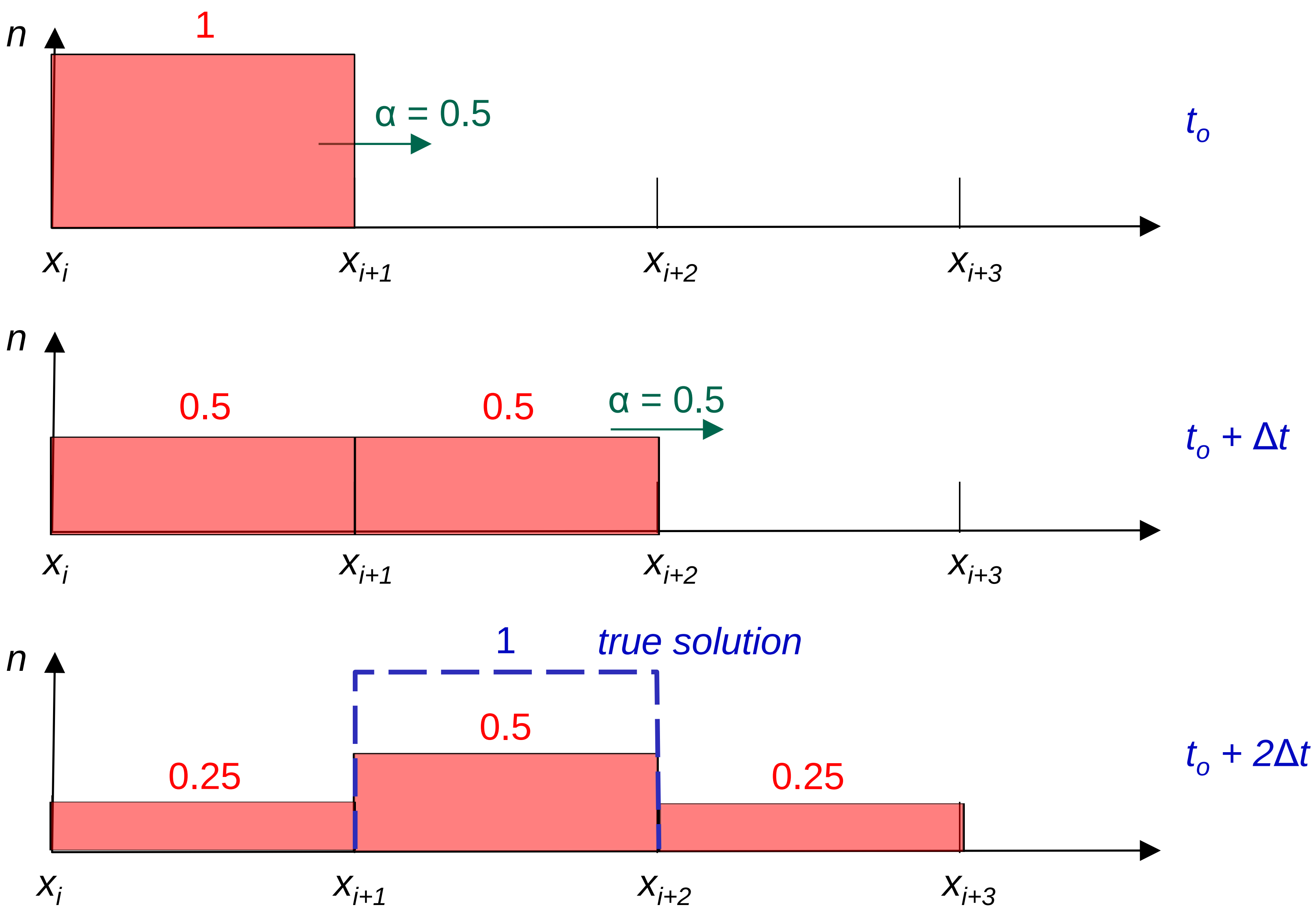


$$\frac{n_{i,t+\Delta t} - n_{i,t}}{\Delta t} = (un)_{i-1/2,t} - (un)_{i+1/2,t}$$

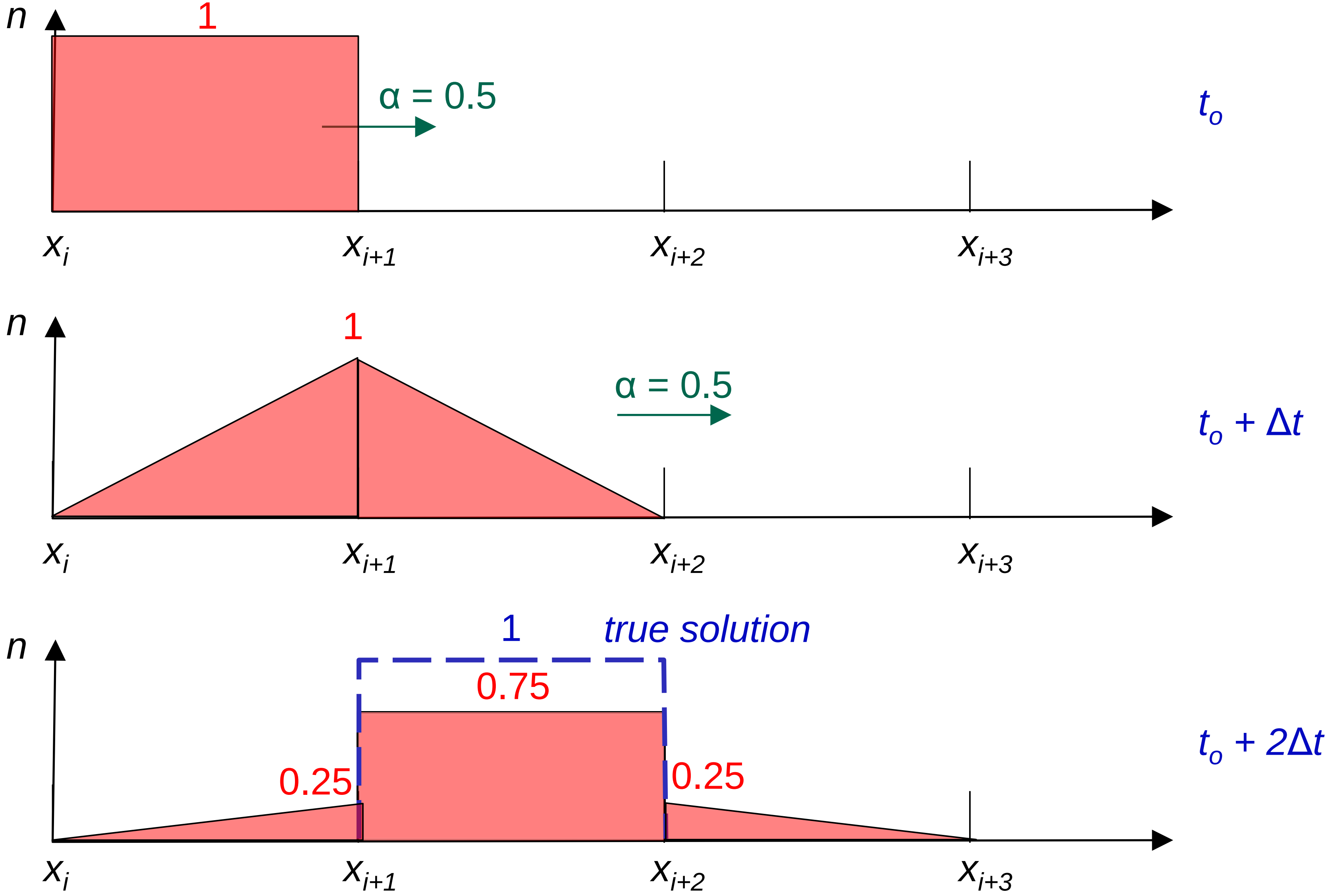
- Mass conservation is ensured;
- Interpolation error at gridbox edges is reduced by solving for momentum and scalars on a staggered grid (C-grid):



Numerical diffusion in a finite-volume upstream scheme

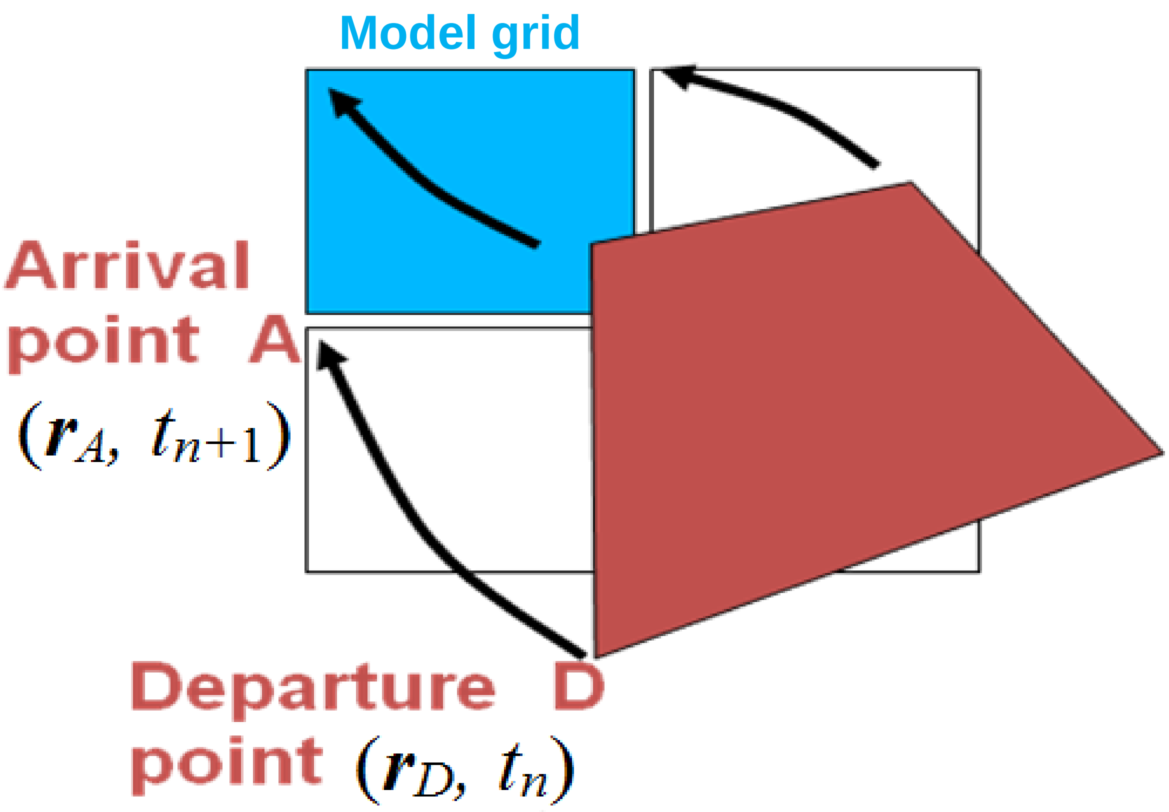


Numerical diffusion in a finite-volume upstream scheme with conservation of first-order moments (slopes scheme)



Piecewise parabolic method (PPM) used in GEOS-Chem resolves subgrid distribution with a quadratic function to reduce numerical diffusion

Semi-Lagrangian advection

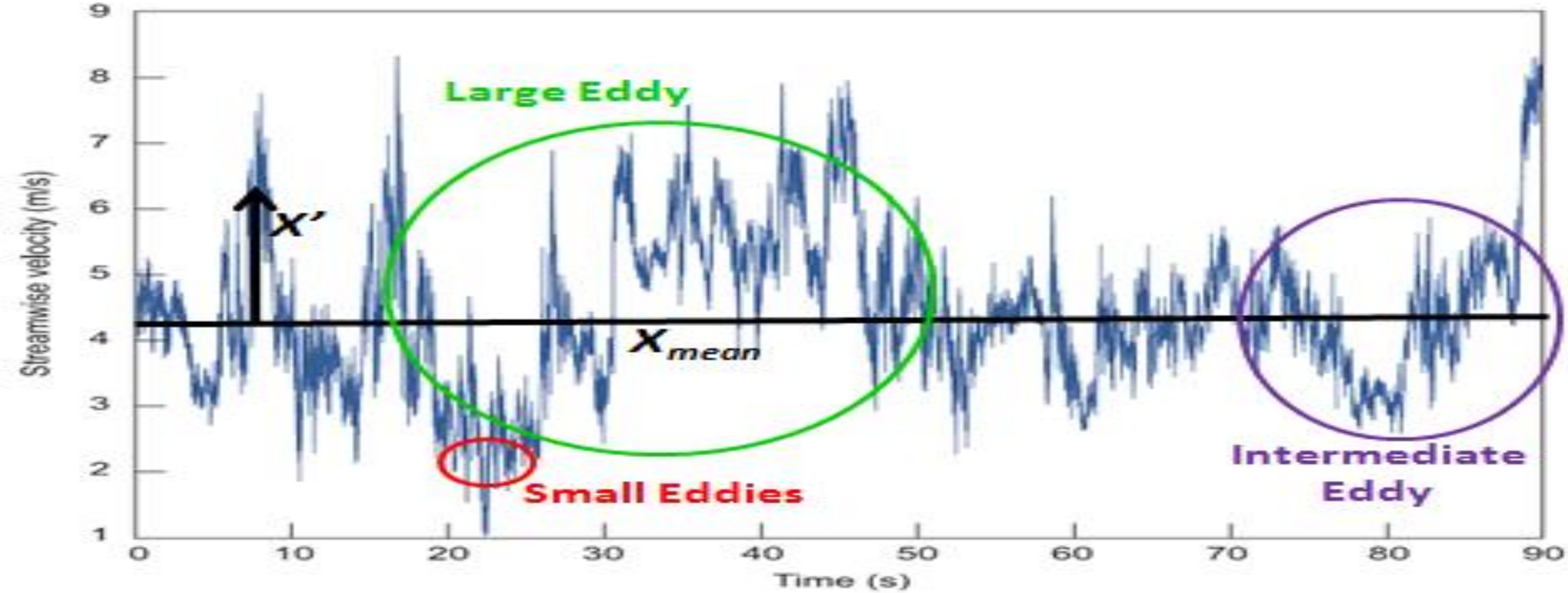


- Allows transport time steps larger than the Courant limit
- Single transport calculation for all species
- But does not conserve mass (posterior correction needed)

Dealing with subgrid transport

Atmospheric flow is turbulent down to mm scale where molecular diffusion takes over

Typical observations of surface wind (10 Hz)

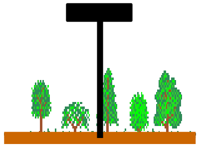


Advection in models must cut off the subgrid scales:

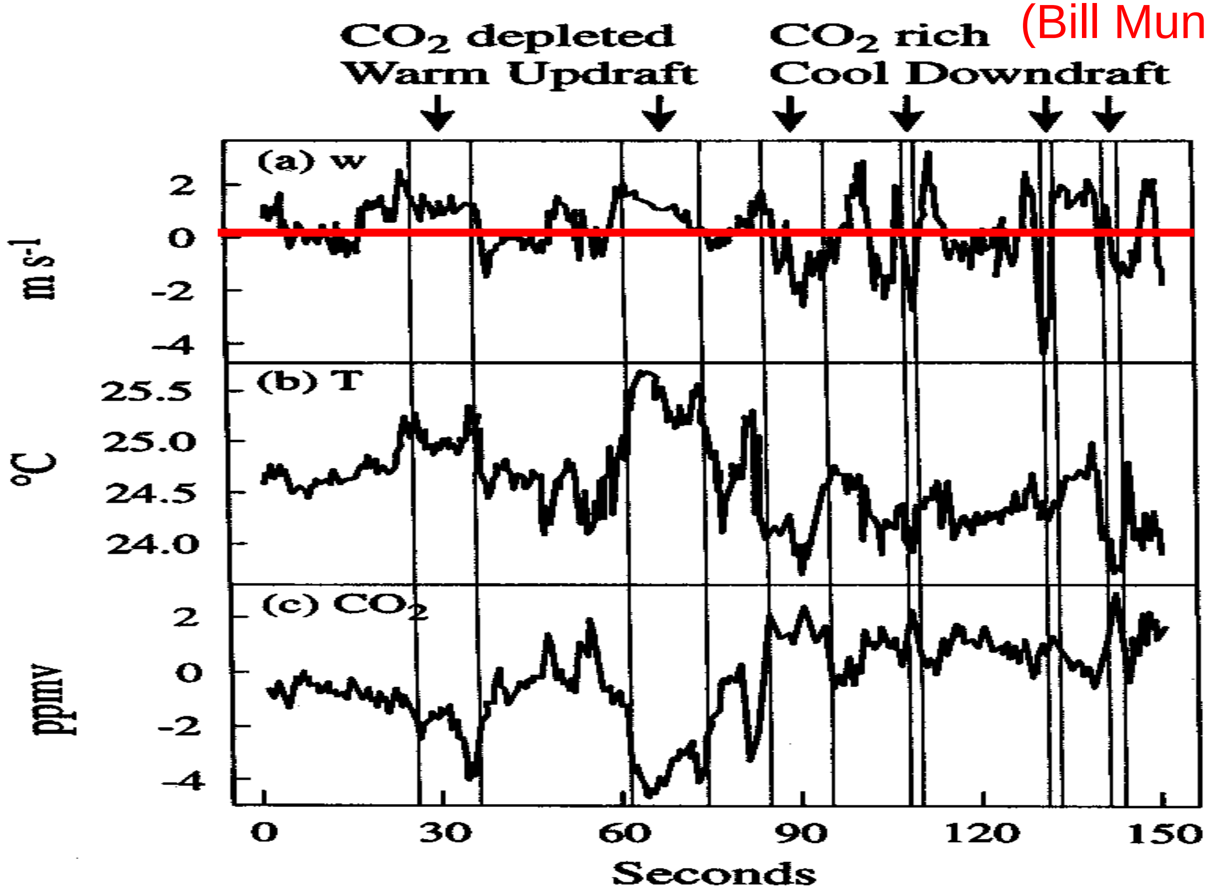
u	=	$\langle u \rangle$	+	u'
instantaneous		grid average resolved deterministic		fluctuating unresolved (turbulent) stochastic

Subgrid turbulence accounts for most of vertical flux in PBL

tower



Observations from Harvard Forest tower on a typical summer day
(Bill Munger, Harvard)



vertical wind *w*

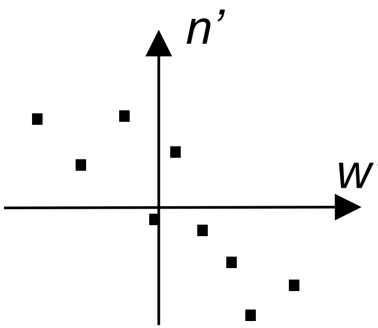
T

CO_2 (*n*)

$w = \langle w \rangle + w'$ $n = \langle n \rangle + n'$

Time-averaged vertical flux $\langle F \rangle = \langle nw \rangle = \langle n \rangle \langle w \rangle + \langle n'w' \rangle$

resolved (small) turbulent (large)



Turbulent flux is covariance between fluctuating components

Turbulent diffusion parameterization for small-scale eddies

In 1-D (vertical) $F_z = nw \quad - \quad K_z n_a \dfrac{\partial C}{\partial z}$

resolved turbulent

K_z is a turbulent diffusion coefficient, same for all species (similarity assumption)

implies Gaussian plumes for point sources

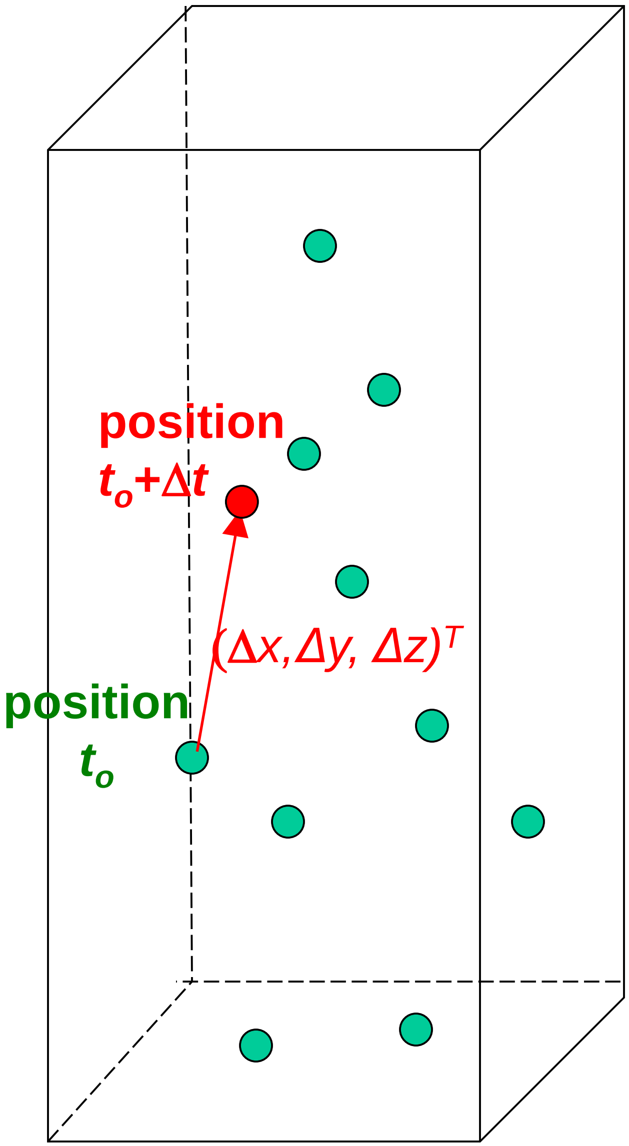
California fire plumes, Oct 2004

Industrial plumes

Generalized continuity equation in 3-D (Eulerian):

$$\frac{\partial n_i}{\partial t} = -\nabla \bullet (n_i \mathbf{U}) + \nabla \bullet \mathbf{K} n_a \nabla C_i + P_i - L_i \qquad \text{with} \qquad \mathbf{K} = \begin{pmatrix} K_x & 0 & 0 \\ 0 & K_y & 0 \\ 0 & 0 & K_z \end{pmatrix}$$

Lagrangian treatment of small-scale eddies



Treat turbulent component as Markov chain:

$$\Delta x = u\Delta t + \sqrt{2K_x}\Delta\xi_x$$

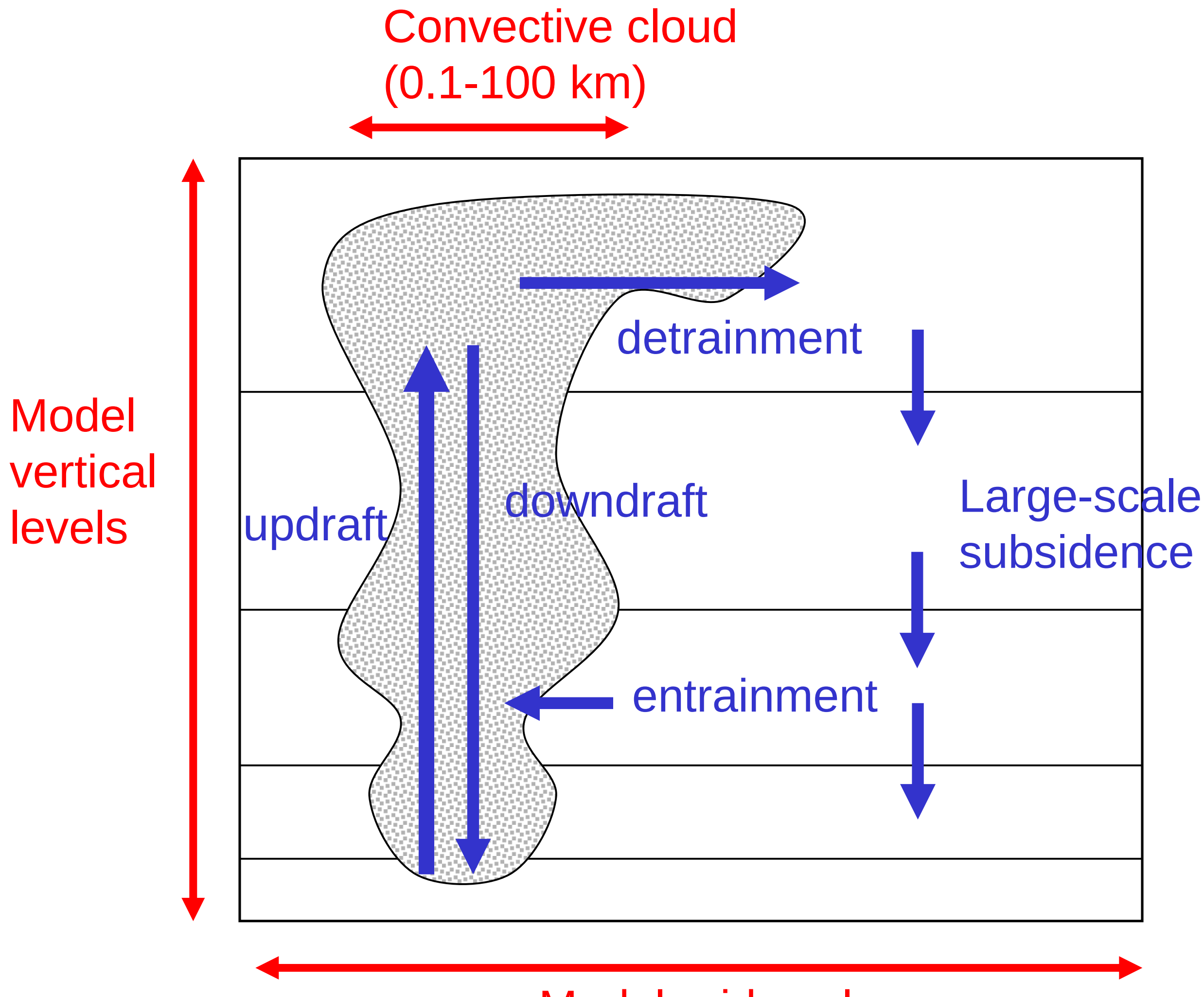
$$\Delta y = v\Delta t + \sqrt{2K_y}\Delta\xi_y$$

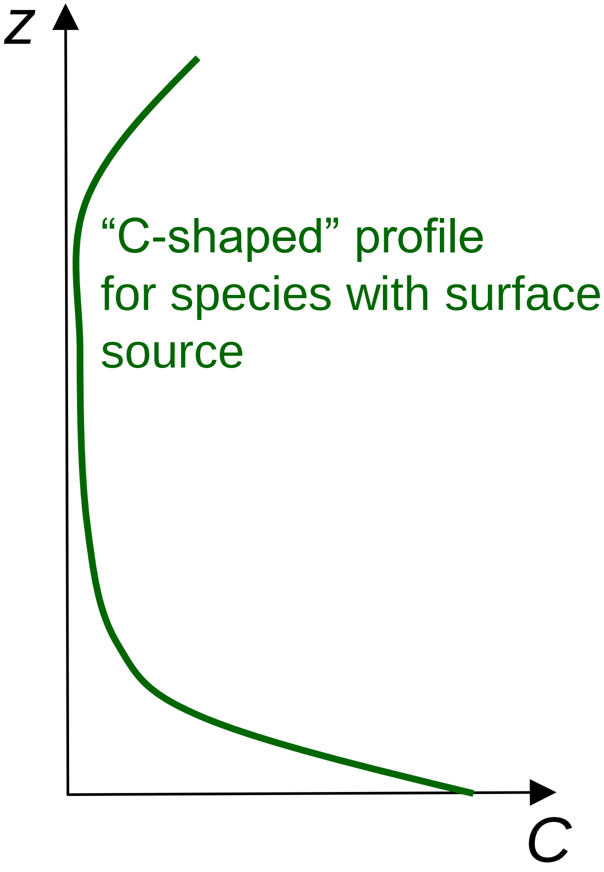
$$\Delta z = w\Delta t + \sqrt{2K_z}\Delta\xi_z$$

where the $\Delta\xi$ random components have expected value of zero and variance Δt

Deep convection

- Subgrid in horizontal but organized in vertical
- Requires non-local parameterization of mass transport





Construction of emission inventories

"Bottom-up" knowledge of processes driving emissions

Activity rate

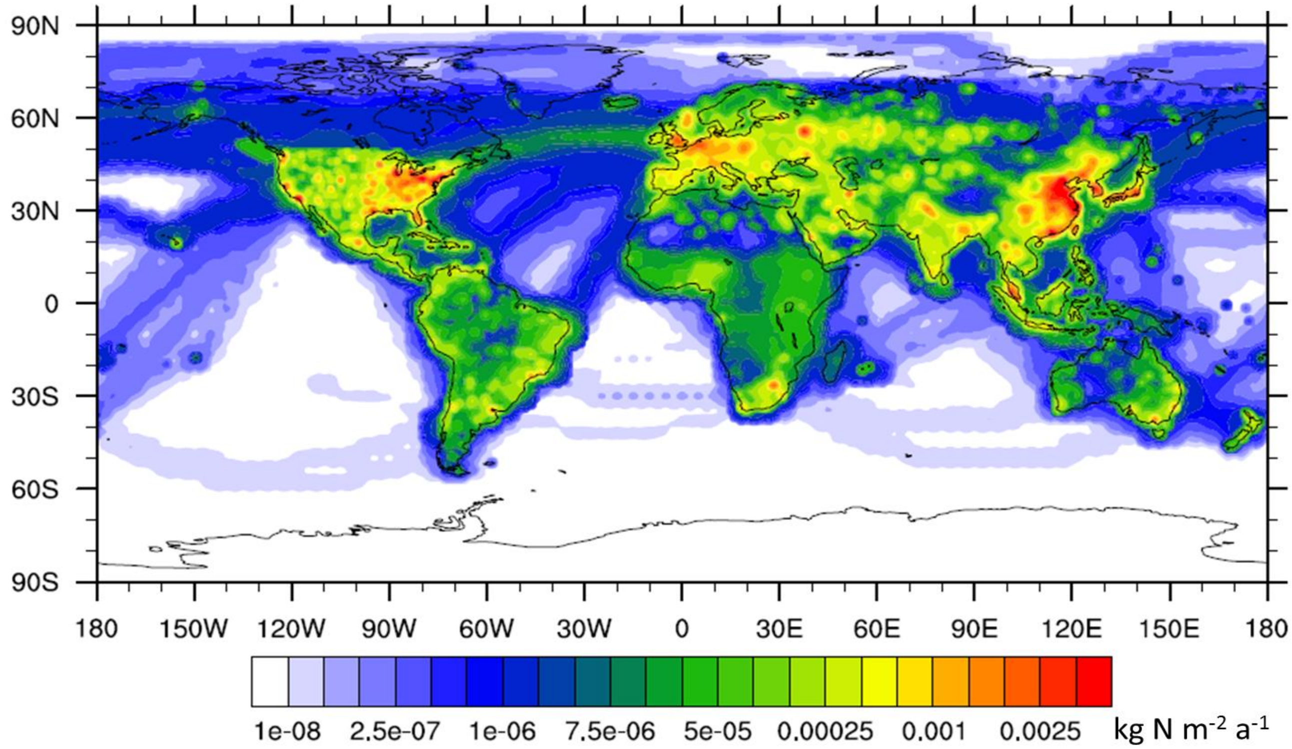
Emission factor

Scale factor

emission flux of species *i*

$$E_i = A \times F_i \times S_i$$

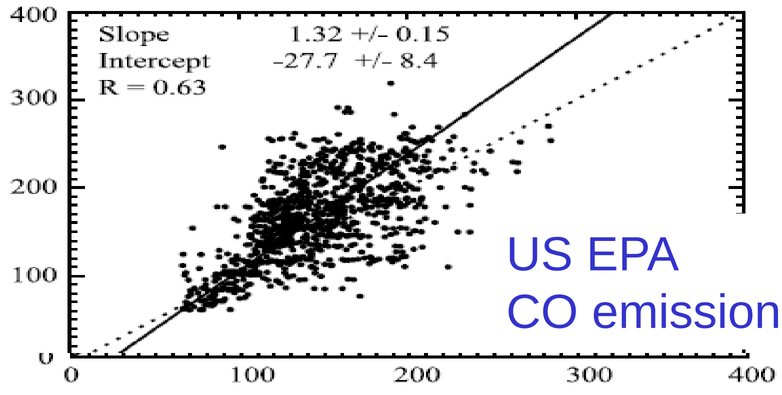
Anthropogenic NO_x emissions for 2013 [Keller et al., 2014]



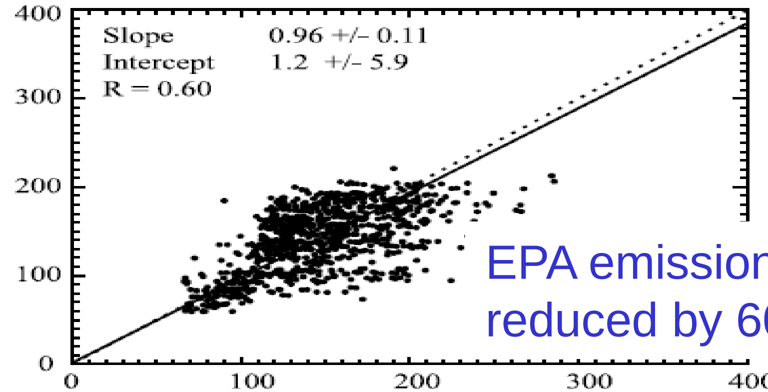
Atmospheric observations as top-down constraints on emissions

Aircraft data over eastern US [Hudman et al., 2008]

Model CO (ppb)



Observed CO (ppb)



Observed CO (ppb)

Bayesian inverse analyses blend error-weighted bottom-up and top-down information:

Bottom-up prior estimate
$\mathbf{E_A} \pm \boldsymbol{\sigma_A}$

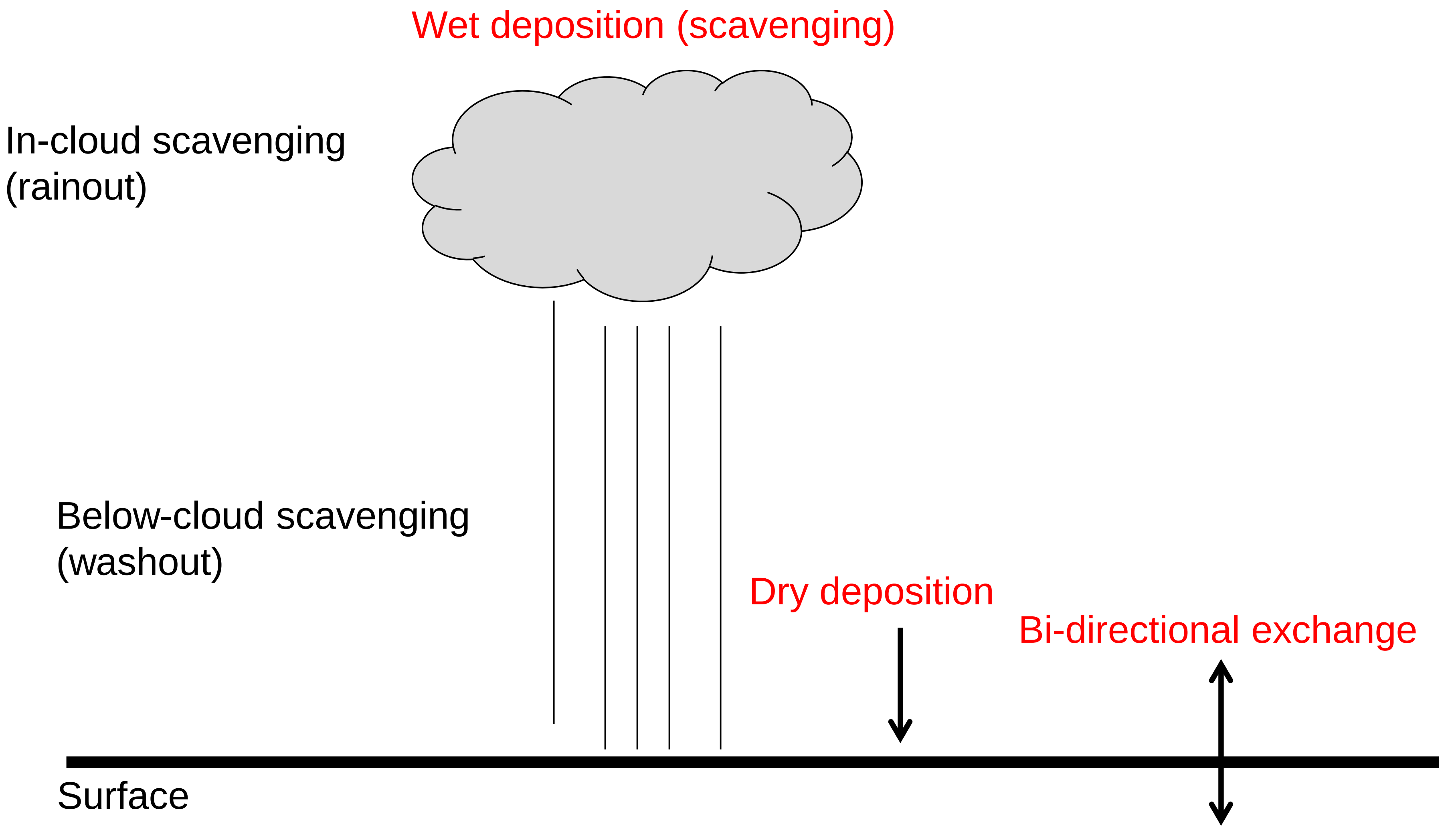
Model concentrations
$\mathbf{n_M} \pm \boldsymbol{\sigma_M}$

Observed concentrations
$\mathbf{n_O} \pm \boldsymbol{\sigma_O}$

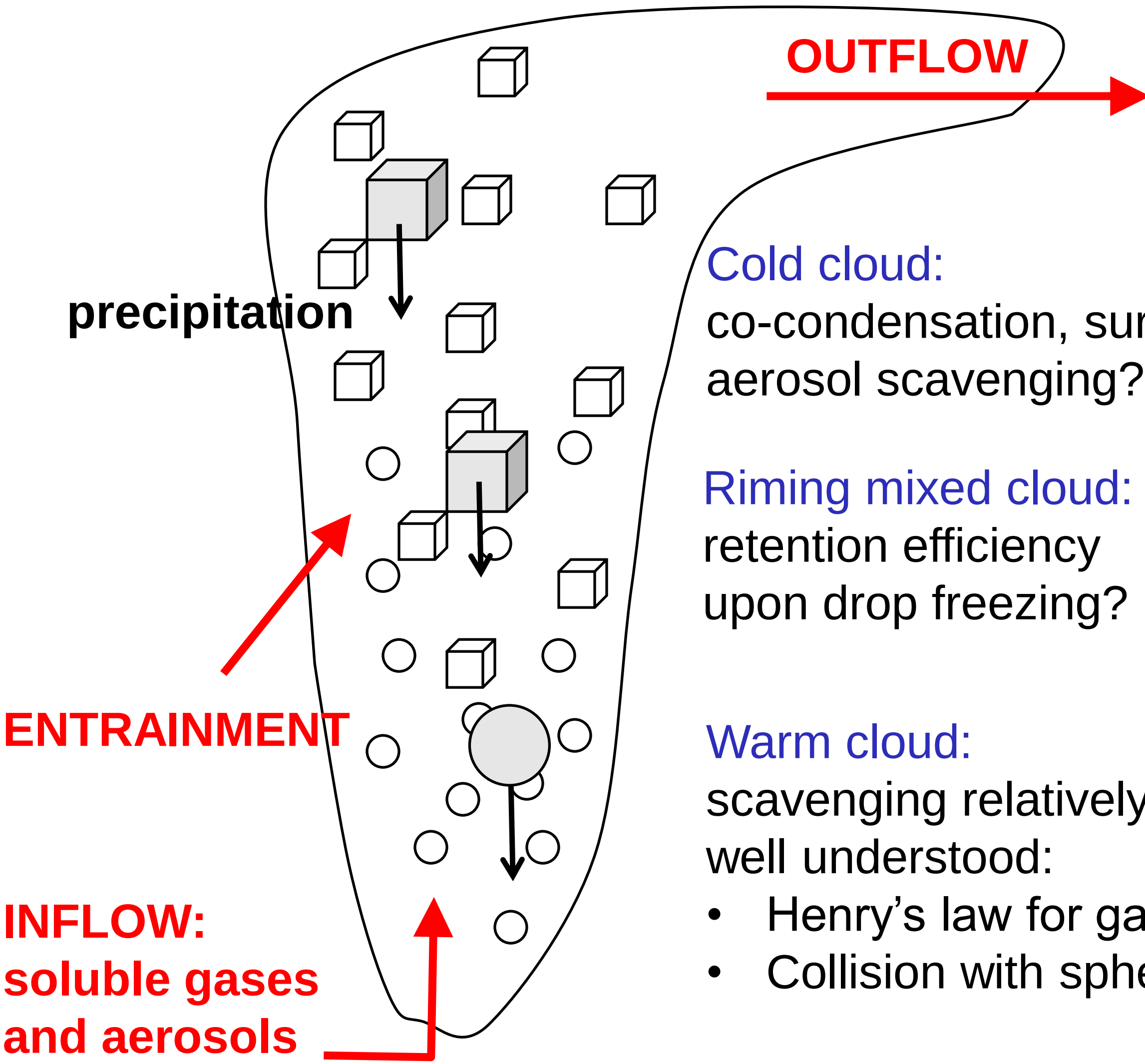
Bayesian optimization

Posterior emission estimate
$\mathbf{E} \pm \sigma$

Deposition processes



Scavenging processes in convective updrafts



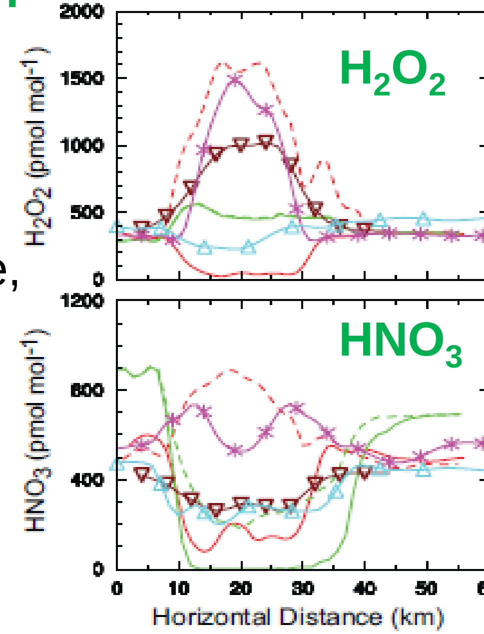
Cold cloud:
co-condensation, surface uptake, aerosol scavenging?

Riming mixed cloud:
retention efficiency upon drop freezing?

Warm cloud:
scavenging relatively well understood:

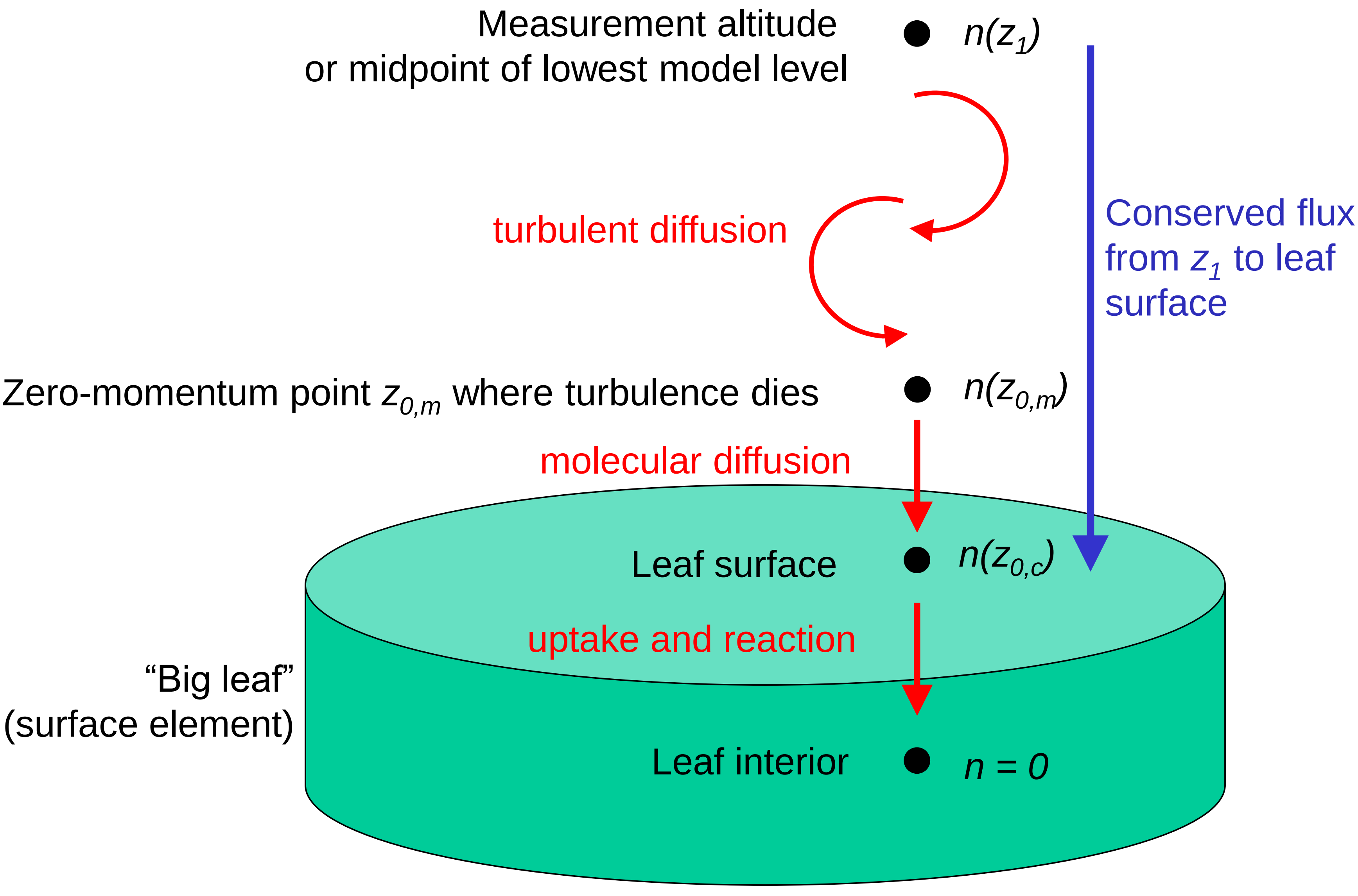
- Henry's law for gases
- Collision with spherical drops for aerosols

Model intercomparison deep convective outflow



Barth et al. [2007]

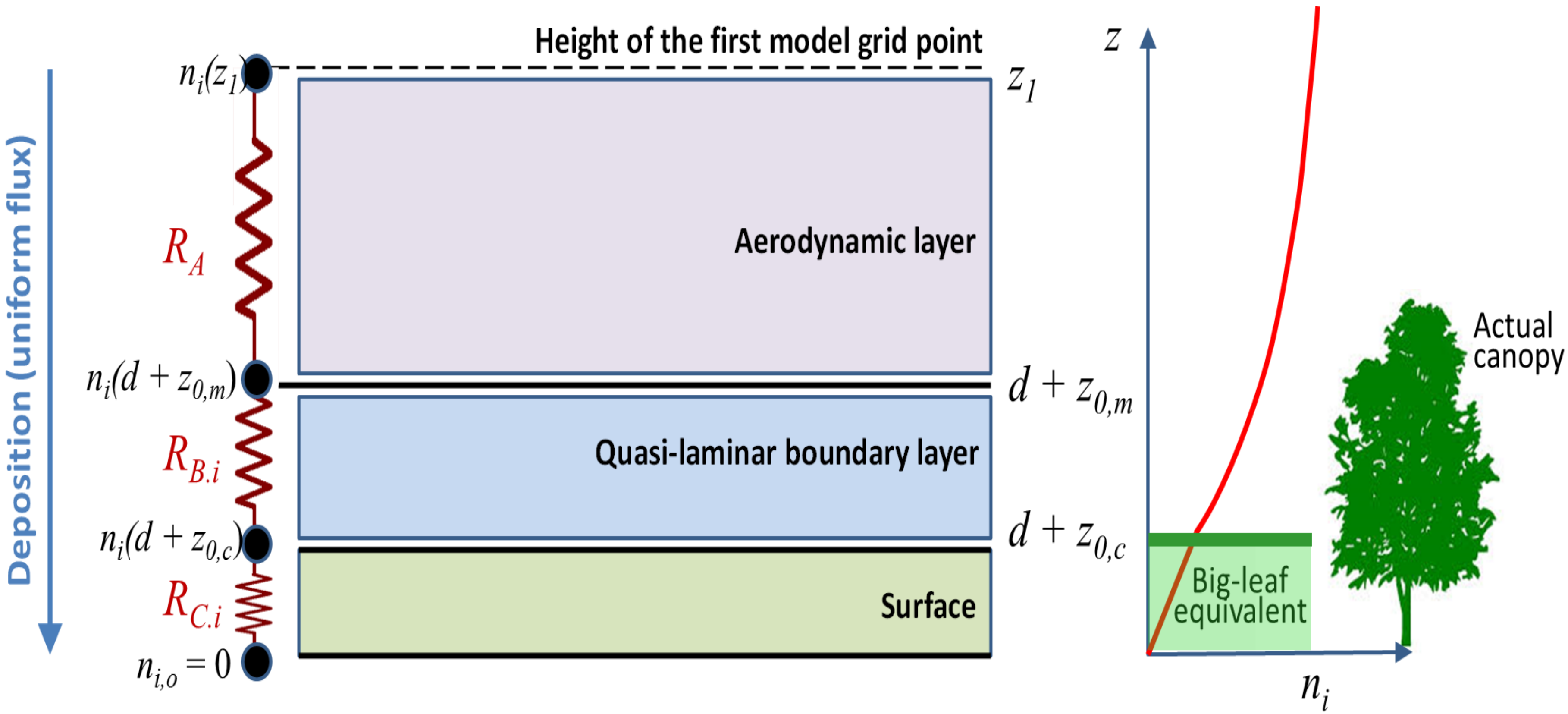
“Big-leaf” modeling of dry deposition



Big-leaf resistance-in-series model for dry deposition

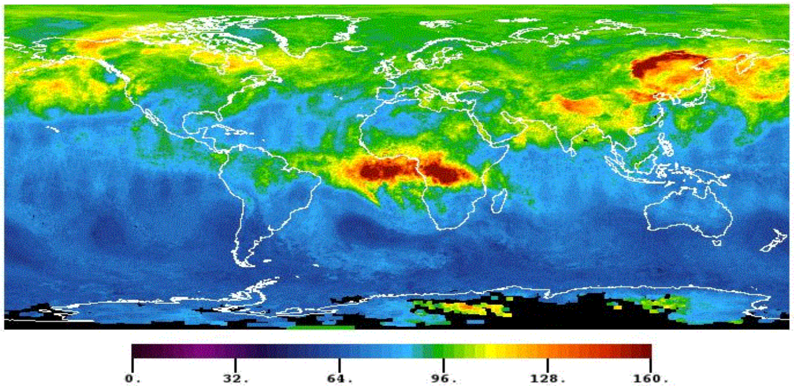
Deposition flux $F = -V(z_1)n(z_1)$

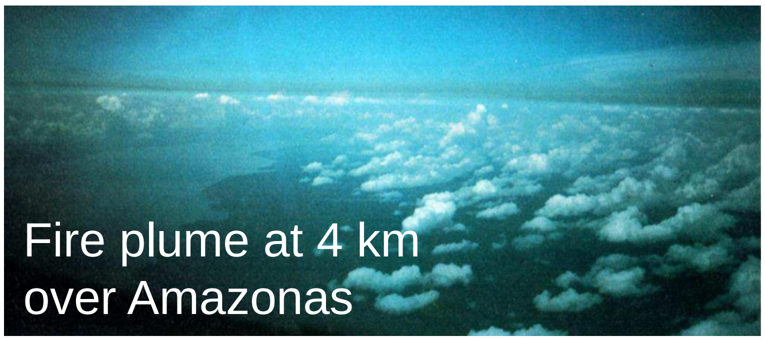
where deposition velocity $V(z_1) = 1/(R_A(z_1) + R_{B,i} + R_{C,i})$



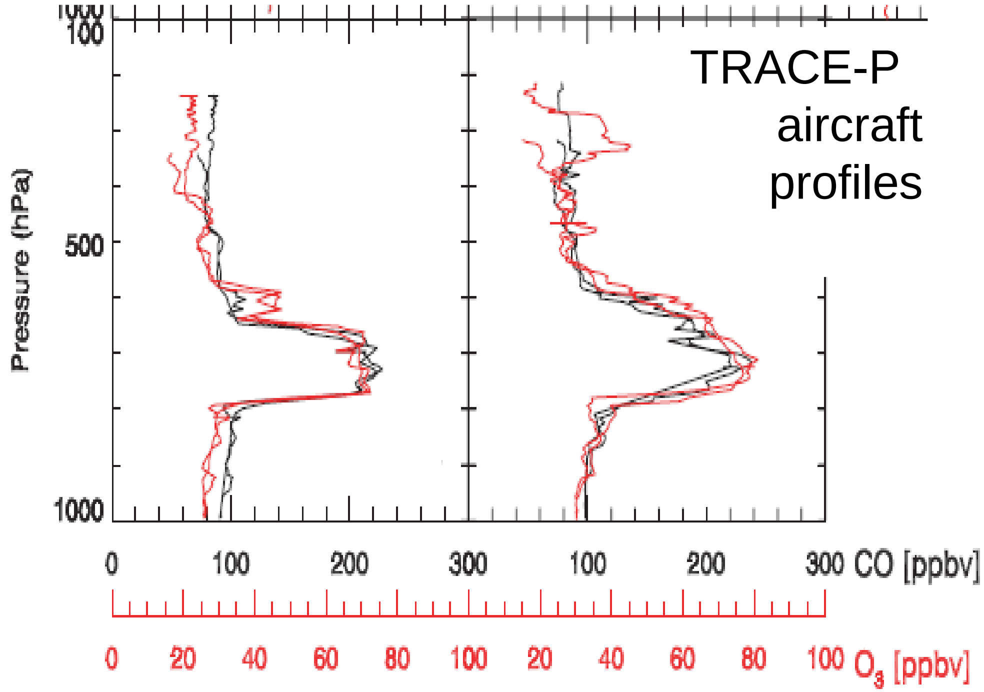
Long-lived chemical plumes in the free troposphere

Free tropospheric CO from AIRS



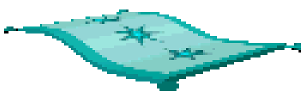


CO and ozone Asian pollution over Pacific



Much of pollution transport on global scale takes place in layers that retain their integrity for over a week, spreading/filamenting horizontally over 1000s of km and vertically over ~1 km

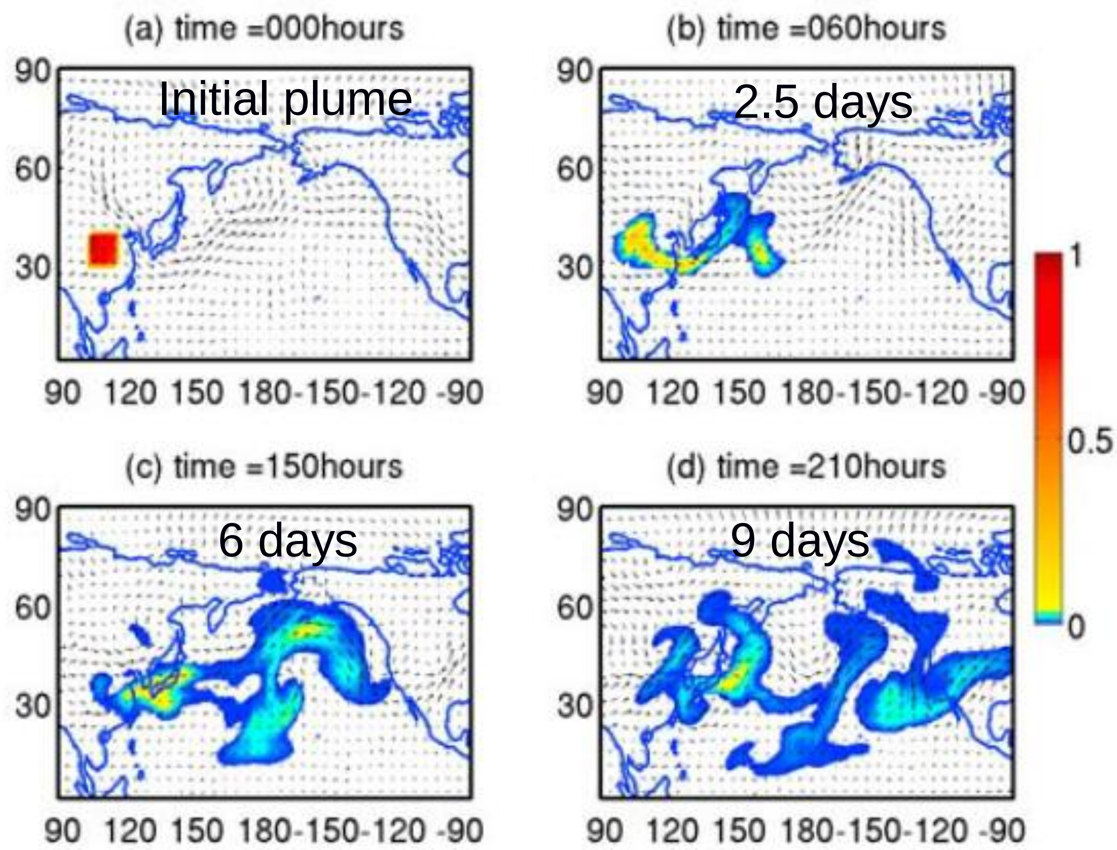
Think of them as “pancakes” or “magic carpets”

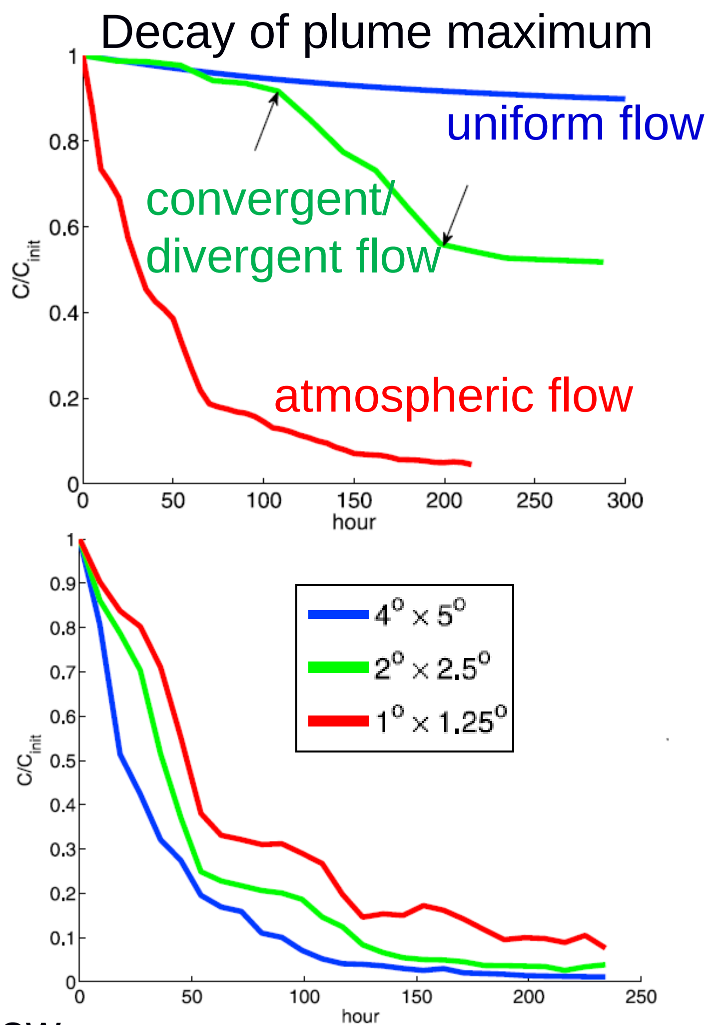


Andreae et al., 1988; Heald et al., 2003

Difficulty of preserving free tropospheric layers in Eulerian models

2-D pure advection $\partial C / \partial t = -\mathbf{u}\nabla C$ of inert Asian plume in GEOS-Chem
Advection scheme is 3rd-order piecewise parabolic method (PPM)

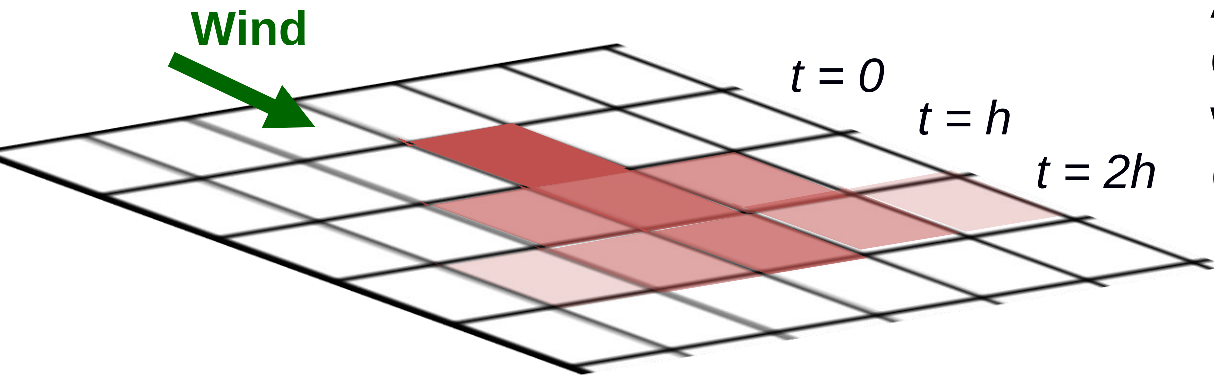




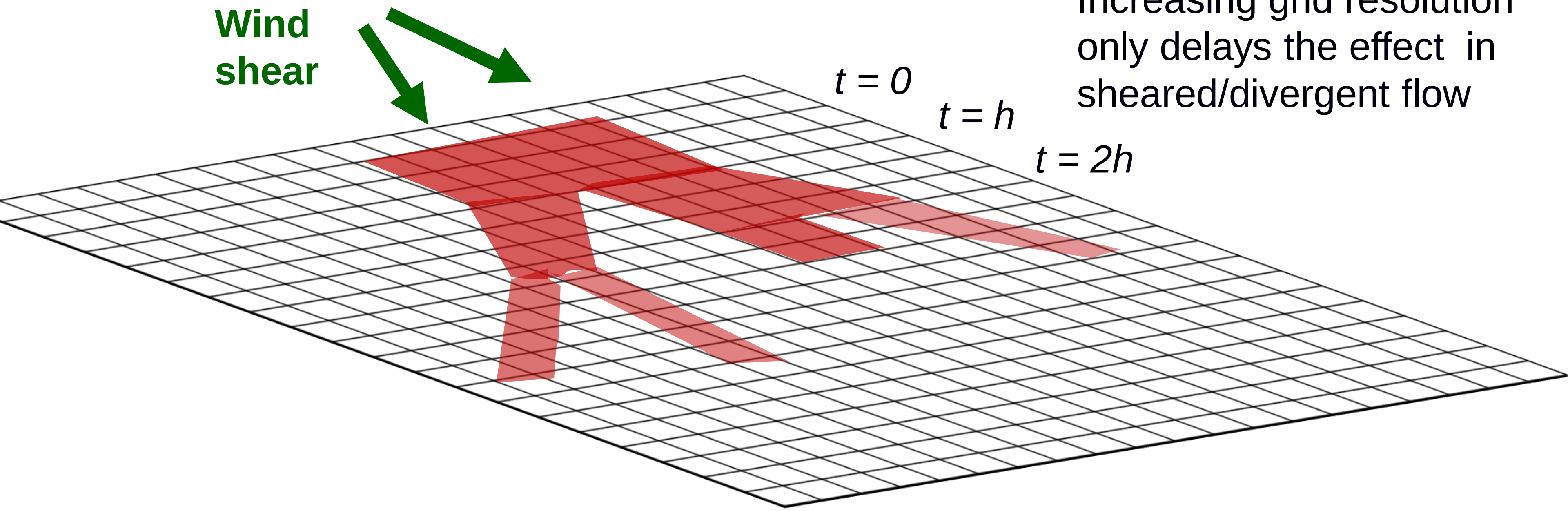
- Advection equation should conserve mixing ratio
- 3rd-order advection scheme fails in divergent/shear flow
- Increasing resolution yields only moderate improvement

Rastigejev et al. [2010]

Why this difficulty? Numerical diffusion as plume shears



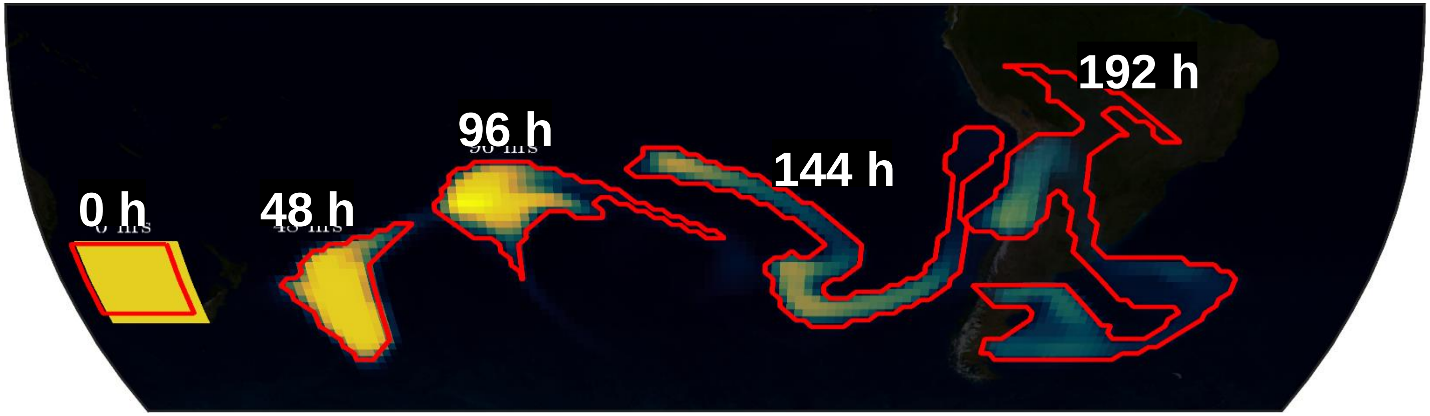
A high-order advection scheme decays to 1st-order when it cannot resolve gradients (plume width ~ grid scale)



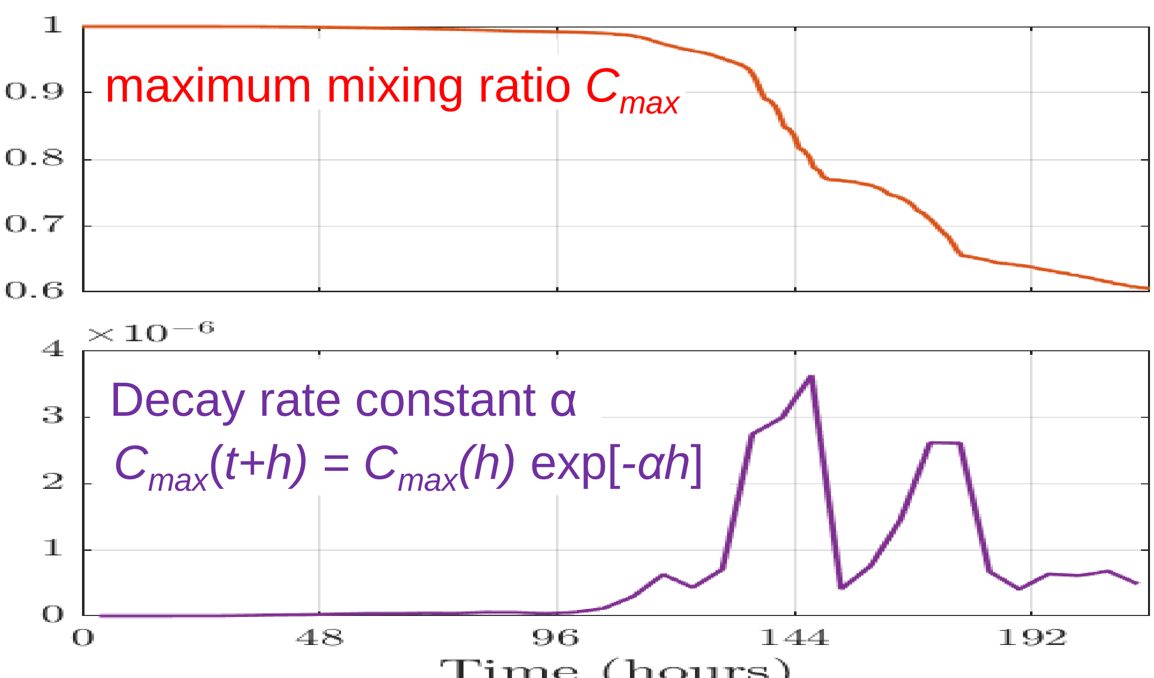
Increasing grid resolution only delays the effect in sheared/divergent flow

Further investigation with 0.25ºx0.3125º version of GEOS-Chem

2-D model grid at 0.25ºx0.3125º, initial plume is 12ºx15º



Color measures volume mixing ratio (VMR)

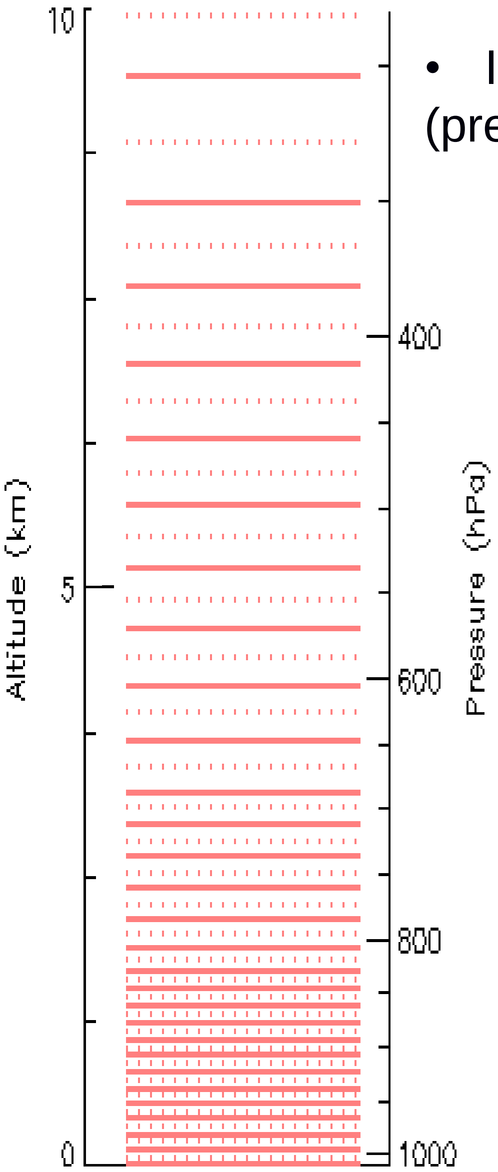


Plume is preserved for 5 days but then collapses rapidly

Eastham et al. [2017]

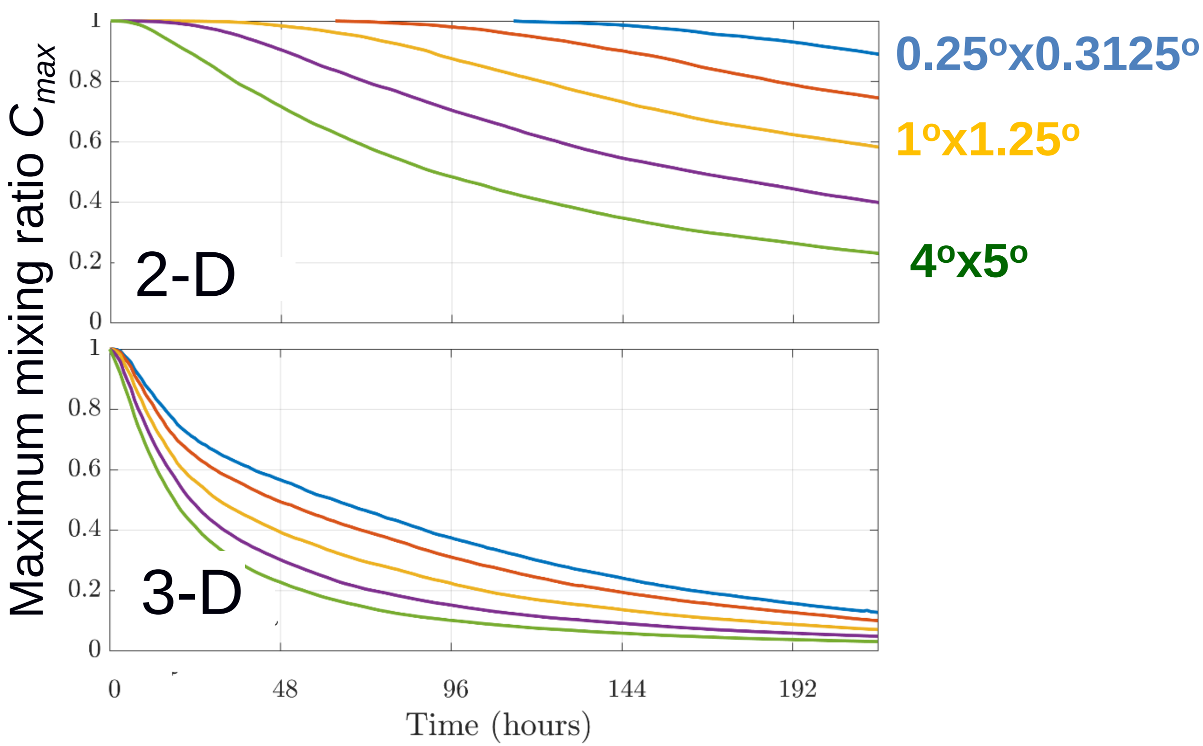
Vertical grid resolution is even more limiting at present

GEOS-Chem vertical levels



- Increasing vertical resolution in free troposphere (presently ~0.5 km) has received low priority in models so far

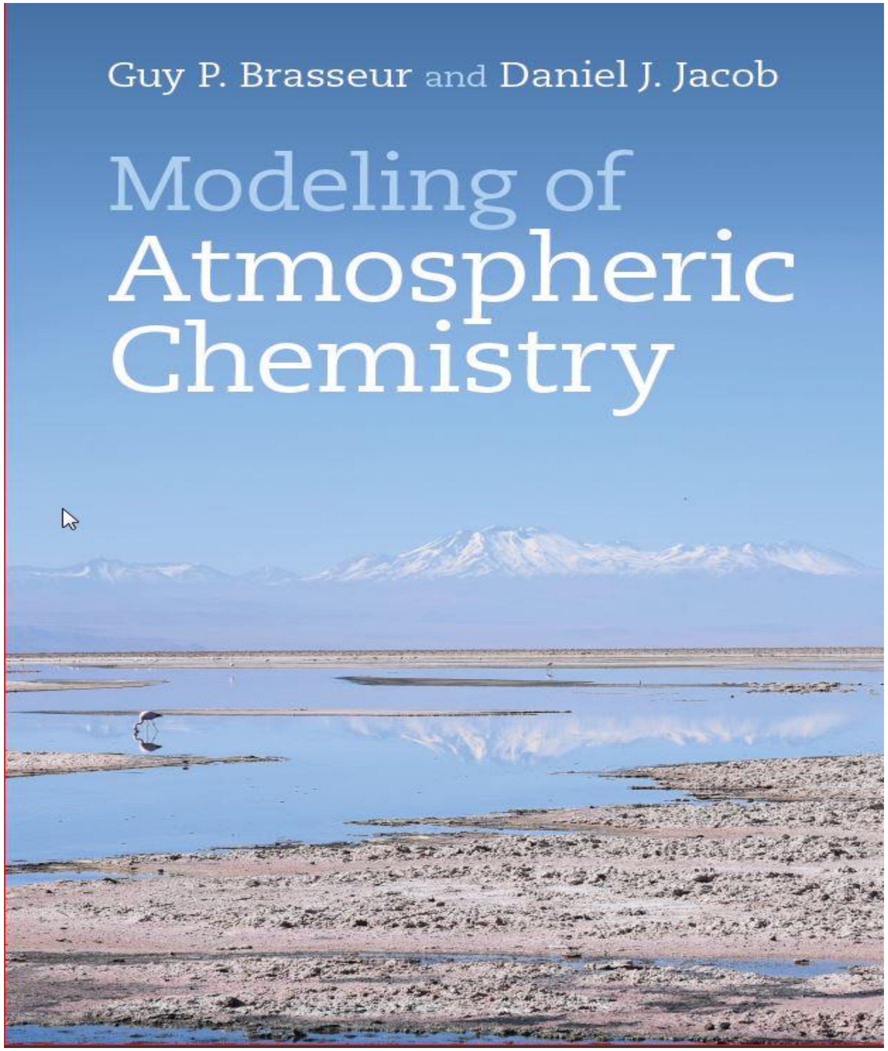
Plume decay rate – 3D vs. 2D



Eastham et al. [2017]

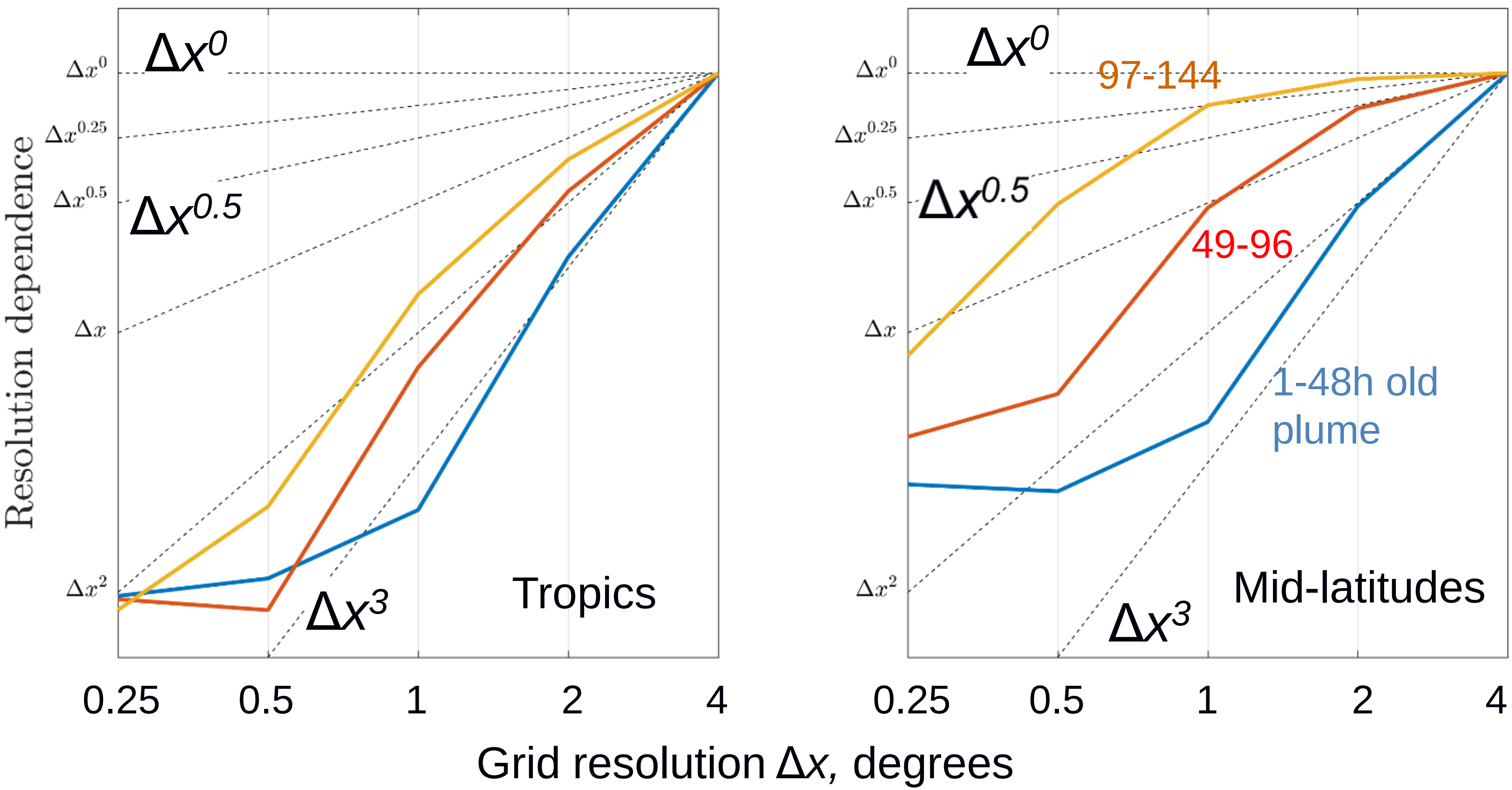
TO KNOW MORE:

Brasseur and Jacob, *Modeling of Atmospheric Chemistry,* Cambridge University Press, 2017



Grid resolution dependence of plume dissipation

How does the plume decay rate constant α depend on the grid resolution Δ*x*?

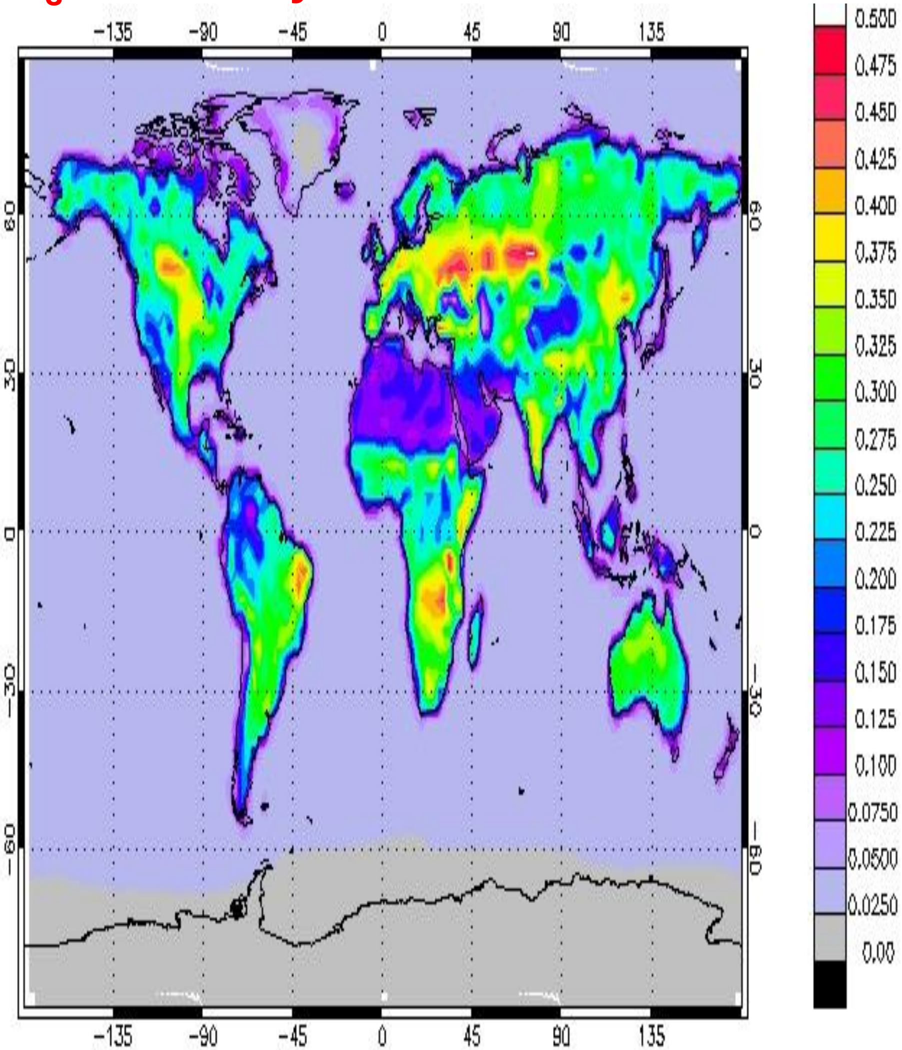


- Numerical diffusion limited by intrinsic numerical accuracy has $\alpha \sim \Delta x^3$
- Numerical diffusion limited by shear/stretching has $\alpha \sim \Delta x^{0.25\text{-}0.5}$

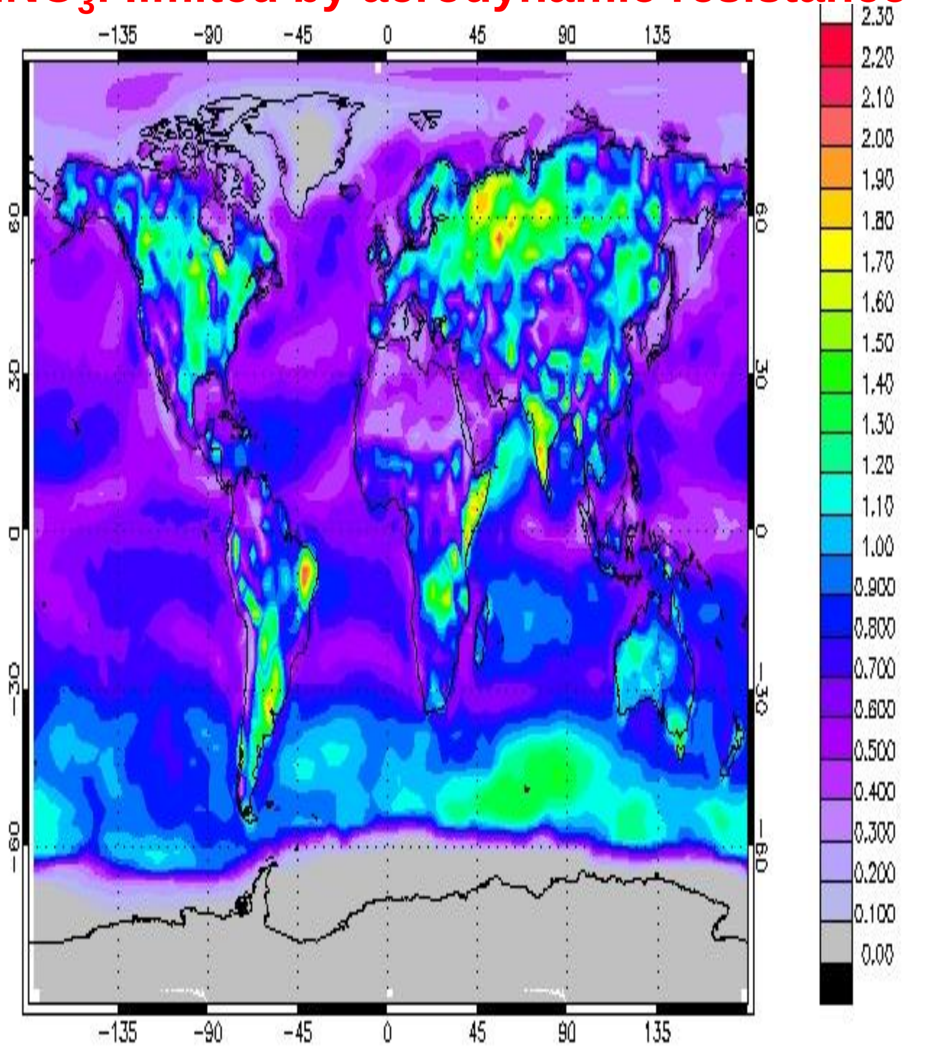
Sebastian Eastham, Harvard

July mean deposition velocities of ozone and nitric acid

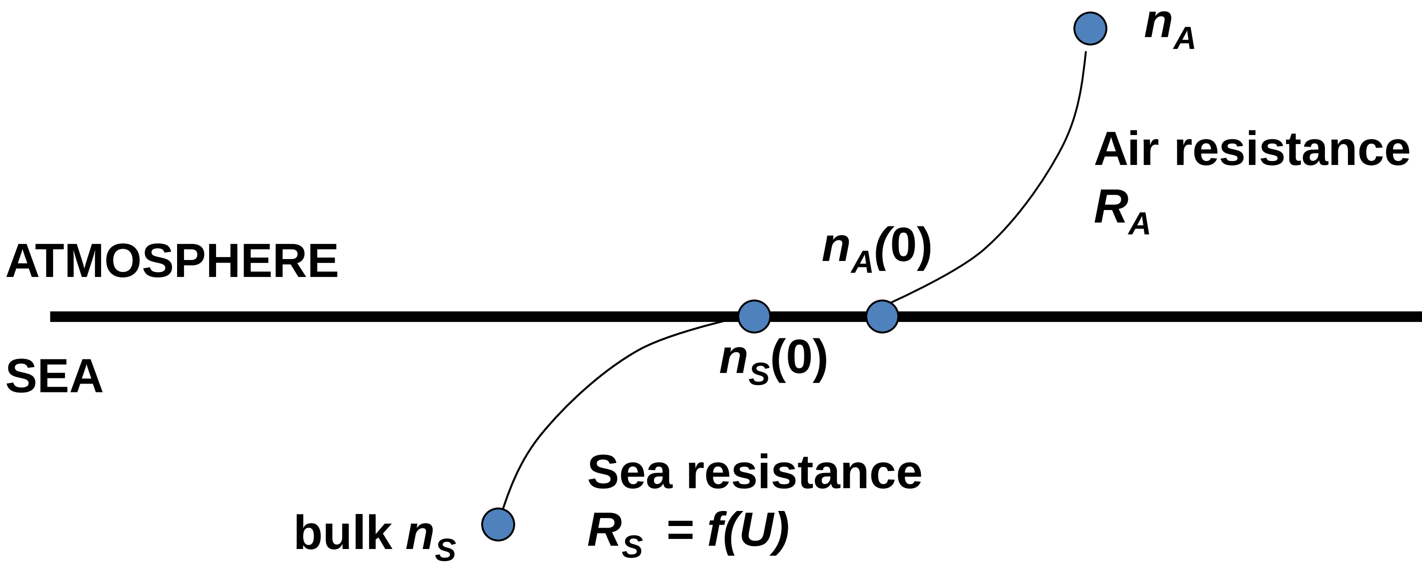
O_3: limited by surface resistance



HNO_3: limited by aerodynamic resistance



Bi-directional exchange



exchange
velocity

Net deposition flux

$$F = \frac{1}{R_A + \frac{R_S}{K_H}}\left(n_A - \frac{n_S}{K_H}\right)$$

Two-way air-sea exchange of acetone

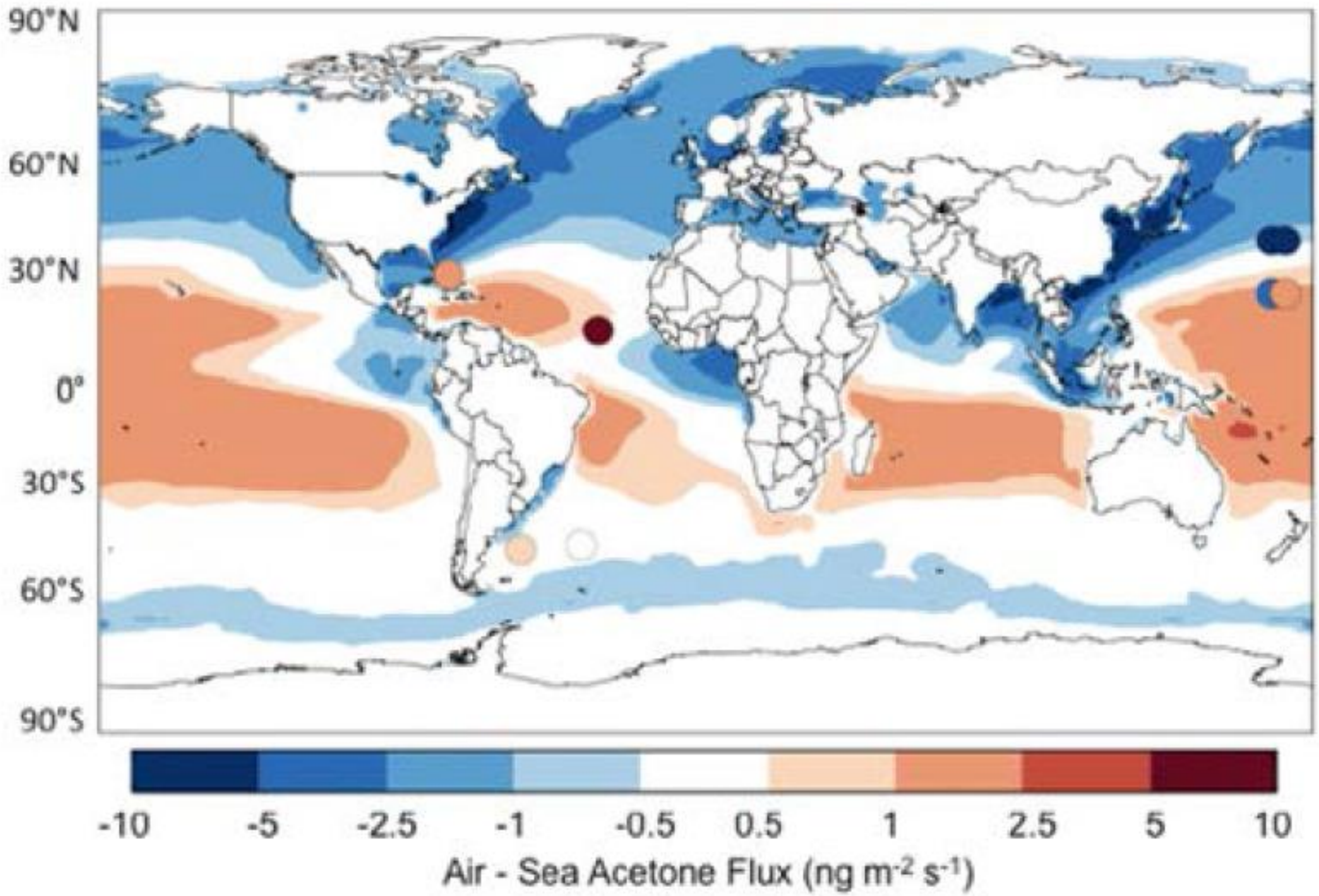


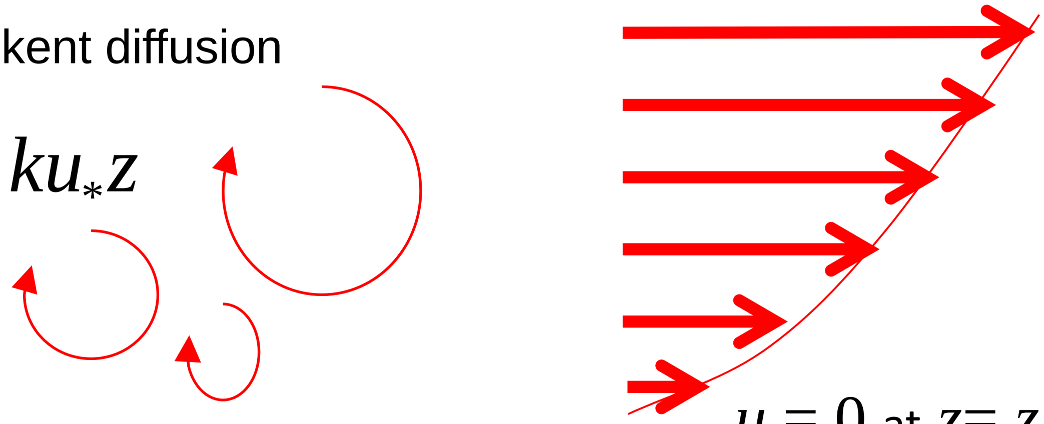
Figure 9.22. Annual mean net air-sea fluxes of acetone calculated with a global chemical transport model assuming a fixed surface ocean acetone concentration of 15 nM. Circles indicate ship observations. From Fischer et al. (2012).

Modeling dry deposition: turbulent flow over flat surface

mean wind

Turbukent diffusion

$$K_z = k u_* z$$



$u = 0$ at $z = z_{o,,m}$ (roughness height)

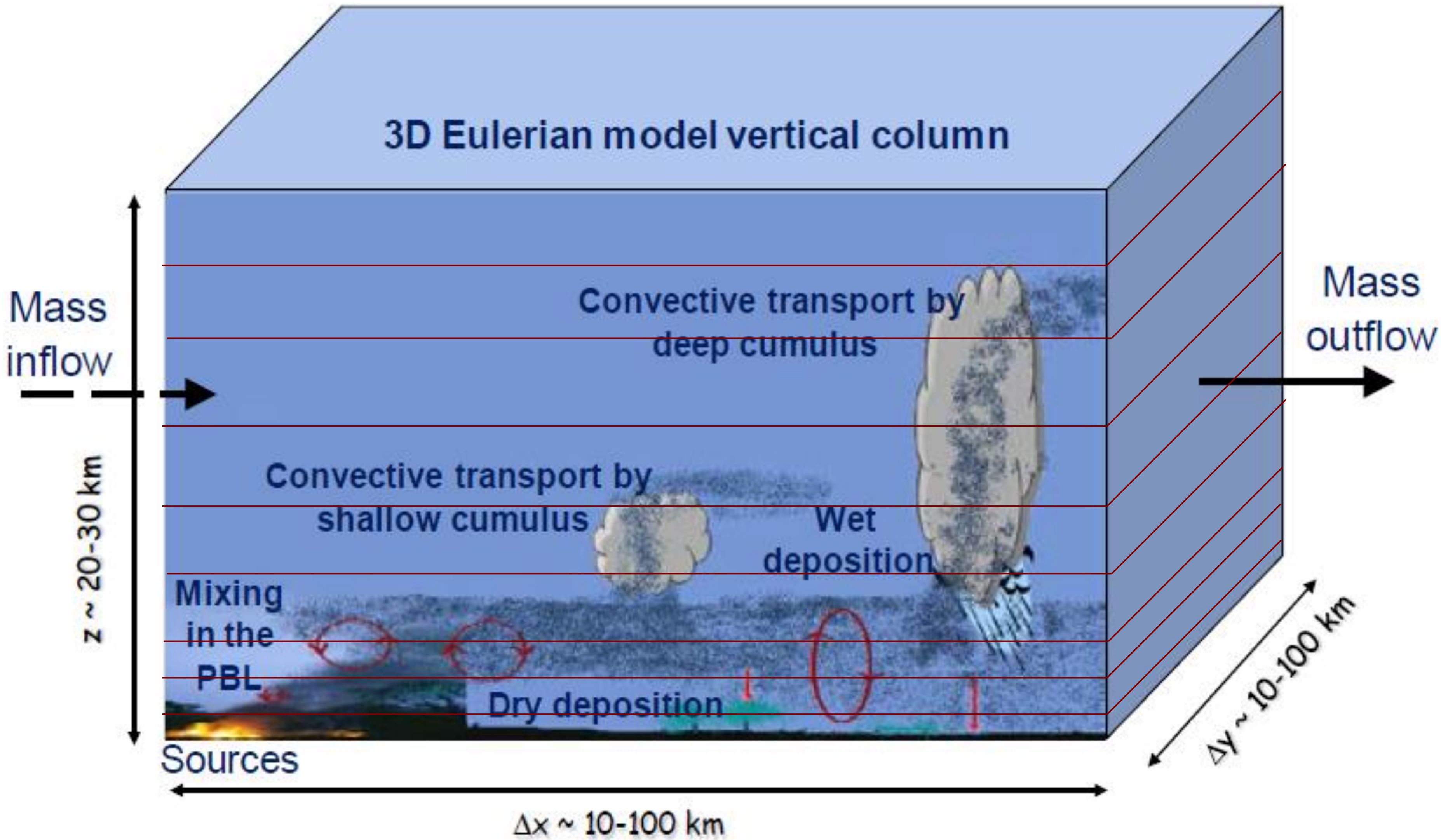
quasi-laminar flow for $z < z_{o,m}$

FLAT ROUGH SURFACE

Friction velocity $$u_* = \left[\frac{|F_m|}{\rho_a} \right]^{1/2}$$ **where F_m is the surface momentum flux**

$$F_m = -K_z \rho_a \frac{du}{dz} \Rightarrow \qquad u = \frac{u_*}{k} \ln \frac{z}{z_{o,m}} \qquad \text{log law for wind}$$

Subgrid-scale transport requiring parameterization in models



GEOS-Chem Chemical Transport Model:

off-line model using NASA GEOS operational meteorological archive

Input data

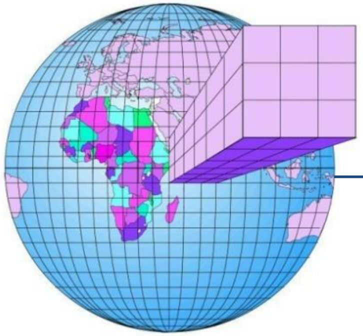
NASA GEOS-5 meteorological fields:

0.25^{o}x0.3125^{o} horizontal resolution, 72 vertical levels up to 0.1 hPa

GEOS-Chem solves 3-D chemical continuity equations on global or nested Eulerian grid

Modules

- emissions
- transport
- chemistry
- aerosols
- deposition
- sub-surface



Model adjoint

Applications

- chemical, aerosol processes
- inversions of surface fluxes
- radiative forcing
- air quality
- biogeochemistry
- …

Developed and used by over 100 research groups worldwide

Stiffness of a system of ODEs

$$\mathbf{n} = (n_1, n_2, ...n_K)^T \qquad\qquad \frac{d\mathbf{n}}{dt} = \mathbf{s}(\mathbf{n})$$

Timescales $\tau_i = -1/\lambda_I$ where λ_I are eigenvalues of Jacobian **K** = **s**/ **n**

Stiffness is defined by $$R = \frac{\max(\tau_i)}{\min(\tau_i)}$$

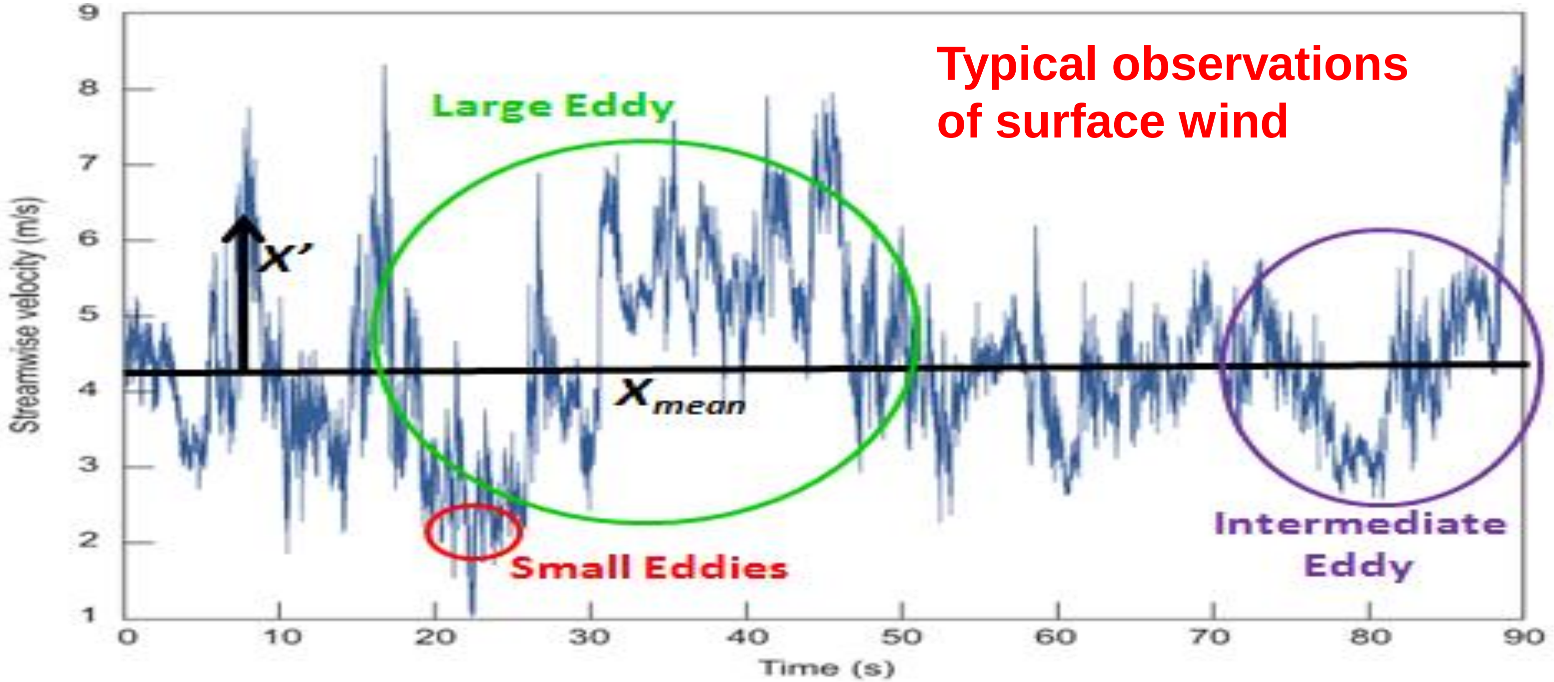
R ~ number of time steps that would be required for an explicit solver

Typical atm chem mechanisms have *R* ~ 10^9 so explicit solver is impractical

Brasseur and Jacob ch. 7.2

Dealing with subgrid turbulence

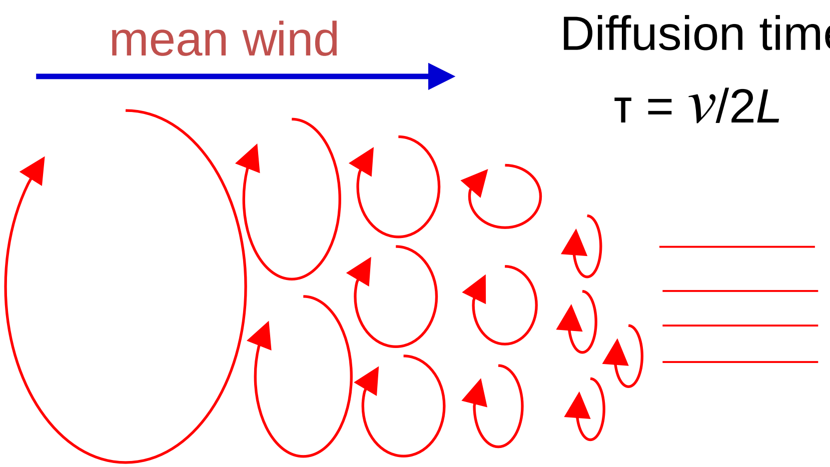
Atmospheric flow is turbulent down to mm scale where diffusion takes over



"Big whirls have little whirls,
Which feed on their velocity.
And little whirls have lesser whirls
And so on to viscosity"
Lewis Fry Richardson

Reynolds number:

Re = UL/ν



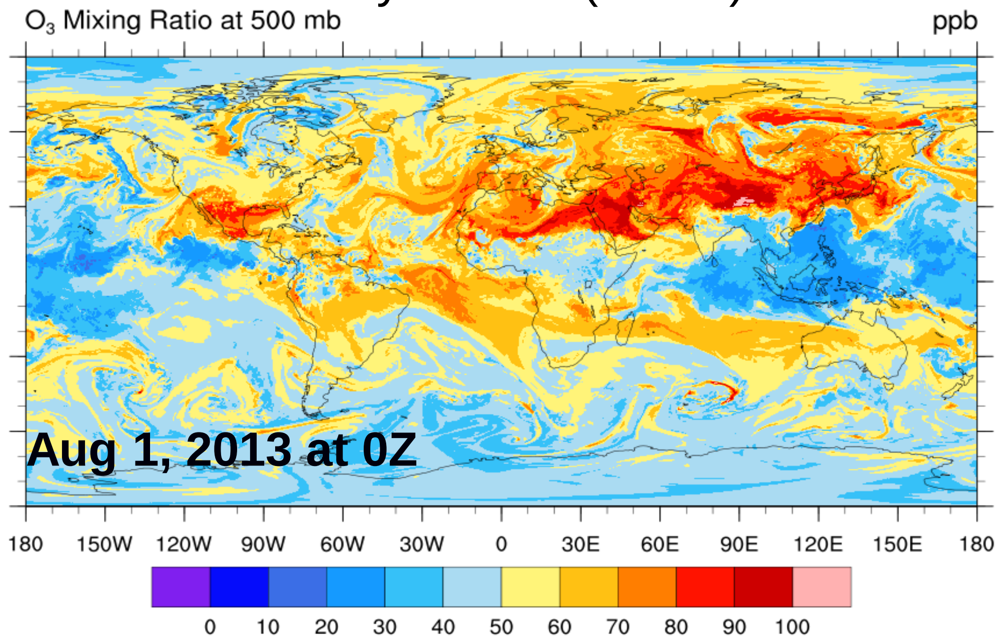
Diffusion time scale:

$\tau = \nu/2L$

On-line applications may benefit from large computational resources

GEOS-Chem chemistry in c720 (12 km) GEOS-5 GCM

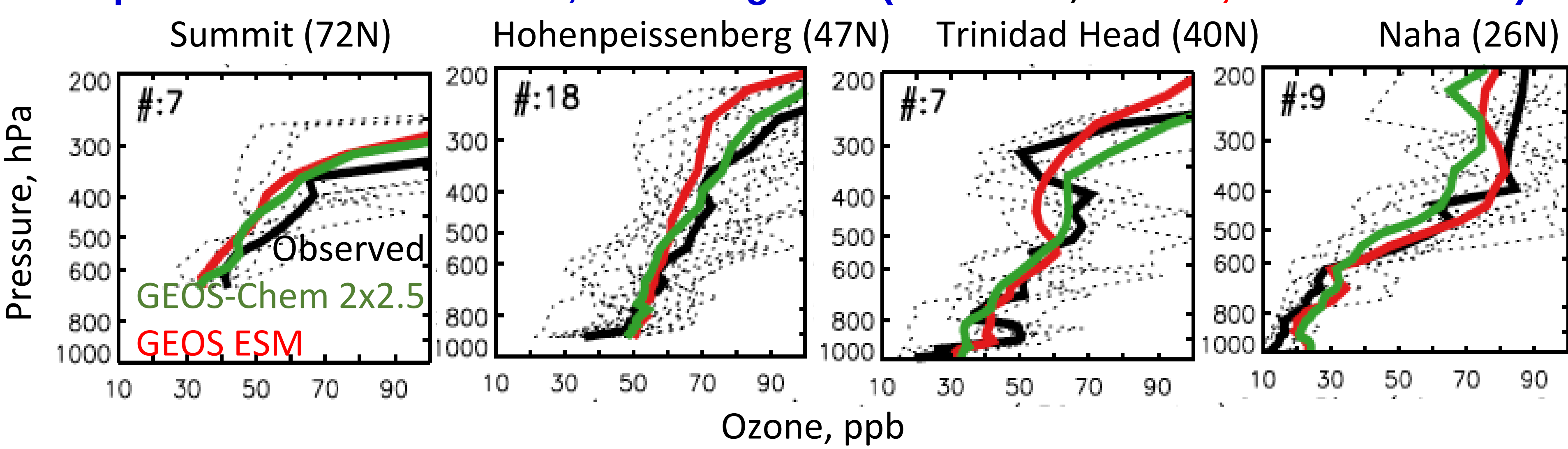
Ozone at 500 hPa



Full-year simulation:

Mike Long, Lu Hu (Harvard), Christoph Keller (NASA)

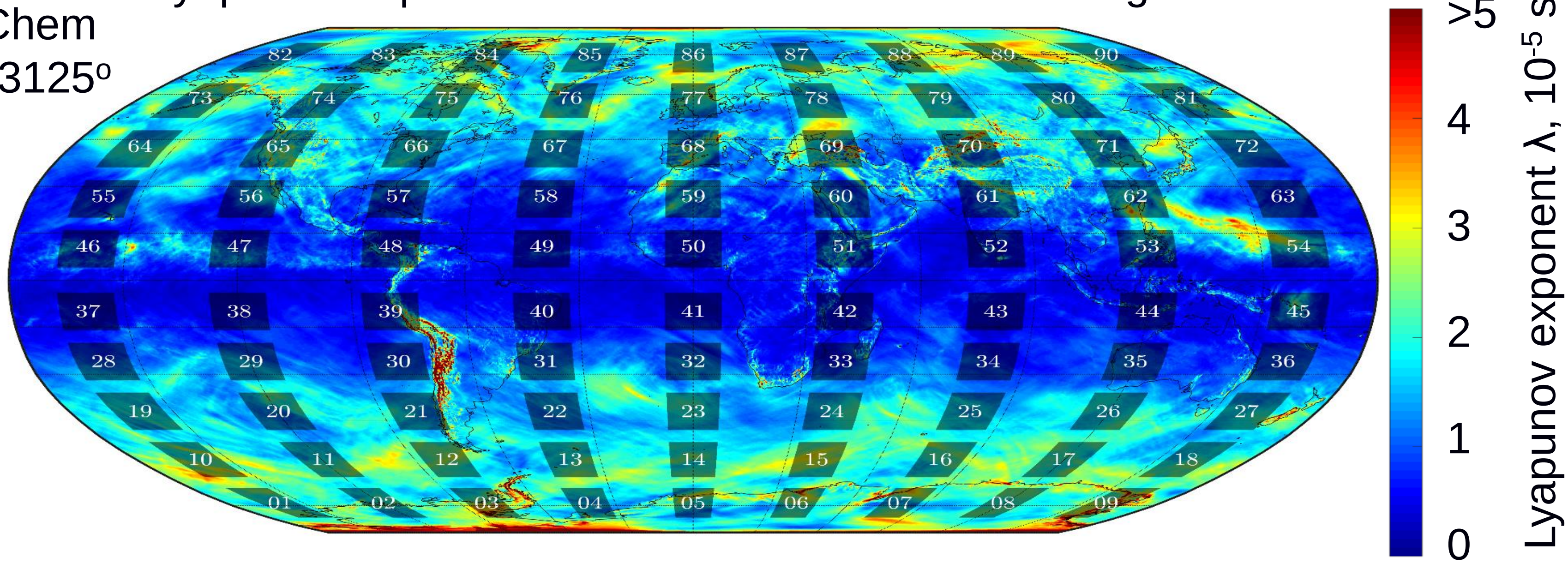
Comparison to ozonesondes, June-Aug 2013 (observed, on-line, off-line $2^o x 2.5^o$)

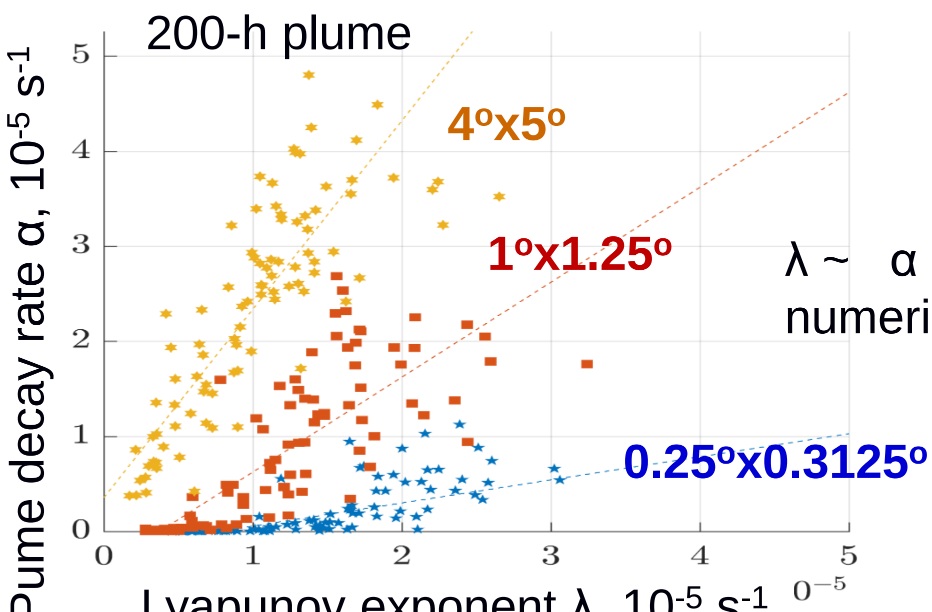


Mapping out the problem with 2-D plumes initialized worldwide

Lyapunov exponents $\lambda = \partial u/\partial x$ measure flow divergence

GEOS-Chem
0.25°x0.3125°





λ ~ α is expected for plumes where numerical diffusion is controlled by stretching

Eastham et al. [2017]