Atmospheric Chemistry - Simple Models

Casas Del Bosque winery in Casablanca valley Chile on September 26, 2013.

The atmospheric evolution of a species X is given by the continuity equation:

$$\frac{\partial [X]}{\partial t} = E_X - \nabla \bullet (\mathbf{U}[X]) + P_X - L_X - D_X$$

Local Change in Concentration with Time

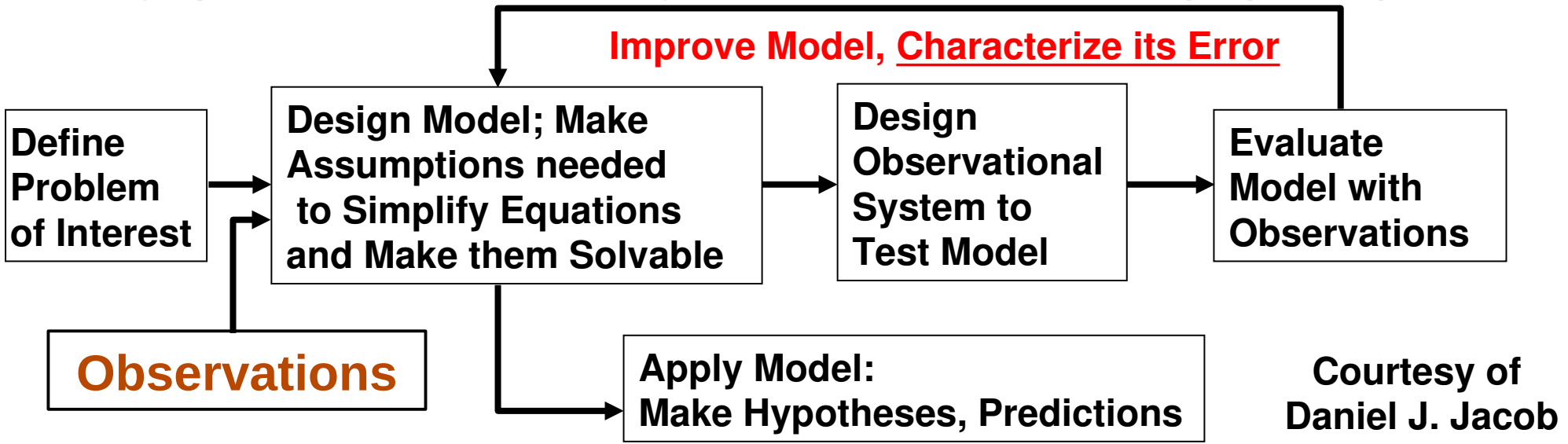
Emission

Transport (Flux Divergence; U is wind Vector)

Chemical Production and Loss (Depends on concentrations of other species)

Deposition

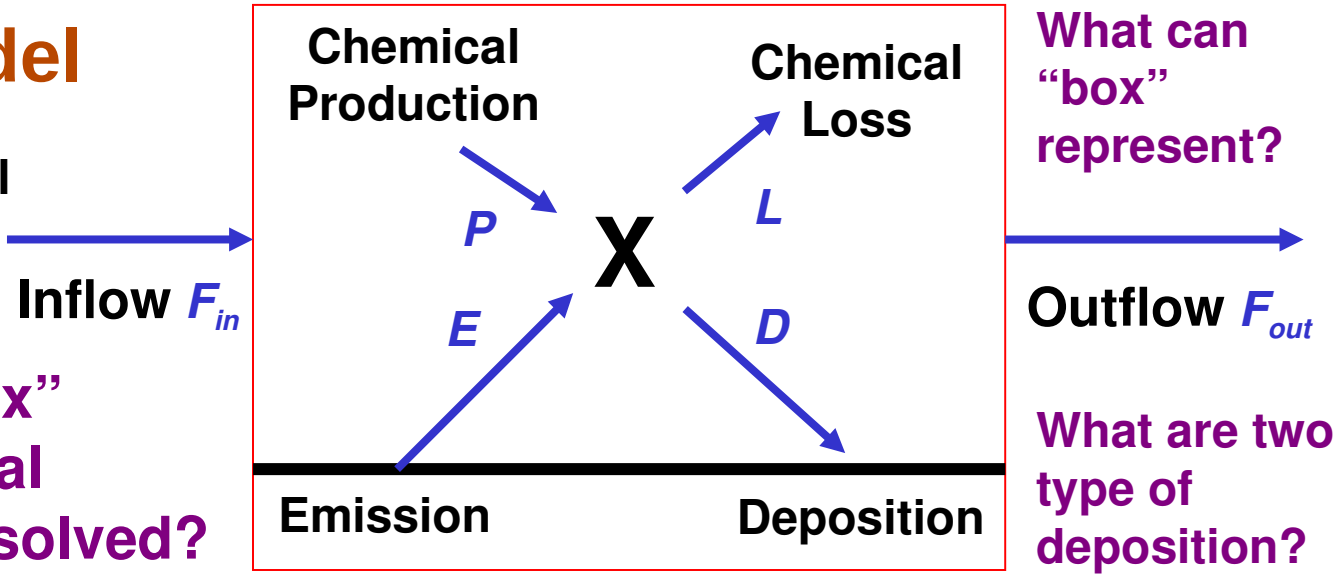
Continuity equation cannot be solved exactly; hence, need to construct model (simplified representation.



Courtesy of Daniel J. Jacob

One-Box Model

Processes that Control Concentration X



What can "box" represent?

In atmospheric "box" models is the spatial distribution of X resolved?

What are two type of deposition?

Mass balance equation: $\frac{dm}{dt} = \sum \text{sources} - \sum \text{sinks} = F_{in} + E + P - F_{out} - L - D$

Atmospheric lifetime: $\tau = \frac{m}{F_{out} + L + D}$ Fraction lost by export: $f = \frac{F_{out}}{F_{out} + L + D}$

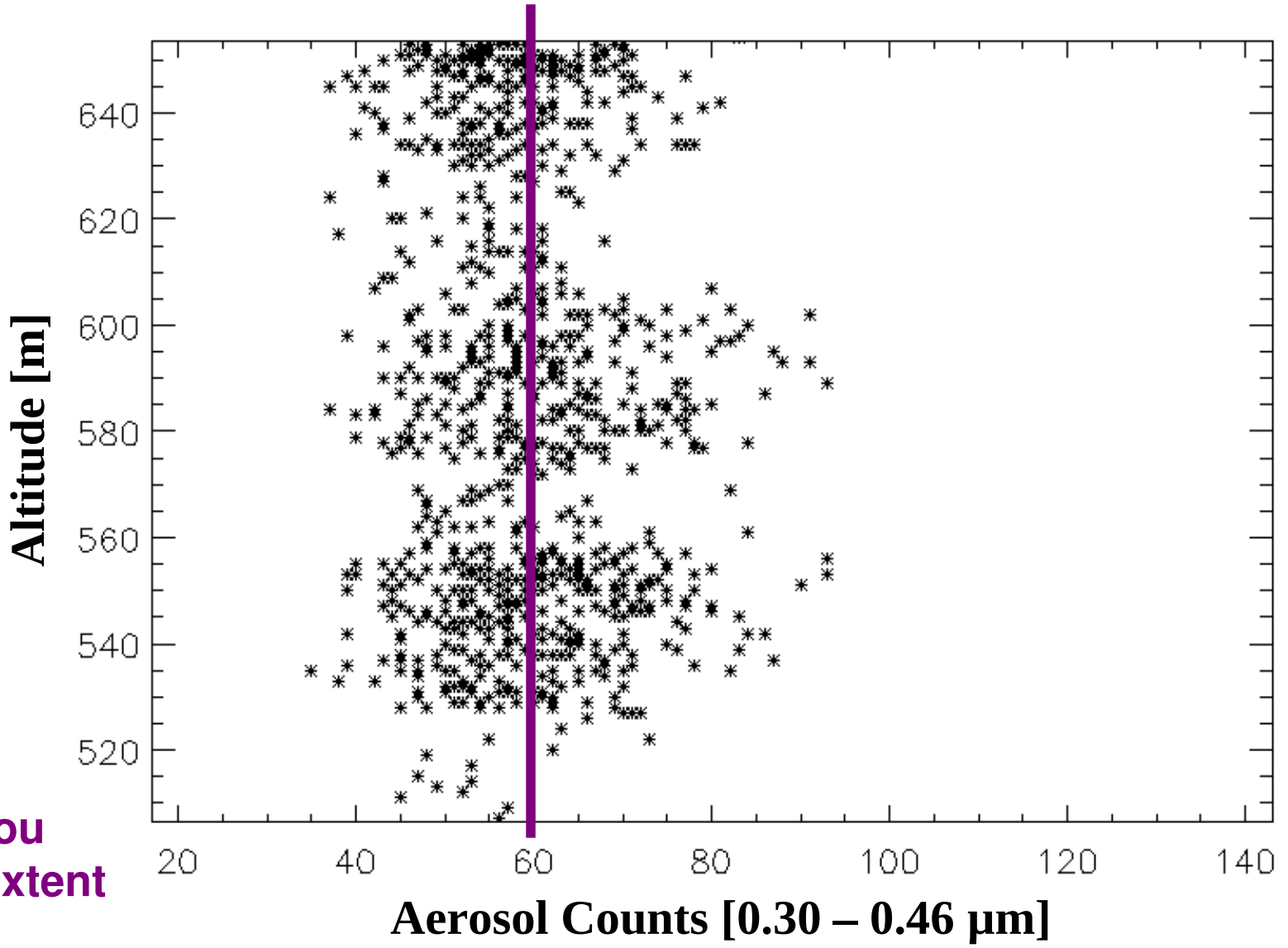
Lifetimes Add in Parallel: $\frac{1}{\tau} = \frac{F_{out}}{m} + \frac{L}{m} + \frac{D}{m} = \frac{1}{\tau_{export}} + \frac{1}{\tau_{chem}} + \frac{1}{\tau_{dep}}$

Loss Rate Constants Add in Series: $k = \frac{1}{\tau} = k_{export} + k_{chem} + k_{dep}$

Courtesy of Daniel J. Jacob

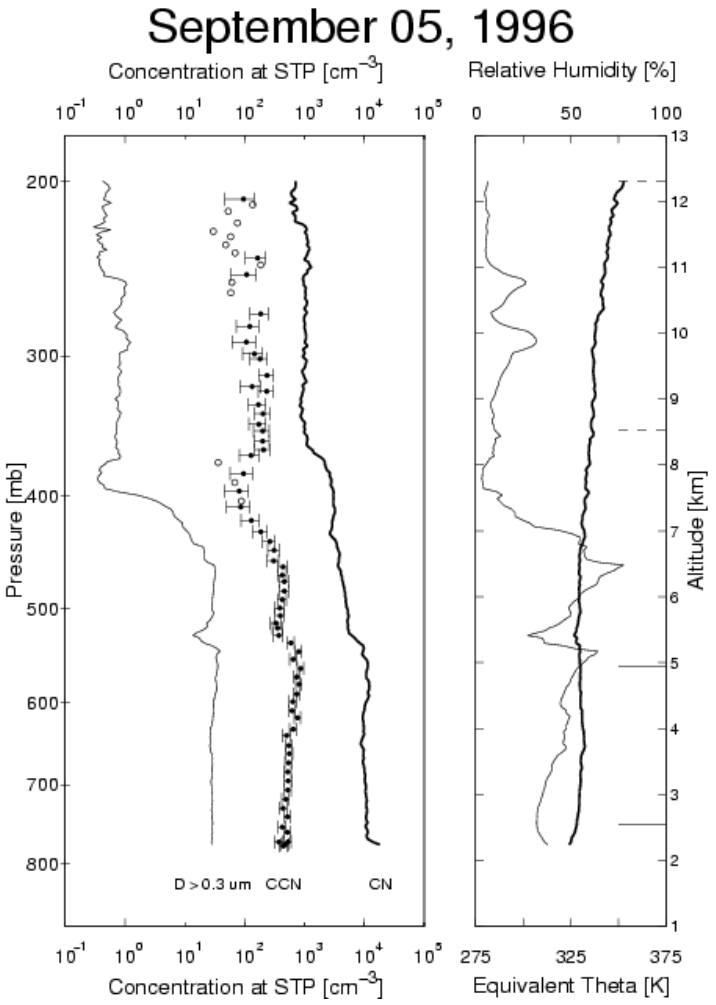
Well Mixed Atmosphere

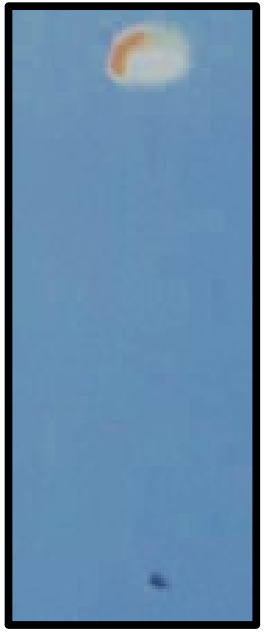
Measurements made 19 September 2011 (10:35-11:00 local time) at Camp Grafton South using the Telemaster Unmanned Aircraft System's Meteorological Package.



What height could you use for the vertical extent of a box model?

Laramie Wyoming Balloon Measurement





Delene, D. J. and T. Deshler, Calibration of a Photometric Cloud Condensation Nucleus Counter Designed for Deployment on a Balloon Package, Journal of Atmospheric and Oceanic Technology, 17, 459-467, 2000.

Example: Global Box Model for CO_2 (Pg C yr^{-1})

	1980s	1990s
Atmospheric Increase	3.3 ± 0.1	3.2 3.3 ± 0.1
Emissions (Fossil Fuel, Cement)	5.4 ± 0.3	6.3 ± 0.4
Ocean-atmosphere Flux	-1.9 ± 0.6	-1.7 ± 0.5
Land-atmosphere Flux	-0.2 ± 0.7	-1.4 ± 0.7
Land-use Change	1.7 (0.6 to 2.5)	NA
Residual Terrestrial Sink	-1.9 (-3.8 to 0.3)	NA

Global CO2budgets (in PgC/yr) based on intra-decadal trends in atmospheric CO2and O2. Positive values are fluxes to the atmosphere;negative values represent uptake from the atmosphere. The fossil fuel emissions term for the 1980s (Marland et al., 2000) has been slightly revised downward since the SAR. Error bars denote uncertainty (±1σ), not interannual variability, which is substantially greater.

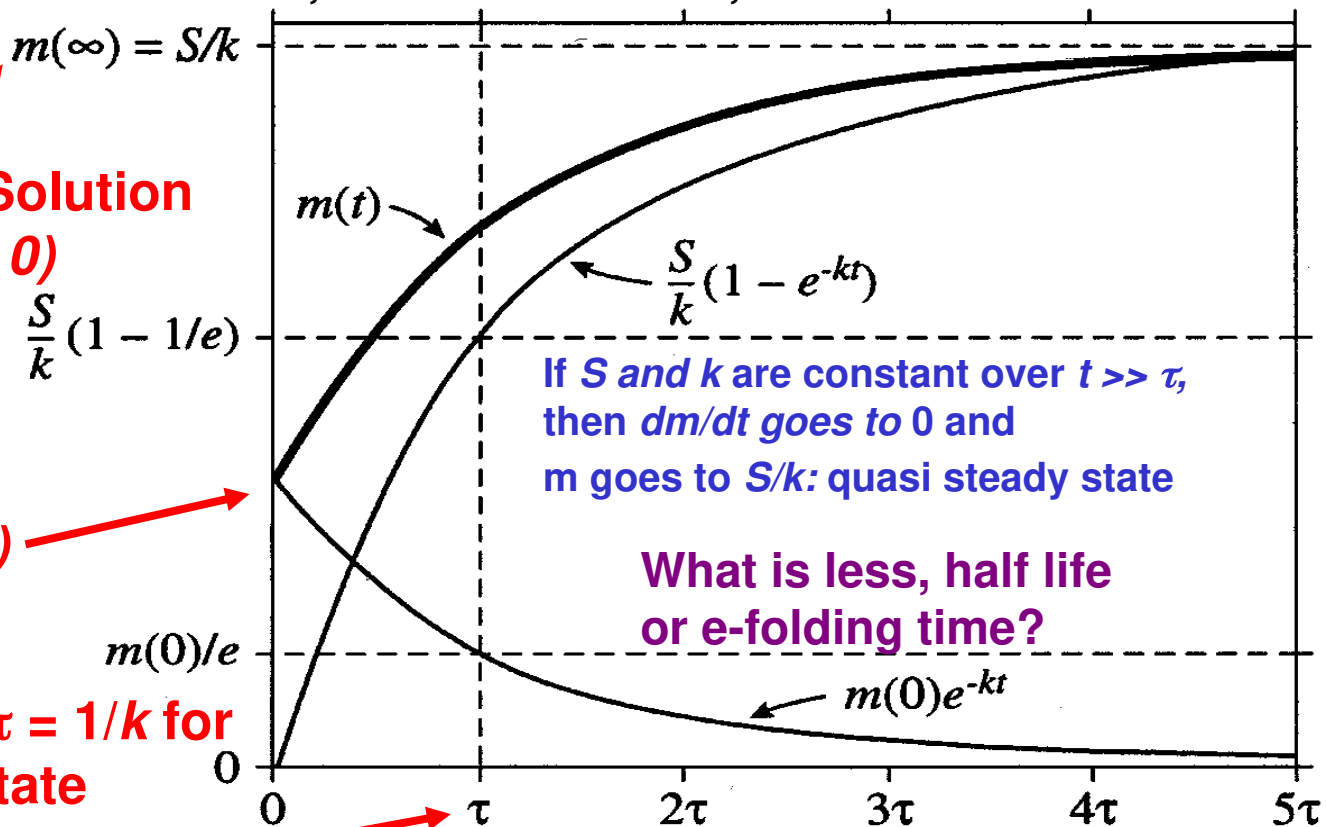
Source: IPCC [2001], Chapter 3 – The Carbon Cycle and Atmospheric Carbon Dioxide

Species with Constant Source, 1st Order Sink

$$\frac{dm}{dt} = S - km \quad \Rightarrow \quad m(t) = m(0)e^{-kt} + \frac{S}{k}(1 - e^{-kt})$$

What does 1st order mean?

τ – Life or Residence Time, k - Rate Constant, S - Source Rate



Steady State Solution (*dm/dt = 0*)

If *S and k* are constant over *t >> τ*, then *dm/dt goes to* 0 and m goes to *S/k:* quasi steady state

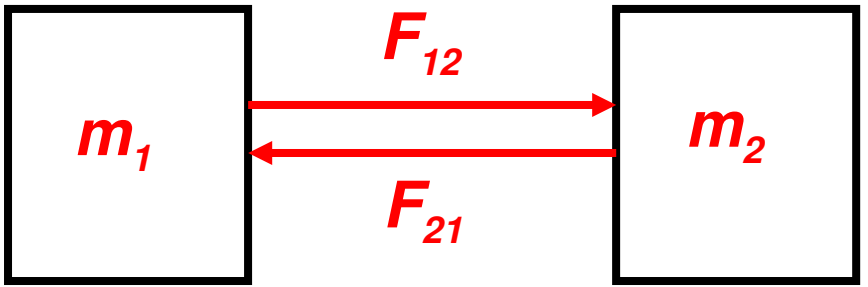
Initial Condition *m(0)*

What is less, half life or e-folding time?

Characteristic Time τ = 1/*k* for
- Reaching Steady State
- Decay of Initial Condition

Courtesy of Daniel J. Jacob

Two-box Model



Mass Balance Equations: $$\frac{dm_1}{dt} = E_1 + P_1 - L_1 - D_1 - F_{12} + F_{21}$$

(similar equation for dm_2/dt)

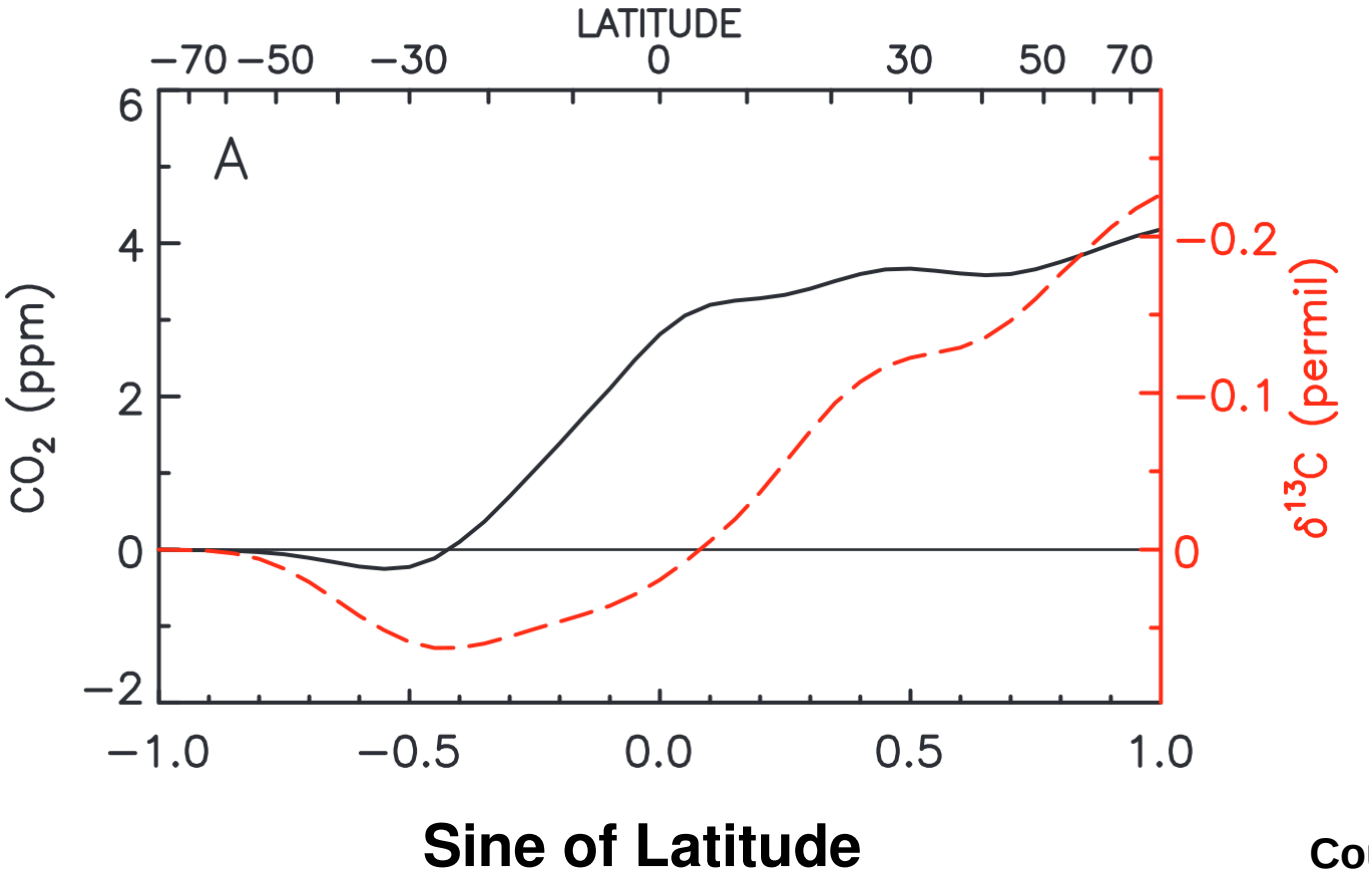
If mass exchange between boxes is first-order:

$$\frac{dm_1}{dt} = E_1 + P_1 - L_1 - D_1 - k_{12}m_1 + k_{21}m_2$$

Therefore, system of two coupled ODEs (or algebraic equations if system is assumed to be at steady state)

Courtesy of Daniel J. Jacob

Latitudinal Gradient of CO_2

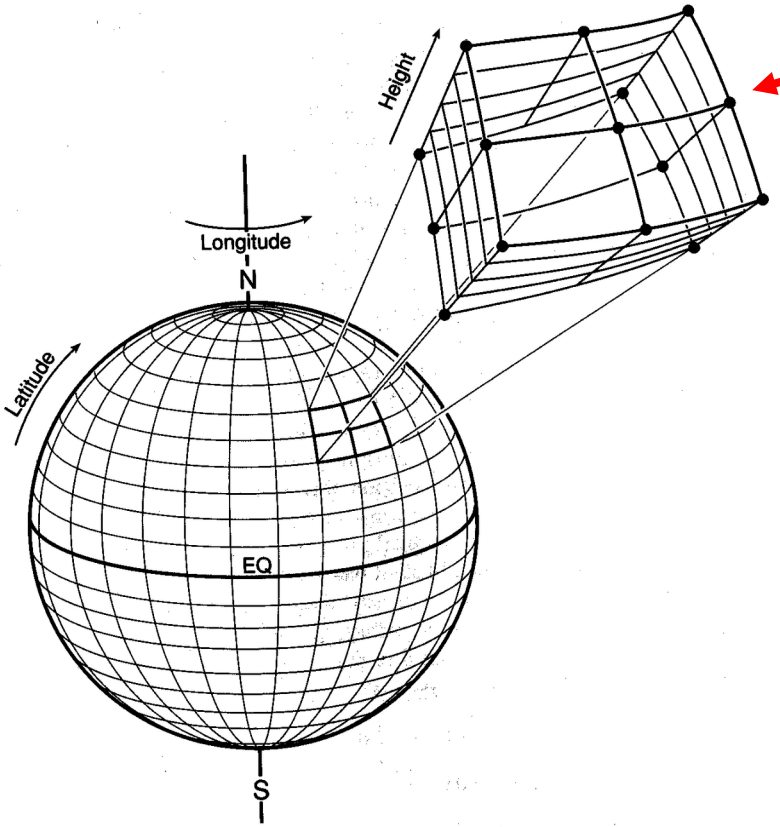


Courtesy of Peter Tans, NOAA

Observed latitudinal gradients of CO2 and δ13 C at CMDL sites located in the marine boundary layer. The δ13 C scale is plotted upside down. Long time scale of interhemispheric exchange can use 2-box model to place constraints on CO_2 sources/sinks in each hemisphere.

Eulerian Research Models Solve Mass Balance Equation in 3-D Assemblage of Grid Boxes

The mass balance equation is the finite-difference approximation of the continuity equation.



Solve Continuity Equation for Individual Grid Boxes

- **Models can presently afford ~ 10^6 grid boxes**
- **In global models, this implies a horizontal resolution of 100-500 km in horizontal and ~ 1 km in vertical**
- **Drawbacks: "numerical diffusion", computational expense**

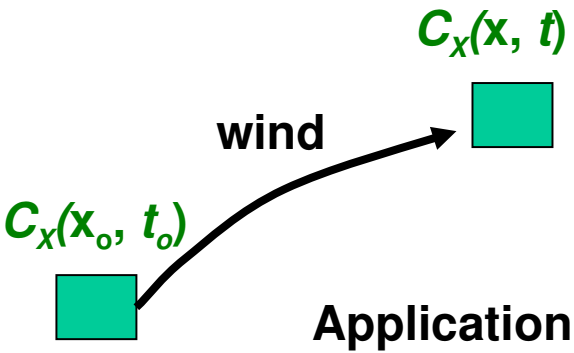
Courtesy of Daniel J. Jacob

In Eulerian Approach, Describing the Evolution of a Pollution Plume Requires a Large Number of Grid Boxes

Fire plumes over southern California on 25 October 2003.

Courtesy of Daniel J. Jacob

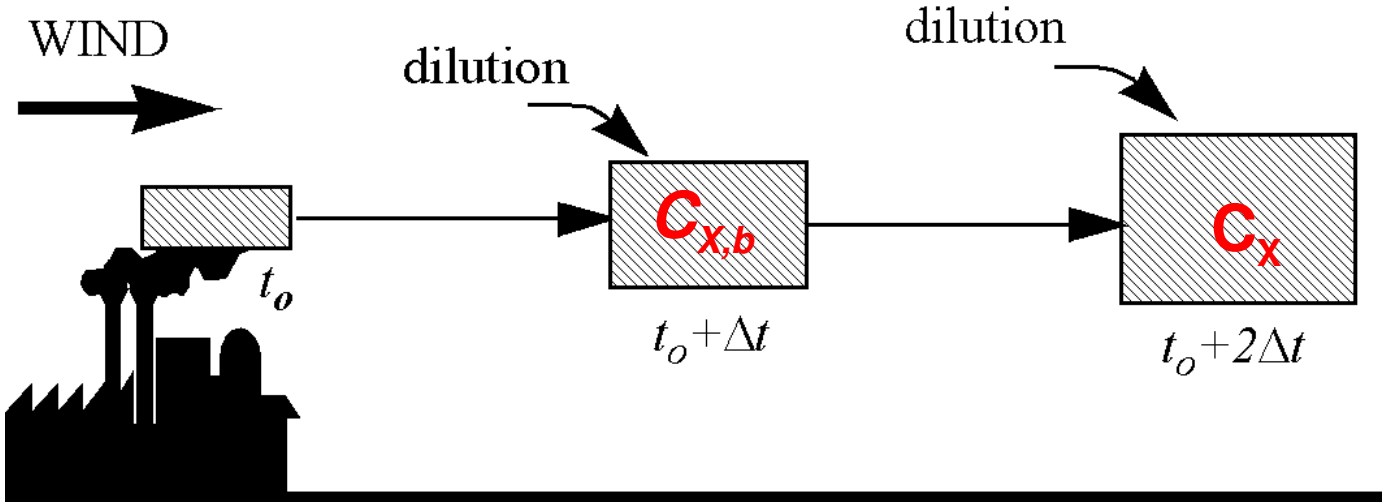
Puff Model: Follow Air Parcel Moving with Wind



In the moving puff, $\frac{dC_X}{dt} = E + P - L - D$

…no transport terms! (they're implicit in the trajectory)

Application to the chemical evolution of an isolated pollution plume:



In pollution plume,

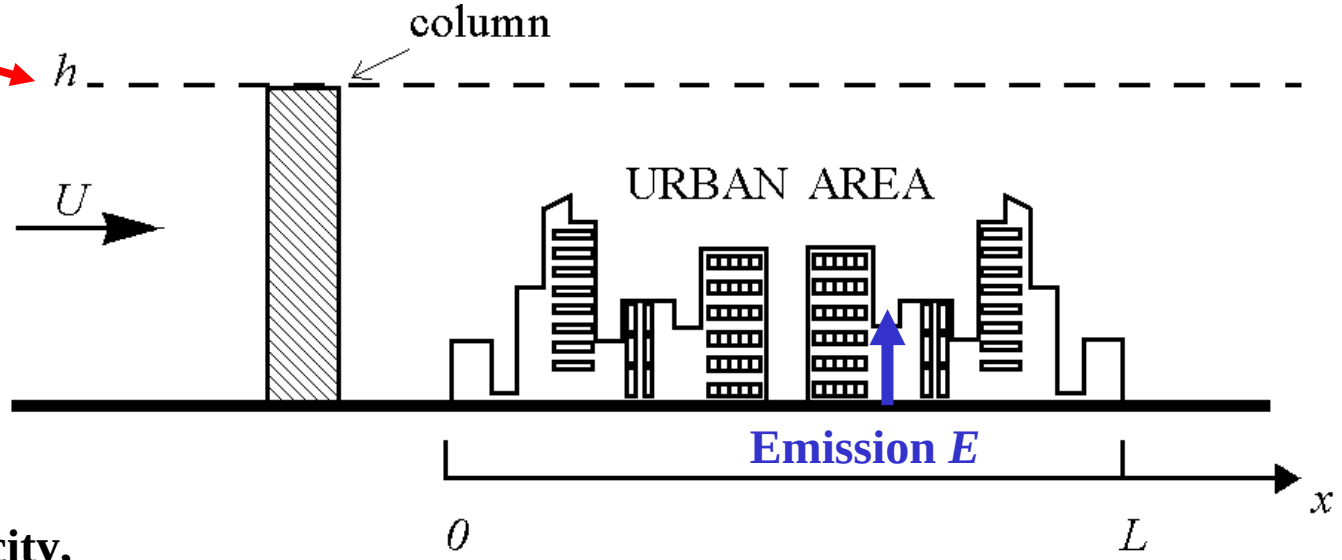
Courtesy of Daniel J. Jacob

$$\frac{dC_X}{dt} = E + P - L - D - k_{dilution}(C_X - C_{X,b})$$

$K_{dilution}$ (s-1) is the dilution rate constant
Also called entrainment rate constant

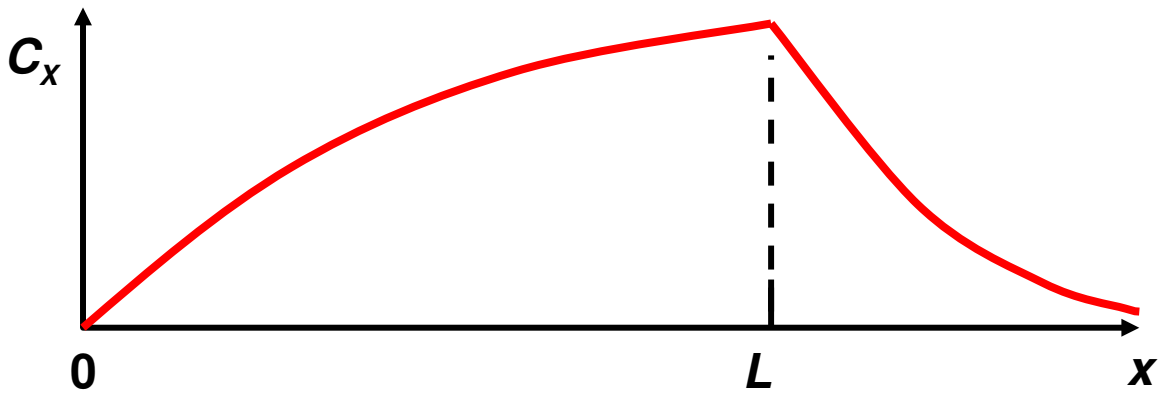
Column Model for Transport Across Urban Airshed

Temperature Inversion (defines "mixing depth")



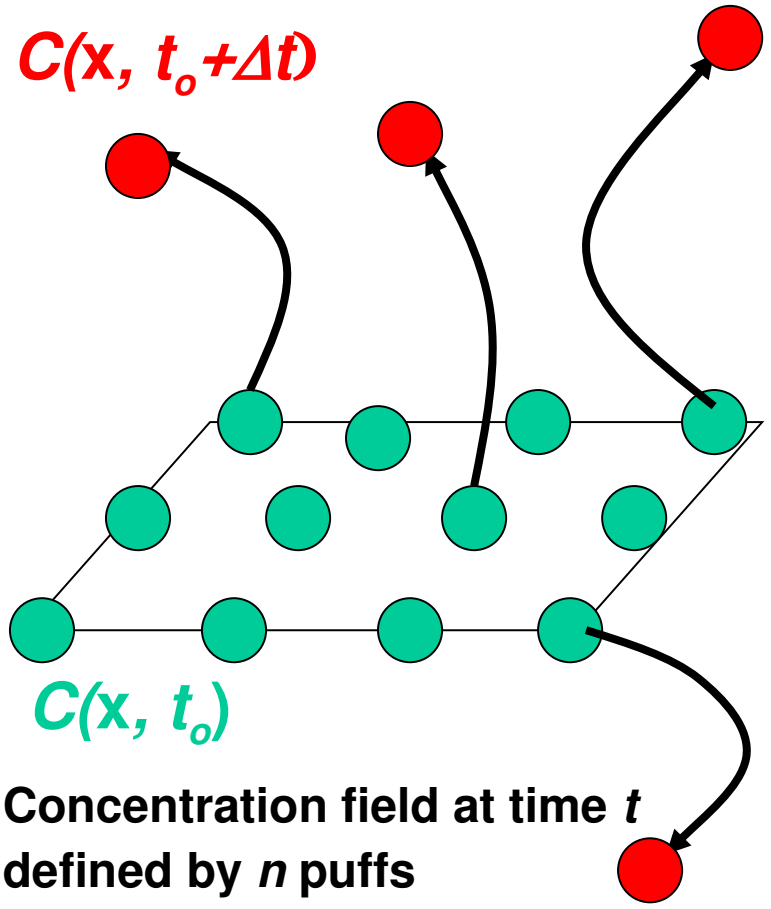
In column moving across city,

$$\frac{dC_X}{dx} = \frac{E}{Uh} - \frac{k}{U} C_X$$



Courtesy of Daniel J. Jacob

Lagrangian Models Follow Large Number of "Puffs"



Concentration field at time *t* defined by *n* puffs

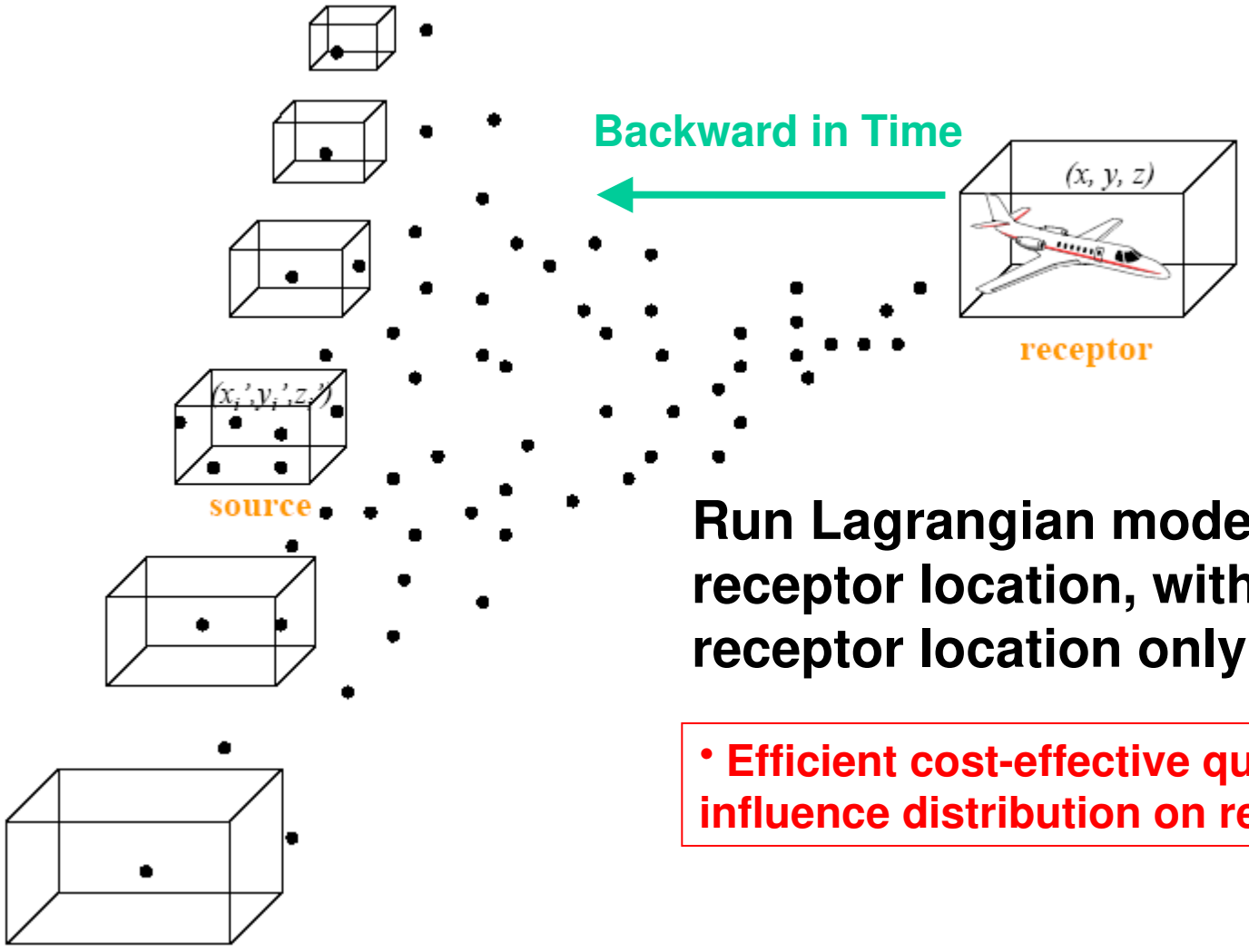
Individual puff trajectories over time Δ*t*.

Advantages of Puff models over Eulerian models:
- **Computational performance (focus puffs on region of interest).**
- **No numerical diffusion.**

Disadvantages of Puff (Lagrangian) models:
- **Can't handle mixing between puffs and can't handle nonlinear processes**
- **Spatial coverage by puffs may be inadequate**

Courtesy of Daniel J. Jacob

Lagrangian Receptor-Oriented Modelling



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

- **Efficient cost-effective quantification of source influence distribution on receptor ("footprint")**

Courtesy of Daniel J. Jacob