Quantifying change

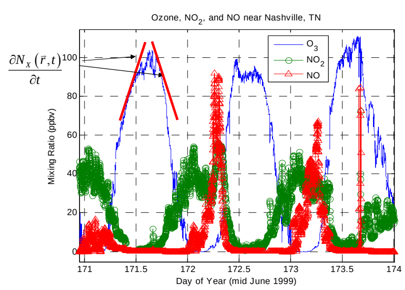
Goal of Atmospheric Chemistry

Concept 1: Mass Balance

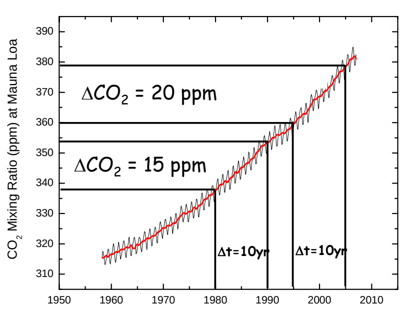
Concept 2: Lifetime

Primary Goal of Atmospheric Chemistry

To describe the change in the atmospheric concentration of chemicals as a function of time and location.

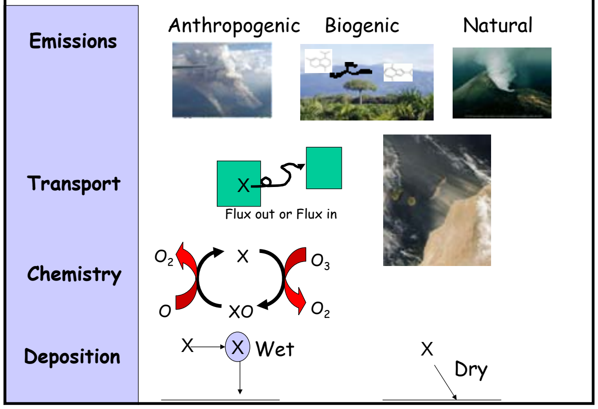


CO_2 Rate of Change



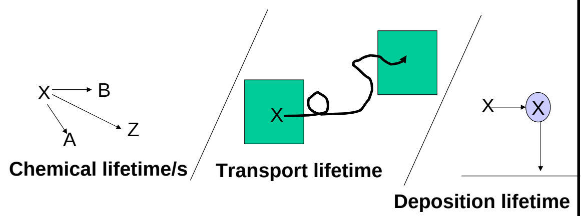
What do we learn about the sources and removal of atmospheric CO_2 based on this graph/analysis?

Factors Affecting d[X]/dt in a Box



Atmospheric Lifetimes

$$\text{Lifetime} = \frac{\text{Amount}}{\text{Removal Rate}}$$



Sink-specific lifetimes allow determination of the importance of a particular process for controlling the fate of a species

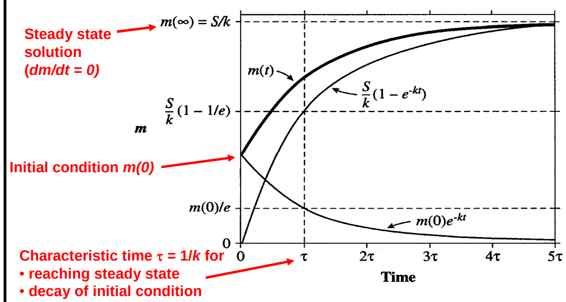
Questions

1. CO_2 is lost from the atmosphere by photosynthesis and physical dissolution into the oceans. Photosynthesis by the biosphere leads to the uptake of ~ 60 Pg C/yr of atmospheric CO_2.What is the atmospheric lifetime of CO_2 w.r.t. uptake by the biosphere? What does this calculation suggest about "fixing global warming"?

2. Fossil fuel burning and deforestation are the major anthropogenic sources of CO_2 to the atmosphere. Together, they add 8 Pg C/yr of CO_2. Given the measured atmospheric growth rate of CO_2 (2ppm/yr), derive a second estimate of the atmospheric lifetime of CO_2.

Steady-State: When is it the case?

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



Question

- The concentration of a species which is in steady state never changes.
  - True or False?

Today: Models

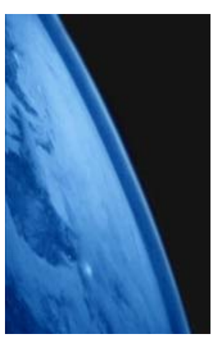
Reading: Chapter 3 and 5 in text

One-box Models

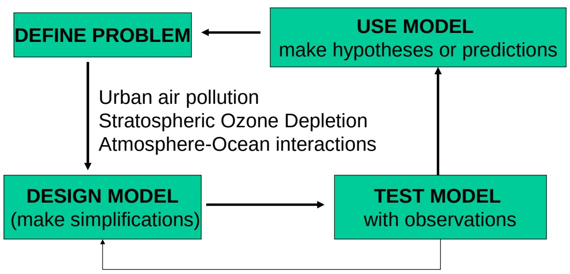
Multi-box Models

Moving the Box Model

Chemical Transport Model (CTM)



Model Development and Application Loop



Models are simplified representations of reality. Observations of the real system are required to test the model.

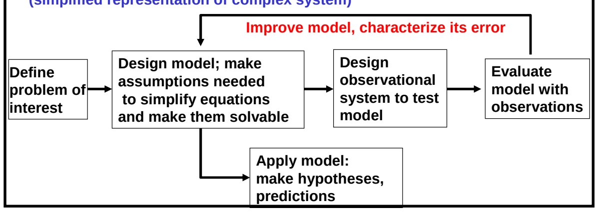
CHAPTER 3: SIMPLE MODELS

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

This equation cannot be solved exactly ⇨ need to construct *model* (simplified representation of complex system)



TYPES OF SOURCES


Natural Surface: terrestrial and marine

highly variable in space and time, influenced by season, T, pH, nutrients…
eg. oceanic sources estimated by measuring local supersaturation in water and using a model for gas-exchange across interface =f(T, wind velocity….)

Natural In situ:


eg. lightning (NO_x) $N_2 \rightarrow NO_x$, volcanoes (SO_2, aerosols)
→ generally smaller than surface sources on global scale but important b/c material is injected into middle/upper troposphere where lifetimes are longer

Anthropogenic Surface:


eg. mobile, industry, fires
→ good inventories for combustion products (CO, NO_x, SO_2) for US and EU

Anthropogenic In situ:


eg. aircraft, tall stacks

Secondary sources: tropospheric photochemistry

Injection from the stratosphere: transport of products of UV dissociation (NO_x, O_3) transported into troposphere (strongest at midlatitudes, important source of NO_x in the UT)

TYPES OF SINKS

Wet Deposition: falling hydrometeors (rain, snow, sleet) carry trace species to the surface

- in-cloud nucleation (depending on solubility)
- scavenging (depends on size, chemical composition)

→Soluble and reactive trace gases are more readily removed

→Generally assume that depletion is proportional to the conc (1st order loss)

Dry Deposition: gravitational settling; turbulent transport

particles > 20 µm → gravity (sedimentation)

particles < 1 µm → diffusion

→ rates depend on reactivity of gas, turbulent transport, stomatal resistance and together define a deposition velocity (v_d)

$$F_d = v_d C_x$$

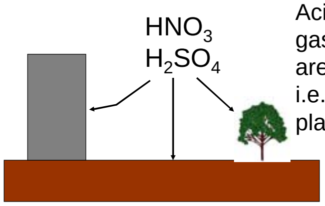
Typical values v_d:
Particles:0.1-1 cm/s
Gases: vary with srf and chemical nature (eg. 1 cm/s for SO_2)

In situ removal:

chain-terminating rxn: OH●+HO_2● → H_2O + O_2

change of phase: SO_2 → SO_4^{2-} (gas → dissolved salt)

Dry Deposition



Acids (and other gas molecules) are taken up by surfaces, i.e. ground, buildings, plants (also respiration)

Factors that govern dry deposition rates:

→Level of atmospheric turbulence

→Chemical properties of depositing species

→Nature of surface itself

Gravitational Settling

Diam. (µm)	Time to Fall 1 km
0.02	228 y
0.1	36 y
1.0	328 d
10	3.6 d
100	1.1 h
1000	4 m
5000	1.8 m

from M.Z. Jacobson "Atmospheric Pollution"

Terminal settling velocity:

$$v_t \propto \frac{D_p^2}{\mu}$$

D_p = diameter of particle

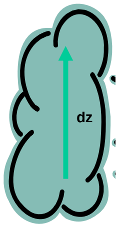
μ = viscosity of air

Only particles smaller than 10 µm reach the global atmosphere

Processes of Wet Deposition

[Liu et al., 2001]

1. CONVECTIVE UPDRAFTS

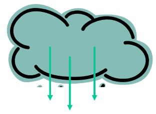


Fraction lost during ascent = αdz
Scavenging efficiency (α) = 4×10^{-4} m^{-1}

$f_{scav} = 1 - e^{-\alpha \Delta z}$

→ 40% scavenged in 1 km

2. RAINOUT

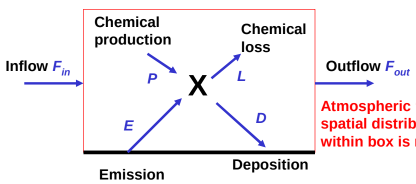


Depends on fraction of grid square experiencing precipitation
(global avg = 2.5% stratiform, 0.4% convective)

3. WASHOUT

Washout rate constant = 0.1 per mm precip applied to max fraction of grid square experiencing precipitation above.

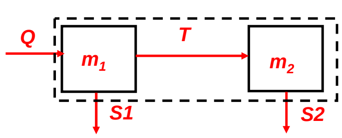
One Box Model



Atmospheric "box"; spatial distribution of X within box is not resolved

$\sum \text{sources} = F_{in} + E + P \qquad \sum \text{sinks} = F_{out} + L + D$

TWO-BOX MODEL (with loss)



Lifetimes: $\tau_1 = \frac{m_1}{T + S_1} \quad \tau_2 = \quad \tau_0 = \frac{m_1 + m_2}{S_1 + S_2}$

If at steady state sinks=sources, so can also write:

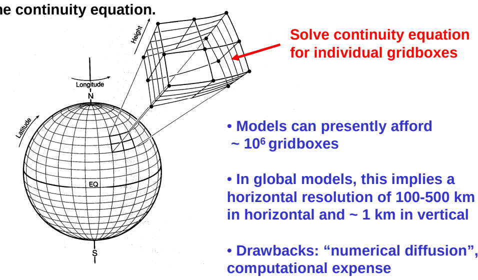
$$\tau_1 = \frac{m_1}{Q} \quad \tau_2 = \frac{m_2}{T} \quad \tau_0 =$$

$$\tau_o = \tau_1 + \alpha \tau_2$$

Global 3D Models

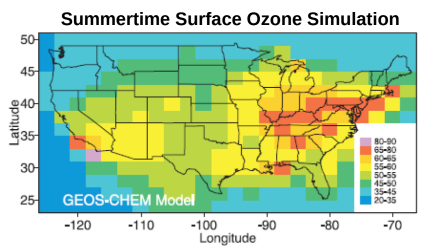
EULERIAN RESEARCH MODELS SOLVE MASS BALANCE EQUATION IN 3-D ASSEMBLAGE OF GRIDBOXES

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



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

EULERIAN MODEL EXAMPLE

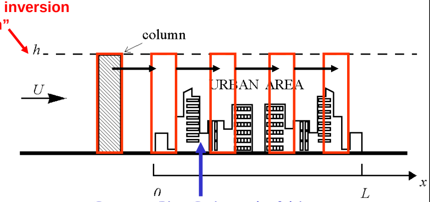


Here the continuity equation is solved for each 2°x2.5° grid box. They are inherently assumed to be well-mixed

[Fiore et al., 2002]

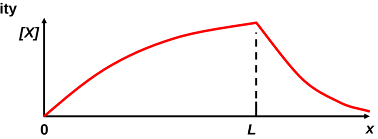
Column Model: A Moving Box

Typically temperature inversion defines "mixing depth"



If X has first order loss, then in column moving across city

$$\frac{d[X]}{dx} = \frac{E}{Uh} - \frac{k}{U}[X]$$



Questions

1. Choose the most appropriate modeling strategy for the following problems (1-box, n-box, plume/column model):

    a. exchange of a uniformly mixed greenhouse gas between the stratosphere and troposphere

    b. production of ozone downwind of an urban area

    c. the abundance of a moderately reactive emission like carbon monoxide

2. Suppose operators of a 1-box model of Seattle's urban "air shed" predicted that the concentration of pollutant emitted downtown was going to rise to a unhealthy level only in the U-District. Should you believe them, why or why not?