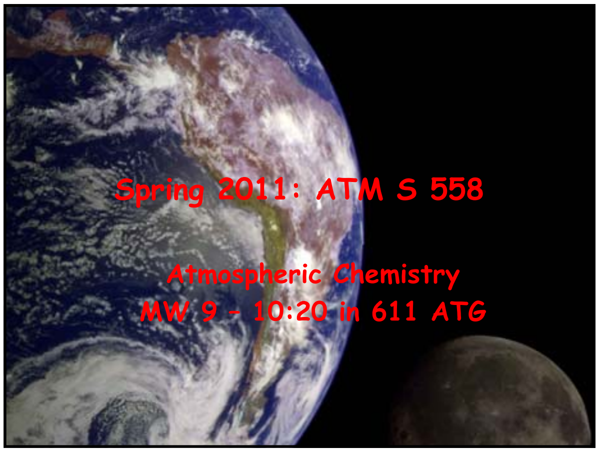


Spring 2011: ATM S 558

Atmospheric Chemistry
MW 9 - 10:20 in 611 ATG

Course Goals

This class will provide an overview of atmospheric chemistry and the fundamental underpinnings so that you will be able to:

1) Understand quantitatively how emissions, transport, chemistry and deposition impact atmospheric chemical composition

2) Explain the chemical and physical mechanisms behind ozone depletion, air pollution and acid rain from the molecular to the global scale

3) Critically evaluate and participate in public discussions of air pollution and climate change

Course Related Activities

(see course website for more information)
http://www.atmos.washington.edu/academics/classes/2011Q2/558/

Lectures/Discussions

Board-work, power point, problem solving, recent literature. Lectures are for you, not me. Please interact!

Problem Sets (not graded) and Exams

Mix of "pencil and paper" and MATLAB based exercises – I will randomly ask students to provide solution method in class. Exams directly based on problem sets and lecture material.

Final Projects

Choose a topic from class for further investigation, write a 5-10 pg report, and give a 15 minute presentation

Course Overview

- Weeks 1-2: Fundamentals
  Measures of atmospheric composition, chemical kinetics, reaction mechanisms, photochemistry, lifetimes.
- Weeks 3-5: Stratospheric Chemistry
  Stratospheric ozone, catalytic loss cycles and CFCs, polar ozone loss, mid-latitude ozone loss, Montreal Protocol
- Weeks 6-8: Tropospheric Chemistry
  Oxidizing capacity of the atmosphere, air pollution, acid rain
- Week 9: Atmospheric Chemistry and Climate
  Biogeochemical cycles, chemistry-climate feedbacks
- Week 10 and finals week: Student Presentations

Goal of Atmospheric Chemistry

To develop a detailed understanding of the chemical and physical processes which control the amounts and spatial and temporal distributions of atmospheric constituents.

Why?

❖The atmosphere plays a critical role in Earth's energy balance (climate)

❖Protects/Sustains life at the surface

❖Couples land,oceans, equator and poles

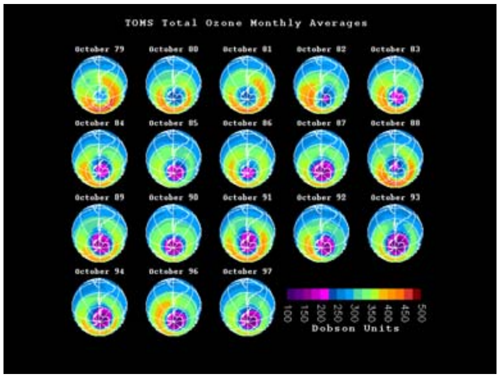
❖Human activity changes its composition

What is Atmospheric Chemistry?

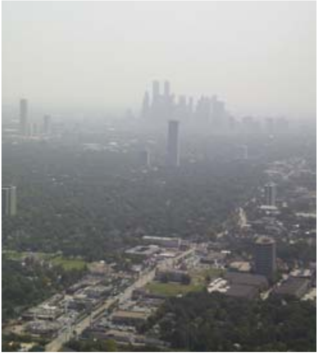
Atmospheric chemistry is the study of the factors controlling the amounts and types of chemical species that make up the atmosphere.

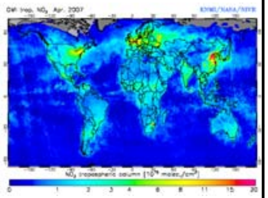
- The "atmosphere" and the chemical species in it, are one and the same.
- This course will highlight the fact that this fluid is a collection of *interacting* atoms and molecules.
- These interactions result in important phenomena which occur on local, regional, and global spatial scales, and over a wide range of temporal scales: seconds to years.
- You are likely very familiar with several phenomena: urban smog, the stratospheric ozone hole, acid rain, the greenhouse effect, just to name a few.

Stratospheric Ozone Depletion



Urban Smog Problem



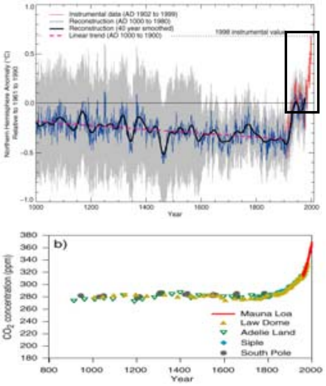


- Global chemistry and climate implications

- Complex regulatory issues

← Houston, TX

Climate – Chemistry Connections



Does composition change drive climate change, or vise versa, or both?

The Atmosphere Moves

CO Movie

How Do We Begin?

Describe the general physical characteristics

mass, temperature, vertical extent, motions

Determine the major and minor components

describe absolute and relative amounts

Develop a physical-chemical framework to:

predict how a species evolves in time and space

Apply this framework to answer:

Why is Earth's atmosphere mainly N_2, O_2, H_2O, and CO_2?

How and where are humans affecting this composition?

What are the implications of such changes?

Measures of Atmospheric Composition

Reading: Chapter 1 in text

How do we describe the amounts of chemical constituents in the atmosphere?

Describing Amounts

Reading: Chapter 1 in text

The atmosphere contains gases (mostly) and some liquids/solids – aerosols and clouds.

All gases can be described by ideal gas law

$$P_X = (n_X/V)RT$$

$$P_{total} = \Sigma(P_X)$$

Aerosols and clouds need:

Size, Number, Composition, and Phase State

mass and volume of particles per volume of air

Average Composition as Mixing Ratios

GAS	MIXING RATIO (dry air) [mol mol^{-1}]
Nitrogen (N_2)	0.78
Oxygen (O_2)	0.21
Argon (Ar)	0.0093
Carbon dioxide (CO_2)	365x10^{-6}
Neon (Ne)	18x10^{-6}
Ozone (O_3)	(0.01-10)x10^{-6}
Helium (He)	5.2x10^{-6}
Methane (CH_4)	1.7x10^{-6}
Krypton (Kr)	1.1x10^{-6}

Trace gases

Mixing Ratio is a mole fraction (Moles X/Total Moles)

- **Air also contains variable H_2O vapor (10^{-6}-10^{-2} mol mol^{-1}) and aerosol particles**

- **Trace gas mixing ratio units:**
  - 1 ppmv = 1x10^{-6} mol mol^{-1}
  - 1 ppbv = 1x10^{-9} mol mol^{-1}
  - 1 pptv = 1x10^{-12} mol mol^{-1}

Related Measures of Composition

Mixing Ratio

$$C_X = \frac{\text{moles of X}}{\text{total moles of air}}$$

•Constant w.r.t. changes in air density

Number Density

$$N_X = \frac{\text{\# molecules of X}}{\text{unit volume of air}}$$

proper measure for
- calculation of reaction rates
- optical properties of atmosphere

N_X and C_X are related by the ideal gas law:

$$N_X = N_{air}C_X = \frac{N_{Avag}P_{air}}{RT}C_X$$

Also define the mass concentration (g cm^{-3} of air):

$$\rho_X = \frac{\text{mass of X}}{\text{unit volume of air}} = \frac{M_X N_X}{N_{Avag}} = \frac{(g/mol)(molec/cm^3)}{(molec/mol)}$$

*Not to be confused with the **density of a substance** **(g cm^{-3} of substance)***

Example

- The mixing ratio of CO_2 is currently ~ 380 ppm throughout the atmosphere, what is its partial pressure?

Visibility Reduction by Aerosols (Haze)

clean day

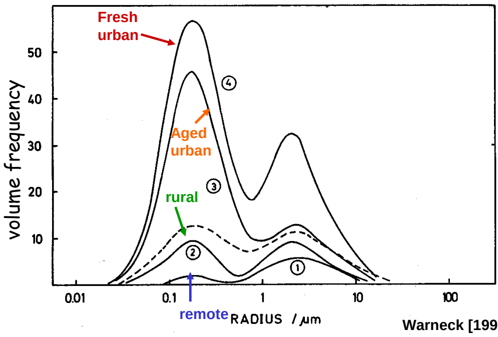
moderately polluted day

Acadia National Park (Northeastern Maine)

http://www.hazecam.net/

Typical U.S. Aerosol Size Distributions

Maxima are most common sizes



Warneck [1999]

Particulate Matter <2.5 microns ($PM_{2.5}$)

U.S. air quality standard:
PM2.5 = 15 μg m^{-3}
(annual mean)
Yellow/red in violation

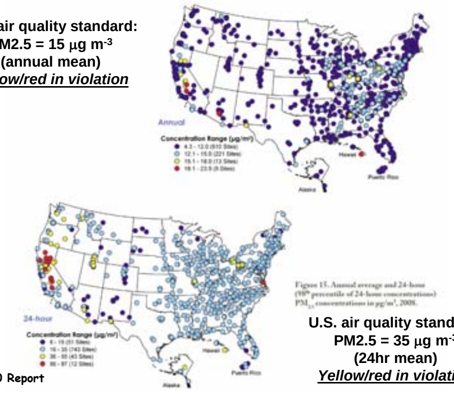


Figure 15. Annual average and 24-hour (98th percentile of 24-hour concentrations) $PM_{2.5}$ concentrations in µg/m³, 2008.

U.S. air quality standard:
PM2.5 = 35 μg m^{-3}
(24hr mean)
Yellow/red in violation

EPA 2010 Report

Seasonal Composition of $PM_{2.5}$

EPA 2010 Report

Figure 18. $PM_{2.5}$ composition by season for 15 U.S. cities.

Kinetics and Photochemistry

Reading: Chapter 9 in text

Rate laws for homogeneous gas-phase reactions
- Unimolecular
- Bimolecular $A + B \rightarrow C + D$
- Termolecular
- Rate constants

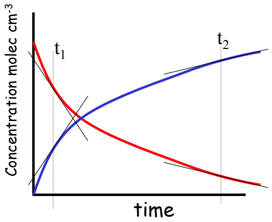
Photolysis Rate Constants $A + h\nu \rightarrow C + D$
- Solar radiation spectrum and bond breaking
- Actinic flux, absorption cross sections, quantum yields

Mechanisms and Overall Reactions

Chemical Kinetics (Reaction Rates)

Rate of reaction at any time, t, is the slope of the tangent to curve describing change in concentration with time

$A + B \rightarrow C + D$

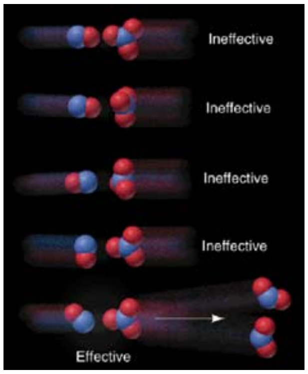


Rates can change w/time because reactant concentrations can change w/time.

d[A]/dt = d[B]/dt = -d[C]/dt = -d[D]/dt (by mass conservation)

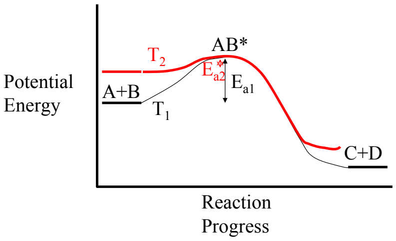
Steric Requirements

$NO + NO_3 \rightarrow 2\ NO_2$



Energy Requirements Affect Rates

Reaction rate constants are often functions of Temperature due to energy requirements



Energy barriers are common: higher T gives higher energy collisions, increasing the probability of a reaction

Rate Expressions for Gas-phase Reactions

Unimolecular: $A \longrightarrow B$

$$-\frac{d[A]}{dt} = k^{I}[A] = \frac{d[B]}{dt}$$

First order process

Lifetime = 1/k; k has units of s^{-1}

Examples - decomposition: $N_2O_5 \rightarrow NO_3 + NO_2$

photolysis: $O_3 + h\nu \rightarrow O_2 + O$

Bimolecular: $A + B \longrightarrow C$

$$-\frac{d[A]}{dt} = k^{II}[A][B] = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

k^{II}, bimolecular rate constant, has units of cm^3 $molec^{-1}$ s^{-1}

Example- $OH + CH_4 \rightarrow H_2O + CH_3$

Special cases:

1. *B=A, rate law becomes 2nd Order in [A]*
2. [B]>>[A] rate law becomes *pseudo-first order in [A]*

Termolecular: $A + B + M \longrightarrow C + M$

M is total air number density

AKA: Pressure dependent bimolecular reactions

Termolecular (Pressure Dependent) Reactions

A bimolecular reaction which requires activated complex to be stabilized by collisions with surrounding gas molecules "M"

1. $A + B \rightarrow AB^*$ k_1
2. $AB^* \rightarrow A + B$ k_2
3. $AB^* + M \rightarrow C + M^*$ k_3
4. $M^* \rightarrow M + \text{heat}$ k_4

$$\frac{d[C]}{dt} = k_3[AB^*][M]$$

[M] is TOTAL AIR NUMBER DENSITY

Assume lifetime of AB* very short, reacts as soon as its formed (quasi steady state approximation):

$$\frac{d[AB^*]}{dt} \approx 0 \approx k_1[A][B] - k_2[AB^*] - k_3[AB^*][M]$$

$$[AB^*]_t = \frac{k_1[A][B]}{k_2 - k_3[M]} \longrightarrow \frac{d[C]}{dt} = \frac{k_3 k_1[A][B]}{k_2 - k_3[M]}[M]$$

Questions

OH is produced in the atmosphere by the reaction of an energetically "hot" oxygen atom (we'll talk about why its "hot" later) with H_2O

$$H_2O + O^* \rightarrow 2OH$$

1. What is the rate expression for the *loss* of O^* by this reactive process?
2. What is the rate expression for the *production* of OH by this reactive process?

Radiation and Photochemical Processes

Questions:

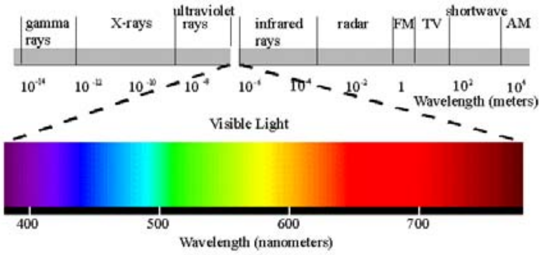
- How does radiation interact with molecules?
- What determines the products and rates of photolysis reactions?
- How do radical and non-radical species react together? At what rate?

Energy from the sun drives the chemistry of the atmosphere through the production of radicals.

Radical = atom or molecule with an unpaired electron = very reactive!

Electromagnetic Spectrum

Radiation (light): Energy carried by oscillating electric and magnetic fields traveling through space at $3\text{x}10^8$ m/s



Photon = quantized packet of energy with zero mass traveling at the speed of light

Interaction of Radiation with Molecules

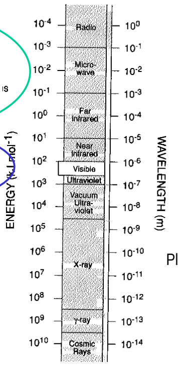
Greenhouse gases

Rotational transitions:
Far Infrared (20 μm <λ)

Vibrational transitions:
Infrared (0.7 <λ< 20 μm)

Electronic transitions:
Ultraviolet (λ <0.4 μm)

Photolysis



Speed of light [$3\text{x}10^8$m s^{-1}]

$$\lambda = c/\nu$$

Wavelength [m]

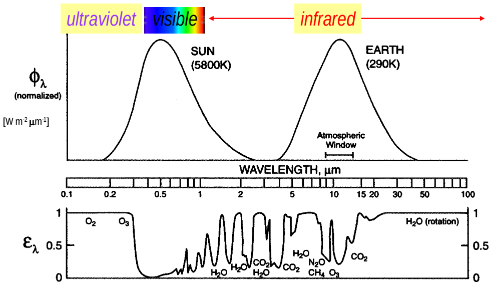
Frequency [s^{-1}]

Energy of one photon [J]:

$$E = h\,\nu = hc/\lambda$$

Planck's constant [$6.62\text{x}10^{-34}$ J s^{-1}]

Absorption of Radiation in the Atmos



Jacob

Fig. 7-11 Efficiency of absorption of radiation by the atmosphere as a function of wavelength. Major absorbers are identified.

Both Sun and Earth behave as blackbodies (absorb 100% incident radiation; emit radiation at all wavelengths in all directions)

Solar Flux

Certain wavelengths of solar radiation are absorbed when traveling through the atmosphere.

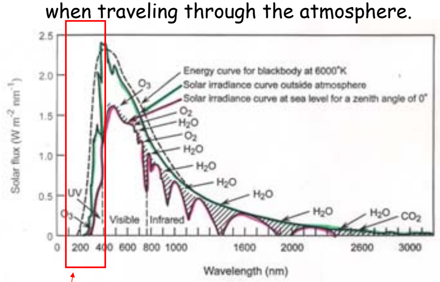


FIGURE 3.12 Solar flux outside the atmosphere and at sea level, respectively. The emission of a blackbody at 6000 K is also shown for comparison. The species responsible for light absorption in the various regions (O_3, H_2O, etc.) are also shown (from Howard *et al.*, 1960).

UV region: Driver of most (but not all) photochemical reactions in the atmosphere

Photochemical Reactions

AB* = Excited electronic state

AB + *h*ν → AB* →	AB + *h*ν	luminescence
→	AB + M	quenching
→	A + B	photodissociation

Photolysis rate:

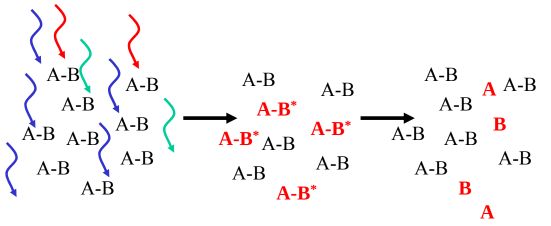
$$d[AB]/dt = -J\,[AB],$$

with J [s^{-1}]= unimolecular rate constant for photodissociation loss of AB

$$J = \int_\lambda \sigma_\lambda\, \phi_\lambda\, q_\lambda\, d\lambda$$

σ_λ Absorption cross section [cm^2/molec]
ϕ_λ quantum yield (unitless)
q_λ solar actinic flux (photons cm^{-2}s^{-1}nm^{-1})

Photolysis



Probability of photon-molecule collision × Probability of absorption of photon energy × Probability of bond-breaking given absorption

I (actinic flux)*[A-B]

Absorption cross-section (σ)

Quantum Yield (ϕ)

Actinic Flux vs. Altitude

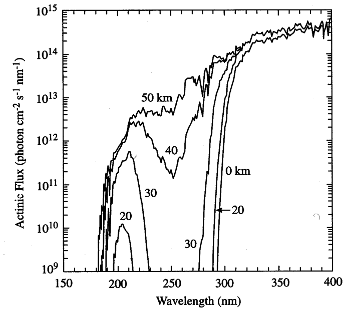
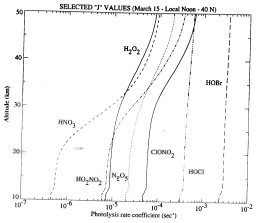
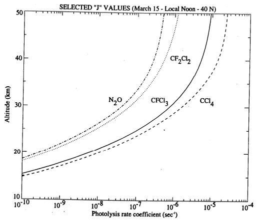


Fig. 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

Altitude Dependence of Photolysis





Two Important Photolysis Reactions

1) Photolysis of O_2 leads to production of ozone in stratosphere

$O_2 + h\nu \rightarrow O + O$ [wavelengths<240 nm]
$O + O_2 + M \rightarrow O_3 + M$

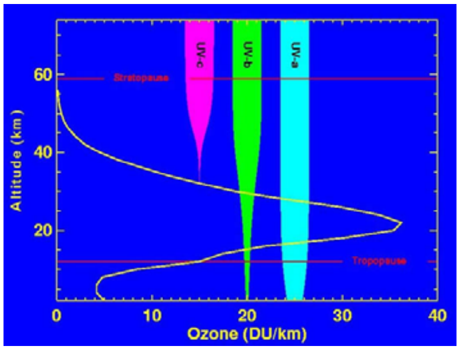
$h\nu$ = energy from one photon; M = unreactive 3rd body (N_2 or O_2)

2) Photolysis of O_3 leads to production of the hydroxyl radical

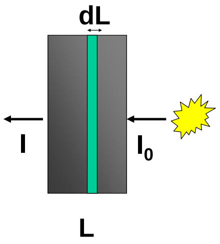
$O_3 + h\nu \rightarrow O(^1D) + O_2$ [wavelengths<310 nm]
$O(^1D) + H_2O \rightarrow OH + OH$

Role of Ozone in Absorbing UV

UV-A: 315-400 nm UV-B: 280-315 nm UV-C: 200-280 nm



Beer-Lambert Law



Attenuation of radiation proportional to thickness and concentration

$$\frac{dI}{I} = -\sigma(\lambda)\, n\, dL$$

σ= absorption cross-section [cm^2/molecule]
n = concentration of absorber [molecules/cm^3]
dL = thickness [cm]

$$\int \frac{dI}{I} = \int_0^L -\sigma\, n\, dL$$

$$I = I_0 \exp[-\sigma\, n\, L]$$

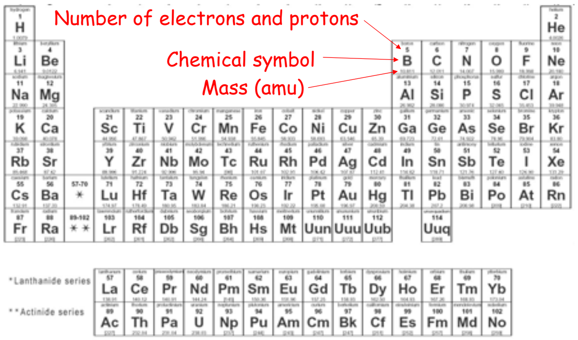
Radicals

- Gases in atmosphere are present at low concentrations → collisions between molecules are infrequent and reactions which proceed at fast rates generally involve at least one radical species
- Radical = chemical species with an unpaired electron in outer (valence) shell
- How do you know whether species is a radical? Generally odd number of electrons in outer shell (exception: oxygen)

Element	# e$^-$	Valence e$^-$	Molar mass (g/mol)	Lewis symbol	Orbitals	
Hydrogen	1	1	1	H•	1s	
Carbon	6	4	12	$\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot$	$1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$	
Nitrogen	7	5	14	$\cdot\overset{\cdot}{\underset{\cdot\cdot}{N}}\cdot$	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	
Oxygen	8	6	16	$:\overset{\cdot}{\underset{\cdot\cdot}{O}}\cdot$	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	Ground state O(^{3}P)
Oxygen	8	6	16		$1s^2 2s^2 2p_x^2 2p_y^2$	Excited state O(^{1}D)

e- occupy different orbitals of a sub-shell before doubly occupying any one of them

Periodic Table of the Elements



H																		He
Li	Be													B	C	N	O	F	Ne
Na	Mg													Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	57-70 *	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89-102 **	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq				

*Lanthanide series	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**Actinide series	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

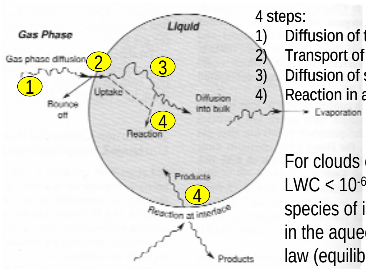
Image from:
http://www.bpc.edu/mathscience/chemistry/images/periodic_table_of_elements.jpg

Questions

1. At a single location on the ground, the photolysis of NO_2 begins earlier in the morning than the photolysis of O_3. Why might this temporal difference exist?

Aqueous-Phase Reactions

Clouds, fog, rain, or particulate matter (few microns in diameter)



4 steps:
1) Diffusion of the gas to surface of droplet
2) Transport of gas across air-water interface
3) Diffusion of solvated species into bulk phase
4) Reaction in aqueous phase or at interface

For clouds or fog droplets (10^{-8} < LWC < 10^{-6} [cm^3 cm^{-3}]), most species of interest are well-mixed in the aqueous-phase → Henry's law (equilibrium) is achieved between the phases

Finlayson-Pitts & Pitts, p 151, Chemistry of the upper and lower atmosphere.

Equilibrium (Henry's Law)

(applicable to dilute solutions, such as cloud droplets)

$$[X] = H_x P_x$$

[X] → equilibrium concentration of X in solution (mol L^{-1})
P_x → gas-phase equilibrium pressure of X (atm)
H_x → Henry's law constant (mol L^{-1} atm^{-1})

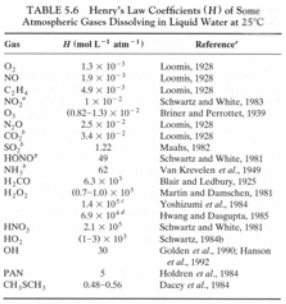


TABLE 5.6 Henry's Law Coefficients (H) of Some Atmospheric Gases Dissolving in Liquid Water at 25°C

Gas	H (mol L^{-1} atm^{-1})	Reference^e
O_2	1.3×10^{-3}	Loomis, 1928
NO	1.9×10^{-3}	Loomis, 1928
C_2H_4	4.9×10^{-3}	Loomis, 1928
NO_2^a	1×10^{-2}	Schwartz and White, 1983
O_3	$(0.82–1.3) \times 10^{-2}$	Briner and Perrottet, 1939
N_2O	2.5×10^{-2}	Loomis, 1928
CO_2^b	3.4×10^{-2}	Loomis, 1928
SO_2^b	1.22	Maahs, 1982
$HONO^a$	49	Schwartz and White, 1981
NH_3^b	62	Van Krevelen *et al.*, 1949
H_2CO	6.3×10^3	Blair and Ledbury, 1925
H_2O_2	$(0.7–1.0) \times 10^5$	Martin and Damschen, 1981
	1.4×10^{5c}	Yoshizumi *et al.*, 1984
	6.9×10^{4d}	Hwang and Dasgupta, 1985
HNO_3	2.1×10^5	Schwartz and White, 1981
HO_2	$(1–3) \times 10^3$	Schwartz, 1984b
OH	30	Golden *et al.*, 1990; Hanson *et al.*, 1992
PAN	5	Holdren *et al.*, 1984
CH_3SCH_3	0.48–0.56	Dacey *et al.*, 1984

Finlayson-Pitts & Pitts, p 151, Chemistry of the upper and lower atmosphere.

Heterogeneous Reactions

Reactions on the surface of aerosol particles are often represented as a 1st order loss processes: $d[X]/dt = -k_{het} [X]$

Reaction probability: γ (unitless, 0-1)
= probability that a molecule impacting an aerosol surface undergoes reaction (measured in lab.)

Net loss of gas due to aerosol reaction (first-order loss):

$$-\frac{d[X]}{dt} = \left(\frac{a}{D_g} + \frac{4}{\upsilon\gamma}\right)^{-1} A[X]$$

a = radius of aerosol [cm]
D_g = gas-phase molecular diffusion coefficient of X [cm^2/s]
υ = mean molecular speed of X in the gas-phase [cm/s]
A = aerosol surface area per unit volume of air [cm^2/cm^3]
[X] = gas phase concentration of X [$molec/cm^3$]

Applicable to both solid and liquid aerosols

Kinetic and Photochemical Data

NASA/JPL: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies
http://jpldataeval.jpl.nasa.gov/index.html

IUPAC (International Union of Pure and Applied Chemistry) Gas Kinetic Data Evaluation
http://www.iupac-kinetic.ch.cam.ac.uk/

Quantifying change

Reading: Chapter 3 in text

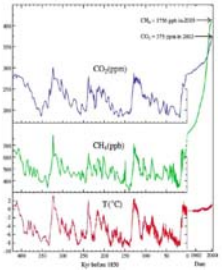
Goal of Atmospheric Chemistry

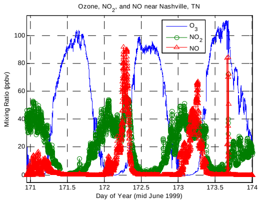
Concept 1: Mass Balance

Concept 2: Lifetime

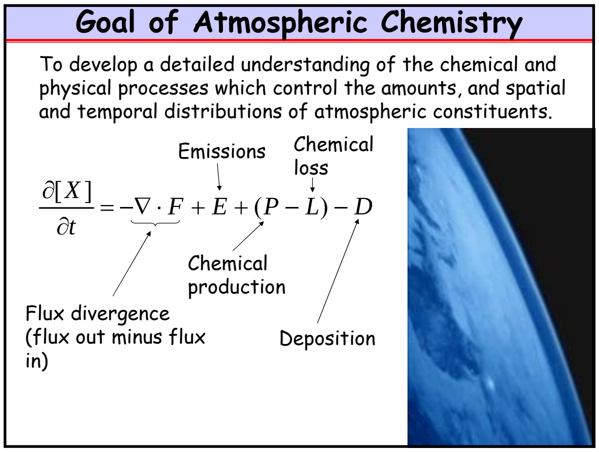
Spatial and Temporal Scales of Change

Gases trapped in ice show changes over millenial and annual timescales.





Chemical change occurs on time scales ranging from <1 second to >millennia



Goal of Atmospheric Chemistry

To develop a detailed understanding of the chemical and physical processes which control the amounts, and spatial and temporal distributions of atmospheric constituents.

Emissions

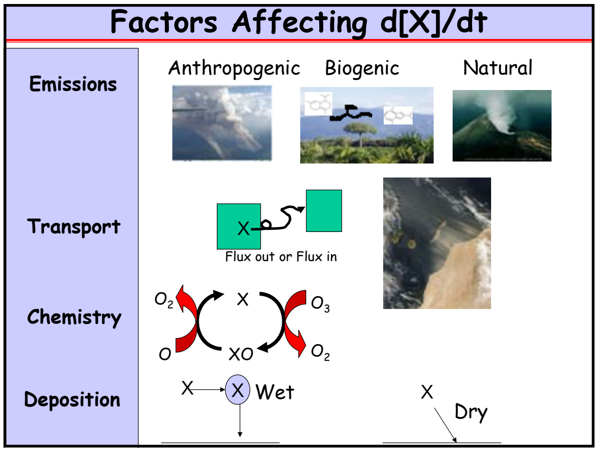
Chemical loss

$$\frac{\partial[X]}{\partial t} = \underbrace{-\nabla\cdot F}_{} + E + (P-L) - D$$

Chemical production

Flux divergence (flux out minus flux in)

Deposition



Factors Affecting d[X]/dt

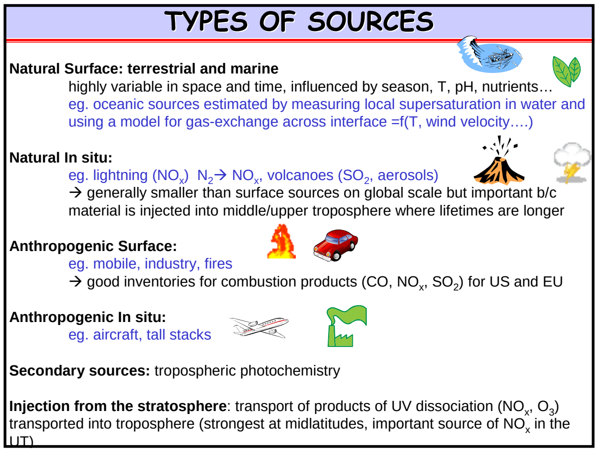
Emissions

Anthropogenic Biogenic Natural

Transport

Chemistry

Deposition



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→ 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)

$$F_d = v_d C_x$$

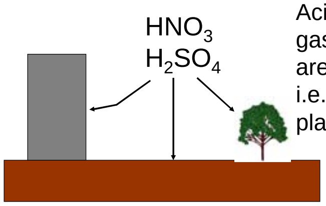
Typical values v_d:
Particles:0.1-1 cm/s
Gases: vary with srf and chemical nature (eg. 1 cm/s for SO_2)

In situ removal:

chain-terminating rxn: $OH\bullet + HO_2\bullet \rightarrow H_2O + O_2$

change of phase: $SO_2 \rightarrow SO_4^{2-}$ (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"

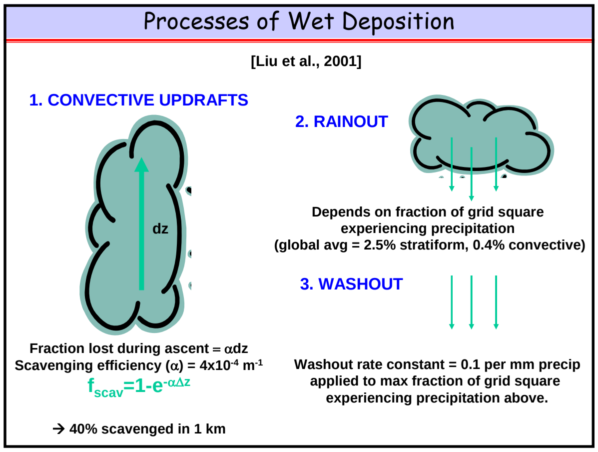
Terminal settling velocity:

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

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}

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

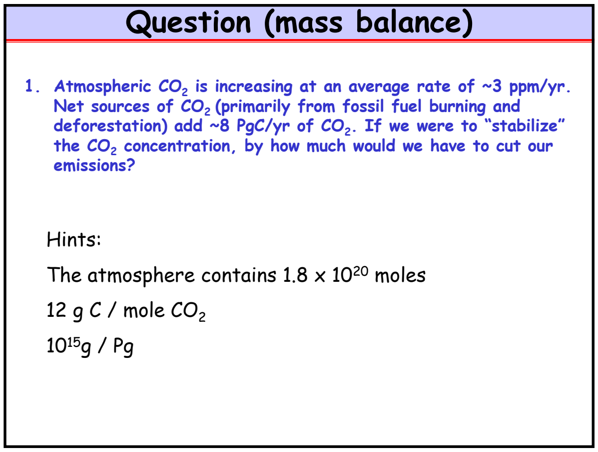
→ **40% scavenged in 1 km**

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.



Question (mass balance)

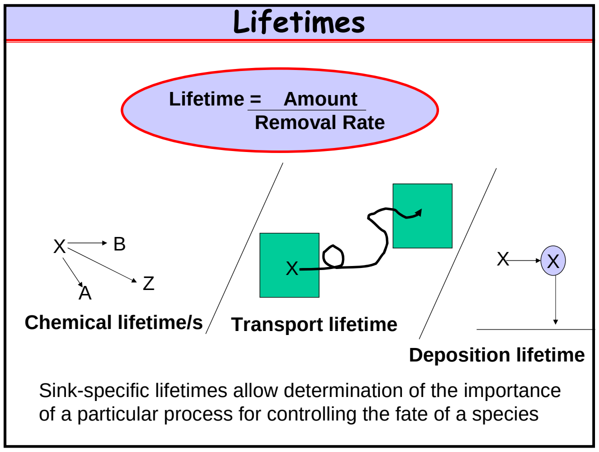
1. **Atmospheric CO_2 is increasing at an average rate of ~3 ppm/yr. Net sources of CO_2 (primarily from fossil fuel burning and deforestation) add ~8 PgC/yr of CO_2. If we were to "stabilize" the CO_2 concentration, by how much would we have to cut our emissions?**

Hints:

The atmosphere contains 1.8×10^{20} moles

12 g C / mole CO_2

10^{15}g / Pg



Lifetimes

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

Chemical lifetime/s

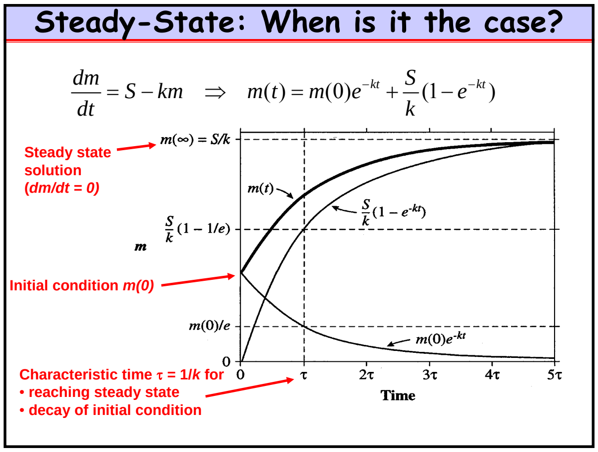
Transport lifetime

Deposition lifetime

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

Questions (lifetime)

1. CO_2 is removed 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. Recall that fossil fuel burning and deforestation net add 8 Pg C/yr of CO_2. Given the measured atmospheric growth rate of CO_2 (~3ppm/yr), and that there's ~380 ppm CO_2, derive a second estimate of the atmospheric lifetime of CO_2. Does this approach seem valid?



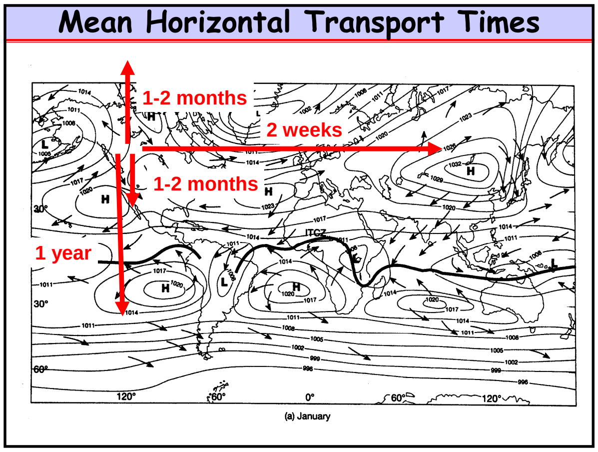
Steady-State: When is it the case?

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

Steady state solution ($dm/dt = 0$)

Initial condition $m(0)$

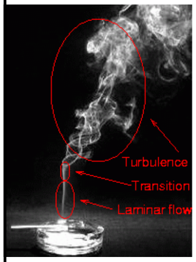
Characteristic time $\tau = 1/k$ for
- reaching steady state
- decay of initial condition

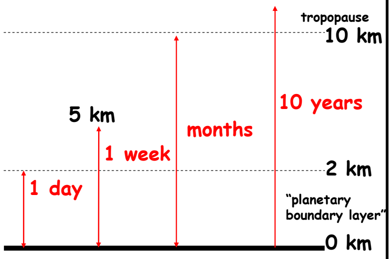


Mean Horizontal Transport Times

(a) January

Vertical Mixing Timescales



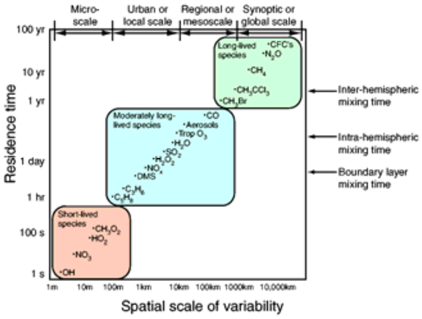


Treat eddy transport as analogous to molecular diffusion

$$F_z = -K_z \frac{\partial N_x}{\partial z}$$

K_z('eddy diffusivity') ~ 1×10^5 cm^2 s^{-1}

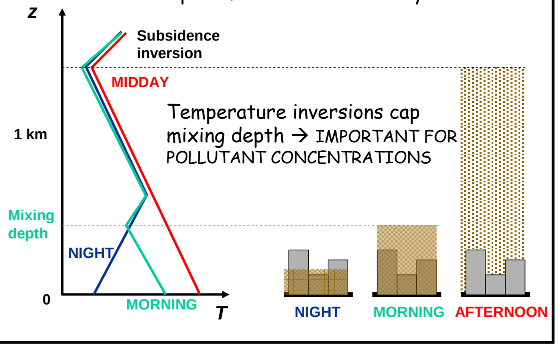
Residence Times and Spatial Variability



Wallace and Hobbs Figure 8.

Mixed Layer Depth

Daily cycle of surface heating and cooling
and the depth of the "well mixed" layer



Temperature inversions cap mixing depth → IMPORTANT FOR POLLUTANT CONCENTRATIONS

Vertical Transport

Vertical transport critical for air quality and the vertical distribution of surface emitted species (CO_2, PM, H_2O, CFCs, etc).

Often associated with cloud processing → multiphase chemistry and scavenging/redistribution of gases and particles


LA Smog/Fog


Cumulonimbus

Models

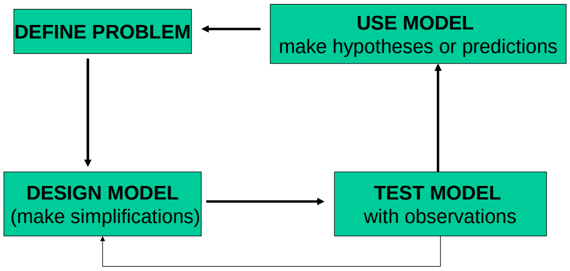
Reading: Chapter 3 in text

One-box Models

Multi-box Models

Moving the Box Model

Model Development and Application Loop

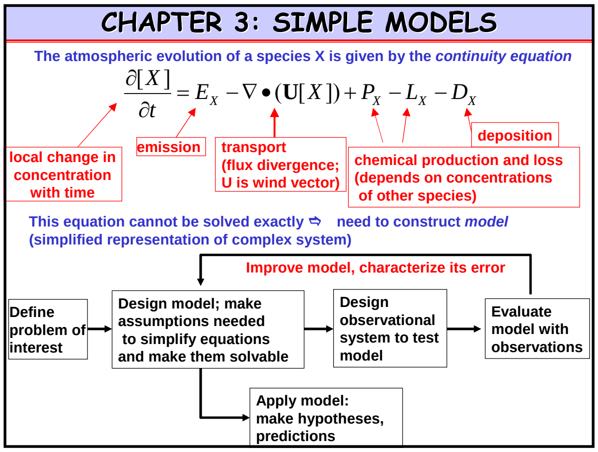


DEFINE PROBLEM

USE MODEL
make hypotheses or predictions

DESIGN MODEL
(make simplifications)

TEST MODEL
with observations



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)

Improve model, characterize its error

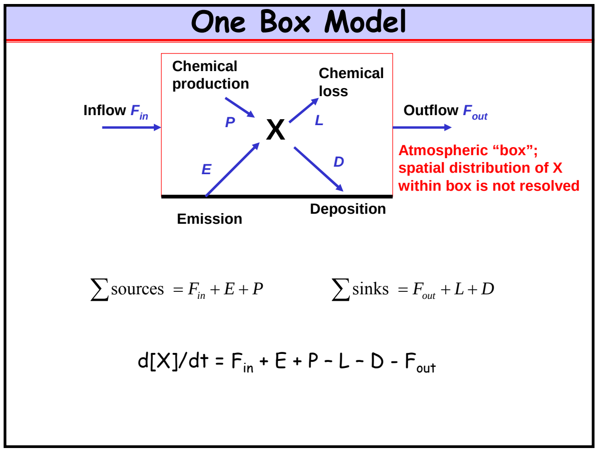
Define problem of interest

Design model; make assumptions needed to simplify equations and make them solvable

Design observational system to test model

Evaluate model with observations

Apply model: make hypotheses, predictions

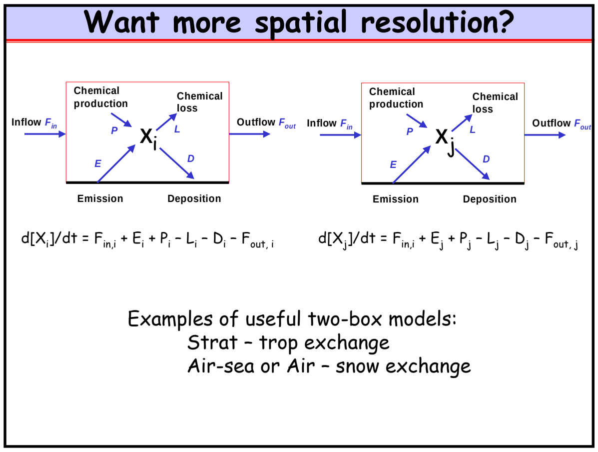


One Box Model

Atmospheric “box”; spatial distribution of X within box is not resolved

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

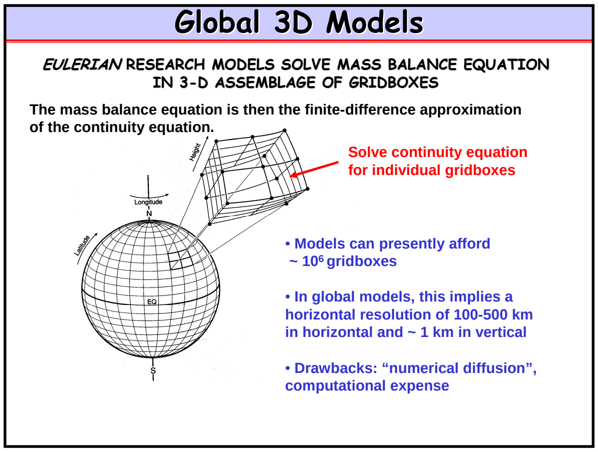
$$d[X]/dt = F_{in} + E + P - L - D - F_{out}$$



Want more spatial resolution?

$$d[X_i]/dt = F_{in,i} + E_i + P_i - L_i - D_i - F_{out,\,i} \qquad d[X_j]/dt = F_{in,i} + E_j + P_j - L_j - D_j - F_{out,\,j}$$

Examples of useful two-box models:
Strat – trop exchange
Air-sea or Air – snow exchange



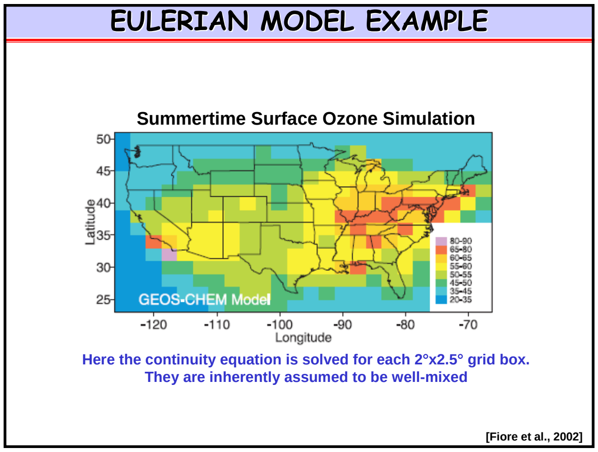
Global 3D Models

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.

Solve continuity equation for individual gridboxes

- 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

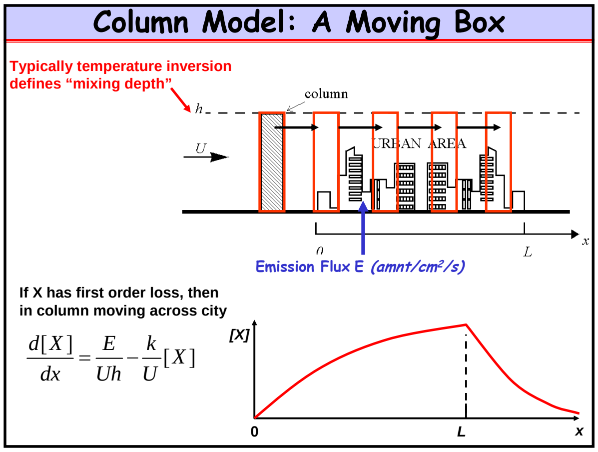


EULERIAN MODEL EXAMPLE

Summertime Surface Ozone Simulation

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"

Emission Flux E *(amnt/cm²/s)*

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?