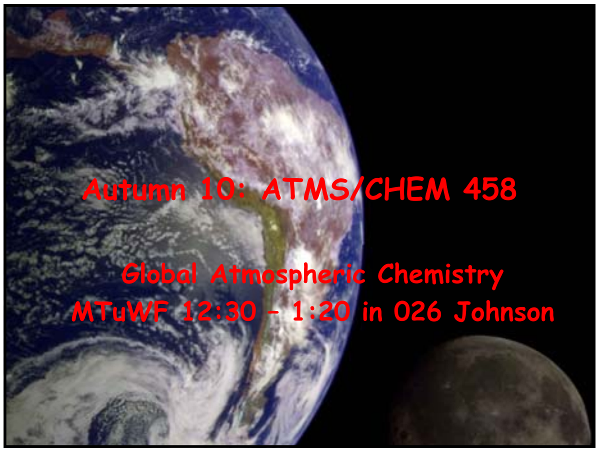


Course Goals

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) Develop skills to evaluate discussions of air pollution and climate change based on scientific evidence and organized knowledge

Course Related Activities

(see course website for more information)

http://www.atmos.washington.edu/academics/classes/2010Q4/458/

Lectures/Discussions

Lectures are for you, not me. Please interact!

Problem Sets and Data Analysis

Are certainly doable, but require some thought. Never wait until the last minute. You are welcome to form groups for these activities.

Final Projects

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

This Week

READING: Chapter 1 - 2 of text

- Goals, Topic Overview
- Atmospheric Physical and Chemical Properties
- Fundamentals

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?

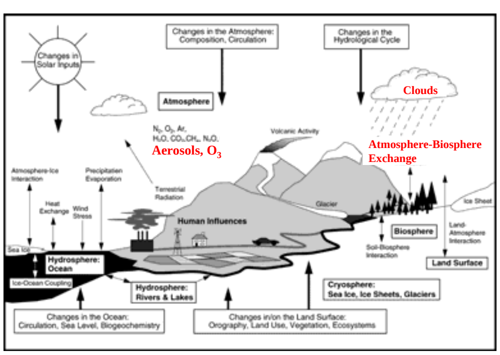
❖The atmosphere plays a critical role in Earth's energy balance (climate)

❖Protects/Sustains life at the surface

❖Couples land,oceans, equator and poles

❖Human activity changes its composition

Atmosphere in the Earth System



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

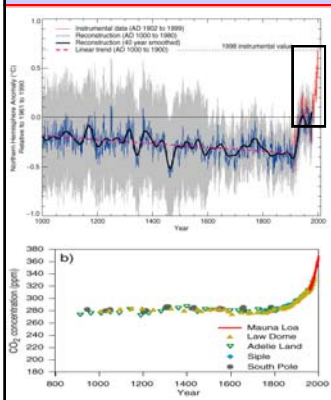
Apply this framework to answer:

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

How and where are humans affecting this composition?

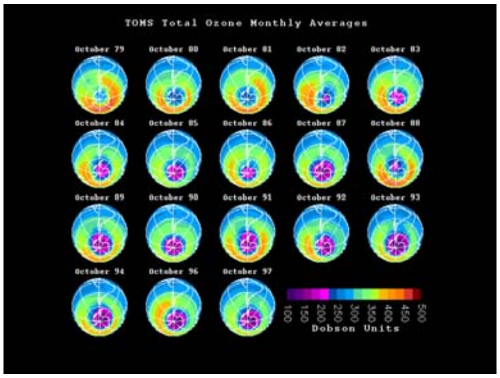
What are the implications of such changes?

Climate – Chemistry Connections

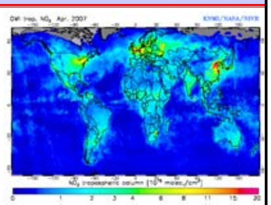


Does composition change drive climate change, or vise versa, or both?

Stratospheric Ozone Depletion



Urban Smog Problem

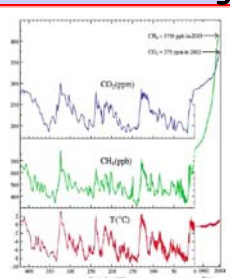


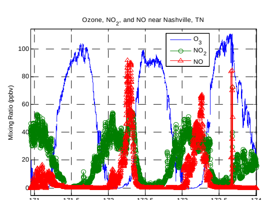
- Global chemistry and climate implications
- Complex regulatory issues

← Houston, TX

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

Today: Describing Amounts

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 (Carbon dioxide through Krypton)

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):

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

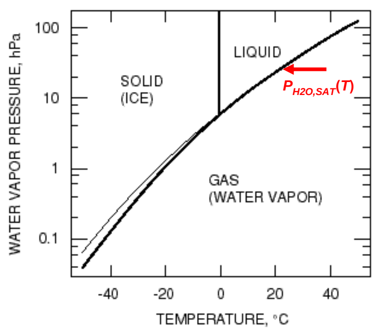
Not to be confused with the ***density of a substance*** ***(g cm^{-3} of substance)***

Examples

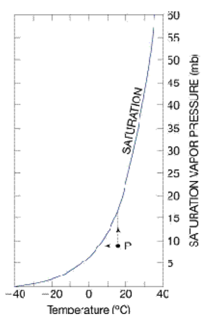
1. How many molecules of air are in 1 cm^3 of this room?

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

H_2O Phase Diagram



Saturation Vapor Pressure



Maximum amount of water vapor volume of air can hold.

Determines when condensed phase H_2O can exist i.e. clouds!

Relative humidity (%) = 100(P_{H2O}/$P_{H2O,SAT}$)

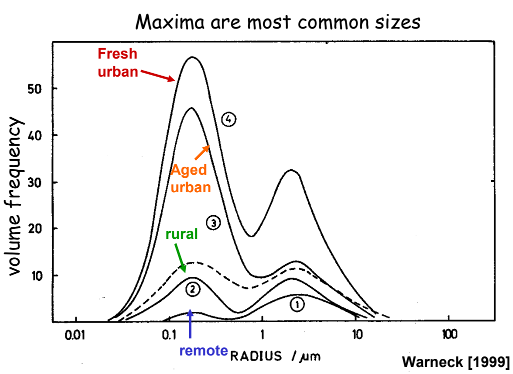
Visibility Reduction by Aerosols (Haze)

clean day

moderately polluted day

Acadia National Park (Northeastern Maine)
http://www.hazecam.net/

Typical U.S. Aerosol Size Distributions

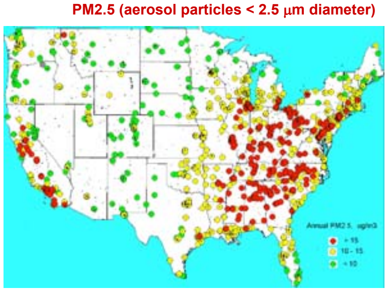


Annual Mean Particulate Matter (PM)

Concentrations at U.S. Sites, 1995-2000

EPA particulate matter assessment document (NARSTO), 2003

PM2.5 (aerosol particles < 2.5 μm diameter)

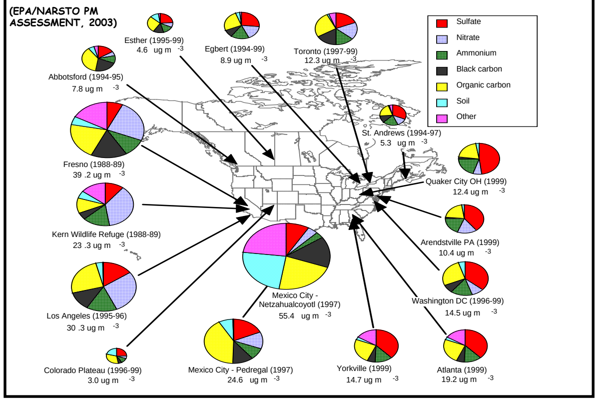


U.S. air quality standard:
PM2.5 = 15 μg m^{-3}
(annual mean)

Red circles indicate sites in violation of the standard

STANDARD IS EXPRESSED AS A MASS CONCENTRATION
Total Mass of Particles PER UNIT VOLUME AIR

Chemical Composition of PM2.5



Questions

1. Liquid water cloud droplets are typically ~20 micrometers in diameter. If there are ~100 droplets per cubic centimeter of air, what is the liquid water mass concentration?

Mass m_a of the Atmosphere

Radius of Earth: 6378 km

Mean surface pressure: 984 hPa

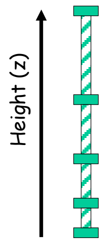
$$m_a = \frac{4\pi R^2 P_S}{g} = 5.2\times10^{18}\ \text{kg}$$

Total number of moles of air in atmosphere:

$$N_a = \frac{m_a}{M_a} = 1.8\times10^{20}\ \text{moles}$$

Air is a Compressible Fluid

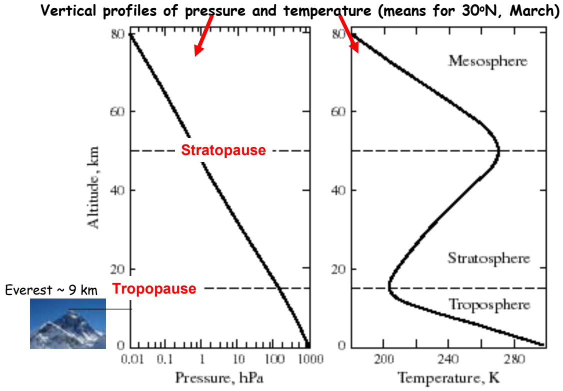
Gases (air) are compressible
fluids unlike most liquids.



Constant-mass bricks of air
stacked on each other

Atmospheric Structure

Vertical profiles of pressure and temperature (means for 30°N, March)



Transport Timescales

READING: Chapter 4 of text

Today: Horizontal Motions

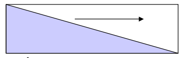
Global Heat Engine (Eq to Pole T gradient)

Coriolis Effect

General Circulation
- Upper level westerlies and surface trades
- Convergence/Divergence
- Uplift/Subsidence

Making Air Move

Pressure Gradient Force



Fluid with horizontal pressure gradient

Fluid will move from high to low pressure

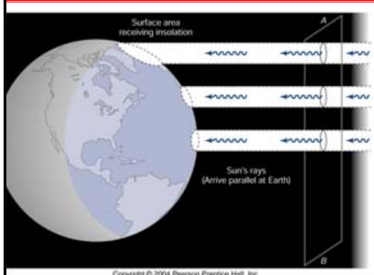
Applies to horizontal (parallel to earth's surface) and vertical (perpendicular to earth's surface)

Buoyant Forces (Tomorrow) Recall: density $\propto$ 1/T

buoyancy: when pressure gradient force in vertical direction not equal to force due to gravity

When an air parcel's density is lower/higher than the surrounding air, it will rise/sink

The Engine's Heat Source

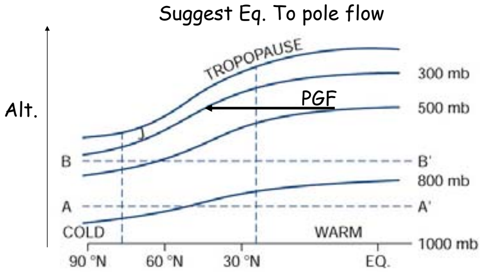


Latitudinal gradient in solar insolation

The equator receives a greater solar radiation energy flux (J/m^2/s) than the poles

Isobars (Constant Pressure Lines)

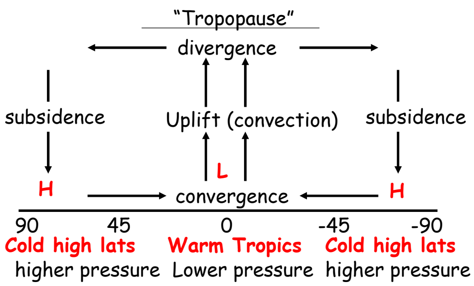
Suggest Eq. To pole flow



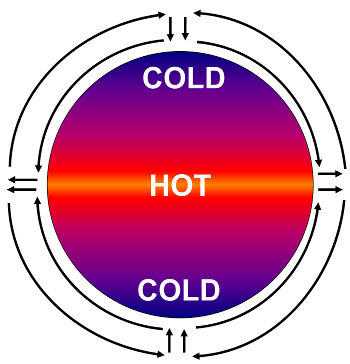
The picture is roughly symmetric for the Southern Hemisphere (SH)

Early Picture of General Circulation

Based on Hadley's 1735 paper:



Hadley Circulation (in 1735)

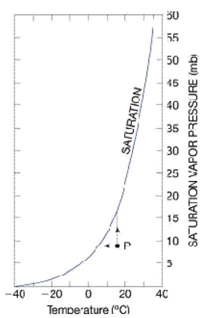


Explains:
Intertropical Convergence Zone (ITCZ)

Wet Tropics
Dry Poles

But it has some problems.

Saturation Vapor Pressure



Amount of water vapor volume of air can hold.

Determines when condensed phase H_2O can exist

Formation of condensed phase H_2O often leads to removal by precipitation

Relative humidity (%) = $100(P_{H2O}/P_{H2O,SAT})$

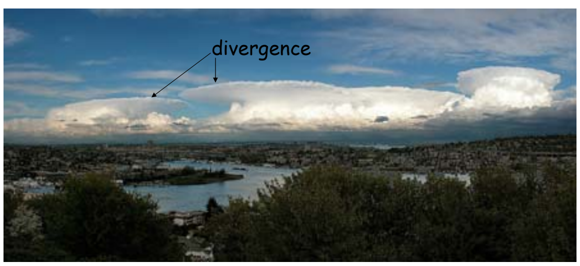
Dew point: Temperature T_d such that $P_{H2O} = P_{H2O,SAT}(T_d)$

Intertropical Convergence Zone (ITCZ)

Surface warming by intense solar radiation leads to warm air rising, creating surface low pressure.

Convergence and uplift leads to saturation/condensation

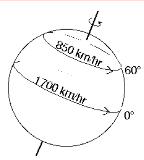
Moist Deep Convection—Where?



Hadley Didn't Know About Coriolis Effect

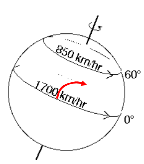
Earth rotates from West to East (an Easterly direction)

The equator is rotating with a larger velocity than higher latitudes

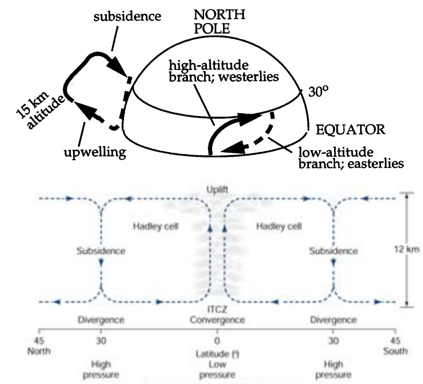


Air (or any object) on Earth always has an easterly velocity component.

Object moving northward from the equator has easterly velocity greater than the Earth at northern latitudes



Coriolis Effect: Modifies Hadley Circulation



Question

Imagine you are standing on the North Pole and you throw a ball in the southward direction. From the point of view of the observer (you), the ball will be deflected to the right. If you are standing on the South Pole and throw a ball in the northward direction,

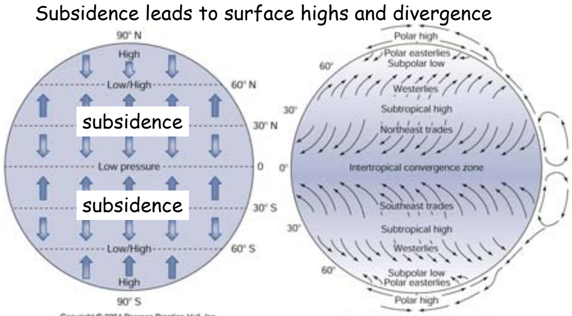
a) it will also curve to the right
b) it curve to the left

The Coriolis effect deflects winds to the right in the Northern Hemisphere and to the left in the Southern Hemisphere.

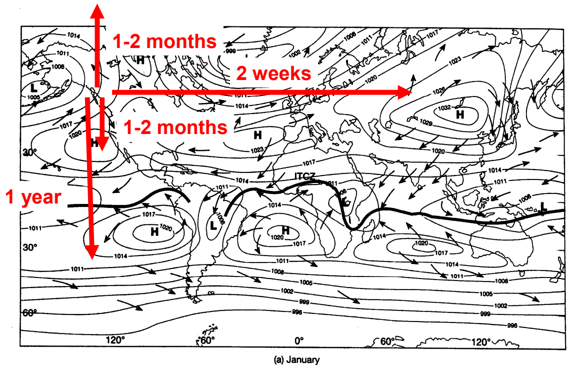
Surface Winds

In the tropics air flows towards the ITCZ, impacted by Coriolis effect and friction. These are the "trades"

Subsidence leads to surface highs and divergence



Mean Horizontal Transport Times



Today: Vertical Transport

Importance to composition

Buoyancy

Stability and Instability

Vertical Transport: Overview

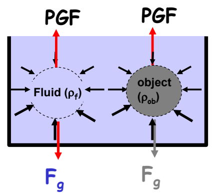
1. Vertical transport critical for air quality and the vertical distribution of surface emitted species (CO_2, PM, H_2O, etc).
2. Determined by temperature differences between air parcels and their surroundings.

LA Smog/Fog

Cumulonimbus

Vertical Transport: Buoyancy

Buoyancy refers to the density of an object in a fluid, relative to the density of that fluid.



$F_{buoyancy}$ = PGF - F_g

If $\rho_{obj} > \rho_{fluid}$, F_g^{obj} will be > PGF, and so object will sink.

If $\rho_{obj} < \rho_{fluid}$, PGF > F_g^{obj} and so object will rise.

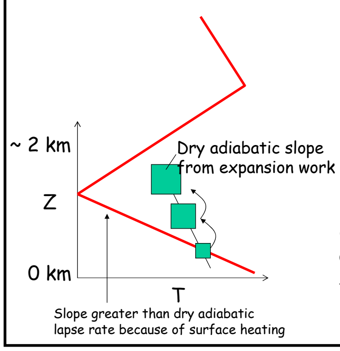
Vertical Transport: Buoyancy

Key Points

- "Warmer air rises and colder air sinks"-- BUT as it rises/sinks, it cools/warms at the adiabatic rate (~10K/km), i.e. when does "warmer" air become "colder"?
- Must compare "parcel" T to "surrounding" atmosphere T to know extent of vertical mixing
- Solar heating and "latent heat" of condensation drive temperature differences between a parcel of air and the surrounding atmosphere.

Vertical Transport: Stability/Instability

How do vertical motions get started and stopped?



Conduction: air warmed by contact w/surface.

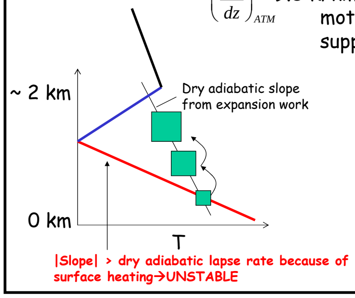
Warm parcels become buoyant or are lifted mechanically to where they are buoyant.

Compare T_{parcel} to T_{ATM} at a given (z) to determine sign of buoyancy

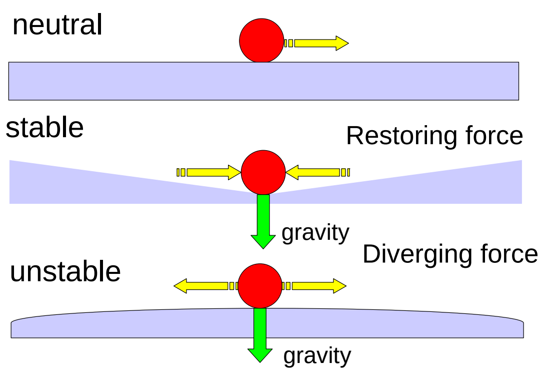
Vertical Transport: Stability/Instability

$-\left(\frac{dT}{dz}\right)_{ATM}$ > 9.8 K/km: UNSTABLE w.r.t. vertical motion (well mixed)

$-\left(\frac{dT}{dz}\right)_{ATM}$ < 9.8 K/km: STABLE w.r.t. vertical motion (vertical mixing suppressed)



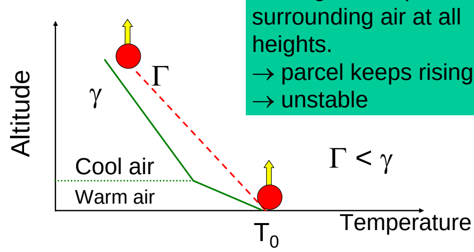
Stability



Atmospheric Stability

Unstable case:

Temp. of rising air parcel has higher temp. than surrounding air at all heights.
→ parcel keeps rising
→ unstable

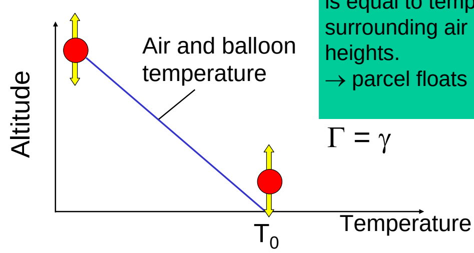


Atmospheric Stability

Neutrally stable case:

Temp. of air parcel is equal to temp. of surrounding air at all heights.
→ parcel floats

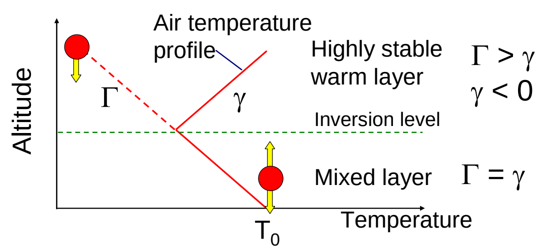
$\Gamma = \gamma$



Atmospheric Stability

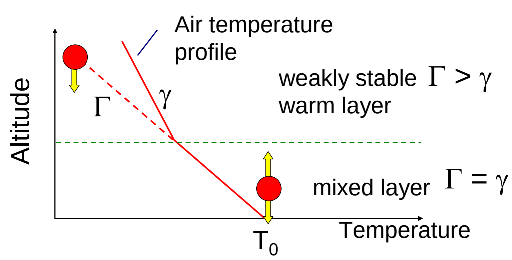
Stable case:

Rising air parcel above inversion is always colder than surrounding air
→ parcel will not rise and be pushed back to its original altitude.



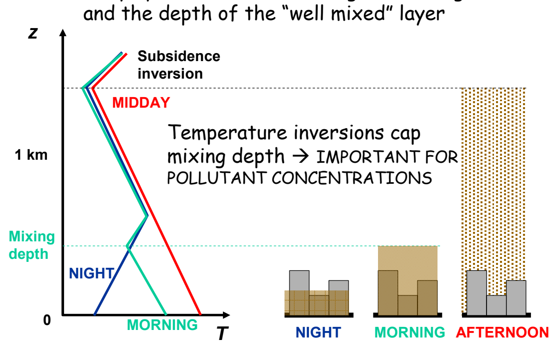
Atmospheric Stability

Stable case:



Temperature Structure and Air Quality

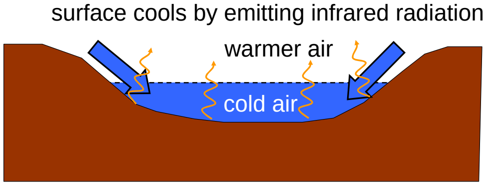
Daily cycle of surface heating and cooling and the depth of the "well mixed" layer



Radiation Inversions

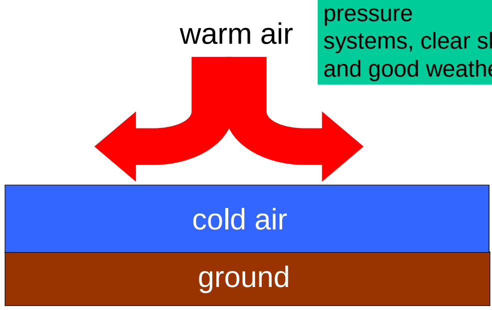
occur at night when the ground cools down

surface cools by emitting infrared radiation

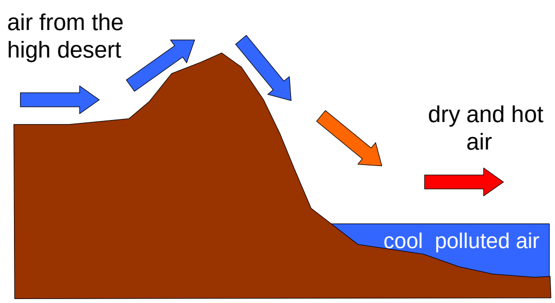


Subsidence Inversions

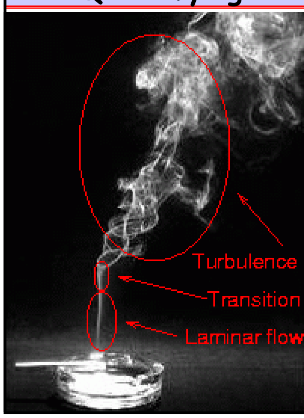
associated with high pressure systems, clear skies, and good weather



Regional Subsidence Inversion



Quantifying Vertical Transport

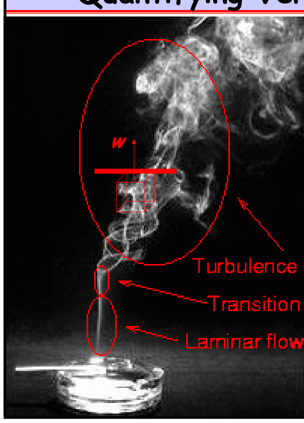


Two regimes for fluid flow

1. Laminar – smooth and steady, all elements have similar velocity
2. Turbulent – irregular and fluctuating ("swirling eddies")

Atmospheric flows largely turbulent

Quantifying Vertical Transport



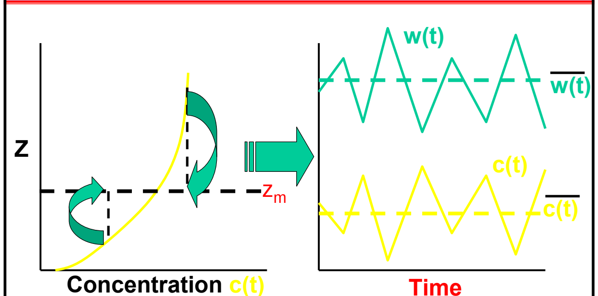
Want Flux of X at some point in space

Volume element (red box) has X number density N_x vertical velocity w and area dA

$$F_x = N_x * w$$

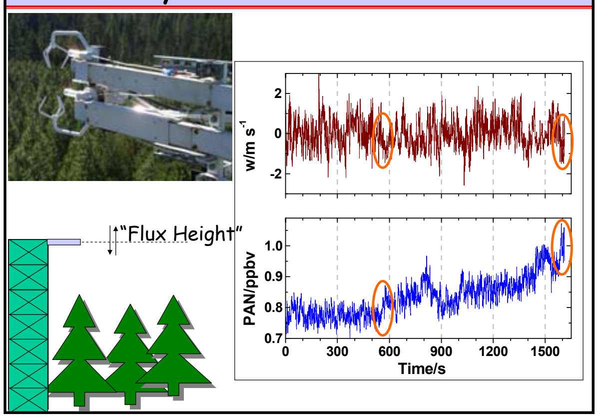
Instantaneous value of F_x not useful, effectively random, need to average.

Measuring Fluxes by Eddy Covariance

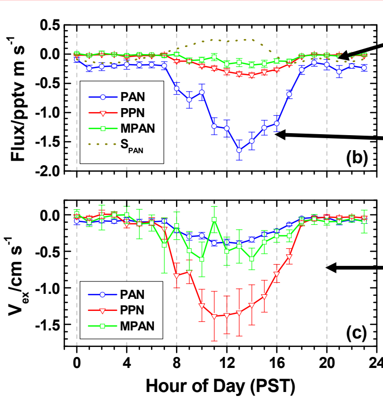


$$F_{net} = \overline{c'w'}$$
$$V_{ex} = F/\bar{c}$$

Eddy Covariance Time Series



Diurnal "Depositional" Flux Example

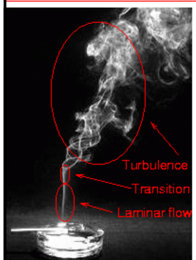


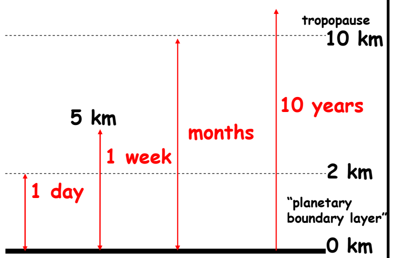
Nighttime-- highly stable → little to no turbulent mixing

Daytime– net downward transport of these compounds

Flux/concentration: measure of relative propensity to be transported

Typical Timescales for Vertical Mixing





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}

Questions

1. Subsidence of air leads to compression, which causes an air parcel to warm. This will lead to:
   - a) rainy weather
   - b) dry weather
   - c) lower pressure at the surface

2. Large scale subsidence tends to occur near 30°N/S as a result of the Hadley circulation. This subsidence exacerbates air quality problems in cities like Los Angeles, Houston, Athens, Cairo, Shanghai, etc.
   - A) True
   - B) False

3. If it only takes months for air at the surface to mix to the top of the troposphere (tropopause), why does it then take 10 years for air in the troposphere to cross into the stratosphere?