

CE558

Air Pollution and its Mitigation



Odd semester (Aug-Dec) 2023

Objective of the course

To understand what a sentence like this means, what it generalizes, what it leaves out, and what it gets wrong.. and how this understanding helps in prioritizing mitigation requirements.

- Why do we care about severity?
- What determines the severity of a pollution episode?
- Is the scale of determination absolute or relative?
- What about the time?



NDTV, 26th Dec 2017

- Air pollution – probably the most generalized of all terms.
- What are the nuances?
- What are the processes and species involved?
- What is so special about Delhi? Or any place, for that matter?

Approach to the course (practical aspects)

- Please pay attention to the slides
 - Slides compile info from multiple sources – questions (I'll upload slides on Moodle)
- We'll be using multiple book chapters and reports
 - I'll share the resources (provide link/upload on Moodle)
 - If you have trouble accessing any of them, let me know
- I'll provide a list of resources prior to starting each topic
- Attendance: 80% (as per Institute policy; will be enforced)
- Assessment: a tentative structure is as follows:
 - Quiz (MCQ): $15 + 15 = 30$ (or Mid-semester exam: 30) (to be finalized soon)
 - Assignments: $15 + 15 = 30$
 - End-semester exam: 40

Organization of the course

Theoretical considerations, real-world applications, case studies

- **Module 1:** The atmospheric system – vertical and horizontal transport, circulation
- **Module 2:** Basics of atmospheric chemistry – major processes, measurement units

- **Module 3:** Stratospheric processes → **Ozone depletion; Global**
- **Module 4:** Tropospheric gas-phase species → **Photochemical smog and acid rain; Case study: USA**
- **Module 5:** Aerosols
- **Module 6:** Air pollution control technologies – stationary and mobile controls
- **Module 7:** Risk assessment and policy intervention → **NAAQS, NAQI; Case study: India**

We will look at case studies with implications ranging from local to regional to global scales

Overall reading material

- Daniel Jacob, 1999 – Introduction to atmospheric chemistry (<http://acmg.seas.harvard.edu/publications/jacobbook/index.html>)
- Finlayson-Pitts and Pitts, 2000 – Chemistry of the upper and lower atmosphere (I will advise as required; selected parts)
- De Nevers, 2000 – Air pollution control engineering (I will advise as required; selected parts)
- Specialized reports on certain topics – e.g., ozone depletion

Module 1: the atmospheric system

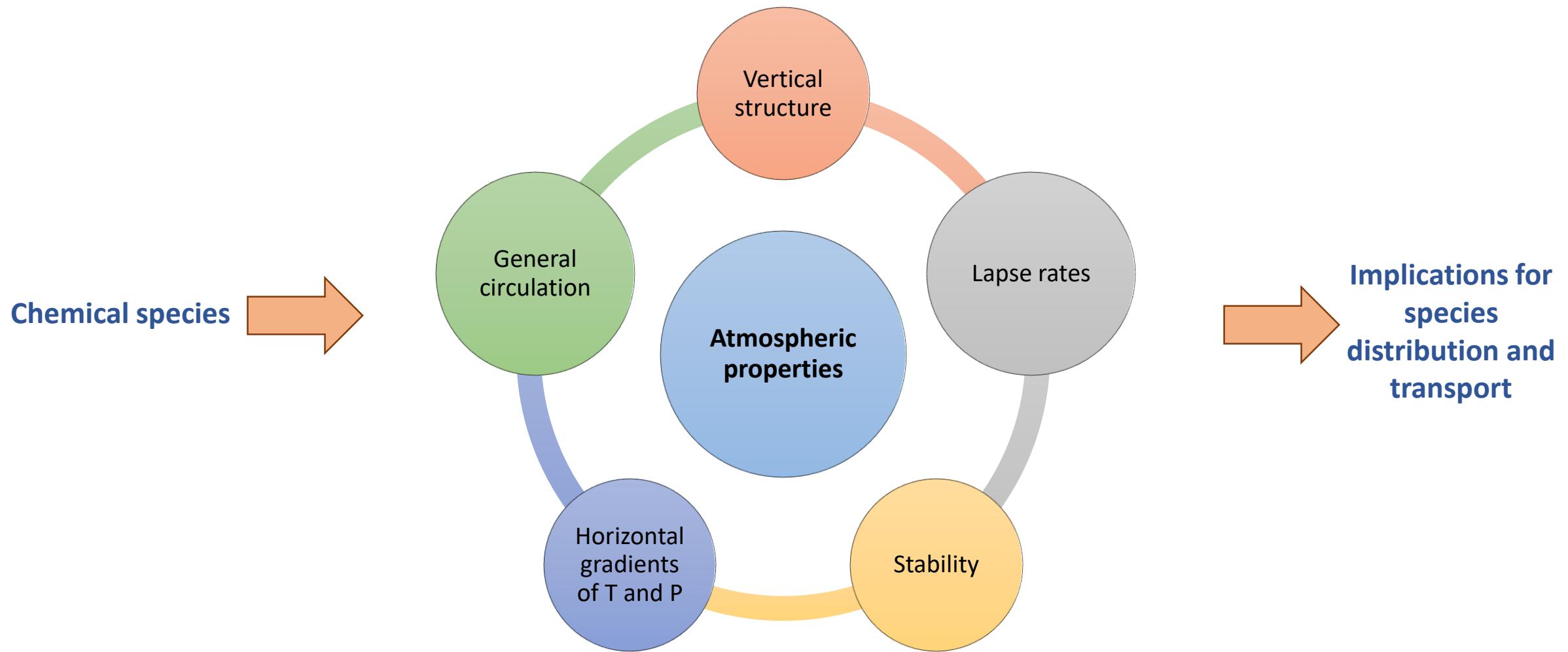
Topics to be covered

- Atmospheric parameters, transport, circulation
 - Structure of the atmosphere
 - Variation of T, P with altitude; vertical transport
 - Horizontal transport
 - General circulation
 - Timescales of transport

Required reading

- Jacob, 1999 – Introduction to atmospheric chemistry (<http://acmg.seas.harvard.edu/publications/jacobbook/index.html>)
 - Chapters 2 and 4
- Finlayson-Pitts and Pitts, 2000 – Chemistry of the upper and lower atmosphere (IIT-Mandi library)
 - Chapter 1A

Properties of the atmosphere



Structure of the atmosphere

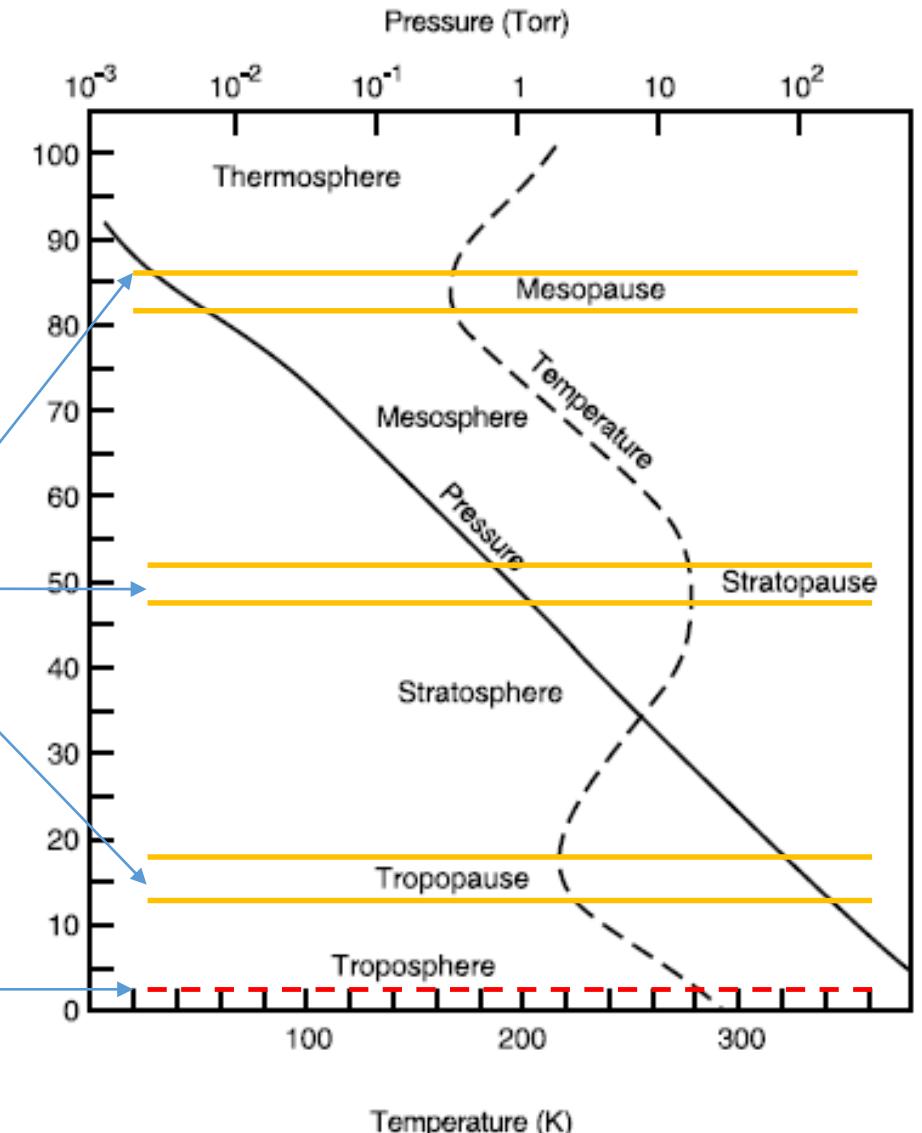
- Variation of T and P; Layers

- **Troposphere:** 0-12 km; ~80% of atmospheric mass; weather, clouds
- **Stratosphere:** 12-50 km; O₃ layer; stable, no vertical mixing; flights
- **Mesosphere:** 50-80 km; Meteorite graveyard
- **Thermosphere:** 80-750 km; International Space Station
- **Exosphere:** Beyond 750 km; Exchange of H, He, N₂, O₂ with space

Note the change of temperature with altitude!

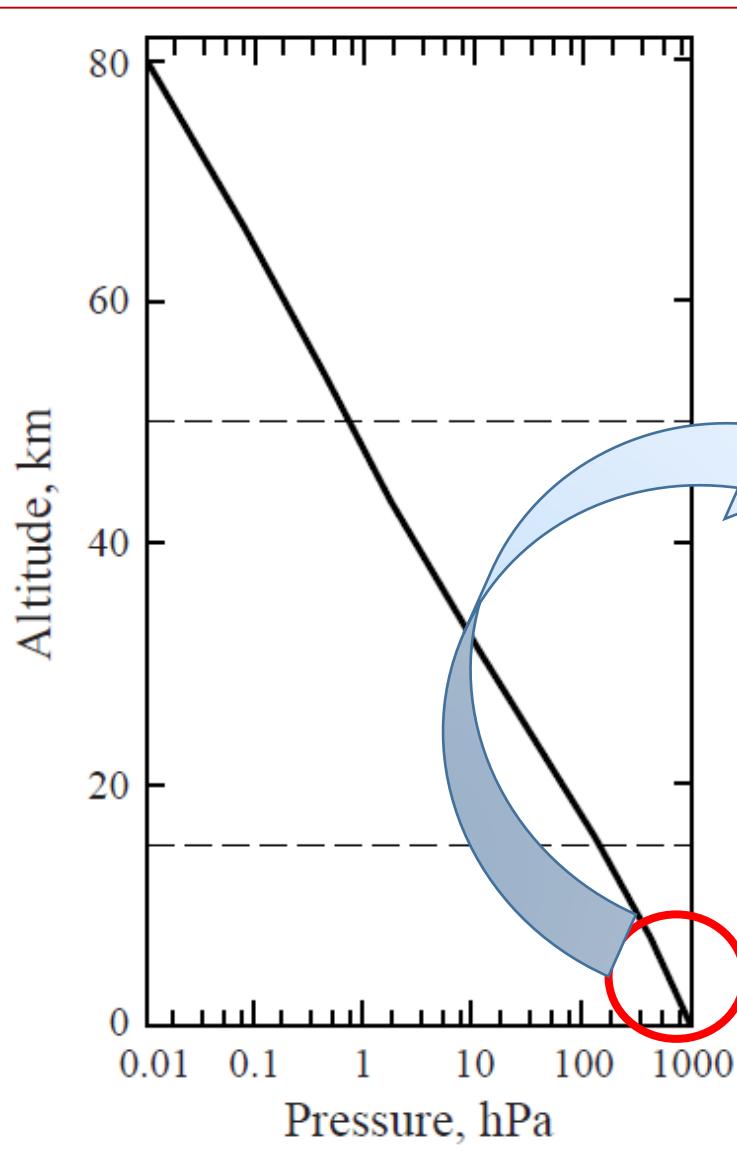
Regions of inflection

Planetary boundary layer (PBL, 1-2 km, region of mixing);
drag forces act



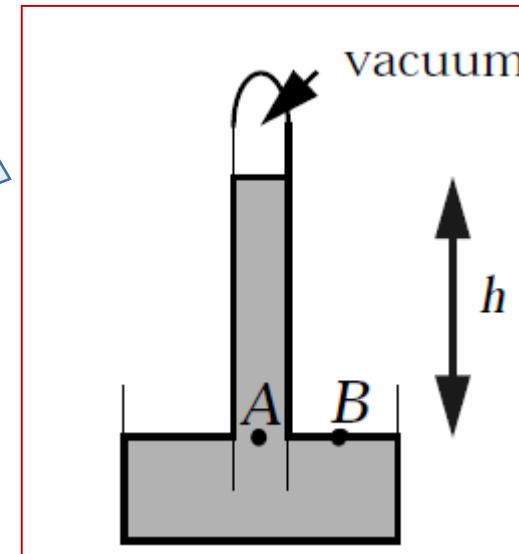
Properties of the atmosphere: Variation of meteorological parameters and vertical transport

Atmospheric profile of pressure



- The pressure profile is NOT linear – it is exponential

Parameterization of pressure



$$P_A = \rho_{Hg}gh$$

where $\rho_{Hg} = 13.6 \text{ g cm}^{-3}$ (density of Hg), $g = 9.8 \text{ m s}^{-2}$, and $h = 76 \text{ cm}$ at sea level

So, sea-level pressure (P_A) = $1.013 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$

Units

$$1 \text{ kg m}^{-1} \text{ s}^{-2} = 1 \text{ Pa}$$

$$\text{Sea-level pressure (P)} = 1.013 \times 10^5 \text{ Pa} = 1013 \text{ hPa} = 1013 \text{ mb} = 1 \text{ atmosphere}$$

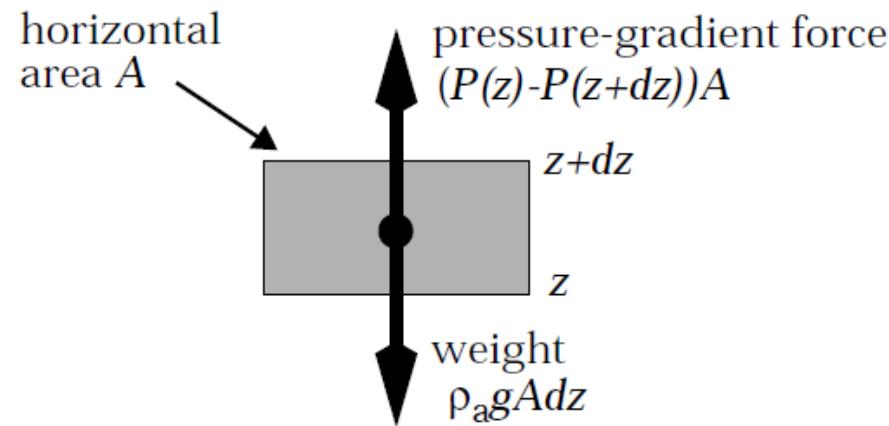
Atmospheric profile of pressure (Contd.)

Now let's take a look at how pressure varies with altitude

At any altitude z , the fraction of pressure above that altitude is $P(z)/P(0)$

At 80 km, $P(z) = 0.01$ hPa. So, 99.999% of the atmosphere lies below 80 km

Deducing the vertical profile of pressure



The net force on the slab = $(P(z) - P(z+dz))A$ and is directed upwards since $P(z) > P(z+dz)$. This is the pressure-gradient force.

For the slab to be in equilibrium, the pressure-gradient force must be balanced by the weight:

$$\rho_a g Adz = (P(z) - P(z + dz))A$$

Rearranging: $\frac{P(z + dz) - P(z)}{dz} = -\rho_a g$

Or, $\frac{dP}{dz} = -\rho_a g$

Now, from the ideal gas law: $\rho_a = \frac{PM_a}{RT}$ (M_a = mol. wt. of air)

Substituting: $\frac{dP}{P} = -\frac{M_a g}{RT} dz$ Assuming T to be constant: $\ln P(z) - \ln P(0) = -\frac{M_a g}{RT} z$

Or, $P(z) = P(0) \exp\left(-\frac{M_a g}{RT} z\right)$

$$H = \frac{RT}{M_a g}$$

$$P(z) = P(0) e^{-\frac{z}{H}}$$

Barometric Law (explains observed exponential dependence of P on z)

- For a mean atmospheric temperature of 250 K, $H = 7.4$ km.
- For each H rise in altitude, pressure and air density drop by a factor of $e = 2.7$

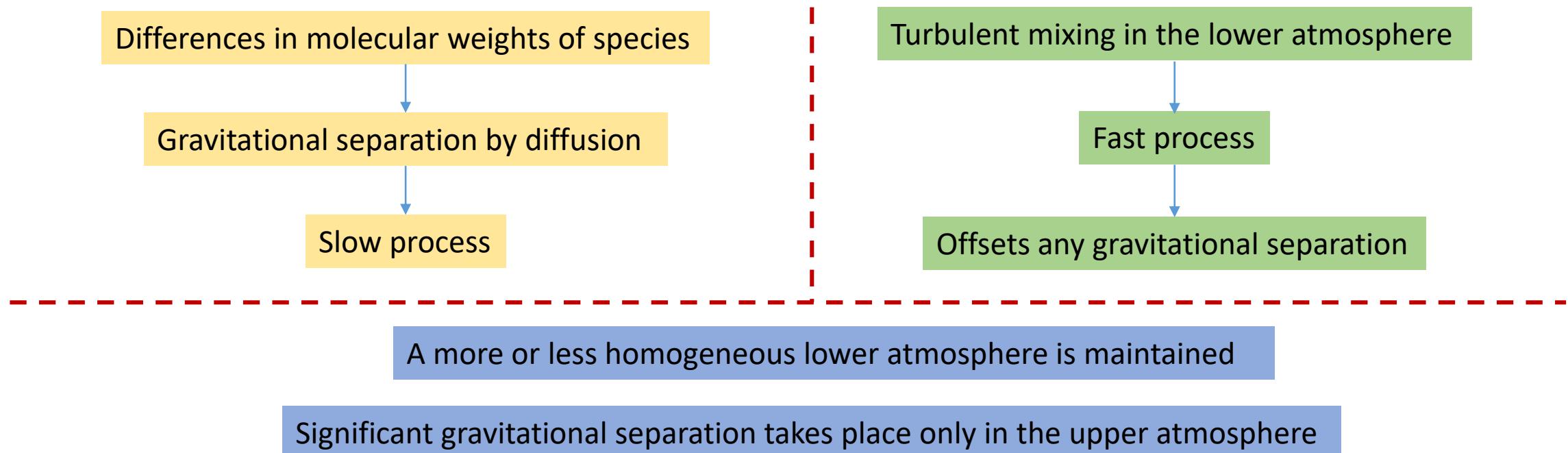
Definition of scale height Barometric law in terms of H

Atmospheric profile of pressure (Contd.)

Will scale height (H) vary for individual chemical species in the atmosphere?

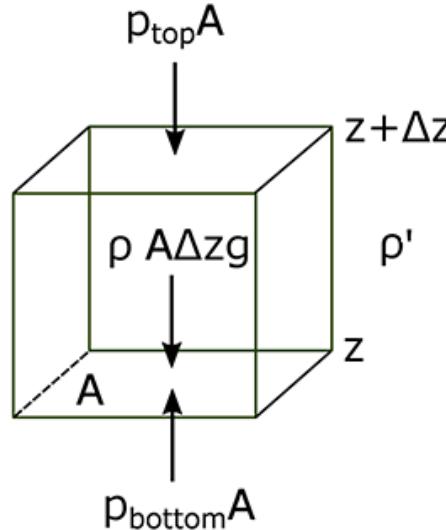
- In the derivation of scale height, we have assumed that air behaves as a homogeneous gas with mol. wt. 29 g mol^{-1}
- But, based on molecular weight, different components should have different scale heights – right? Example: N_2 vs O_2

The answer is: NO. There are 2 processes at play here:



Atmospheric profile of temperature – stability and vertical transport

- Vertical wind speeds (from horizontal convergence/divergence) are generally in the range $0.001\text{-}0.01 \text{ m s}^{-1}$. Resulting timescale for surface-tropopause transport is $\sim 2\text{-}3$ months.
- Faster vertical transport can take place locally – driven by buoyancy (in turn driven by temperature gradients).



$$\gamma_b = \frac{\rho' - \rho}{\rho} g$$

$\gamma_b = \text{buoyant acceleration}$

- If the object is lighter than the fluid it is immersed in, it is accelerated upwards.
- If it is heavier, it is accelerated downward

Whether the air parcel is stable or unstable depends on the buoyancy (both magnitude and direction)

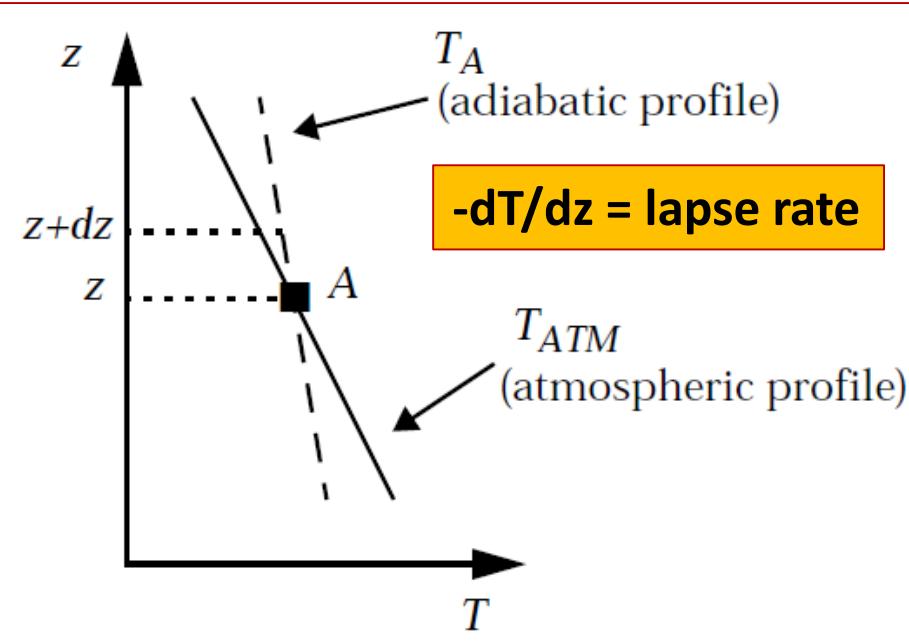
So, the question is: how is buoyancy (i.e., atmospheric stability) driven by temperature?

Buoyant motions (Contd.)

Consider a parking lot painted black where the surface temperature ($T=301\text{ K}$) is slightly higher than that of the surrounding area ($T'=300\text{ K}$). What is the buoyant acceleration of air over the parking lot?

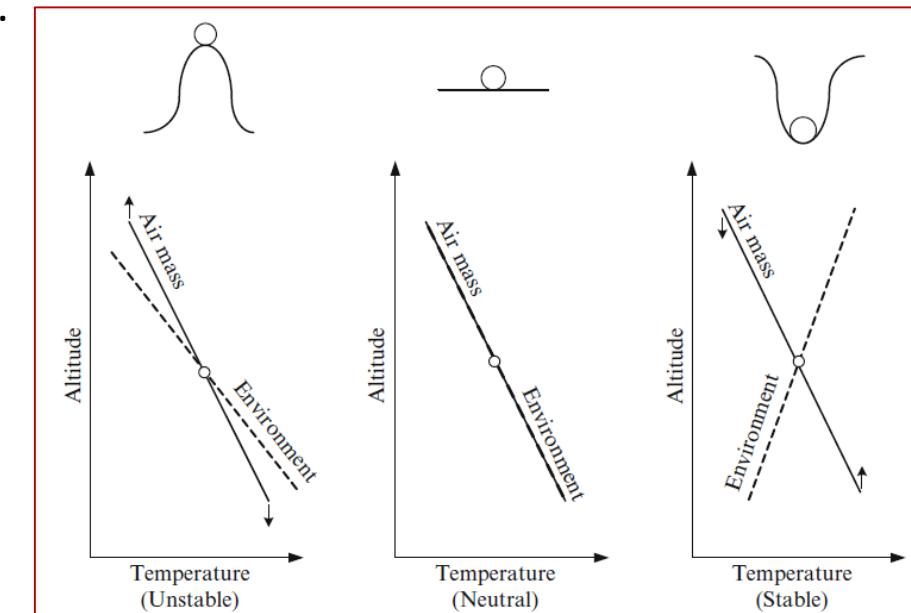
Atmospheric profile of temperature – lapse rates

- Consider a horizontally homogeneous atmosphere with a vertical temperature profile $T_{ATM}(z)$



- Assumption:** the air parcel does not exchange energy with its surroundings as it rises, i.e., the rise is adiabatic.
- The air parcel cools as it rises.
- Whether the air parcel keeps on rising depends on how rapid its adiabatic cooling rate is relative to the change of temperature with altitude in the atmosphere.

- Case 1:** $T_A(z+dz) > T_{ATM}(z+dz)$ – unstable, convective
- Case 2:** $T_A(z+dz) < T_{ATM}(z+dz)$ – stable
- Case 3:** $T_A(z+dz) = T_{ATM}(z+dz)$ – neutral



The dry adiabatic lapse rate

- The dry adiabatic lapse rate can be parameterized as follows:

$$\Gamma = g/C_p = 9.8 \text{ K km}^{-1}$$

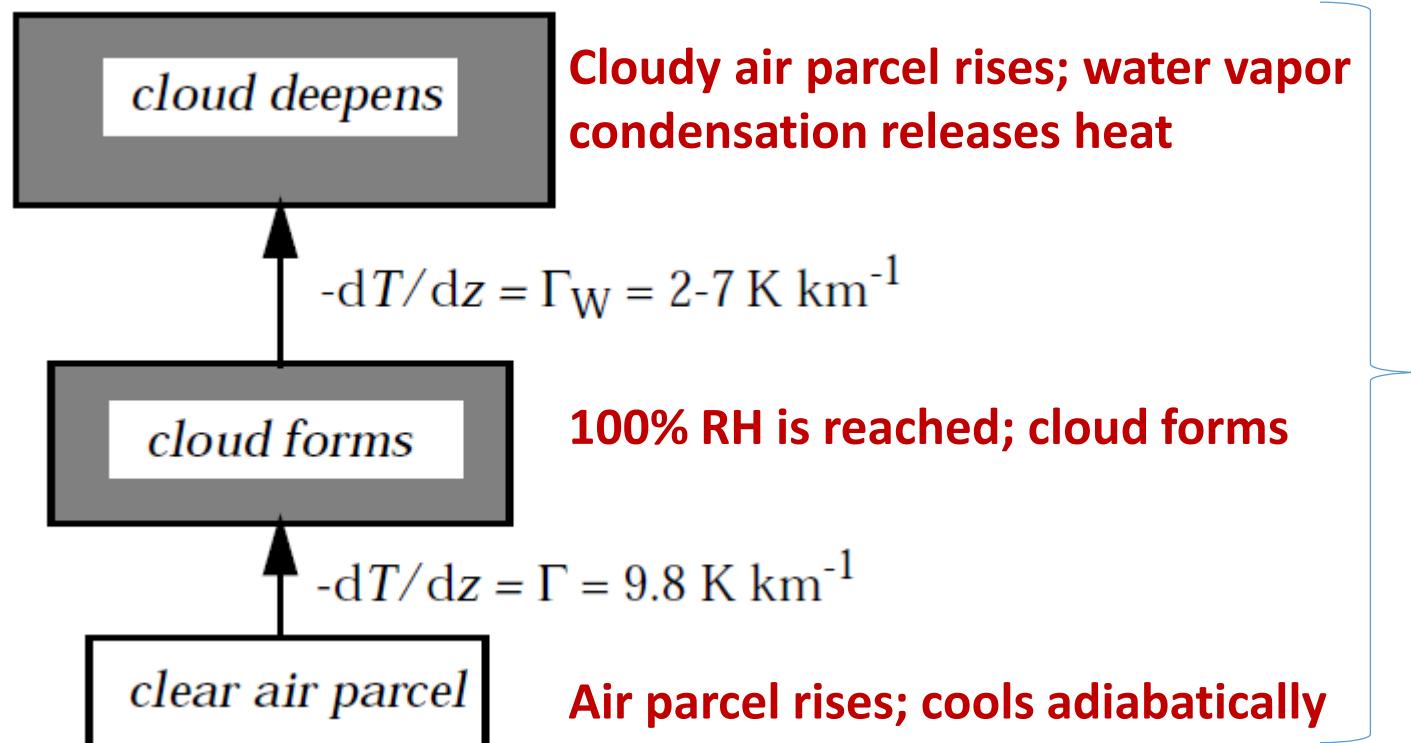
- We can diagnose whether an atmosphere is stable or unstable with respect to vertical motions by comparing its lapse rate to $\Gamma = 9.8 \text{ K km}^{-1}$

$$\begin{aligned}-\frac{dT_{ATM}}{dz} &> \Gamma && \text{unstable} \\ -\frac{dT_{ATM}}{dz} &= \Gamma && \text{neutral} \\ -\frac{dT_{ATM}}{dz} &< \Gamma && \text{stable}\end{aligned}$$

- **Critical assumption: the air parcel is dry.**
- **So, what happens in humid conditions? We invoke a parameter called the “wet adiabatic lapse rate”**

The wet adiabatic lapse rate

- Condensation of water vapor (cloud formation) is an exothermic process
- Provides an internal source of heat that partly compensates for the cooling due to expansion of the parcel
- Increases the buoyancy of the parcel



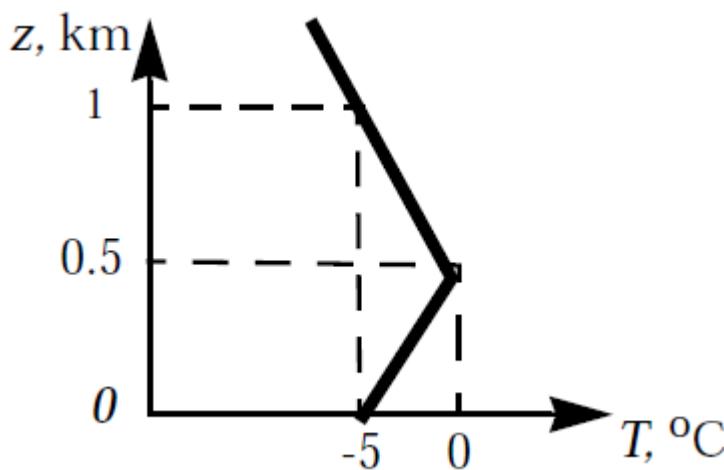
- The rate of cooling of rising humid air is **smaller** than that of dry air.

This is called “**wet adiabatic lapse rate**.”

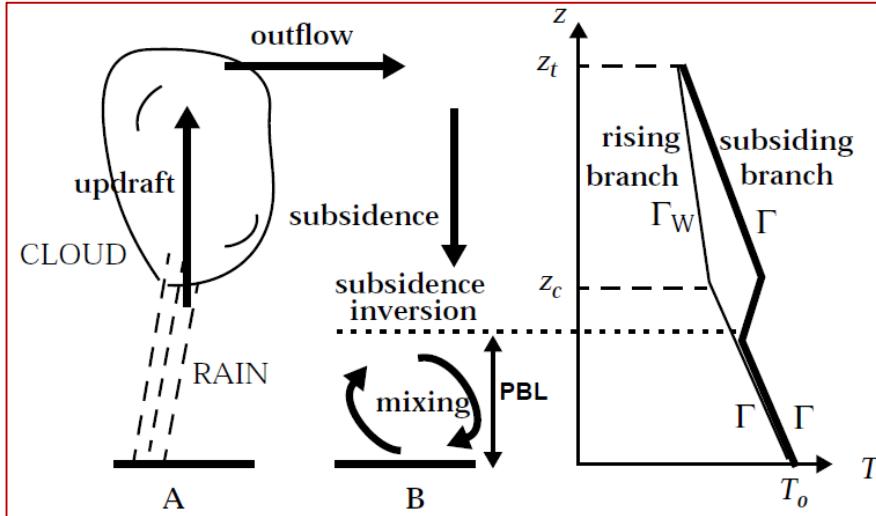
Temperature inversions

- Special cases where temperature increases with altitude – leads to stable equilibrium
- Limits convection and vertical mixing – pollutants are trapped near the surface

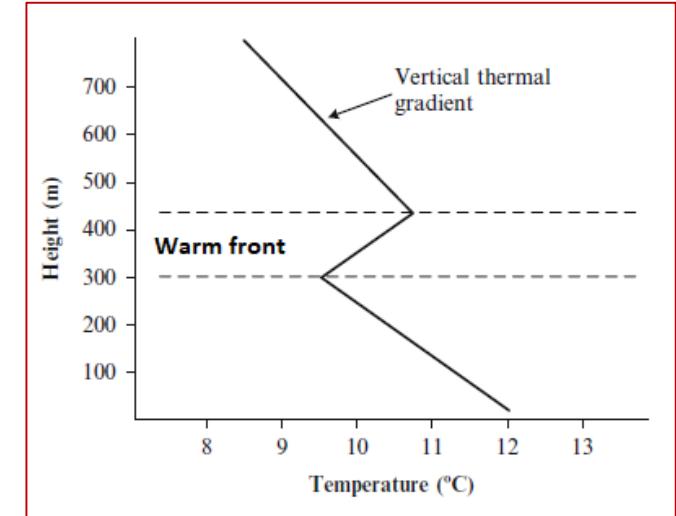
Radiation/Surface inversion: cooling of lower atmospheric layers



Subsidence inversion: adiabatic warming of descending air



Frontal inversion: horizontal transport of warm/cold air



- Mostly nocturnal and wintertime – cooling of surface due to long-wave radiation release
- Clear skies and low wind speeds favor its formation
- Broken up during the day due to solar heating

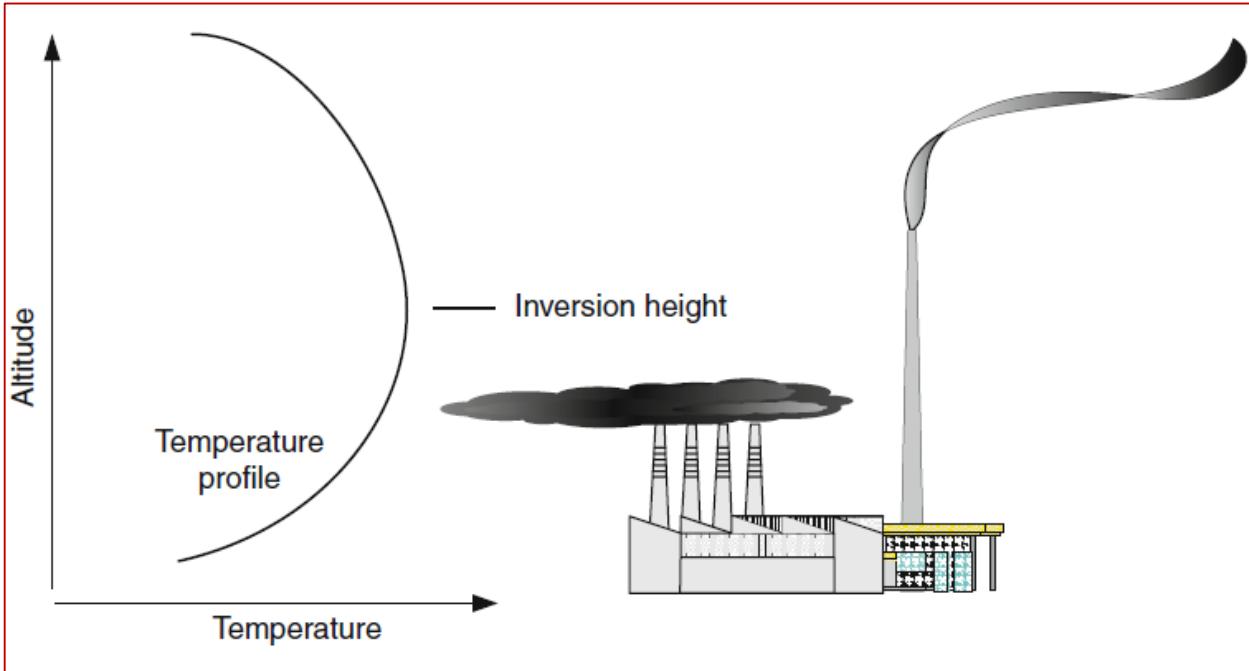
- Descending movement of cold air masses from above – heating due to compression
- Elevated inversion layer (1-3 km) – contrast with surface inversion
- Can last for days – pollution episodes inside the PBL

- Warm air mass overrides a cold layer (or a cold layer slides under a warm layer)
- Frequently associated with weather fronts
- Elevated inversion layer

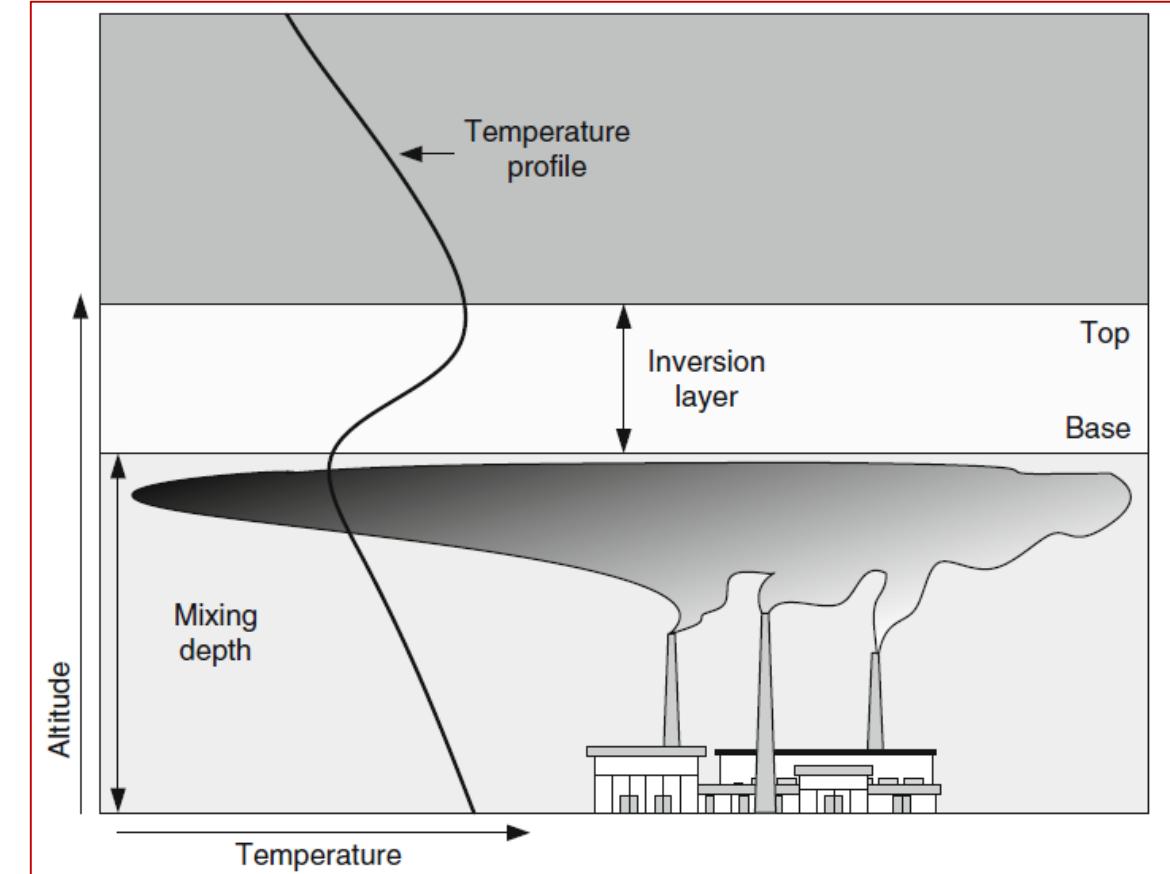
Example of a smoke ceiling



Behavior of a plume under inversion conditions



- Stack height of industrial units is critical
- Low-lying surface inversions can trap emissions from smaller stacks
- Emissions from taller stacks can be dispersed – **good, right?**

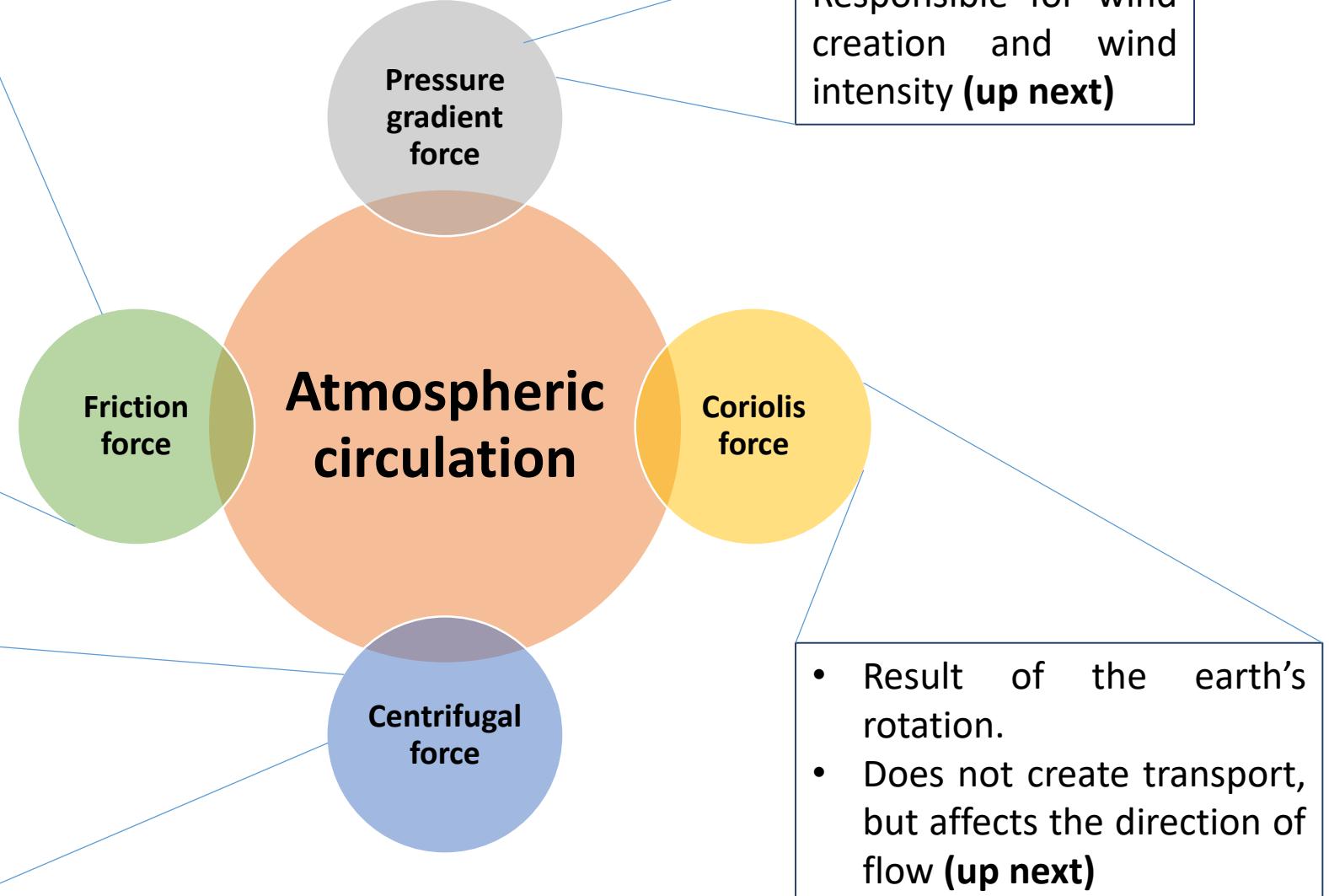


Taller stacks – greater dispersion – long-range transport and deposition (after dilution/mixing) – **case study: acid rain (we'll come back to it)**

Properties of the atmosphere: Horizontal transport and circulation

Major forces that affect atmospheric circulation

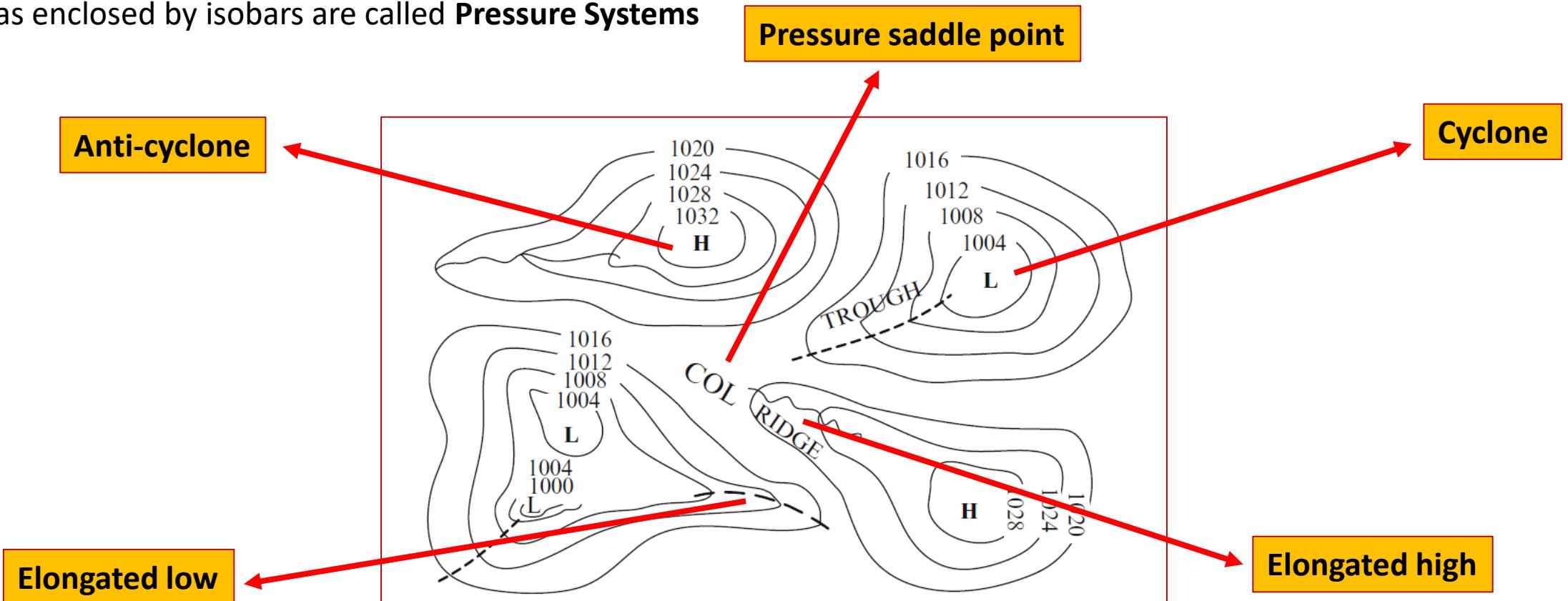
- Result of surface friction – opposes wind movement.
- Causes slowdown and indirectly affects Coriolis force.
- $F_T = -m\alpha V$, where α is the surface roughness coefficient, m is the mass of air, V is the wind velocity



Atmospheric pressure systems

Key points

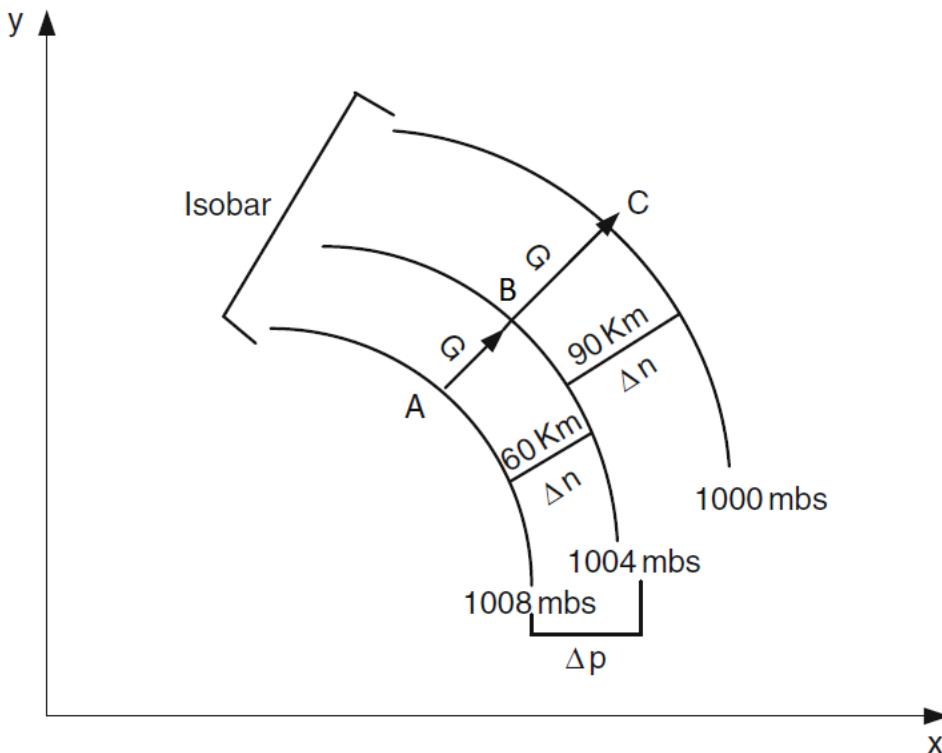
- Pressure is the weight of the air column above a certain location – varies within a small range (950-1050 mb)
- Lower values at higher altitudes (self-evident) – need to standardize to a common elevation for purposes of comparison
- That common reference point is the **Mean Sea Level (MSL)** pressure
- On surface maps, pressure variations are plotted as lines that connect points with same pressure – isobars
- Areas enclosed by isobars are called **Pressure Systems**



Pressure gradient force

The force that tends to move air molecules from high to low pressure areas in order to attain equilibrium is called the pressure gradient force (F_B)

- Pressure gradient is calculated as the ratio of the pressure difference between two successive isobaric lines to their distance, i.e. $\Delta P/\Delta n$



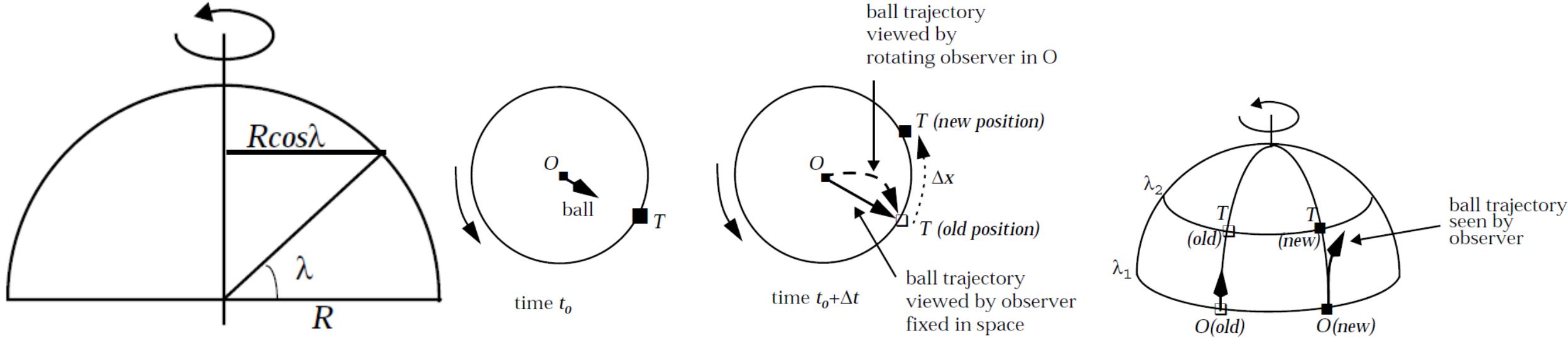
Pressure gradient

- AB: $PG_1 = 4 \text{ mb}/60 \text{ km} = 0.07 \text{ mb km}^{-1}$
- BC: $PG_2 = 4 \text{ mb}/90 \text{ km} = 0.04 \text{ mb km}^{-1}$
- $PG_1 > PG_2$

The same force that we considered while deriving atmospheric stability equations and scale height

Coriolis force

The force that arises out of the earth's rotational motion. Consider an observer fixed in space and watching the earth rotate.



Translational velocity

$$V_E = 2\pi R \cos \lambda / t$$

where λ is the latitude, R is the radius of the earth, t is the time

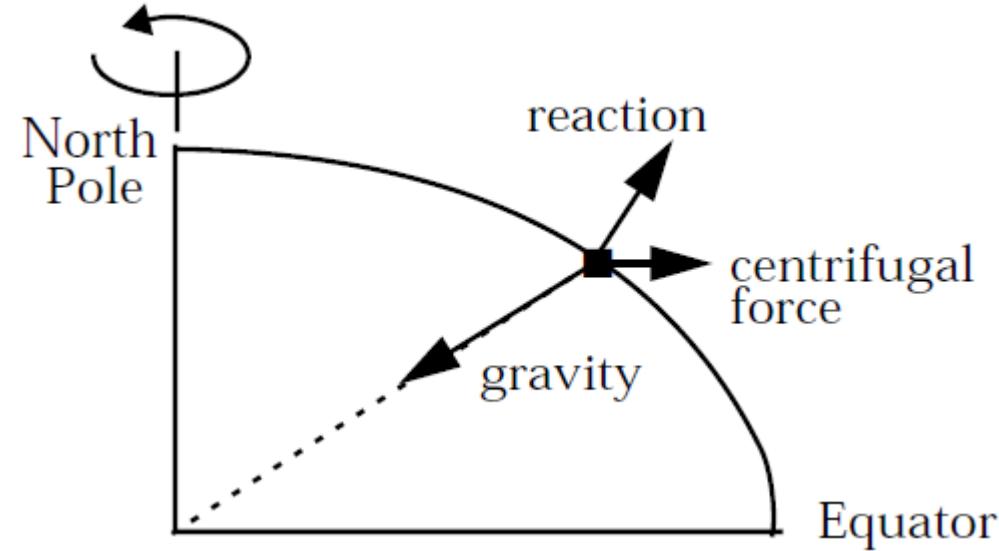
- The Coriolis force is a fictitious force; applies only to a rotating frame of reference
- We must consider it since all atmospheric observations are in this rotating frame of reference

- Ball travels from λ_1 to λ_2
- Conservation of angular momentum $m V_{E(\lambda_1)} R \cos \lambda_1$
- $V_{E(\lambda_2)} < V_{E(\lambda_1)}$
- The ball must acquire an eastward velocity relative to the earth

Coriolis force (Contd.)

The Coriolis force applies similarly to motions at a fixed latitude.

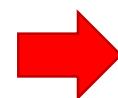
Forces of gravity and reaction applied to an object at rest on the earth's surface combine to balance the centrifugal force.



- Ball thrown from W to E: angular velocity increases – centrifugal force deflects towards the equator
- Ball thrown from E to W – angular velocity decreases – deflection towards the pole

Generalization of the Coriolis effect

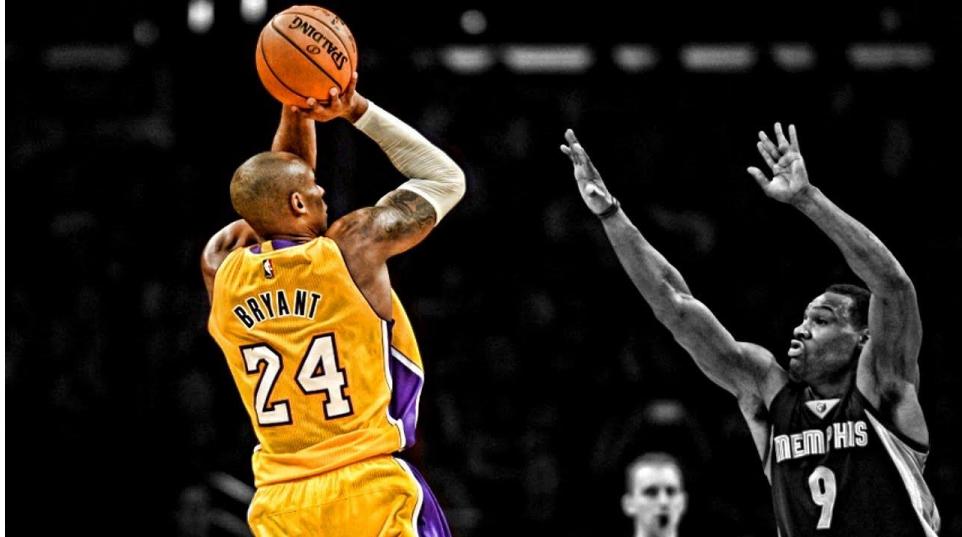
- Coriolis force applies **perpendicular to the direction of motion**
- Deflects air masses towards the **right in the NH** and towards the **left in the SH**
- Significant only for large-scale motions: $\Delta Y = \omega \Delta X^2 \sin \lambda / v$, where ω is the angular velocity of the earth and v is the speed of the moving object in the rotating FOR



But how significant is the Coriolis force in the real world?

How significant is the Coriolis force?

Let's take two examples



Let's say Kobe Bryant has returned from beyond to the LA Lakers and shoots a 3 pointer (10 m s^{-1}) from the top of the box (7 m). How does the ball deflect?

$$\Delta Y = \omega \Delta X^2 \sin \lambda / v \text{ (here, } \lambda = 39^\circ \text{ (Lakers are playing a home game))}$$

Displacement is 0.22 mm (insignificant)



Let's say Kim Jong-un decides to nuke the US; specifically, New York ($\sim 11000 \text{ km}$). He fires an ICBM (5 km s^{-1}) from Pyongyang. What is the displacement?

$$\Delta Y = \omega \Delta X^2 \sin \lambda / v \text{ (here, } \lambda = 39^\circ \text{)}$$

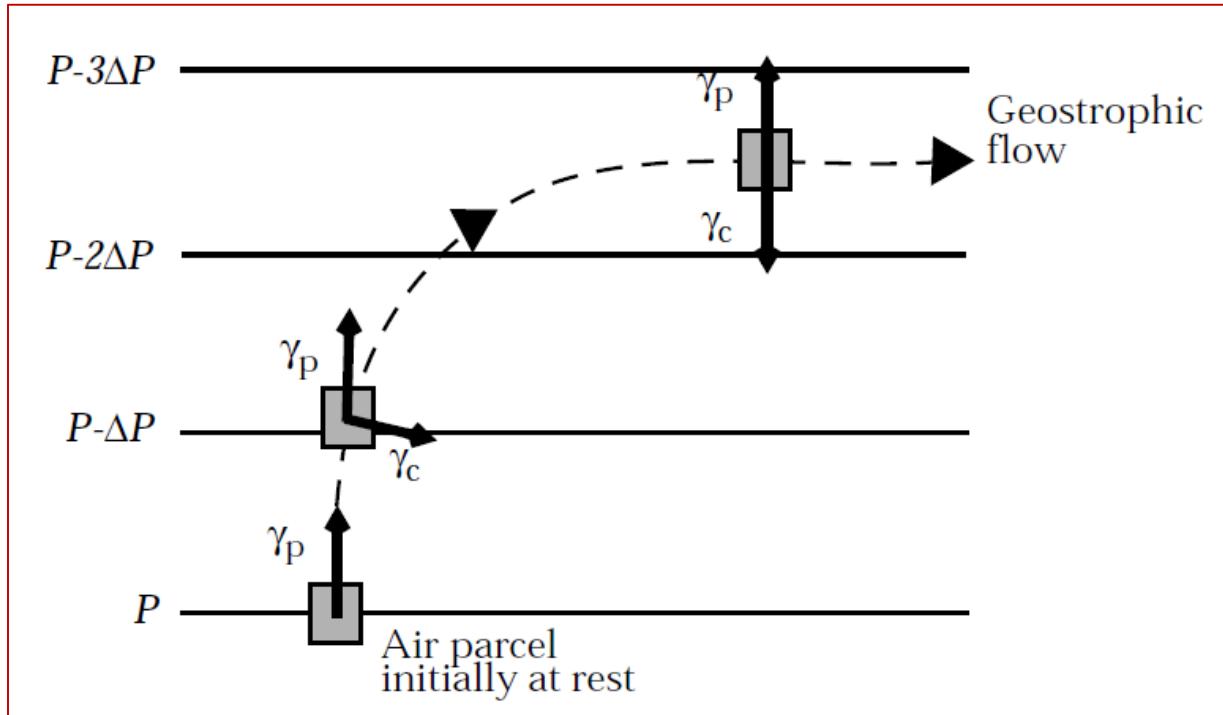
Displacement is $\sim 1100 \text{ km}$ (significant)!
So, New Yorkers should hope that DPRK scientists have forgotten to take the Coriolis effect into consideration!

Geostrophic winds

It is the wind that results from the equilibrium of the pressure gradient force and the Coriolis force.

- Under the pressure gradient force, the air parcel flows perpendicular to the isobars.
- As it acquires speed, the Coriolis force causes it to deflect to the right.
- Eventually, an equilibrium is reached when the Coriolis force balances the pressure gradient force.
- This results in a steady flow (zero acceleration) parallel to isobars – geostrophic flow.
- Note:** higher pressures to the right of the air parcel; lower pressures to the left.

This geostrophic wind is used for approximate calculation of the real wind for areas with no meteorological data.



Example of geostrophic flow in the NH

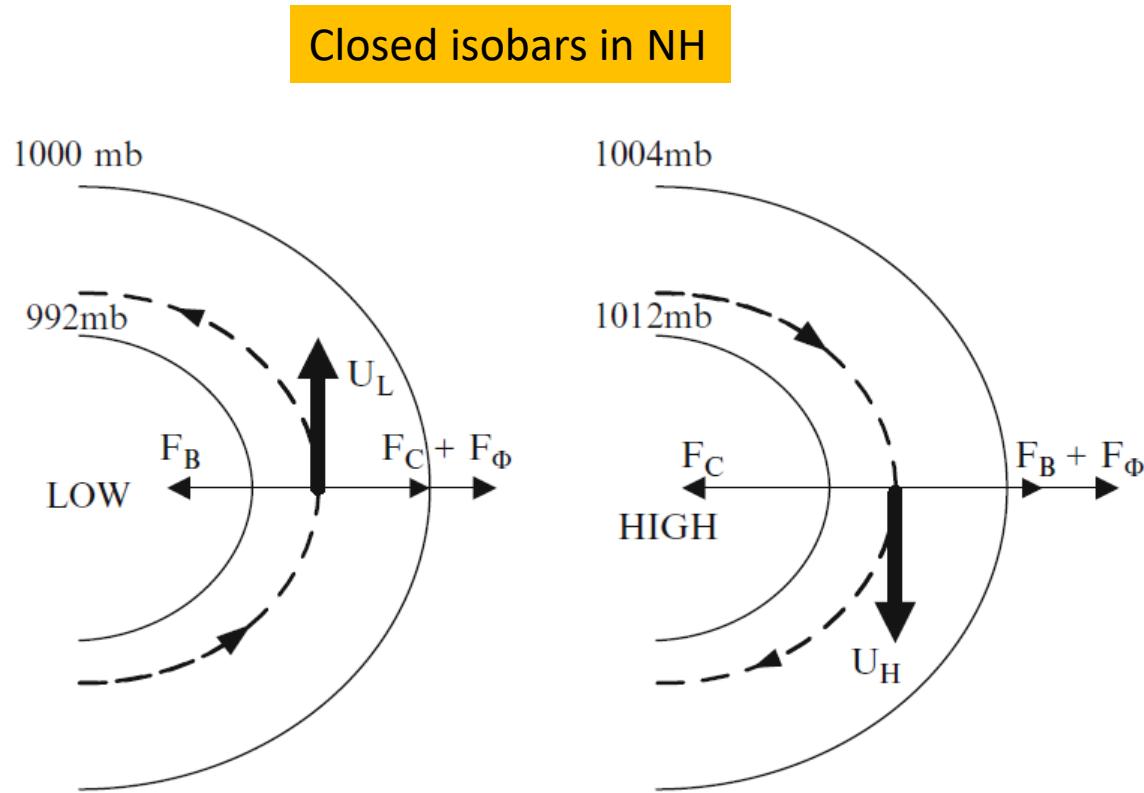
Critical assumptions

Isobars are not curved

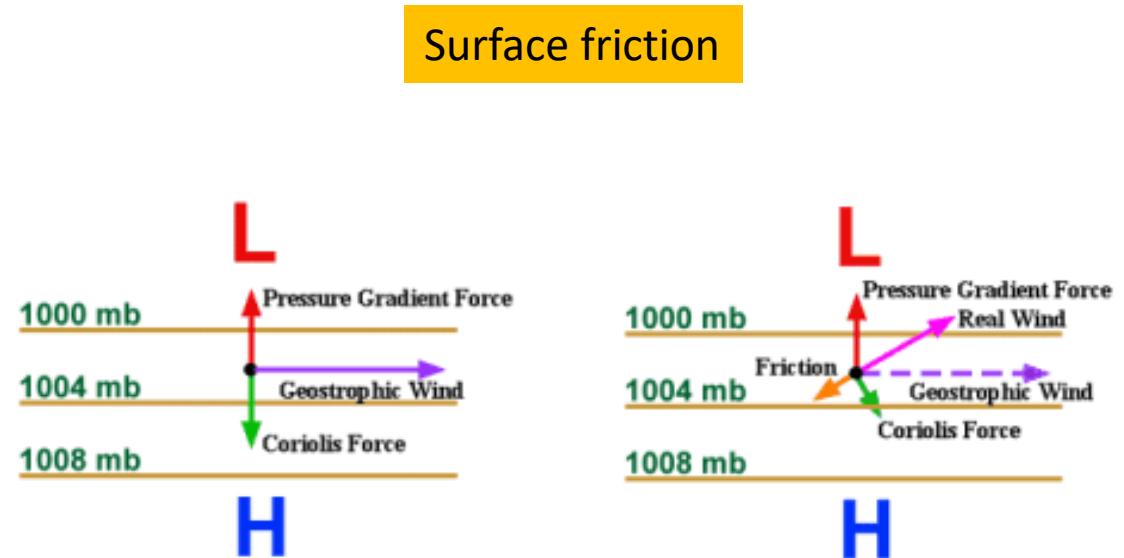
The effect of friction on the wind speed is negligible

Geostrophic winds (Contd.)

Two cases: 1) Isobars are, in reality, curved (closed); 2) Friction affects wind motion close to the surface



- Low pressure system
- Air moves anticlockwise
- Cyclone
- High pressure system
- Air moves clockwise
- Anti-cyclone

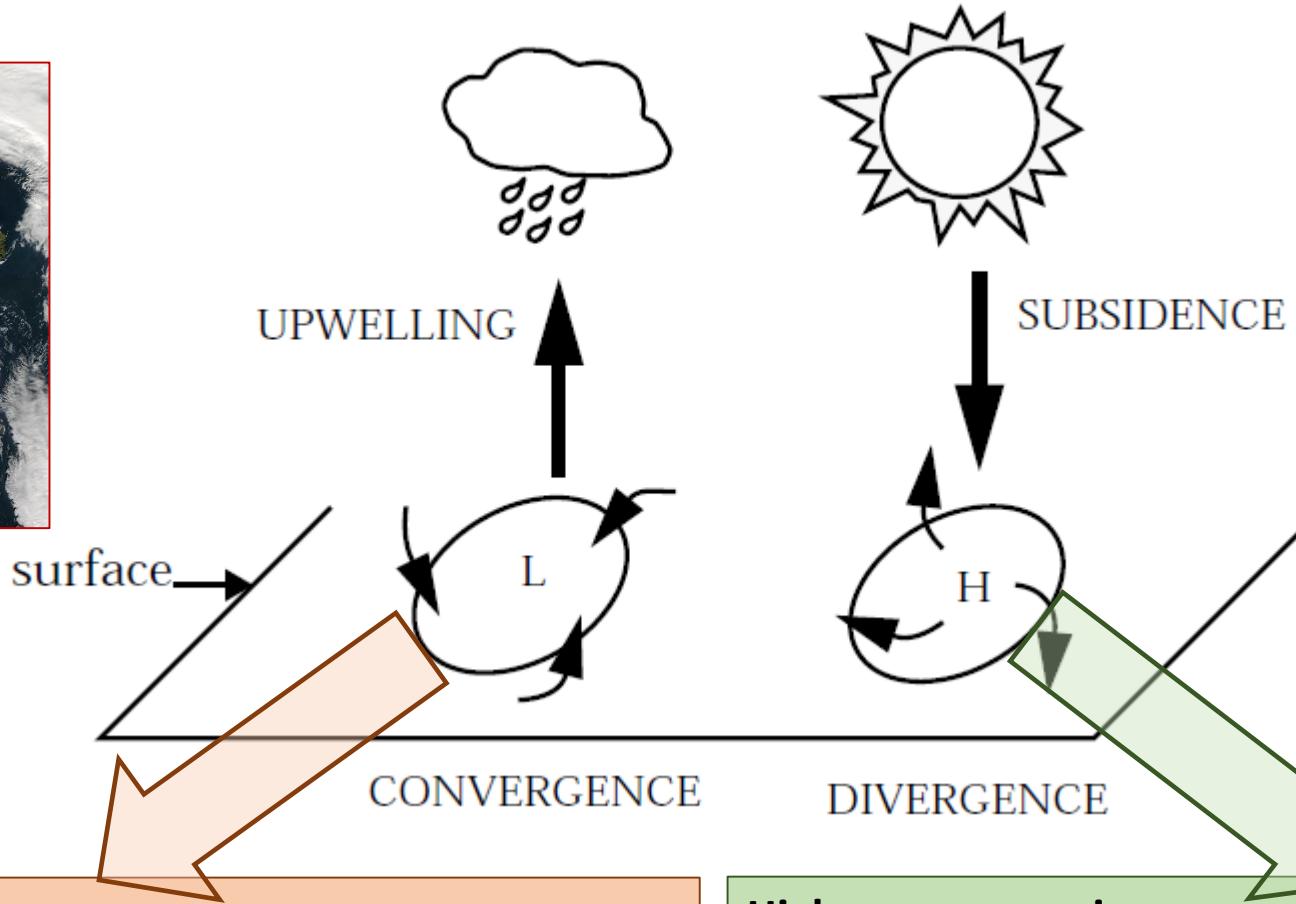


- Friction provided by mountains, trees, buildings, waves
- Loss of momentum in a direction opposite to motion
- Slowdown of Coriolis acceleration
- Geostrophic flow is no longer parallel to the isobars
- The air mass is relatively deflected towards the low pressure region

Weather associated with surface highs and lows



Cyclone



Anti-cyclone

Low pressure region

- Convergent motion at the surface (towards low)
- Upward motion (upwelling) needed for compensation
- Upwelling air cools by expansion – high RH – clouds, rain

High pressure region

- Divergent motion at the surface (away from high)
- Sinking motion (subsidence) needed for compensation
- Subsiding air heats up by compression – low RH – clear, dry

Example: tropics

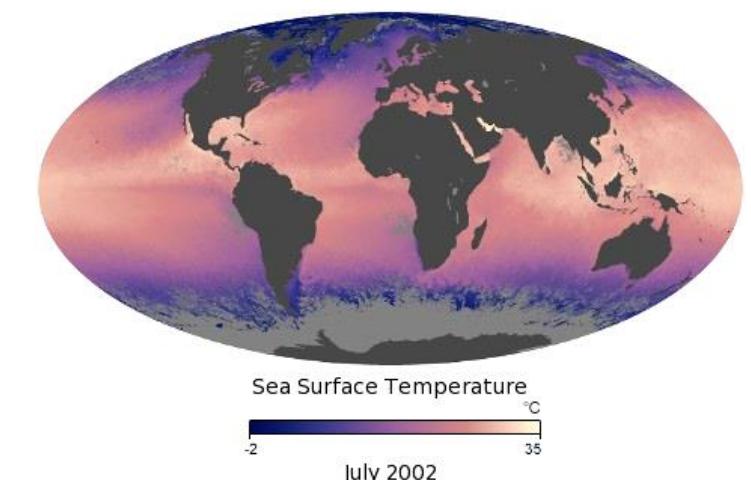
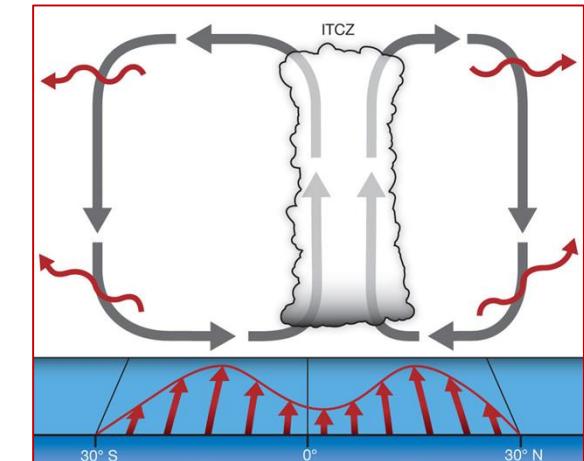
Example: temperate regions

General circulation in the atmosphere

In view of the forces and processes that we've talked about so far, let us now look at the way atmospheric circulation takes place on a global scale

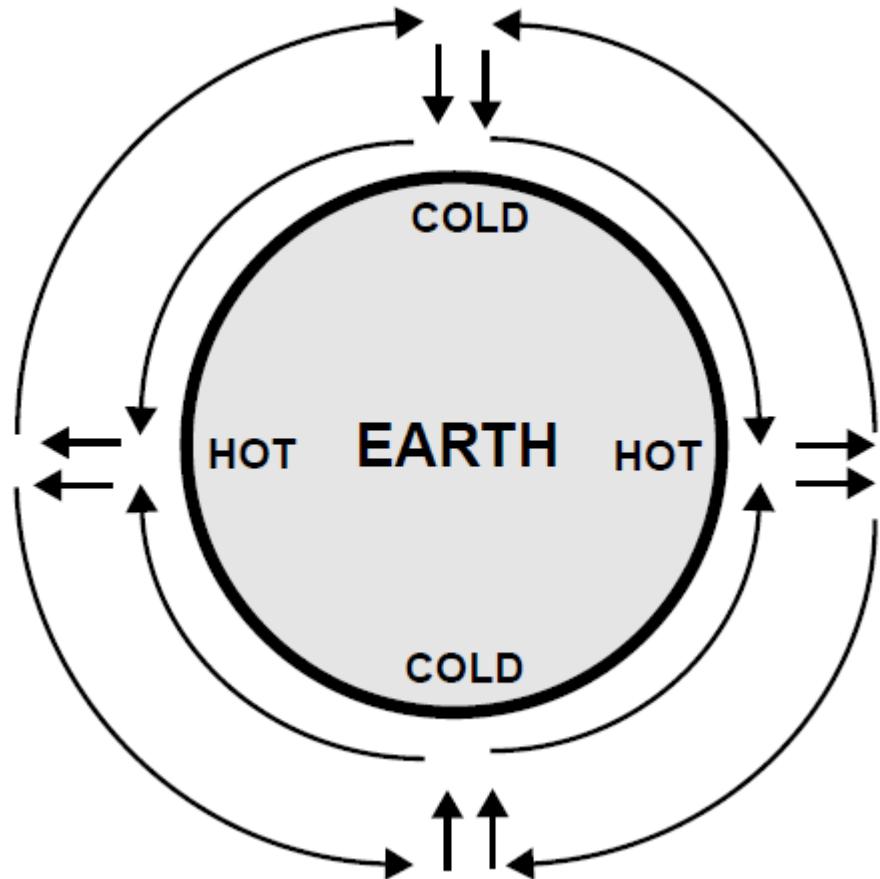
A) Intertropical Convergence Zone (ITCZ)/Equatorial Convergence Zone/Doldrums

- A layer of atmosphere in the equatorial region ($\sim 5^{\circ}\text{N} - 5^{\circ}\text{S}$; a few hundred km wide) that is associated with persistent converging winds, upwelling, clouds and rainfall.
- Clouds can often extend up to the tropopause (Remember this – we'll discuss the effects of this phenomenon while talking about O_3 depletion).
- Only vertical movement of air masses; diminished horizontal winds – termed “doldrums” by ancient sailors.
- The location shifts with season – effect of seasonal heating patterns – moves north of the equator from January to July.
- Region for inter-hemispheric transport (timescale: ~ 1 yr)



General circulation in the atmosphere (Contd.)

B) The single-cell model of general circulation



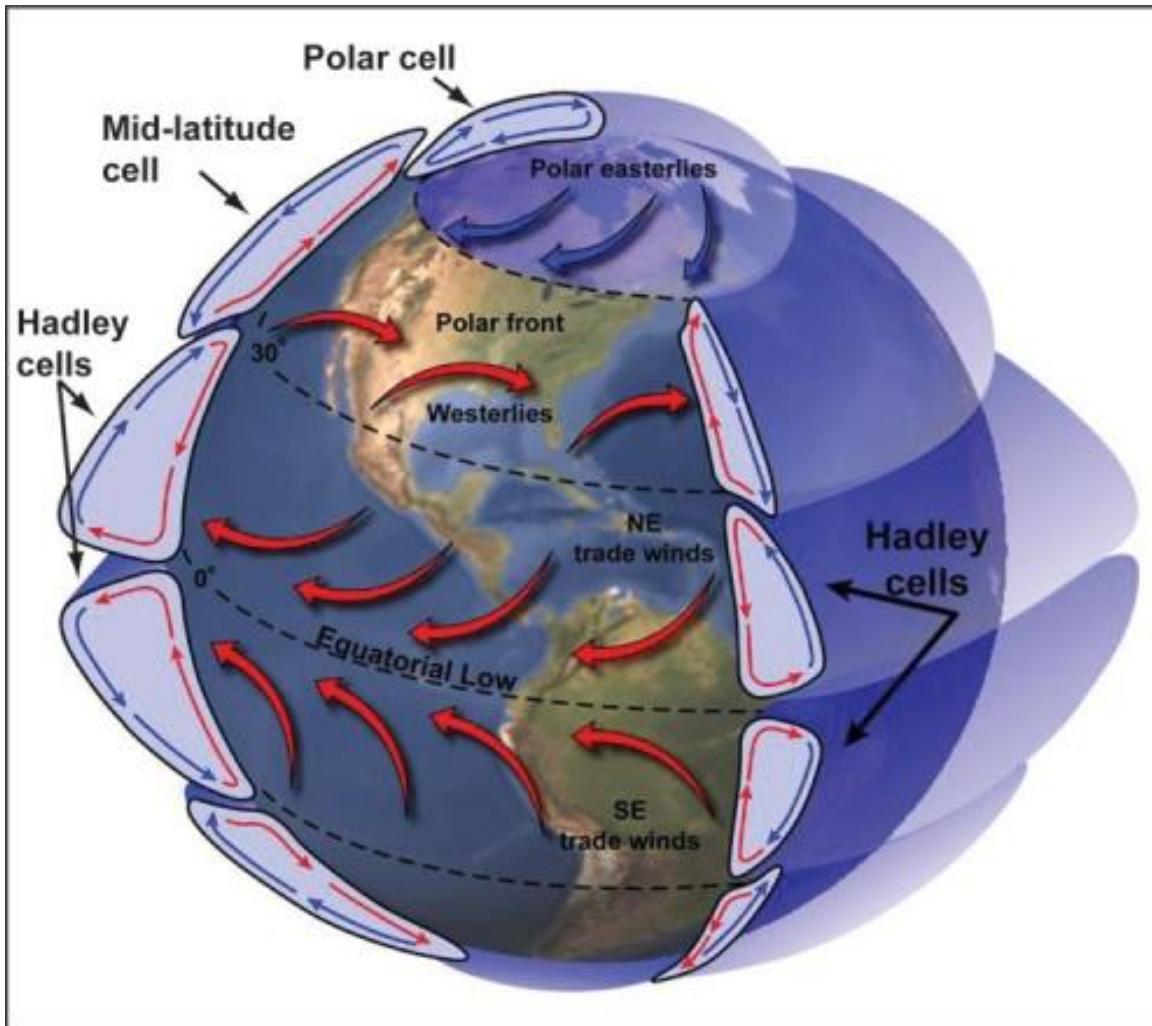
Hadley Cell

- Temperature-driven movement of air **from the equator to the poles above the surface**.
- Compensatory movement of air **from the poles to the equator at the surface**.
- One complete loop each in the NH and the SH.
- **Assumptions**
 - The earth is of uniform composition (i.e., there is no temperature difference between land and ocean surfaces) – **NOT TRUE**.
 - The earth is not tilted (i.e., sunlight strikes directly at the equator) – **NOT TRUE**.
 - The earth rotates negligibly slowly (i.e., there is no Coriolis force) – **NOT TRUE**.

A more realistic picture of the circulation emerges if we take Coriolis force into consideration

General circulation in the atmosphere (Contd.)

C) The 3-cell model of general circulation



Hadley Cell – Equatorial

- Extends from the equator to $\sim 30^{\circ}$ N and S.
- The increasing Coriolis force acting on poleward moving air makes it unstable and breaks it down at around these latitudes.
- Creates sub-tropical high pressure belts (sinking air).
- Creates easterly trade winds (**next slide**).

Ferrel Cell – Mid-latitude

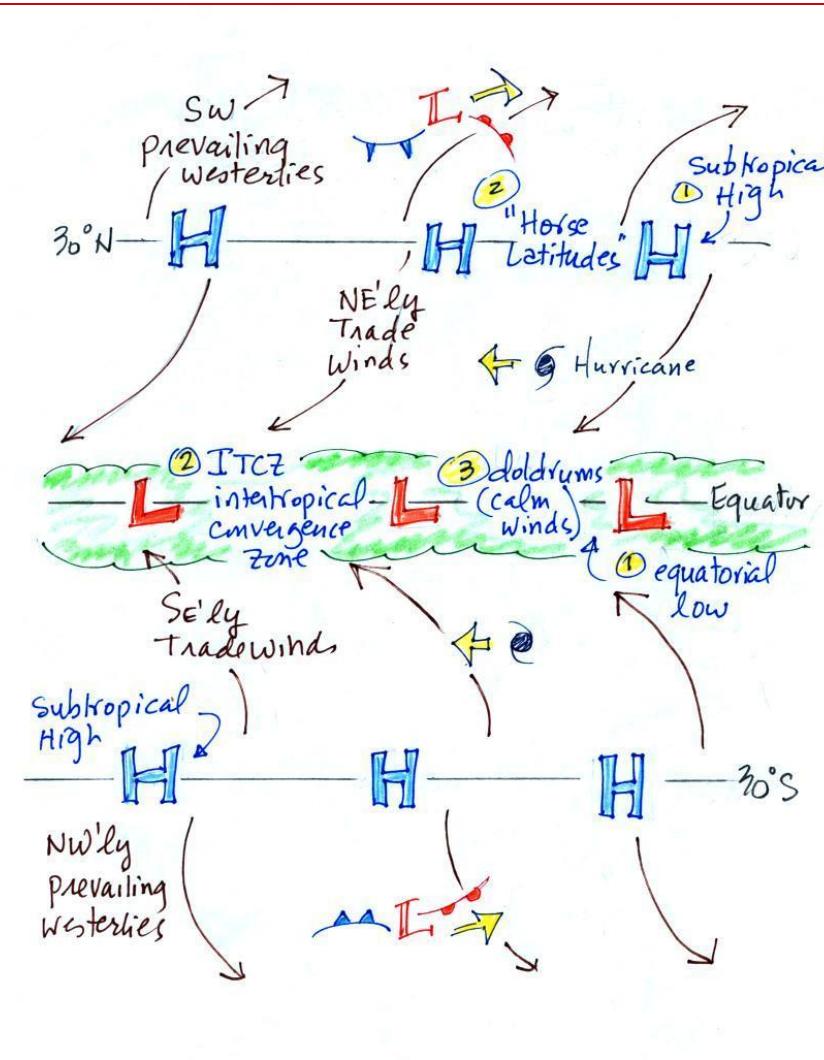
- Secondary circulation feature – existence depends on the Hadley and Polar cells.
- Thermally indirect cell; therefore, weak (the other two cells are thermally direct).

Polar Cell – Well, polar!

- Air masses at 60th parallel are warm and moist enough to undergo a convective thermal loop.
- Creates polar easterlies (**next slide**).

General circulation in the atmosphere (Contd.)

D) The nature of surface winds



The Coriolis force affects the direction of movement of surface winds

Remember the pressure belts – Equator (Low), 30°N/S (High), 60°N/S (Low), Poles (High)

From 30° High towards the equator

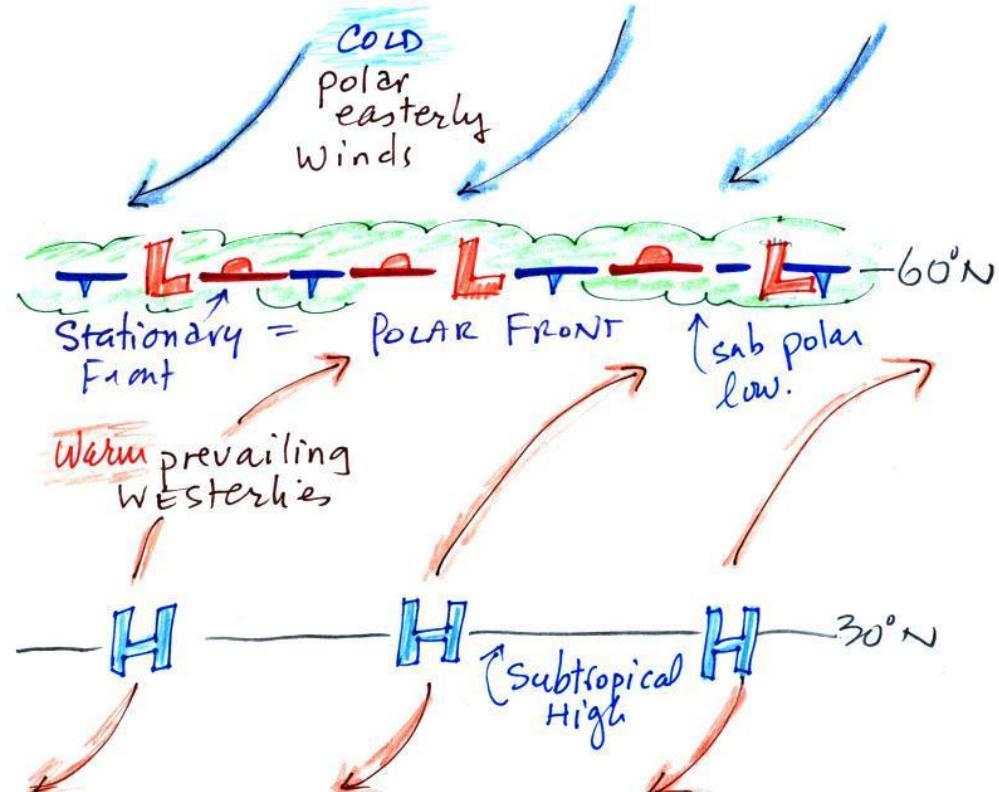
- Coriolis force drives these winds to the right in the NH and to the left in the SH.
- These are Trade Winds (northeasterly in the NH; southeasterly in the SH) – simply referred to as “Easterlies.”
- Sub-tropical Highs associated with sinking air and weak surface winds – “horse latitudes” – **interesting etymology.**

From 30° High towards 60° Low

- Surface winds are deflected to the east.
- Prevailing westerlies (Anti-trade winds).
- 30-60°S is mostly oceans – less friction – westerlies in the SH are more persistent and much stronger than in the NH – “roaring 40s”, “screaming/ferocious 50s”

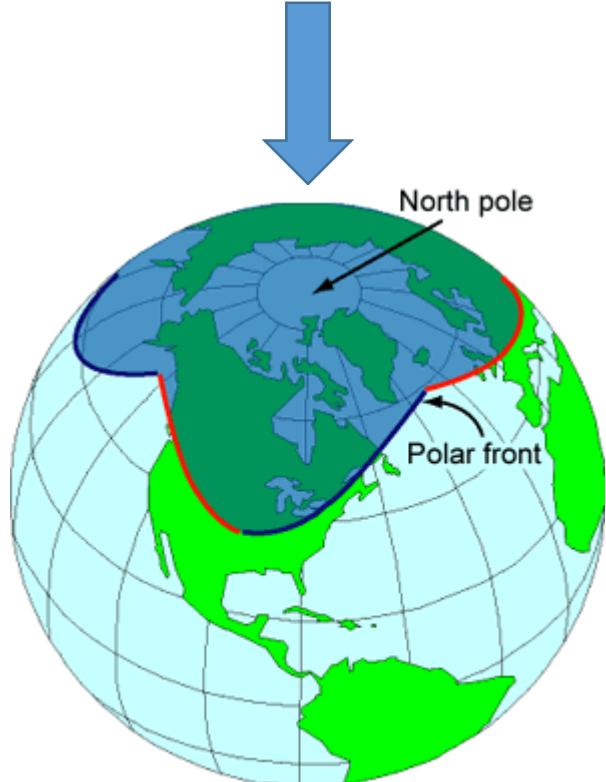
General circulation in the atmosphere (Contd.)

D) The nature of surface winds

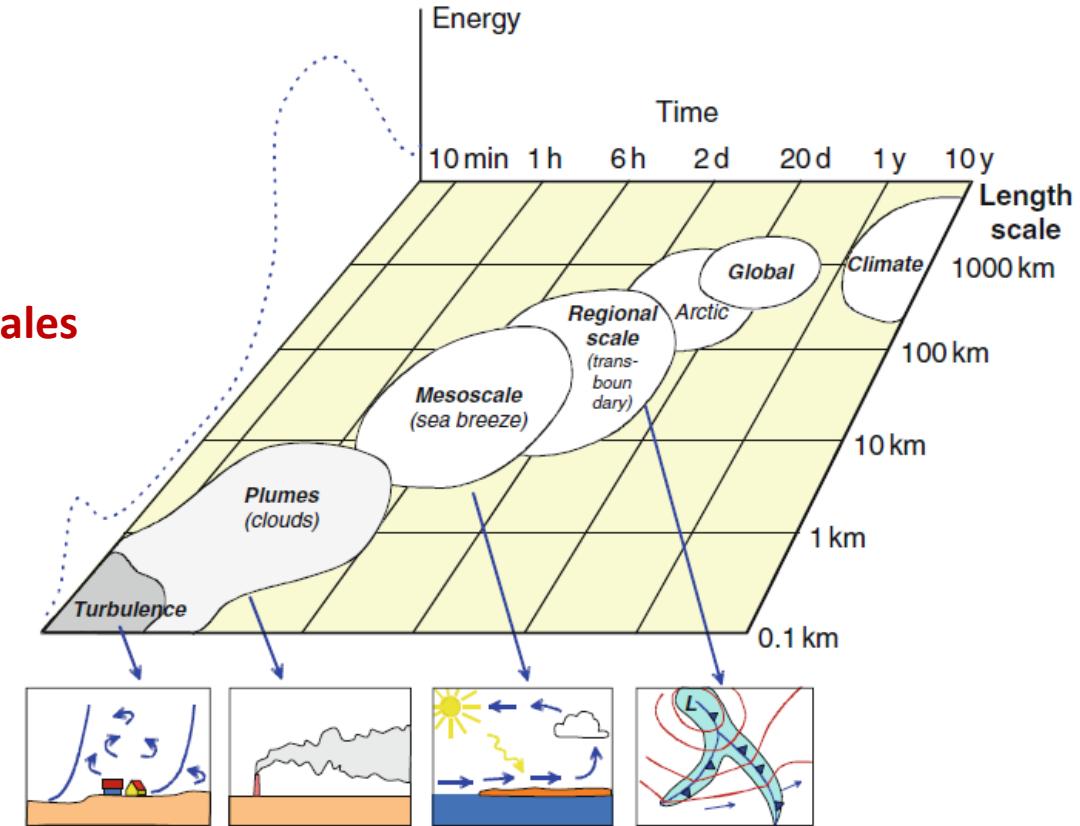
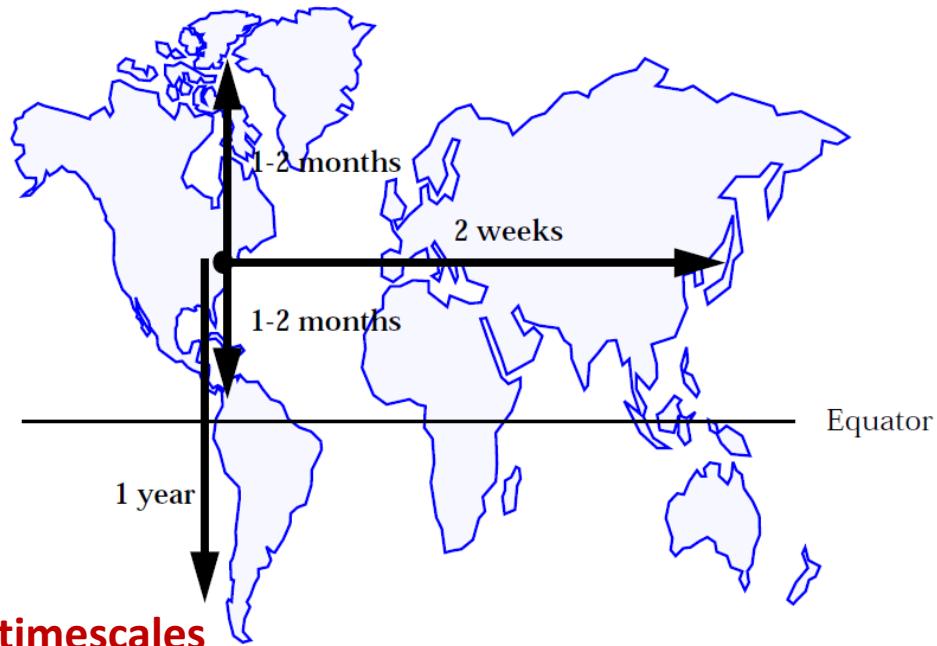
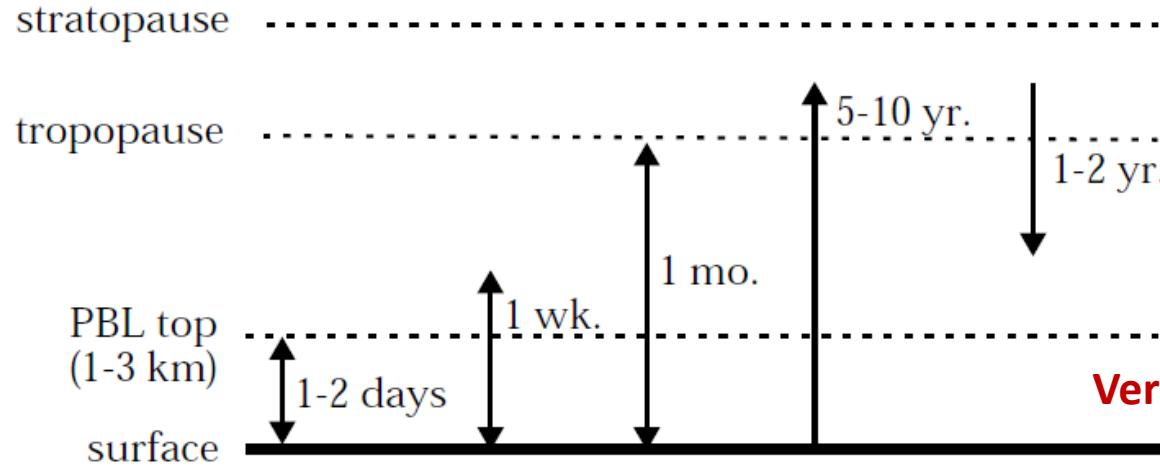


From polar High towards the 60° Low

- Cold winds from high pressure regions over the poles are deflected towards the west.
- Creates Polar easterlies.
- Convergence zone where the polar easterlies meet the warmer westerlies – Polar front.
- Position of the polar front is variable.
- In places, the transition between polar and tropical air is smooth, giving rise to a discontinuity in the polar front.
- Summer – polar front is compressed north of 60°; Winter – polar front invades south of 60°



Timescales of atmospheric transport



These timescales affect pollutant mixing and transport
(local vs regional vs global pollutants)

Key messages

Discussed so far

Parameters such as T and P vary in specific ways in the atmosphere



Gives rise to air flows that depend on the latitude and season



These in turn determine temporal and spatial scales of atmospheric transport



We classify pollutants based on these scales



Pollutants react chemically and photochemically in the atmosphere



Produce health and environmental effects

To be discussed

Feedback on atmospheric parameters, especially, temperature

Module 2: Basics of atmospheric chemistry

Topics to be covered

- Atmospheric measurement units
 - Mole fraction
 - Number density
 - Mass density
- Photochemical and radical-assisted reactions
 - Daytime vs nighttime chemistry
 - Tropical vs polar chemistry

Required reading

- Jacob, 1999 – Introduction to atmospheric chemistry
(<http://acmg.seas.harvard.edu/publications/jacobbook/index.html>)
 - Chapters 1, 9.3, 9.4
- Sportisse, 2010 – Fundamentals in air pollution
 - Chapter 4.1.2

A primer on atmospheric measurement units

- **Gases**

- **Mixing ratio (or mole fraction):** $C_x = N_x/N_{\text{air}}$

- Mol/mol or v/v; ppmv, ppbv or pptv

- Robust measure of atmospheric composition

Major gases (N_2 , O_2 , Ar): %

Trace gases (CO_2 , CO, halocarbons):
ppmv, ppbv, pptv

- **Number density (n_x):** molecules per unit volume (cm^{-3} or m^{-3})

- Calculation of reaction rates, column light extinction

e.g., OH radical

- **Partial pressure:** $P_x = C_x P$

- Phase changes

e.g., water vapor

- **Mass density:** $\mu\text{g m}^{-3}/\text{ng m}^{-3}$

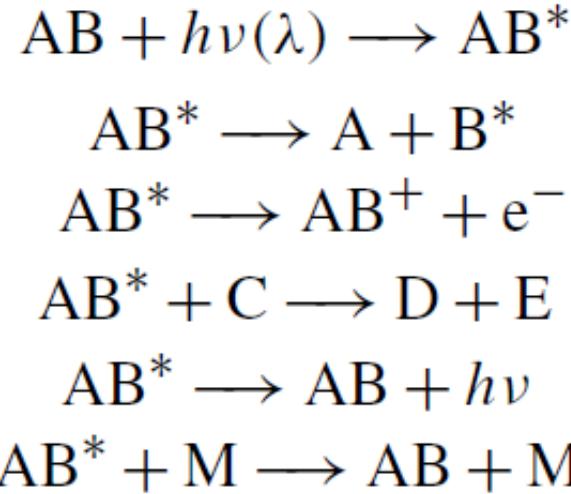
- Health effects

- **Aerosols:** **Mass density** ($\mu\text{g m}^{-3}/\text{ng m}^{-3}$); **Number density** (no. of particles cm^{-3})

- Why not mixing ratio?

Photochemical reactions

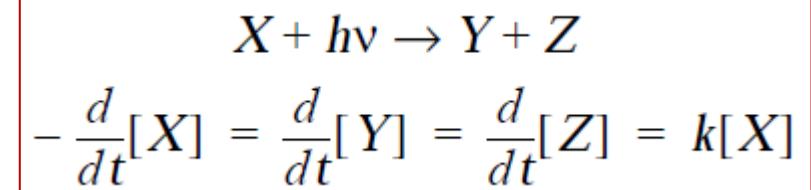
The reaction is initiated by the absorption of photons. Pathways are –



Photon absorption
 Dissociation
 Ionization
 Direct chemical reaction
 Fluorescence with photon emission
 Stabilization by collision (quenching)

Photodissociation is the most significant pathway in the atmosphere

Consider the following photolysis reaction which involves breaking of a chemical bond by an incident photon. Here k (s^{-1}) is the photolysis rate constant.



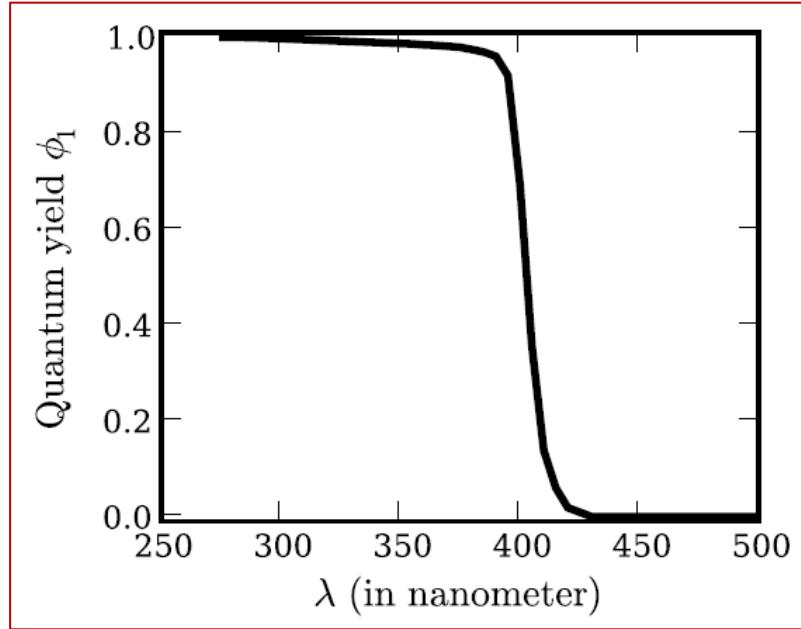
The relationship between k , the actinic flux (I), the absorption cross-section (σ_X) and the quantum yield (q_X) is given by the following equations

$$\begin{aligned} k &= q_X \sigma_X I \\ k &= \int_{\lambda} q_X(\lambda) \sigma_X(\lambda) I_{\lambda} d\lambda \end{aligned}$$

Photochemical reactions (Contd.)

Important points to consider

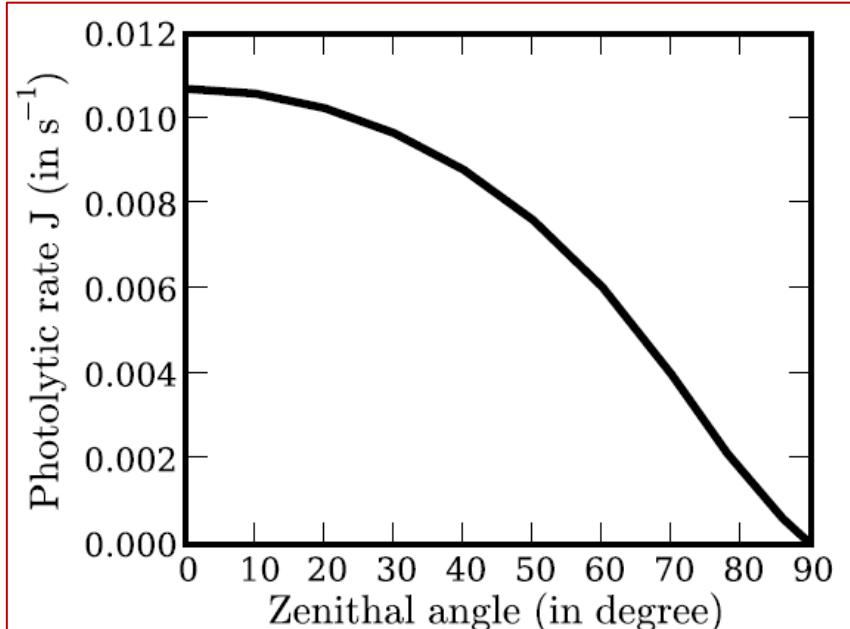
The quantum yield (q_x or ϕ) is dependent on the wavelength



Quantum yield for the dissociation of NO_2 with wavelength

- In the troposphere, the quantum yields of dissociation of pollutants will depend on the incident wavelength range.
- Quantum yields are negligible for $\lambda > 730$ nm. So, terrestrial (long-wave) radiation does not contribute.
- Stratospheric shielding constrains tropospheric photochemistry.

The actinic flux depends on the solar zenith angle



Rate of photolytic dissociation of NO_2 as a function of zenith angle

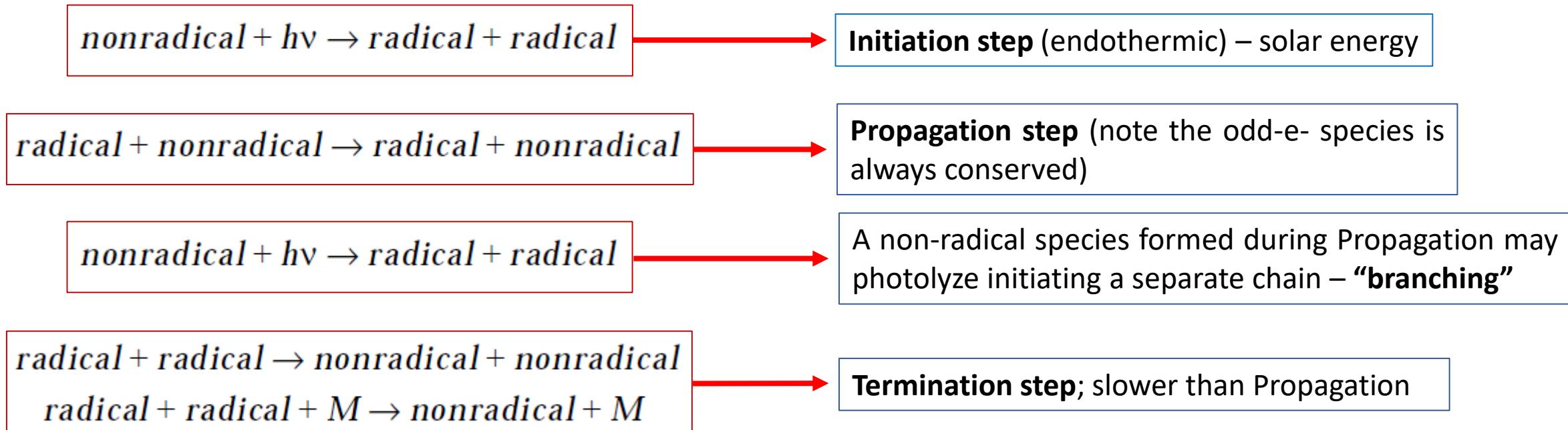
- The actinic flux depends on hour, season, location.
- Critical implications for daytime vs nighttime and tropical vs polar chemistry.
- Also depends on atmospheric screening state (aerosols, clouds).

Radical-assisted reactions

Why are radical-assisted reactions important?

- Gases in the atmosphere are present in low concentrations (much lower than lab-scale values)
- Collisions are relatively infrequent.
- Due to the presence of unpaired e^- , radicals are more reactive and the corresponding reaction rates are faster

Steps in a radical-assisted reaction



Module 3: Stratospheric processes

Topics to be covered

- NARRATIVE
- Development of CFCs and first measurements
 - Mechanisms of O₃ depletion (HO_x, NO_x, Cl, Br)
 - Observational evidence and Antarctic O₃ hole
 - Mitigation policies
 - Effects on O₃ depleting substances
 - Recovery of O₃
 - Replacement products
 - Challenges that we face



- O₃ formation
- Significance
- Measurement methods

Primary text:

WMO, 2010 – Scientific assessment of ozone depletion:
[\(<https://www.esrl.noaa.gov/csd/assessments/ozone/2010/report.html>\)](https://www.esrl.noaa.gov/csd/assessments/ozone/2010/report.html)

- Twenty questions and answers about the ozone layer

Additional resource (if you're interested):

Finlayson-Pitts and Pitts, 2000

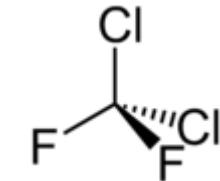
- Chapters 1A, 12A.1, 12A.2, 12B.1

Long-lived halocarbons: invention and properties

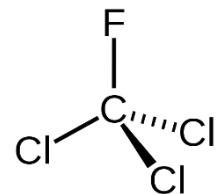
1920-1930 – industry-sponsored development of two chemicals that would later wreak havoc in the environment – CFCs and tetraethyllead (TEL).



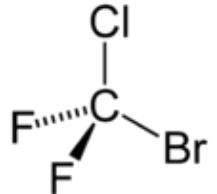
Thomas Midgley Jr.
American engineer and chemist



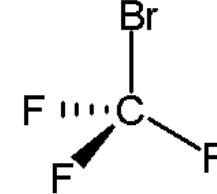
CFC-12



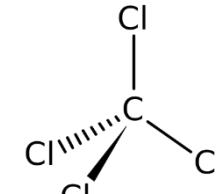
CFC-11



Halon-1211



Halon-1301



CCl_4

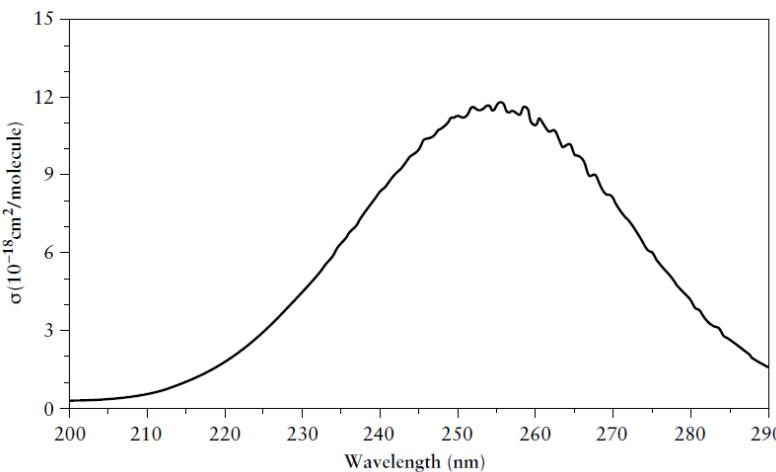
Properties: chemically inert (strength of C-F bonds), non-toxic, non-flammable, volatile (perfect recipe for a refrigerant!)

But nobody wondered at the time: are there special situations in the environment where these compounds can break down?
And what happens if they do?

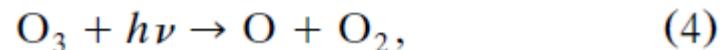
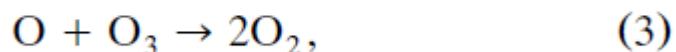
Meanwhile, also in 1930...

- 1880-1930 – evidence was trickling in as to the presence of an O_3 layer in the atmosphere.
- **But no theory was put forward regarding the origin of the O_3 layer.**

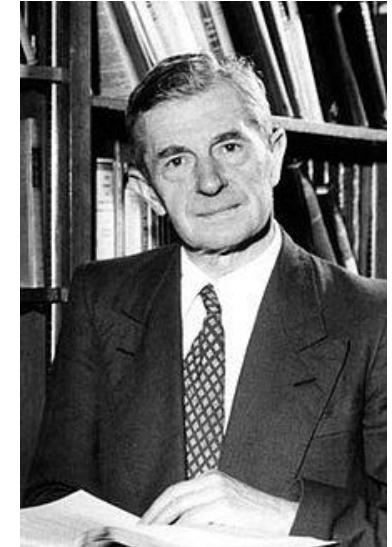
“Chapman cycle” or the “ozone-oxygen cycle”
– the sole source of O_3 in the stratosphere



Wavelength dependence of O_3 light absorption

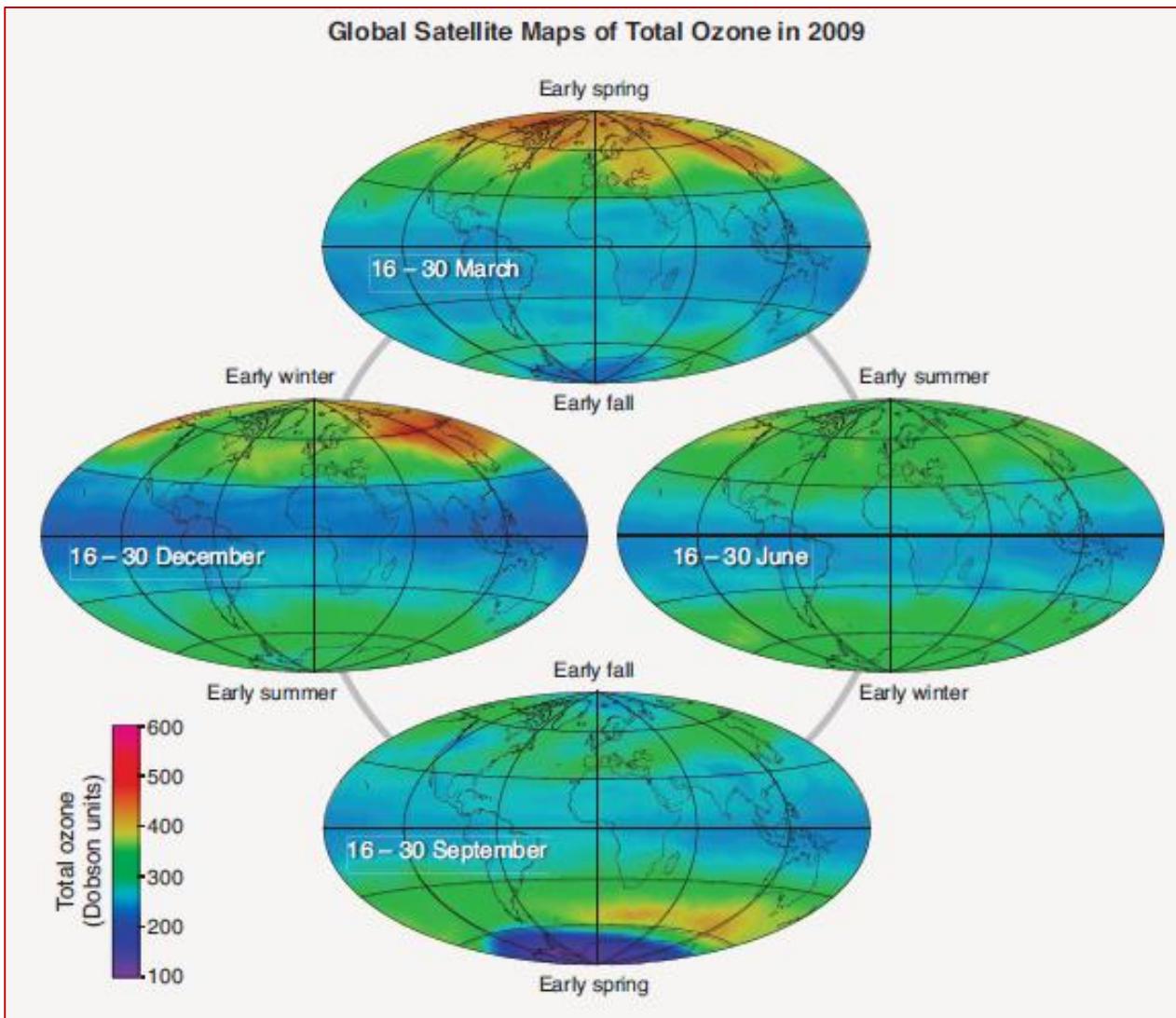


- O_2 dissociates in the presence of $h\nu$ with $\lambda < 240$ nm
- M is a third-body, generally N_2 or O_2
- O_3 absorbs $h\nu$ with $\lambda < 310$ nm ($\lambda_{MAX} = 255$ nm)
- The O_2 - O_3 cycle reactions release heat – leading to T rise in the stratosphere.



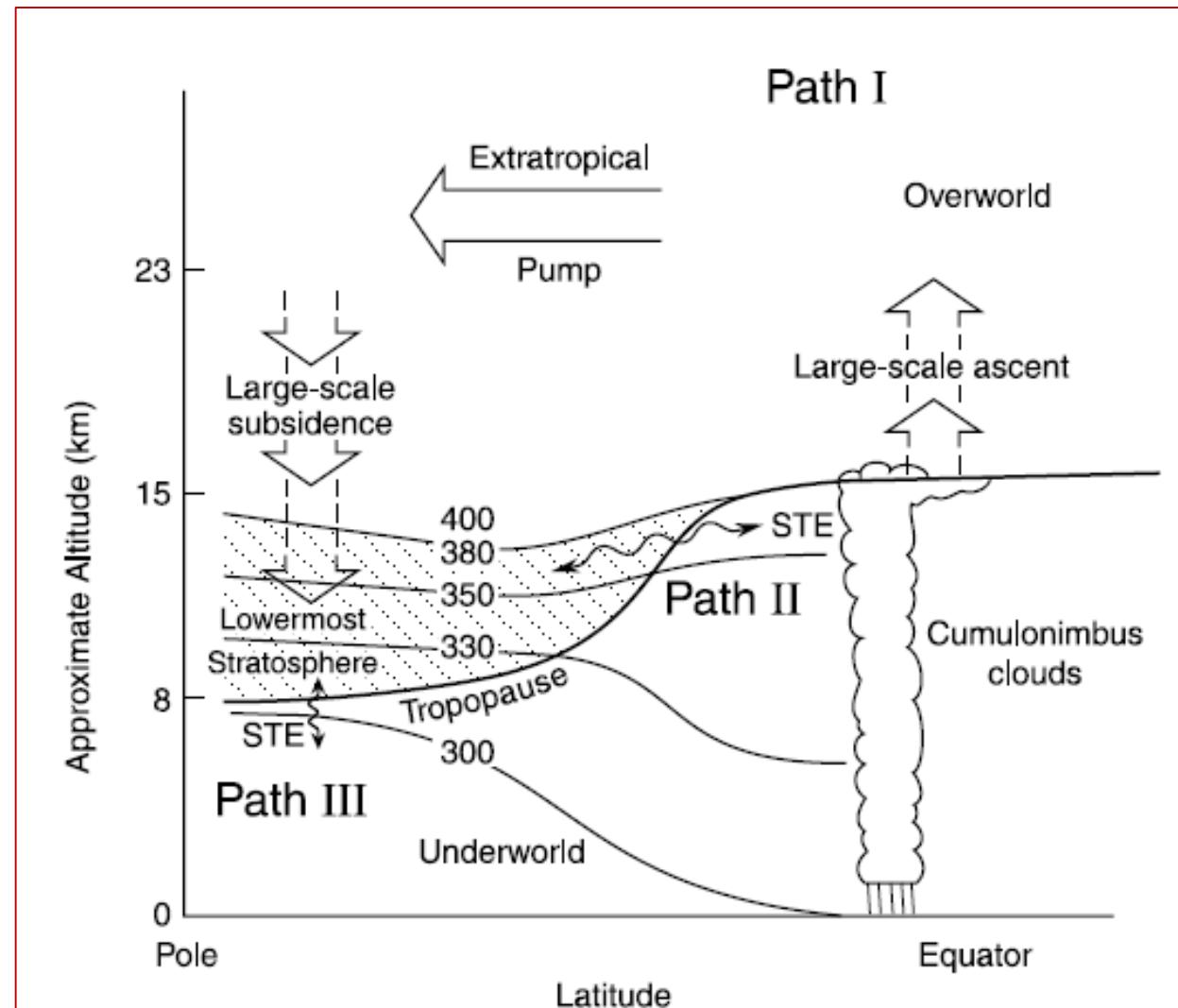
Sydney Chapman
British mathematician

O₃ layer – latitudinal and seasonal variations



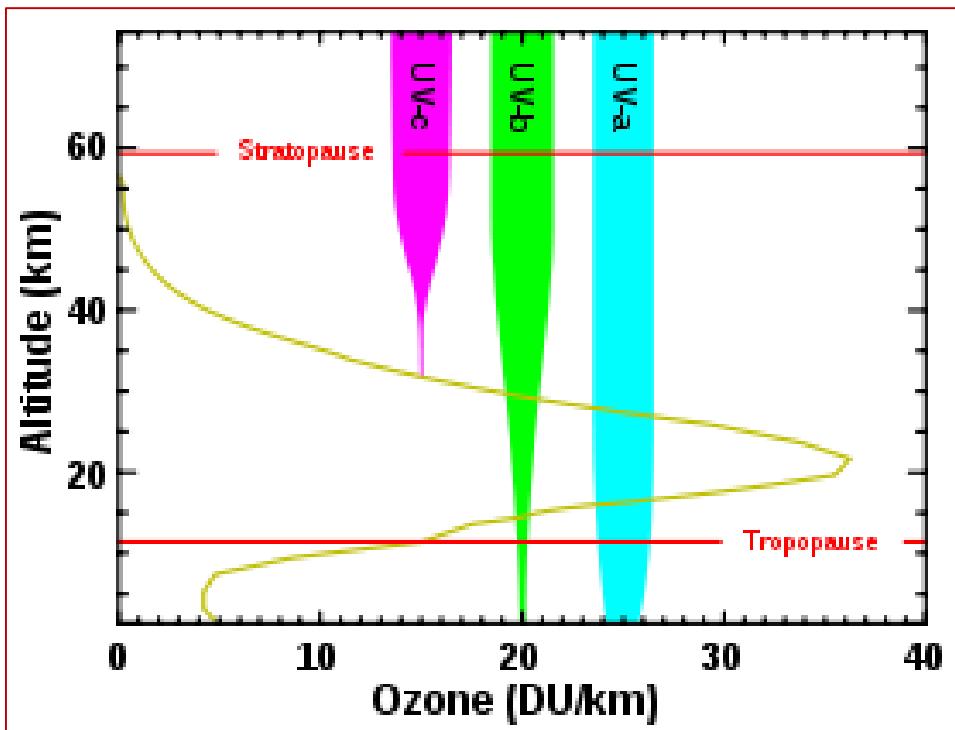
- Latitudinal distribution of O₃ – high in mid- and high-latitudes, low in tropics.
- Higher production rates at the tropics from solar UV + meridional stratospheric transport towards poles.
- Seasonal distribution of O₃ – high during spring in the NH. Note the spring minimum over SH – **we'll come back to it.**
- O₃ peaks at 25-30 km with a mixing ratio of 200-1000 ppb.
- Compare this with the troposphere, where typical O₃ mixing ratio is 20-100 ppb.

Dynamics of stratospheric transport

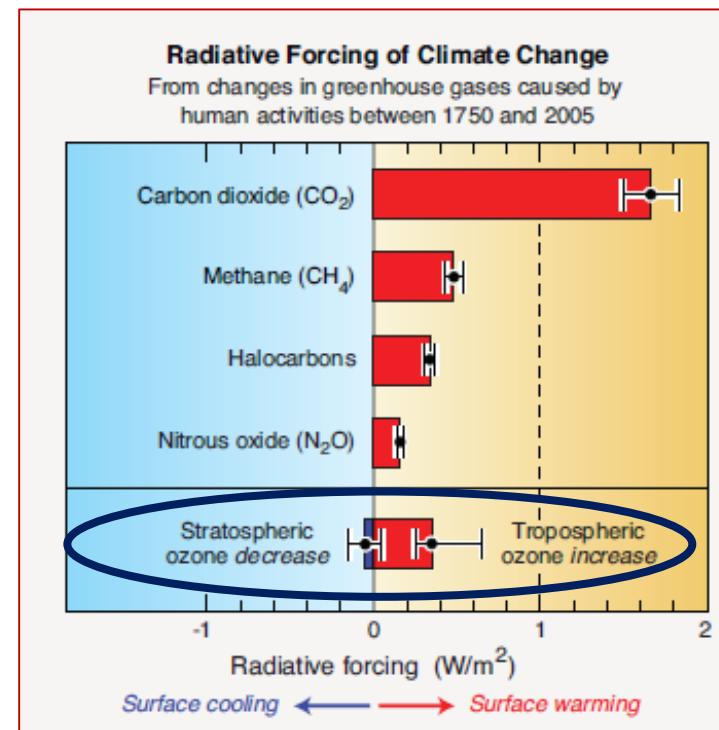


Brewer-Dobson circulation

O₃ layer – significance



- Shields the biosphere from UV-B (280-315 nm) and UV-C (100-280 nm) (Recall photo-dissociation equation of O₃).
- UV-B exposure can cause skin cancer, cataracts, and suppressed immune systems in humans. Affects terrestrial plant life.



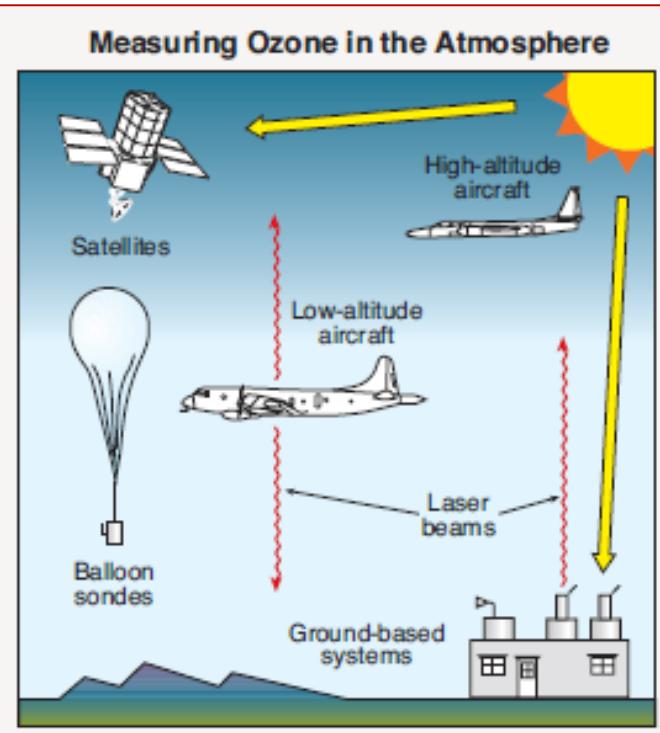
- Stratospheric O₃ depletion and tropospheric O₃ increase have opposite effects on climate forcing.
- Stratospheric O₃ layer acts as a heat reservoir (incoming solar + outgoing IR).

- Increase in UV flux to the troposphere – **warming**.
- Increased UV destroys CH₄ – **cooling**.
- Decrease in downward radiation of thermal energy due to less UV and IR absorption – **cooling**.

Overall: cooling

Measurements of O₃ – ground-based & satellite-borne

- “Total O₃” or “Total columnar O₃” refers to the total amount of O₃ in a column of the atmosphere over a location. It is measured in Dobson Units (DU).
- One DU is the thickness (in 10 µm i.e., 10⁻⁵ m) of the layer of pure O₃ that would be formed by the total column amount at 1 atm and 273 K.



- **Ground-based measurements**
 - Column UV absorption using Dobson spectrophotometers (since 1926)
 - Light detection and ranging (LIDAR)
- **Satellite-borne measurements**
 - Total ozone mapping spectrometer (**TOMS**; NASA satellites; 1978-2006)
 - Ozone monitoring instrument (**OMI**; NASA Aura; 2006-till date)
 - Solar backscattered ultraviolet (**SBUV and SBUV/2**; NOAA satellite; 1985-till date)
 - Global ozone monitoring experiment 2 (**GOME-2**; ESA METOP-A; 2006-till date)

Back to the narrative..

- 1930s – development of CFCs followed by widespread use + understanding of the origin of the O₃ layer.
- **No link yet between the two!**
- Nothing much happens for the next 40 years. And then we come to the 1970s and there are 5 major breakthroughs!

Breakthrough 1: First measurements of CFCs in the atmosphere

NATURE VOL. 230 APRIL 9 1971

Atmospheric Fluorine Compounds as Indicators of Air Movements

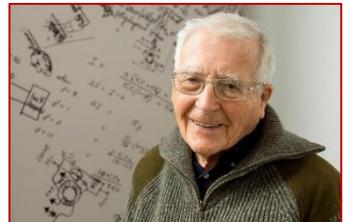
GASEOUS fluorine compounds are supposed not to occur naturally in the atmosphere. Volatile fluorine compounds would not be expected to result from chemical equilibria between fluorine compounds on the surface of the Earth, and it is improbable that biological systems contribute significant quantities of organic fluorine compounds.

It is, however, estimated that about 10⁶ tons of fluorine compounds are released each year into the atmosphere, and these include halomethanes from aerosol dispensers, fire extinguishers, refrigerant fluids and anaesthetics, and sulphur hexafluoride from electrical equipment. By contrast with these stable compounds, reactive compounds such as hydrogen fluoride, which are also industrial products, are rapidly scavenged from the atmosphere by physical and chemical processes.

Table 1 Observations at Adrigole, Co. Cork, Ireland (51° 40' N, 09° 45' W)

Wind heading	Concentration by volume CCl ₃ F	Concentration by volume SF ₆	Turbidity
45°–135°	1.0×10^{-11} (4)	2.9×10^{-14} (3)	0.03 (7)
225°–315°	1.9×10^{-10} (3)	1.2×10^{-13} (3)	0.19 (2)

The number of observations is shown in parentheses.



James Lovelock
British scientist

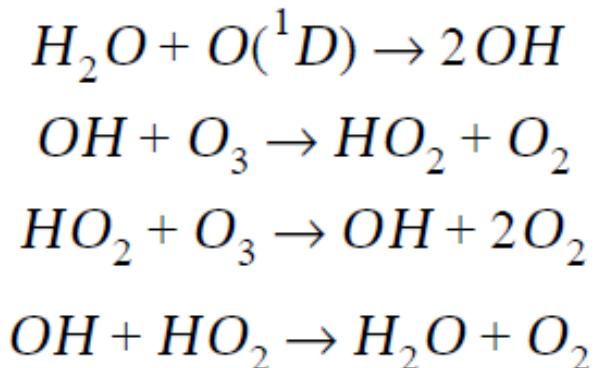
- Lovelock was the first to report the presence of CFC-11 in the atmosphere. He used his own invention – the electron capture detector (ECD).
- Established a NH background, but expressed no concern.
- His calculation of CFC-11 lifetime was later found to be off by a factor of 45.

Back to the narrative..

- Total column O₃ predicted by Chapman Cycle was not reconciled by ground-based measurements.
- Laboratory experiments suggested that additional reactions for O₃ decomposition should be considered with the Chapman Cycle.

Breakthrough 2: Role of HO and HO₂ radicals in O₃ destruction

- The hydroxyl radical (OH) and the hydroperoxy or hydroperoxyl radical (HO₂) are collectively called the HO_x family.
- Small amounts of water vapor are transported from the troposphere to the stratosphere. Additionally, some water vapor is formed in the stratosphere through oxidation of CH₄. Water vapor mixing ratio in the stratosphere is 3-5 ppmv.
- During 1950-1970, it was proposed that catalytic cycles initiated by the oxidation of water vapor could be a significant sink of O₃ in the stratosphere.
- **HO_x catalysis alone could not account for the observations.**



But it introduced the vital new idea that species present at trace levels in the stratosphere could trigger chain reactions destroying O₃.

Back to the narrative..

- The limited catalytic ability of HO_x indicated the presence of additional destruction pathways.

Breakthrough 3: Role of NO and NO_2 in O_3 destruction

- Nitrous oxide (N_2O), produced from microbiological processes at the earth's surface, can be transported to the stratosphere followed by reaction with $\text{O}({}^1\text{D})$.

Shorter Contribution
The influence of nitrogen oxides on the atmospheric ozone content
 P.J. Crutzen
 First published: April 1970 Full publication history
 DOI: 10.1002/qj.49709640815 View/serve citation
 Cited by CrossRef: 697 articles Check for updates Citation tools
 10 Funding information

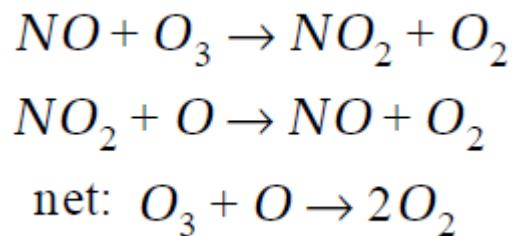
Abstract
 The probable importance of NO and NO_2 in controlling the ozone concentrations and production rates in the stratosphere is pointed out. Observations on and determinations of nitric acid concentrations in the stratosphere by Murcay, Kyle, Murcay and Williams (1968) and Rhine, Tubbs and Dudley Williams (1969) support the high NO and NO_2 concentrations indicated by Bates and Hays (1967).
 Some processes which may lead to production of nitric acid are discussed.
 The importance of $\text{O}({}^1\text{S})$, possibly produced in the ozone photolysis below 2340 Å, on the ozone photochemistry is mentioned.



Paul Crutzen
Dutch chemist



The NO could then catalytically destroy O_3 .



- NO_x emissions from supersonic aircraft (cruise altitude ~ 20 km), rockets and space shuttle contribute to O_3 loss.

- Consequently, US Congress blocked subsidies for development of commercial supersonic aircraft.
- Paul Crutzen was awarded the Nobel Prize in Chemistry in 1995.

- Model calculations showed that NO_x emissions from supersonic aircraft could lead to considerable depletion of the O_3 layer ($\sim 3\%$ for a conservative fleet size).

Back to the narrative..

- The NO_x catalytic cycle was the “missing link” in reconciling stratospheric O_3 measurements with theory.
- But no thoughts yet on the potential effects of halocarbons that had accumulated for ~40 years.

Breakthrough 4: Role of long-lived halocarbons in O_3 destruction

Stratospheric sink for chlorofluoromethanes : chlorine atomc-ataylsed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

HALOGENATED aliphatic hydrocarbons have been added to the natural environment in steadily increasing amounts over several decades as a consequence of their growing use, chiefly as aerosol propellants and as refrigerants^{1,2}. Two chlorofluoromethanes, CF_2Cl_2 and CFCl_3 , have been detected throughout the troposphere in amounts (about 10 and 6 parts per 10^{11} by volume, respectively) roughly corresponding to the integrated world industrial production to date^{3–5,31}. The chemical inertness and high volatility which make these materials suitable for technological use also mean that they remain in the atmosphere for a long time. There are no obvious rapid sinks for their removal, and they may be useful as inert tracers of atmospheric motions^{4–6}. We have attempted to calculate the probable sinks and lifetimes for these molecules. The most important sink for atmospheric CFCl_3 and CF_2Cl_2 seems to be stratospheric

photolytic dissociation to $\text{CFCl}_3 + \text{Cl}$ and to $\text{CF}_2\text{Cl} + \text{Cl}$, respectively, at altitudes of 20–40 km. Each of the reactions creates two odd-electron species—one Cl atom and one free radical. The dissociated chlorofluoromethanes can be traced to their ultimate sinks. An extensive catalytic chain reaction leading to the net destruction of O_3 and O occurs in the stratosphere:



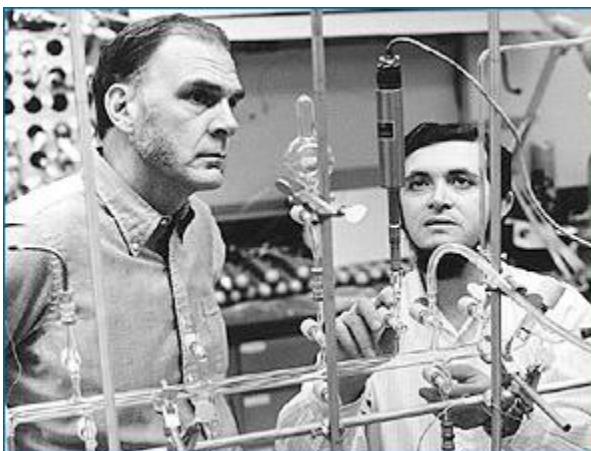
This has important chemical consequences. Under most conditions in the Earth's atmospheric ozone layer, (2) is the slower of the reactions because there is a much lower concentration of O than of O_3 . The odd chlorine chain (Cl, ClO) can be compared with the odd nitrogen chain (NO, NO_2) which is believed to be intimately involved in the regulation of the present level of O_3 in the atmosphere^{7–10}. At stratospheric temperatures, ClO reacts with O six times faster than NO_2 reacts with O (refs 11, 12). Consequently, the $\text{Cl}-\text{ClO}$ chain can be considerably more efficient than the $\text{NO}-\text{NO}_2$ chain in the catalytic conversion of $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$ per unit time per reacting chain¹³.

Photolytic sink

Both CFCl_3 and CF_2Cl_2 absorb radiation in the far ultraviolet¹⁴, and stratospheric photolysis will occur mainly in the ‘window’ at 1,750–2,200 Å between the more intense absorptions of O_3 and the Hartley bands of O_2 .

© 1974 Nature Publishing Group

- Stolarski and Cicerone (1974) first reported the importance of Cl-induced dissociation of O_3 , but the connection with CFCs was not made.
- It took the scientific imagination of F. Sherwood Rowland and Mario J. Molina to connect the dots.

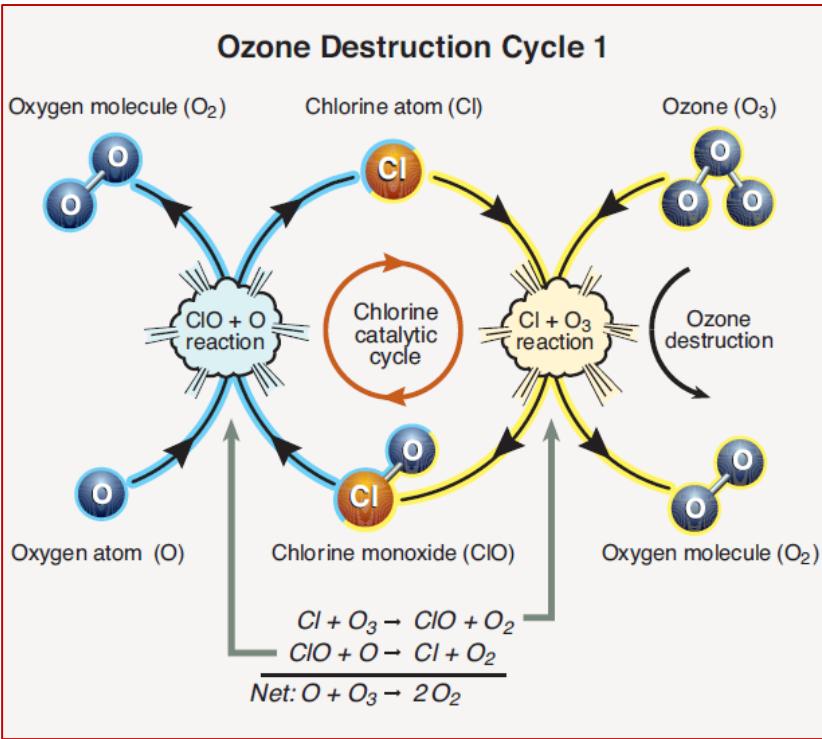


- Presented theoretical calculations of the major sinks of selected CFCs.
- Pointed out the Cl-induced photo-dissociation is much faster than NO-induced ones.
- Predicted a direct link between CFC production and O_3 destruction.

Remember: no observational evidence yet!

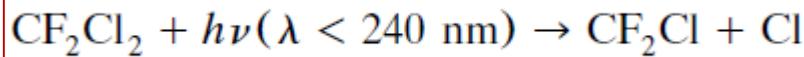
Back to the narrative..

Breakthrough 4: Reaction mechanism with Cl

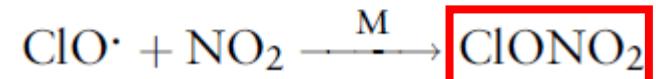


- One Cl atom can destroy $\sim 100,000 O_3$ molecules.
- HOCl, HCl and ClONO₂ serve as reservoir molecules for Cl and ClO.

- CFCs do not have any sinks in the troposphere. Once released, they are transported to the stratosphere and broken down by UV radiation.

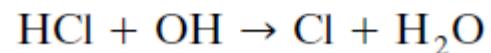
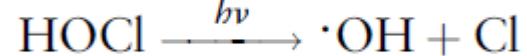
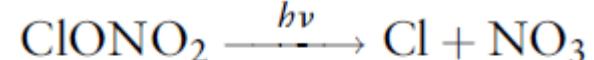


Formation of reservoir molecules

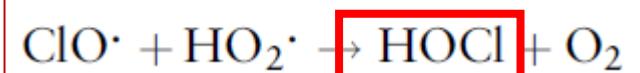
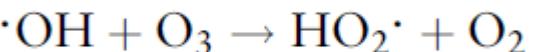


Presence of NO

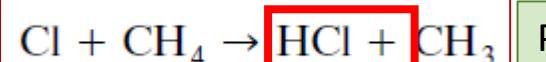
Destruction of reservoir molecules



Leads to reactivation of O_3 -destroying species



Presence of OH

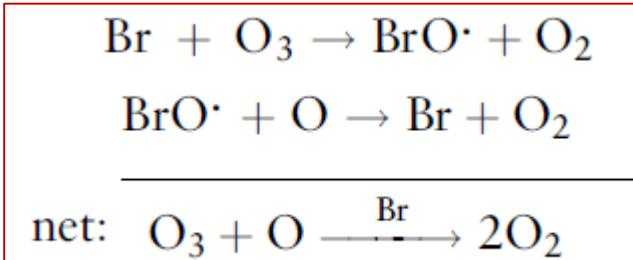


Presence of CH₄

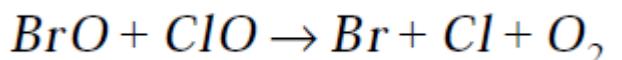
Back to the narrative..

Breakthrough 4: Reaction mechanism with Br

- Br can similarly participate in a catalytic cycle to destroy stratospheric O₃.



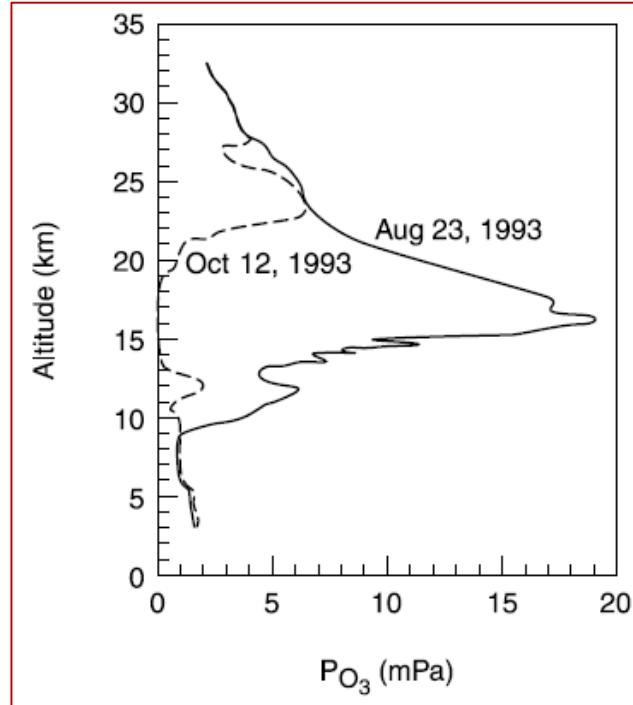
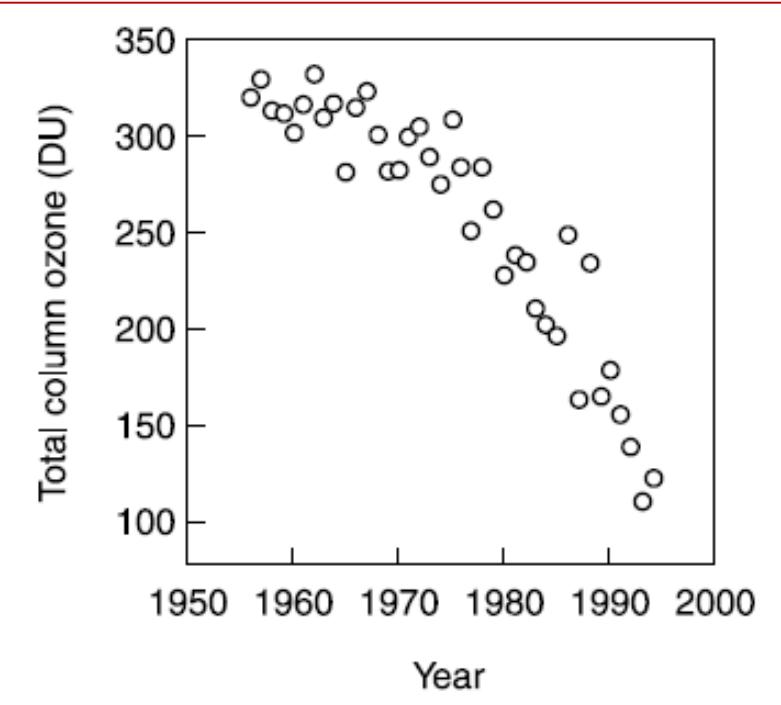
- Stratospheric Br – photolysis of methyl bromide (CH₃Br) and halons (H-1211, H-1301, etc.).
- Sources of CH₃Br: marine/terrestrial biogenic, biomass burning, agricultural and QPS fumigation.
- Major sources of halons: fire extinguishing agents
- No effective stratospheric reservoir for Br and BrO (unlike Cl and ClO)**
- Consequently, Br atoms are ~60 times more destructive to O₃ than Cl atoms on a per-atom basis.**
- Overall, Cl is more destructive due to larger emissions.**
- Synergistic interaction of ClO and BrO – enhanced O₃ depletion



Back to the narrative..

Breakthrough 5: Observational evidence

- It was about a decade after Molina and Rowland's paper that observational evidence for severe O₃ depletion came in.



Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction

J. C. Farman, B. G. Gardiner & J. D. Shanklin

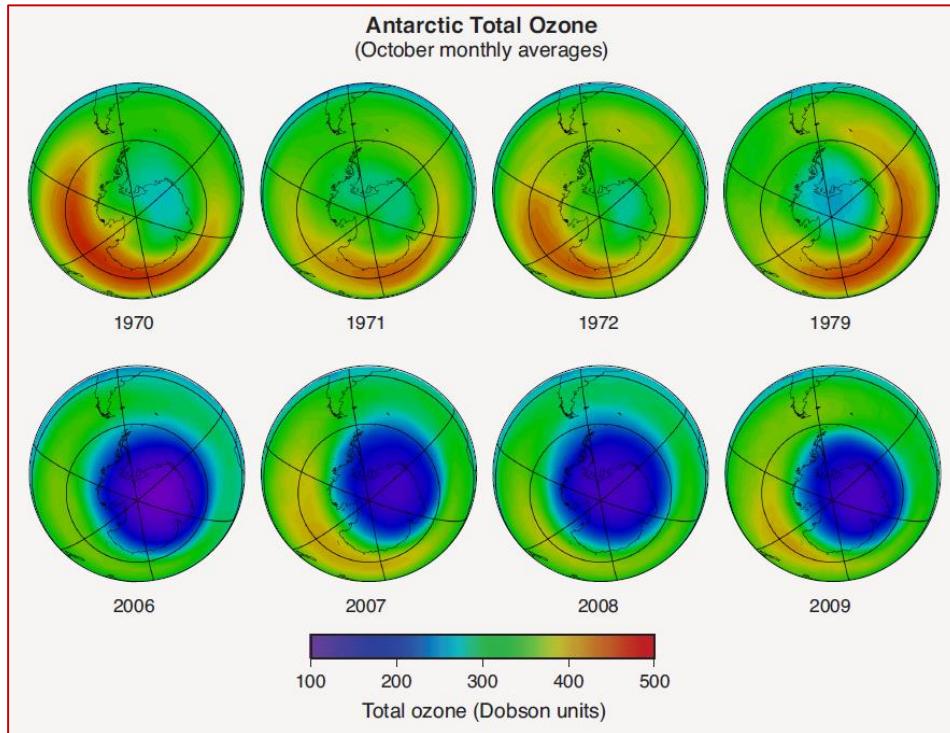
British Antarctic Survey, Natural Environment Research Council,
High Cross, Madingley Road, Cambridge CB3 0ET, UK

- The presence of a late-winter/early-spring Antarctic "Ozone hole" was discovered by Farman et al. and reported in 1985.
 - Values were so low that initially scientists filtered out the data thinking they were outliers.

The Antarctic ozone hole

Why does it happen?

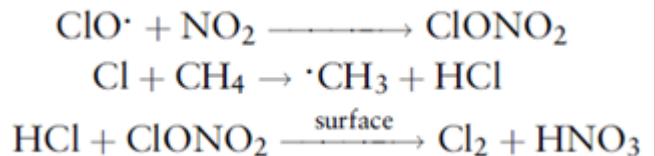
How severe is it?



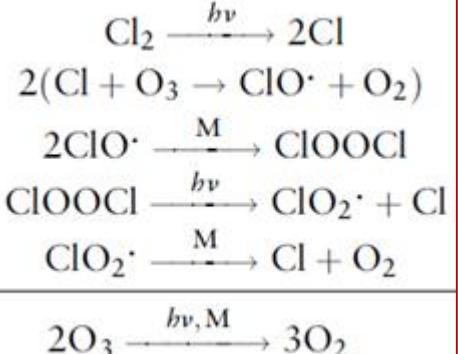
- In 2000, the size of the Antarctic O_3 hole was $28 \times 10^6 \text{ km}^2$, about the size of North America!
- Mean 1990-2009 values were reduced by 90% compared to 1960.

Tropospheric halocarbon emissions transported to the stratosphere and towards the poles.

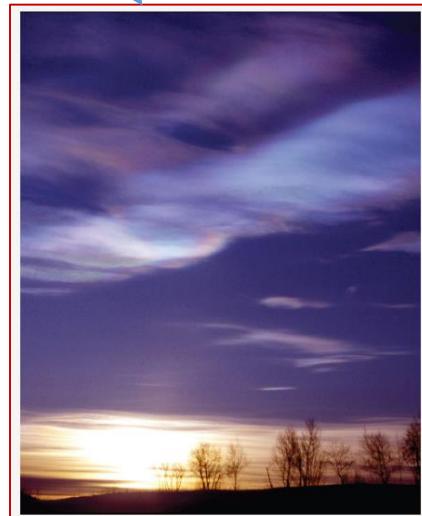
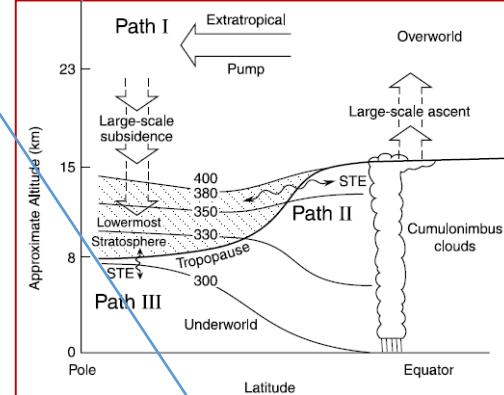
Extremely low winter T over Antarctica (-80 to -90°C) – formation of polar stratospheric clouds (PSCs) inside polar vortex – isolated condition.



Re-activation of Cl reservoir species

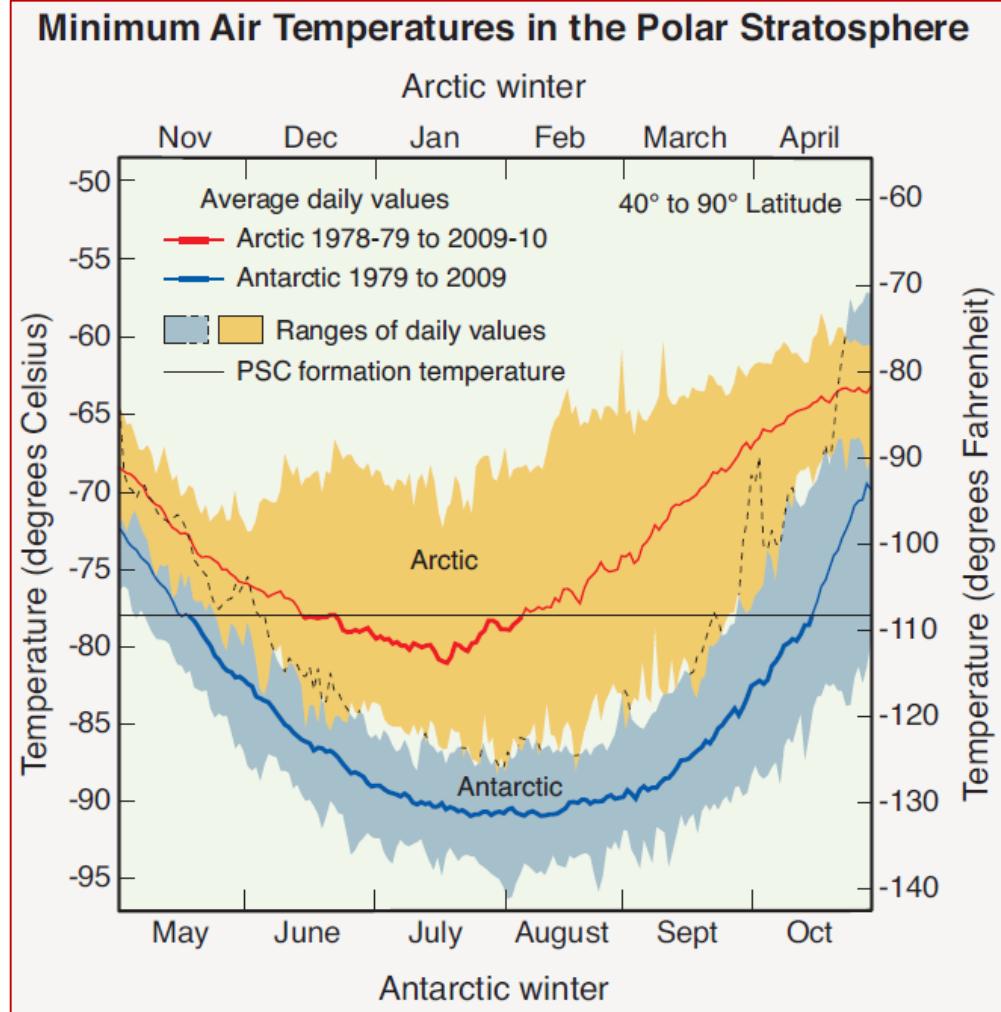


~70% due to ClO self-reaction; ~30% due to ClO-BrO synergy



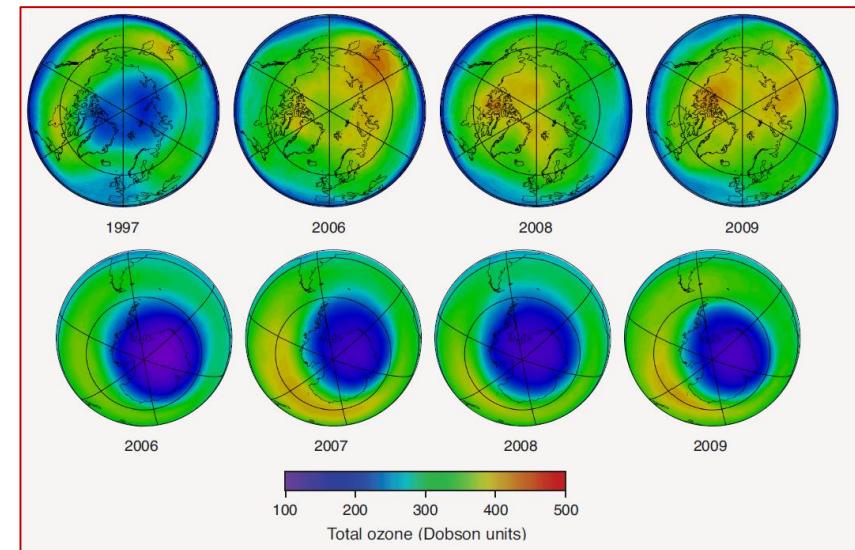
Why isn't there an Arctic ozone hole?

There is significant “depletion” of the Arctic ozone layer, but not an “ozone hole.”



- Arctic winters are far less severe than Antarctic winters.
- Temperatures often do not reach the threshold for PSC formation.
- Isolation of stratospheric air is less effective.
- Break-up of vortex due to atmospheric waves.
- Addition of tropical O₃-rich air by Brewer-Dobson circulation.

*Comparison of Arctic
and Antarctic O₃*



What has been done to address O₃ depletion?

The response of policy-makers to the evidence of O₃ depletion was quick and decisive.

Montreal Protocol (MP) on Substances that Deplete the Ozone Layer (1987) and subsequent amendments

Ratified by all 196 UN member states. Entered into force in 1989

Legally-binding controls on production/consumption of ODS

Developed countries

- CFCs, halons, CCl₄, CH₃CCl₃ – phase-out by 1995
- CH₃Br – phase-out by 2005

Developing countries

- CFCs, halons, CCl₄, CH₃CCl₃ – phase-out by 2010
- CH₃Br – phase-out by 2015

$$EESC(t) = a \left(\sum_{Cl} n_i f_i \rho_i + \alpha \sum_{Br} n_i f_i \rho_i \right)$$

Equivalent effective stratospheric Cl (EESC) (in units of mixing ratio)

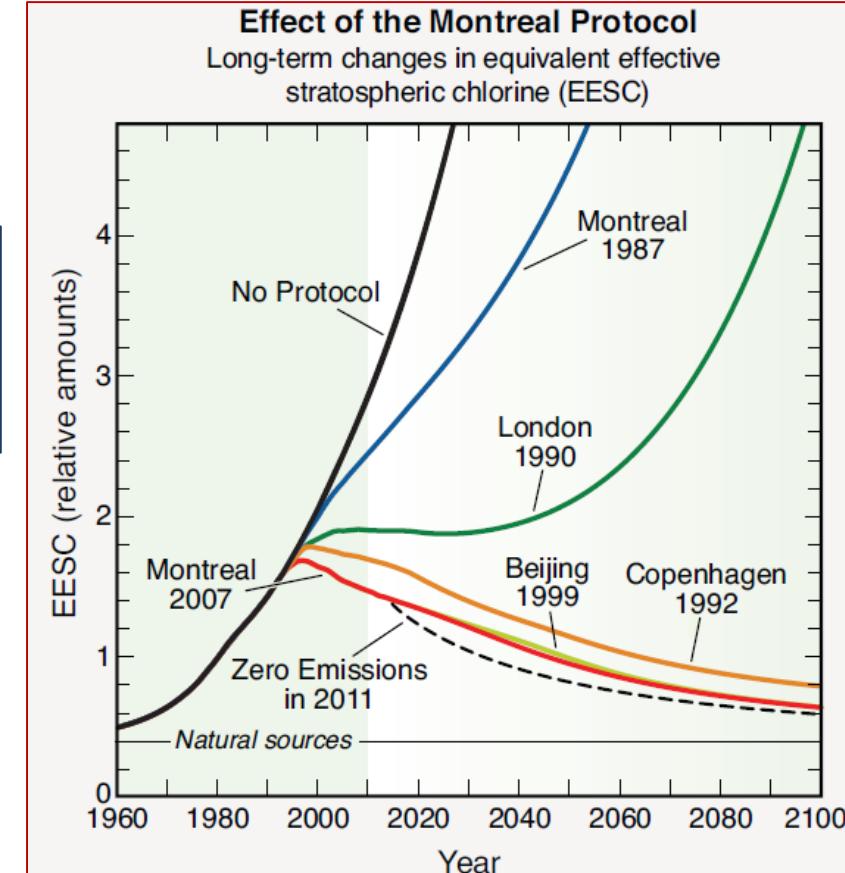
$a = 1.0$ (fractional release with respect to CFC-11)

n_i = number of Cl or Br atoms of gas i

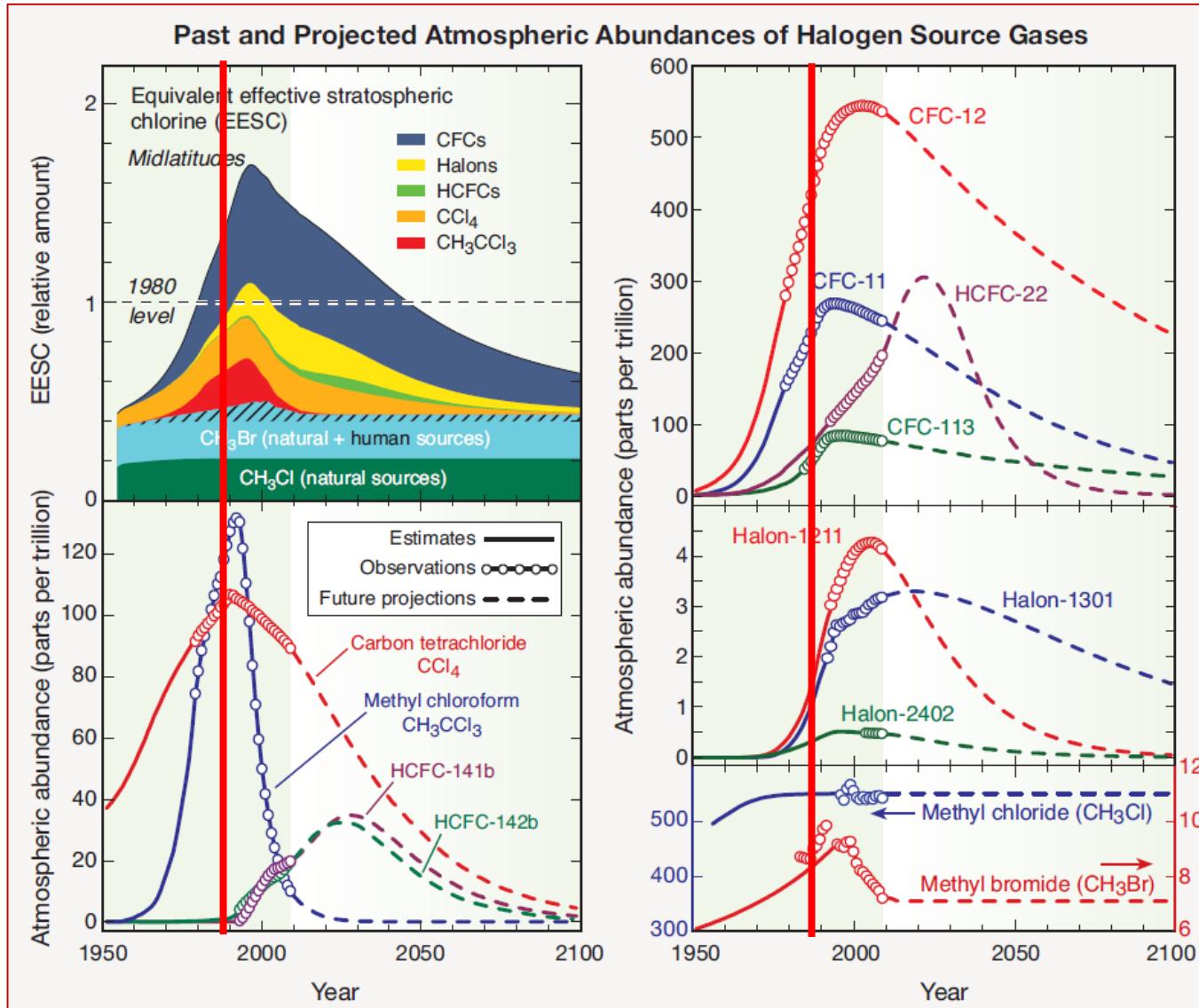
f_i = stratospheric release efficiency (as a fraction) = measure of active Cl or Br

ρ_i = mixing ratio of the gas in the stratosphere

$\alpha = 60$ (relative efficiency of Br with respect to Cl in O₃ depletion)



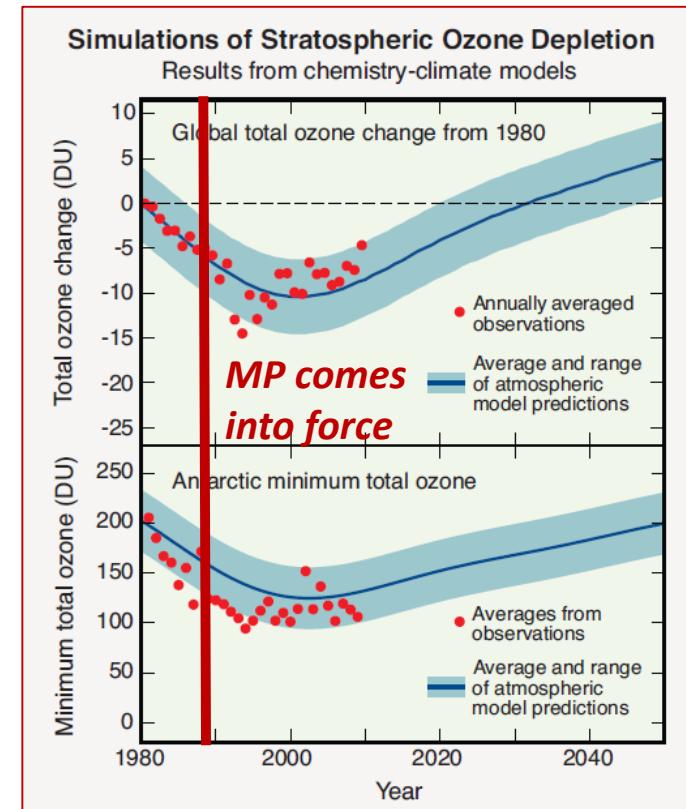
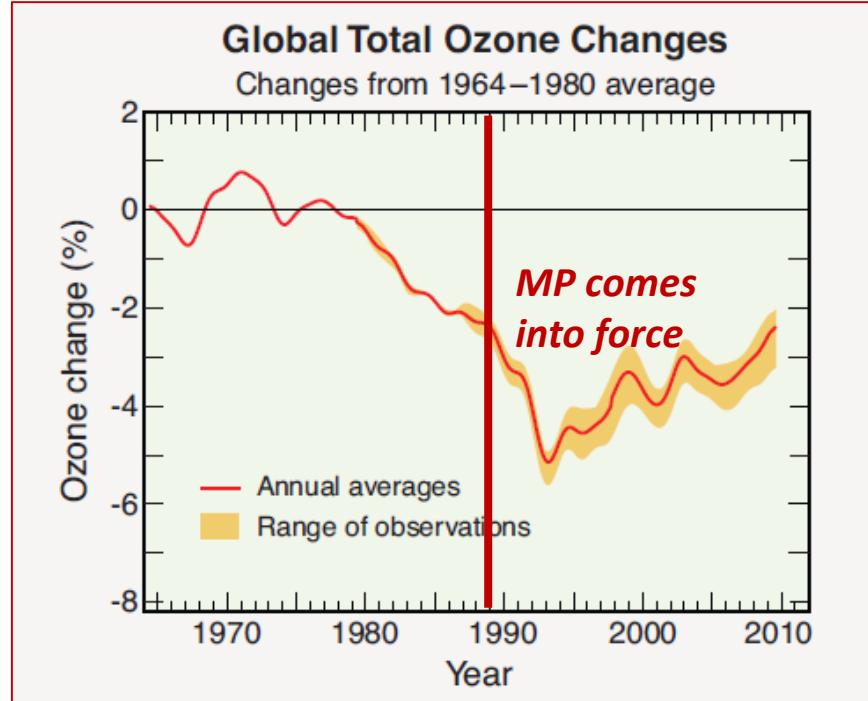
How has MP affected long-term trends of ODS?



- Long-term measurements are made at several remote sites across the world by various campaigns.
- Advanced Global Atmospheric Gases Experiment (AGAGE) – MIT
- NOAA Earth System Research Laboratory (ESRL), Global Monitoring Division (GMD)
- These have publicly available data.
- Provide evidence of the effectiveness of MP (with certain inconsistencies) – We'll discuss this in the “Research Challenges” segment.
- Levels of CFCs, halons and other ODS have peaked in the late 1990s followed by sharp declines

Is stratospheric O₃ recovering due to these efforts?

The answer is: Yes, significantly.



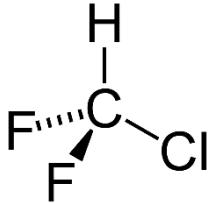
- Measurement data show the largest depletion of ~6% in the 1990s. In 2010, the depletion reduced to ~3.5% of 1964-1980 values.
- Antarctic O₃ is expected to return to 1980 values sometime after 2050. For the Arctic, the projection is during 2020-2035.
- Global O₃ is expected to reach 1960 levels between 2040 and 2080.

A world without the Montreal Protocol: O₃ layer collapse by 2050, UV index 30 by 2070 (>15 is extreme), additional 1.6 million skin cancer deaths in US alone

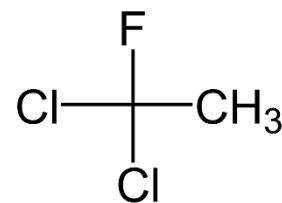
Which products have replaced CFCs? And are they harmful too?

First- and second-generation CFC replacements: hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs)

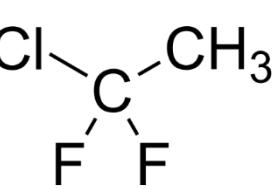
- Rationale: Reduce/remove Cl from the molecule – add H to the molecule to avoid/minimize Cl transport to the stratosphere.
- Developed during 1970-1990.



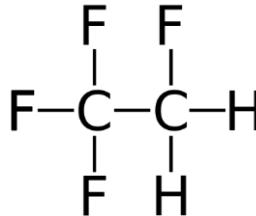
HCFC-22



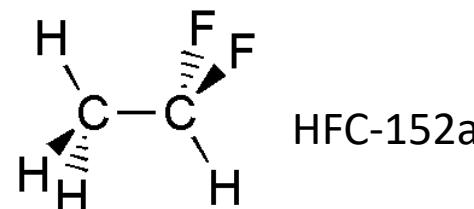
HCFC-141b



HCFC-142b

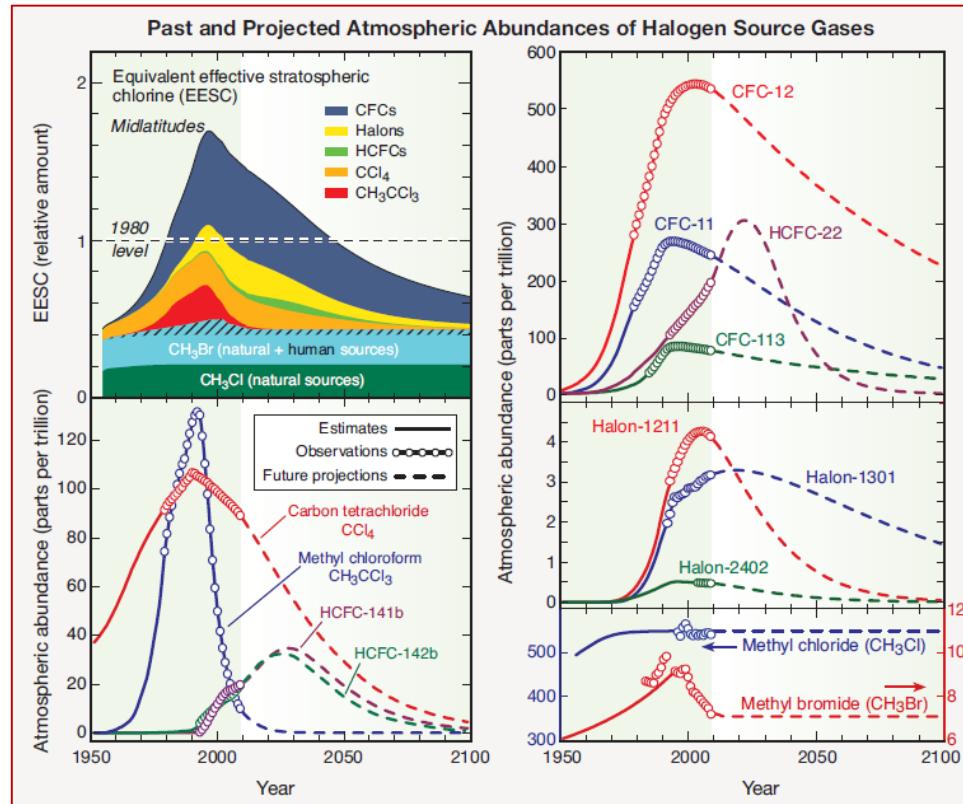


HFC-134a



HFC-152a

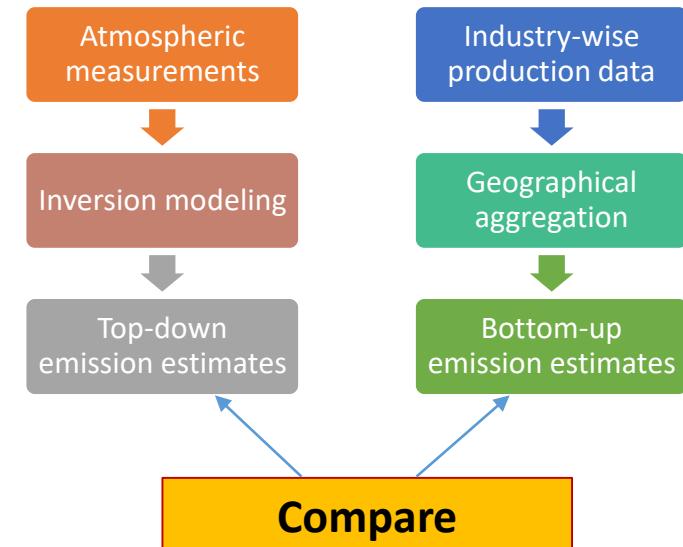
- Small or zero ozone depletion potential – great news, right?
- Can absorb longwave (IR) radiation – contribute to global warming (GWP of few 100s to few 1000s).
- HCFCs are controlled under MP: Developed nations: phase-out by 2020; Developing nations: Freeze in 2016, phase-out by 2040 (later modified to 2030).
- HFCs come under the Kigali Amendment.



Challenges that we face

Assessing the effectiveness of MP regulations on regional/national scales

- Remote monitoring of ODS can assess overall (global) effectiveness of MP, but not on national levels.
- How do we know countries are following MP? *Countries report data to the Ozone Secretariat.*
- Countries cheat sometimes (e.g., unreported production/leakage).
- Spatially-resolved atmospheric measurements, preferably long-term, needed. **No work in India so far.**
- Atmospheric measurements coupled with inverse modeling – top-down emission estimates. **No work in India so far.**
- Proper (and publicly available) bottom-up emission estimates – comparison with top-down – **No work in India so far.**

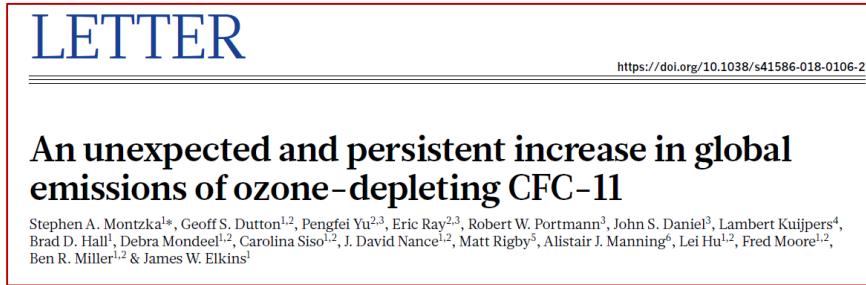


A recent example of (possible) cheating

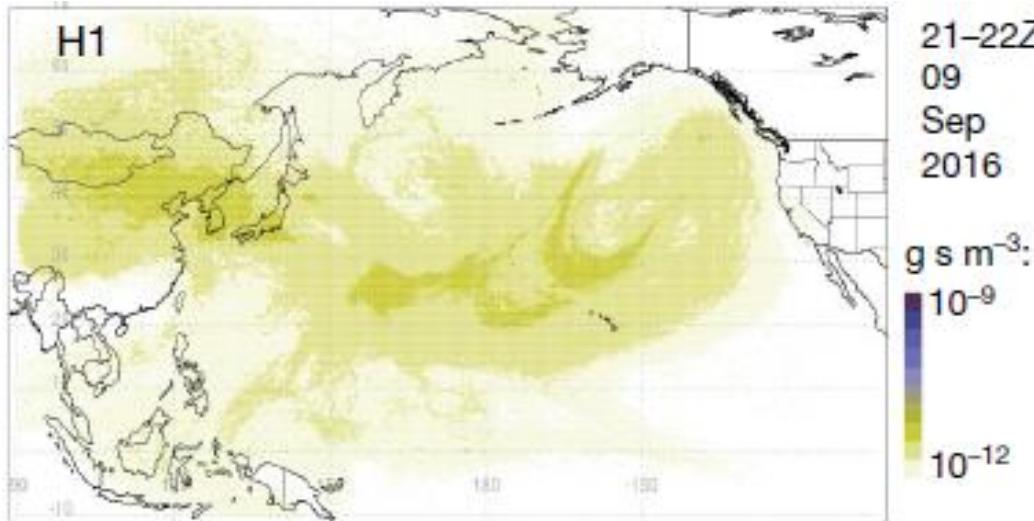
Anomalous trends in view of MP provide evidence for unreported production

- Remote monitoring of ODS has recently revealed an increasing trend of CFC-11 emissions.

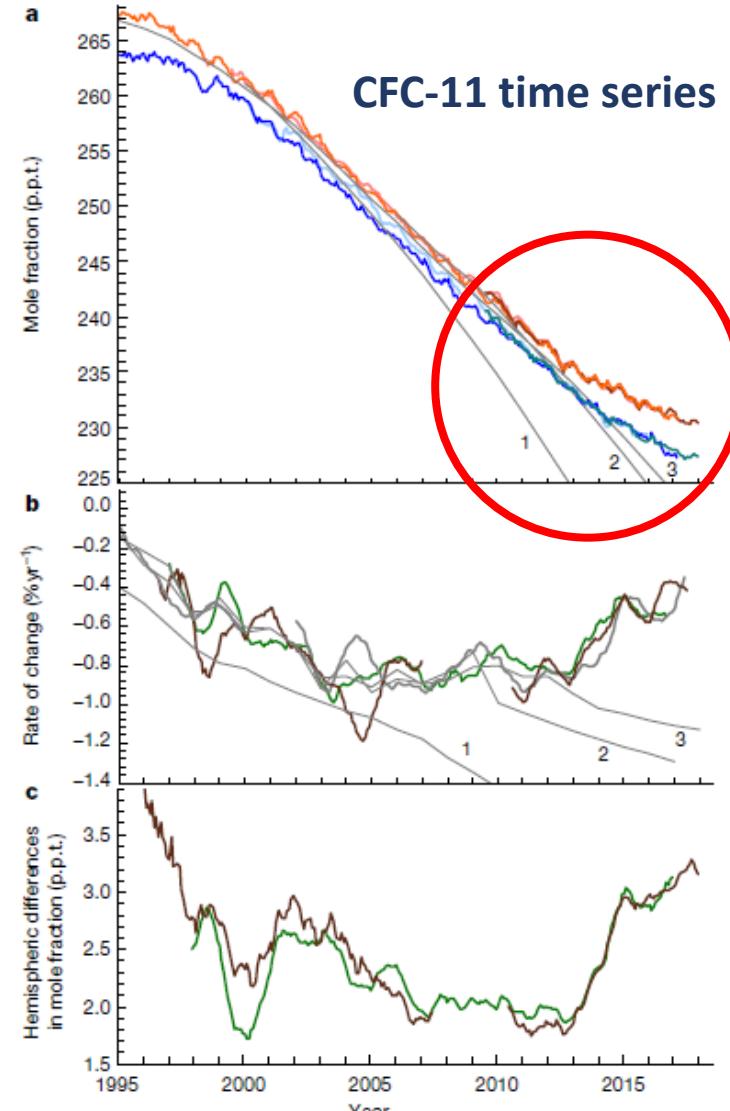
Post-2012 CFC-11 emissions detected from Asia – guess which country it might be?



Montzka et al. (2018) *Nature* 557, 413-417



Cross-checking needed for reported CFC emissions and those estimated from top-down measurements.



Challenges that we face – Contd.

The curious case of CCl_4

- CCl_4 is a major ODS – contributes ~12% of global Cl input to the stratosphere.
- Banned as per MP in mid-1990s.
- Atmospheric mixing ratios should decrease as a function of its lifetime – right?
- Observed rates of decrease are far lower than expected values!**
- A discrepancy of 54 Gg yr^{-1} exists between top-down and bottom-up inventories of CCl_4 .
 - Unknown/unaccounted source
 - Lifetime needs revision

