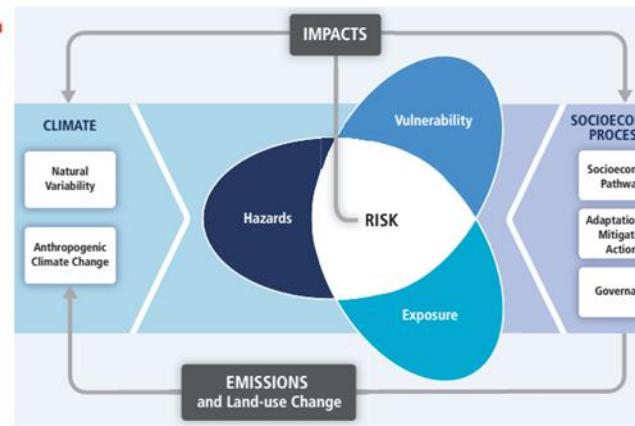
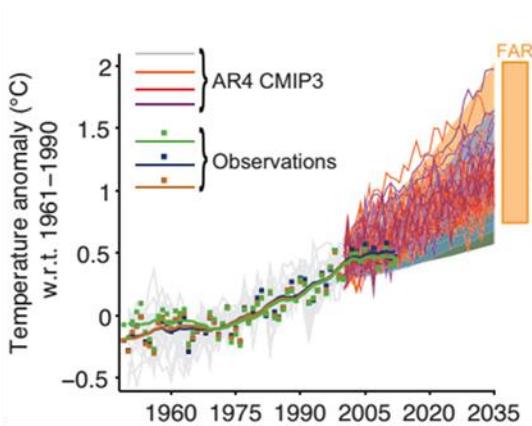


# Energy Systems & Climate Change



Material covered in this Topic:

- Combustion and CO<sub>2</sub>
- Anthropogenic CO<sub>2</sub> emissions
- CO<sub>2</sub> and the greenhouse effect
- CO<sub>2</sub> accounting, the Carbon cycle, and other GHG

## Combustion fundamentals

Simple combustion chemistry reviewed

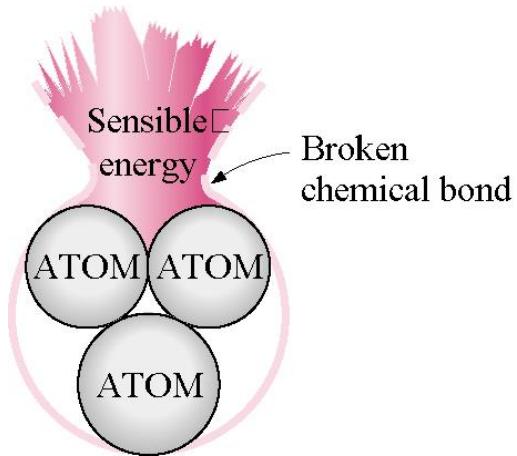
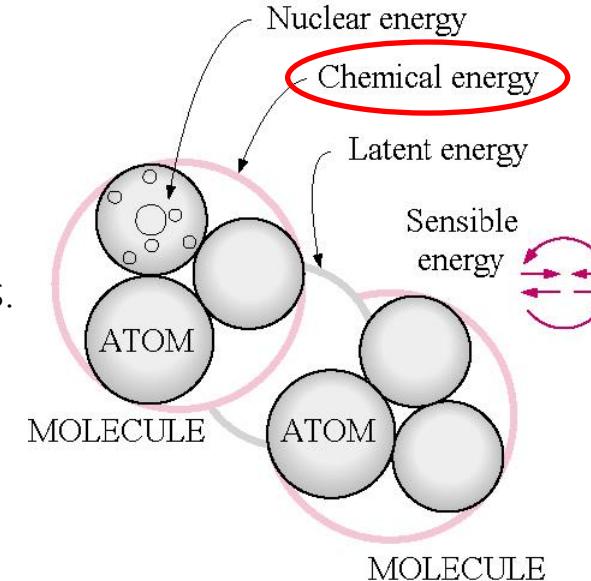
Characteristics of Hydrocarbon fuels

Worked example – CO<sub>2</sub> emissions

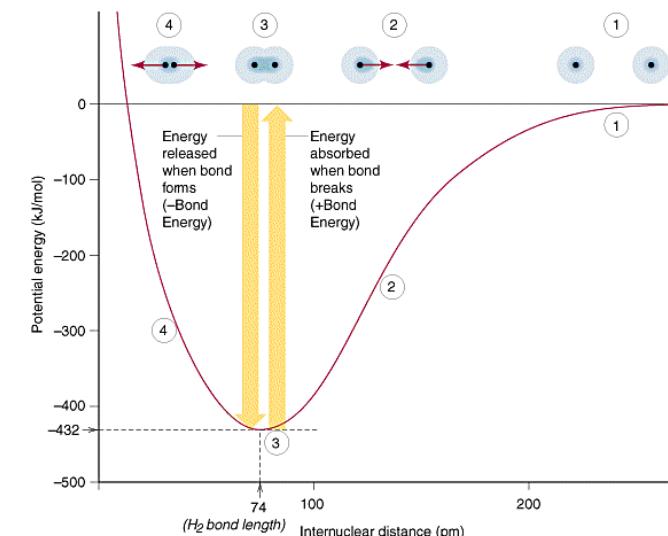
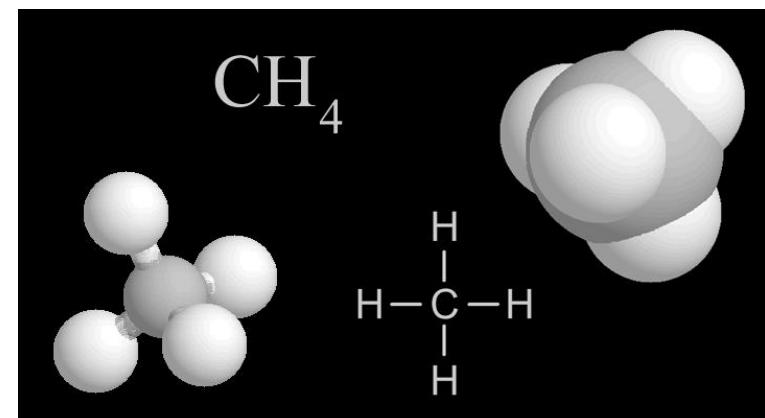


# Chemical Bonds in the Combustion Process

All substances contains energy in sensible, latent, chemical, and nuclear forms.

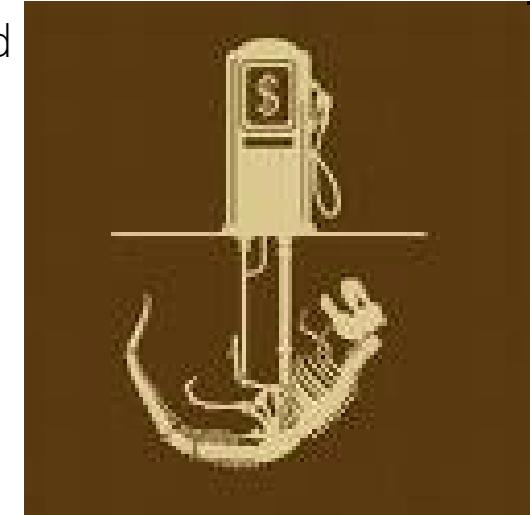


When existing chemical bonds are destroyed and new ones are formed during a combustion process, a large amount of sensible energy is usually released.





- Found naturally
- Formed by the accretion and compression of carbon-based life forms
- Encompasses solids (coal, lignite, etc), liquids (crude oil), and gases (natural gas, propane, etc.).
- Molecular composition is based on a combination of Carbon and Hydrogen atoms, ( $C_aH_b$ ), in a bewildering variety of forms.
- May include small amounts of Sulphur, Nitrogen, Oxygen, and "ash"
- The Carbon (C) and Hydrogen (H) atoms are the primary reactants.



# Hydrocarbon (Fossil) Fuels

The *ratio* of Hydrogen to Carbon atoms is significant:

Hydrogen is a gas under normal atmospheric conditions – Carbon is a solid, so:

- Fuels with a high H:C ratio ( $>2$ ), tend to be gaseous
- Fuels with low H:C ratio ( $<1$ ) tend to be solid
- Fuels with intermediate H:C ratio tend to be liquid



Coal:  $0.1 < \text{H:C} < 1$



Petrol:  $\text{H:C} \sim 1.85$



Natural gas:  $3.5 < \text{H:C} < 4$

Combustion of a fossil (hydrocarbon) fuel comprises two main steps:

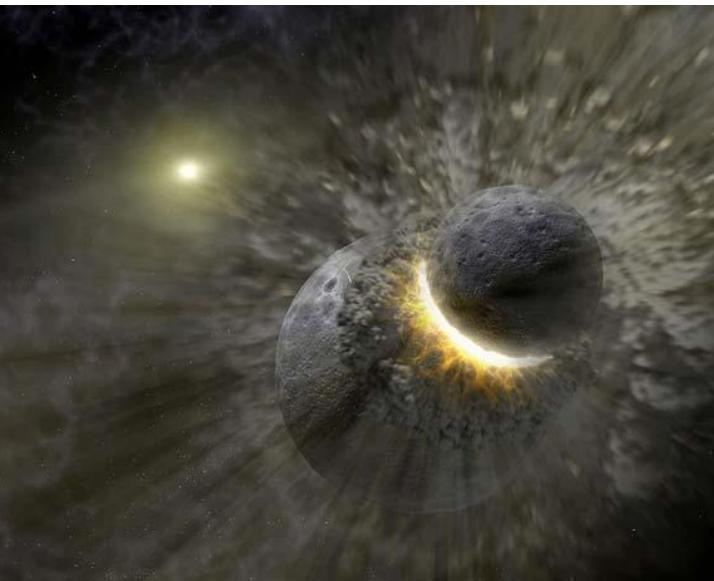
1. The chemical bonds holding the fuel molecule together are broken.

This requires an energy input (match, spark, etc.)

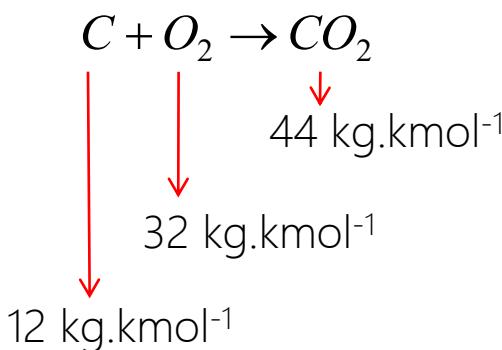


2. The "loose" Carbon and Hydrogen atoms collide with Oxygen atoms, and form new chemical bonds.

This releases a lot more energy than was absorbed in step 1: we get a self-sustaining, or "chain", reaction.



Basic combustion equations for hydrocarbon fossil fuels:

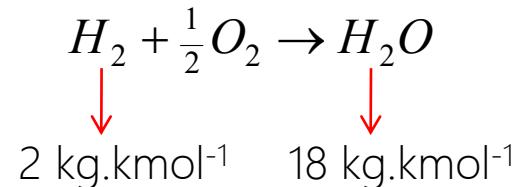


1 kmol of CO<sub>2</sub> formed, per kmol of Carbon oxidised

44 kg of CO<sub>2</sub> formed, per 12 kg of Carbon oxidised

$$\therefore \frac{44}{12} = 3.67 \text{ kg of CO}_2 \text{ formed, per kg of Carbon oxidised}$$

**32.8 MJ** of energy released, per kg of Carbon oxidised



Zero CO<sub>2</sub> formed, per kmol of Hydrogen oxidised

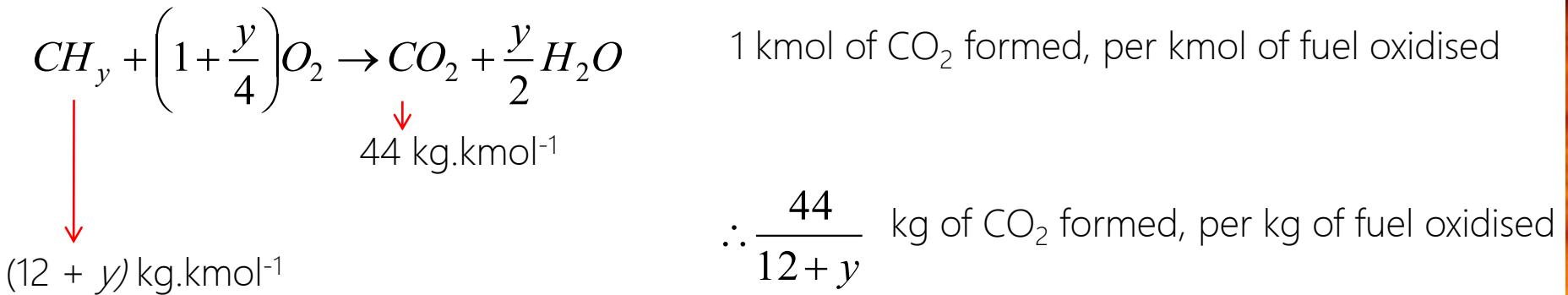
**142.9 MJ** of energy released, per kg of Hydrogen oxidised



Fuels with a higher H:C ratio will tend to:

- release more energy per kg of fuel burned (high energy density)
- produce less CO<sub>2</sub> per kJ of energy released

Basic combustion equations for hydrocarbon fossil fuels:



## Classroom problem #1

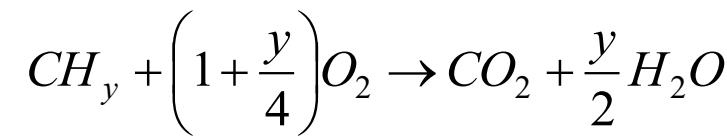
Calculate the approximate CO<sub>2</sub> intensity of the following fuels:

	$\gamma$	kg CO <sub>2</sub> per kg fuel	LHV (MJ.kg <sup>-1</sup> )	kg CO <sub>2</sub> per MJ	SEAI* values
Natural Gas (CH <sub>4</sub> )	4	2.75	50	0.055	0.0569
Diesel or petrol (CH <sub>1.85</sub> )	1.85	3.18	43	0.074	0.07–0.073
Coal (CH <sub>0.5</sub> )	0.5	3.52	33	0.107	0.0947

$$\therefore \frac{44}{12+y} \quad \text{kg of CO}_2 \text{ formed, per kg of fuel oxidised}$$

Note: None of the above fuels consists of a single pure component. The *actual* CO<sub>2</sub> emission per kg of fuel will differ slightly – in some cases significantly – from the values calculated above.

\*Source: Energy in Ireland: Key Statistics 2009. [www.seai.ie](http://www.seai.ie)



Heating value: The amount of heat released when a given amount of a pure substance is burned to form incombustible products ( $\text{MJ} \cdot \text{kg}^{-1}$ ).

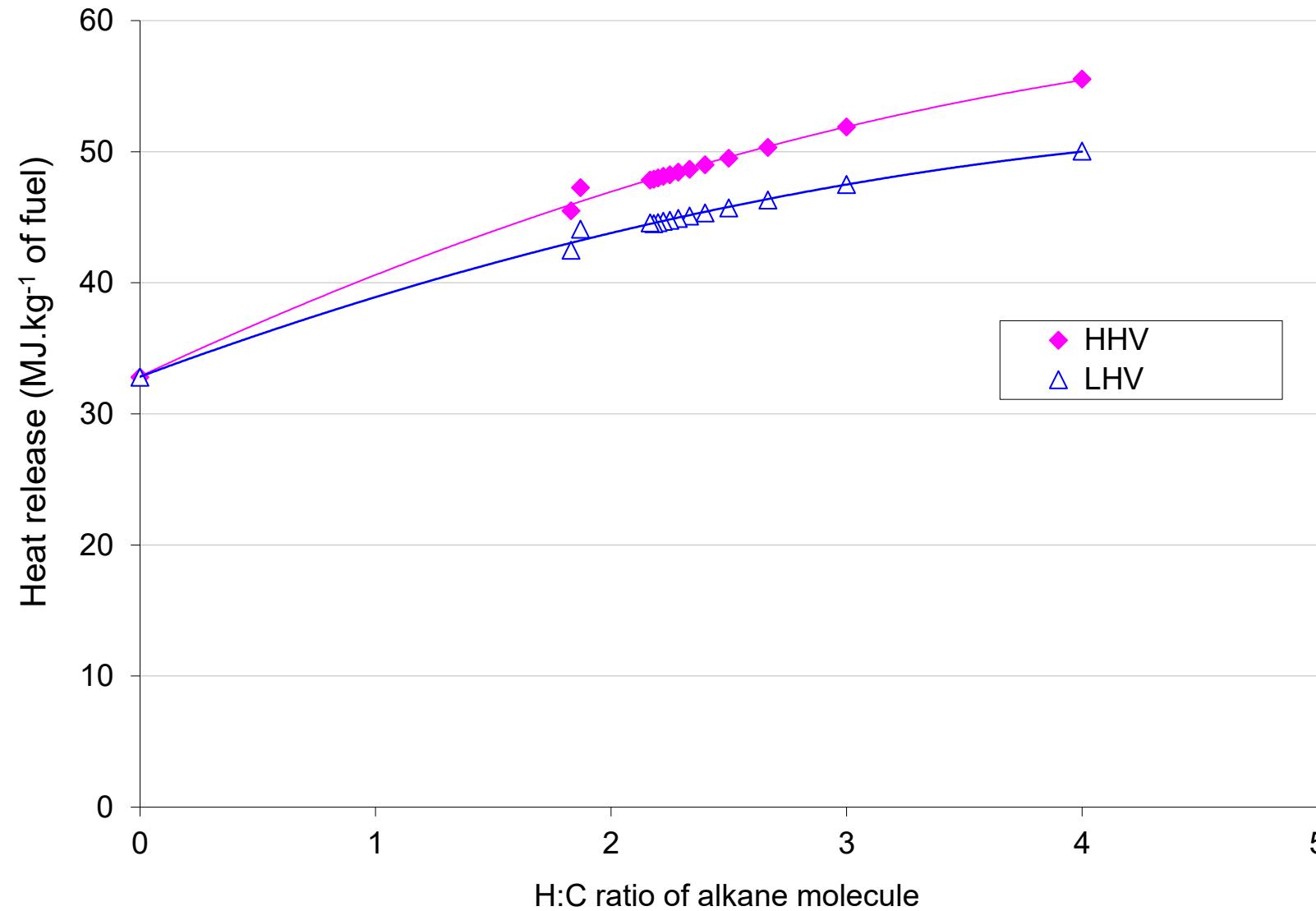
Measured by cooling the products down to a specified temperature.

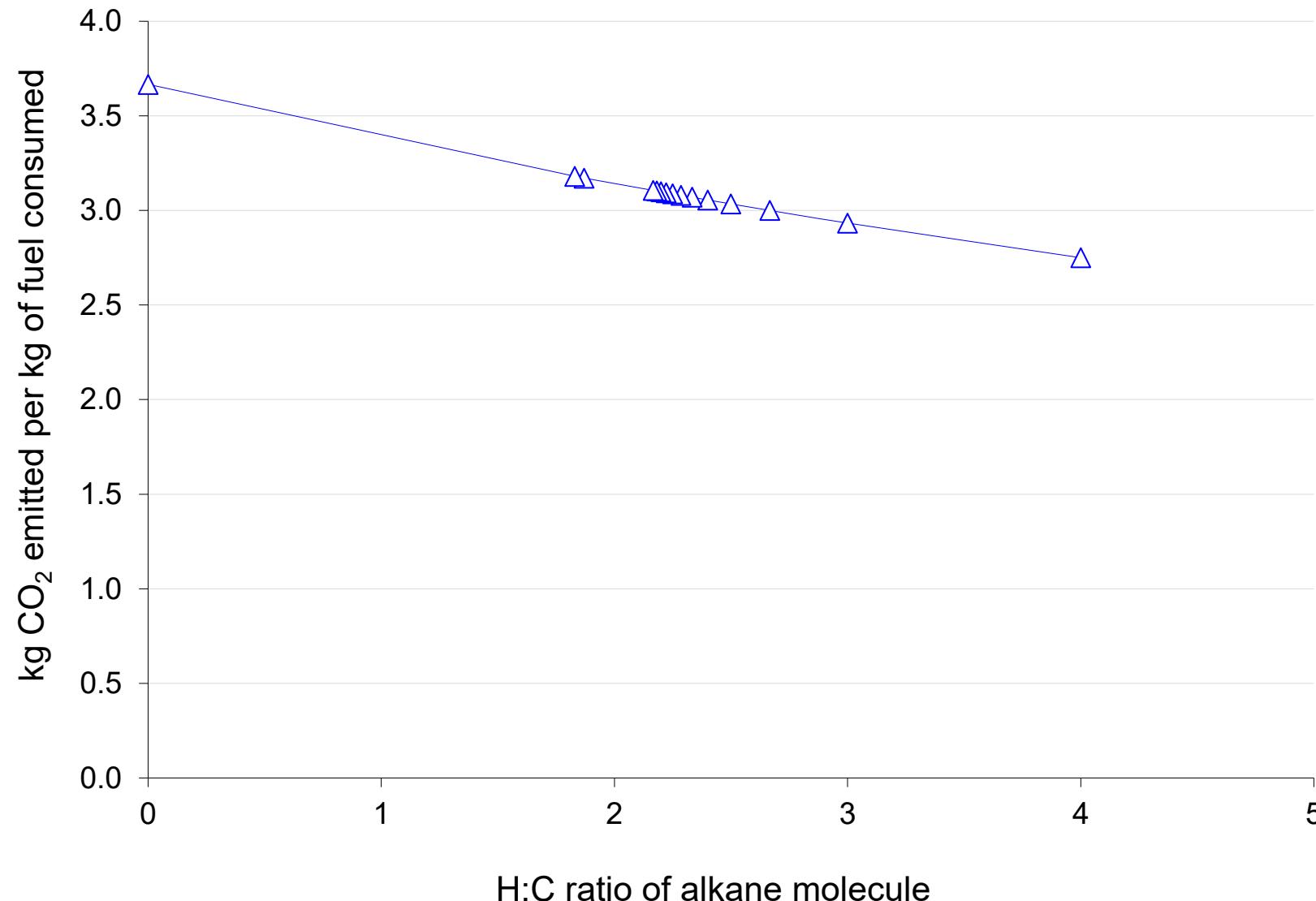
HHV (HCV, GCV):

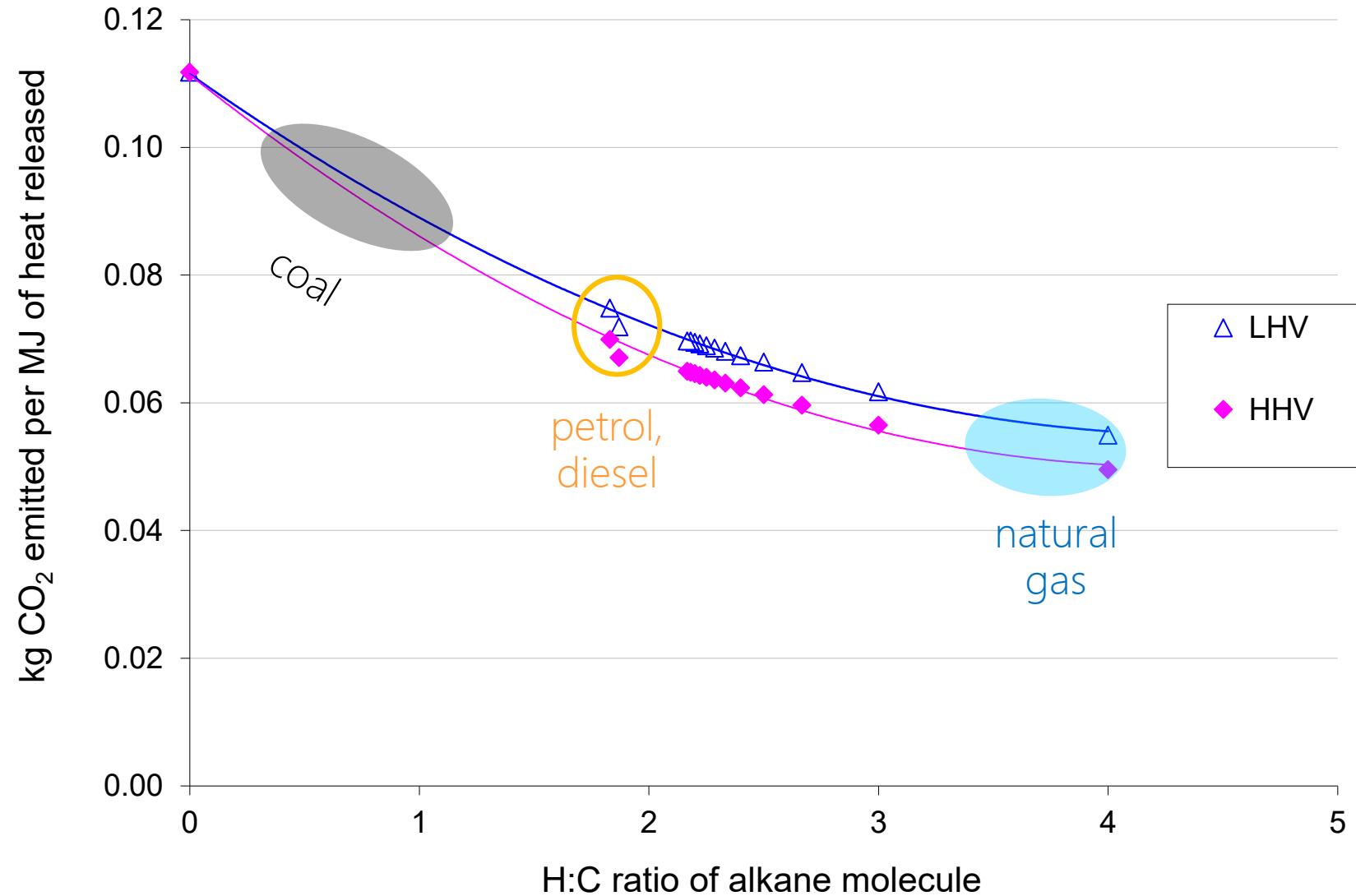
Products are cooled to initial fuel temperature (usually 25 C): most (assumed 100% of) water vapour condenses out.

LHV (LCV, NCV):

Products are cooled to 150 C: most (assumed 100% of) water remains in vapour phase.







## Sample calculation :

Calculate annual CO<sub>2</sub> emissions from a power plant generating 500 MW of electricity for each of three scenarios:

- Coal-fired, Rankine cycle plant
- Natural gas fired, Rankine cycle plant
- Natural gas fired GTCC plant

Assume 8,000 hours of operation per annum in each case

Sample calculation :



500 MW<sub>e</sub>

Coal fired

Rankine cycle

$\eta = 40\%$

500 MW<sub>e</sub>

Natural gas fired

Rankine cycle

$\eta = 40\%$



500 MW<sub>e</sub>

Natural gas fired

Combined cycle

$\eta = 55\%$

Sample calculation :

500 MW<sub>e</sub>

Coal fired

 $\eta = 40\%$ 

$$\text{Heat input rate} = \frac{\text{Power output}}{\text{Plant efficiency}} = \frac{500 \text{ MW}}{0.4} = 1250 \text{ MW}_{\text{th}}$$

$$1250 \text{ MW}_{\text{th}} \times 8,000 \text{ hours} = 10,000 \text{ GWh}_{\text{th}}$$

$$1 \text{ GWh}_{\text{th}} = 3,600 \text{ GJ} = 86 \text{ toe}$$

Hence, annual heat input = 860,000 toe

$\text{CO}_2$  emission factor for coal =  $3.96^* \text{ t CO}_2$  per toe

Annual  $\text{CO}_2$  emissions =  **$3.41 \text{ Mt CO}_2$  per year**

Note:  $500 \text{ MW} \times 8,000 \text{ h} = 4,000,000 \text{ MWh}$

$$\frac{3,410,000 \text{ t CO}_2}{4,000,000 \text{ MWh}} = \frac{3.41 \text{ t CO}_2}{4 \text{ MWh}} = 0.8525 \text{ kg CO}_2 \text{ per kWh}$$

Sample calculation :

500 MW<sub>e</sub>

Natural gas fired

 $\eta = 40\%$ 

$$\text{Heat input rate} = \frac{\text{Power output}}{\text{Plant efficiency}} = \frac{500 \text{ MW}}{0.4} = 1250 \text{ MW}_{\text{th}}$$

Hence, annual heat input = 860,000 toe

CO<sub>2</sub> emission factor for gas = 2.35 t<sub>CO<sub>2</sub></sub> per toeAnnual CO<sub>2</sub> emissions = 2.02 Mt<sub>CO<sub>2</sub></sub> per year

$$\frac{2,020,000 \text{ t CO}_2}{4,000,000 \text{ MWh}} = \frac{2.02 \text{ t CO}_2}{4 \text{ MWh}} = 0.505 \text{ kg CO}_2 \text{ per kWh}$$

Sample calculation :



500 MW<sub>e</sub>

NG fired

GTCC cycle

$\eta = 55\%$

$$\text{Heat input rate} = \frac{\text{Power output}}{\text{Plant efficiency}} = \frac{500 \text{ MW}}{0.55} = 909 \text{ MW}_{\text{th}}$$

$$909 \text{ MW}_{\text{th}} \times 8,000 \text{ hours} = 7,272 \text{ GWh}_{\text{th}}$$

$$1 \text{ GWh}_{\text{th}} = 3,600 \text{ GJ} = 86 \text{ toe}$$

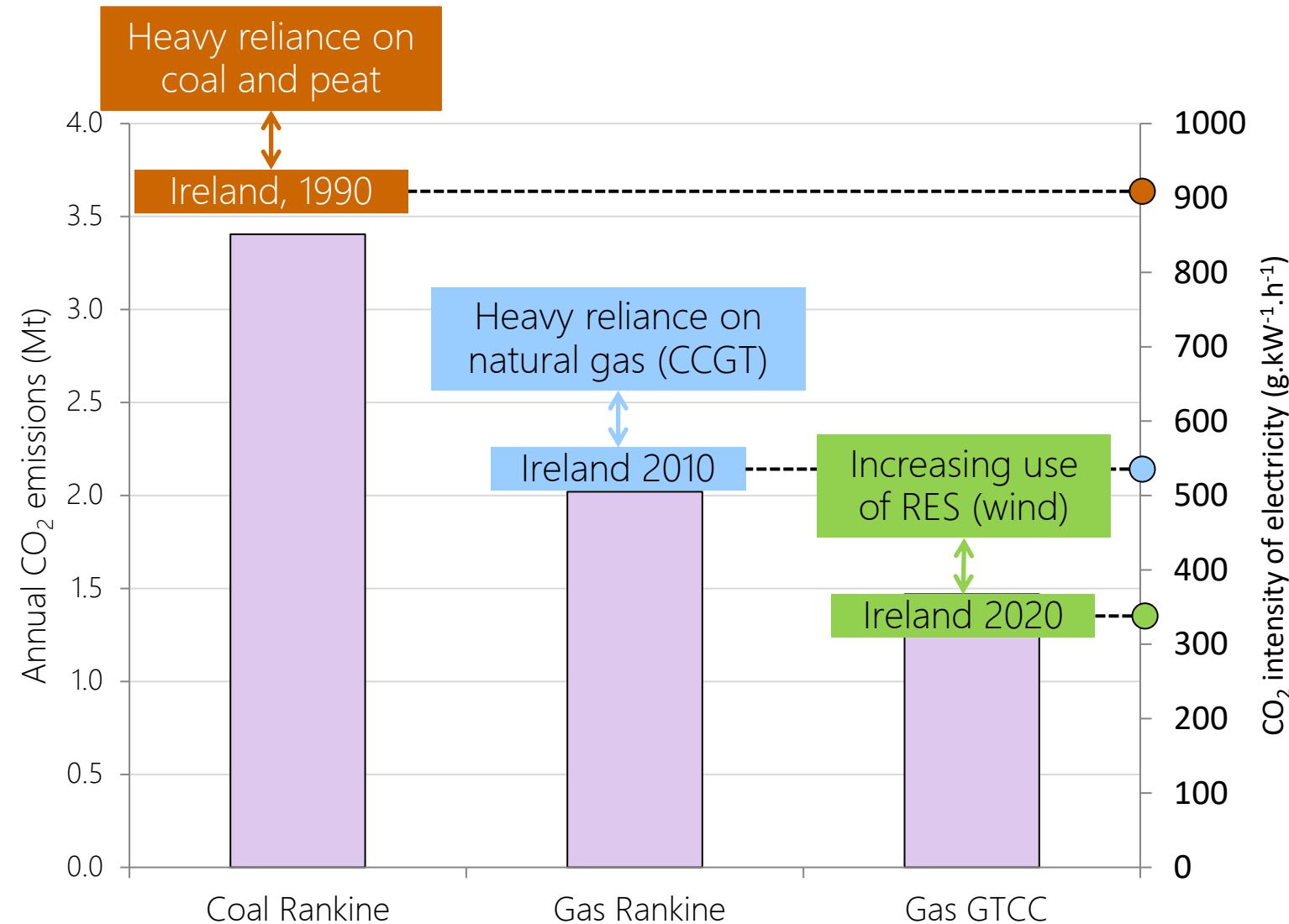
Hence, annual heat input = 625,000 toe

CO<sub>2</sub> emission factor for gas = 2.35 t<sub>CO<sub>2</sub></sub> per toe

Annual CO<sub>2</sub> emissions = 1.47 Mt<sub>CO<sub>2</sub></sub> per year

$$\frac{1,470,000 \text{ t CO}_2}{4,000,000 \text{ MWh}} = \frac{1.47 \text{ t CO}_2}{4 \text{ MWh}} = 0.3675 \text{ kg CO}_2 \text{ per kWh}$$

Summary :



## Note 1:

All fossil fuels contain Carbon.

If you don't want CO<sub>2</sub> to be added to the atmosphere, then:

- don't burn fossil fuels...
- ...or strip off the Carbon before combustion (H<sub>2</sub> synthesis)...
- ...or capture and store (sequester) the CO<sub>2</sub> after combustion.

## Note 2:

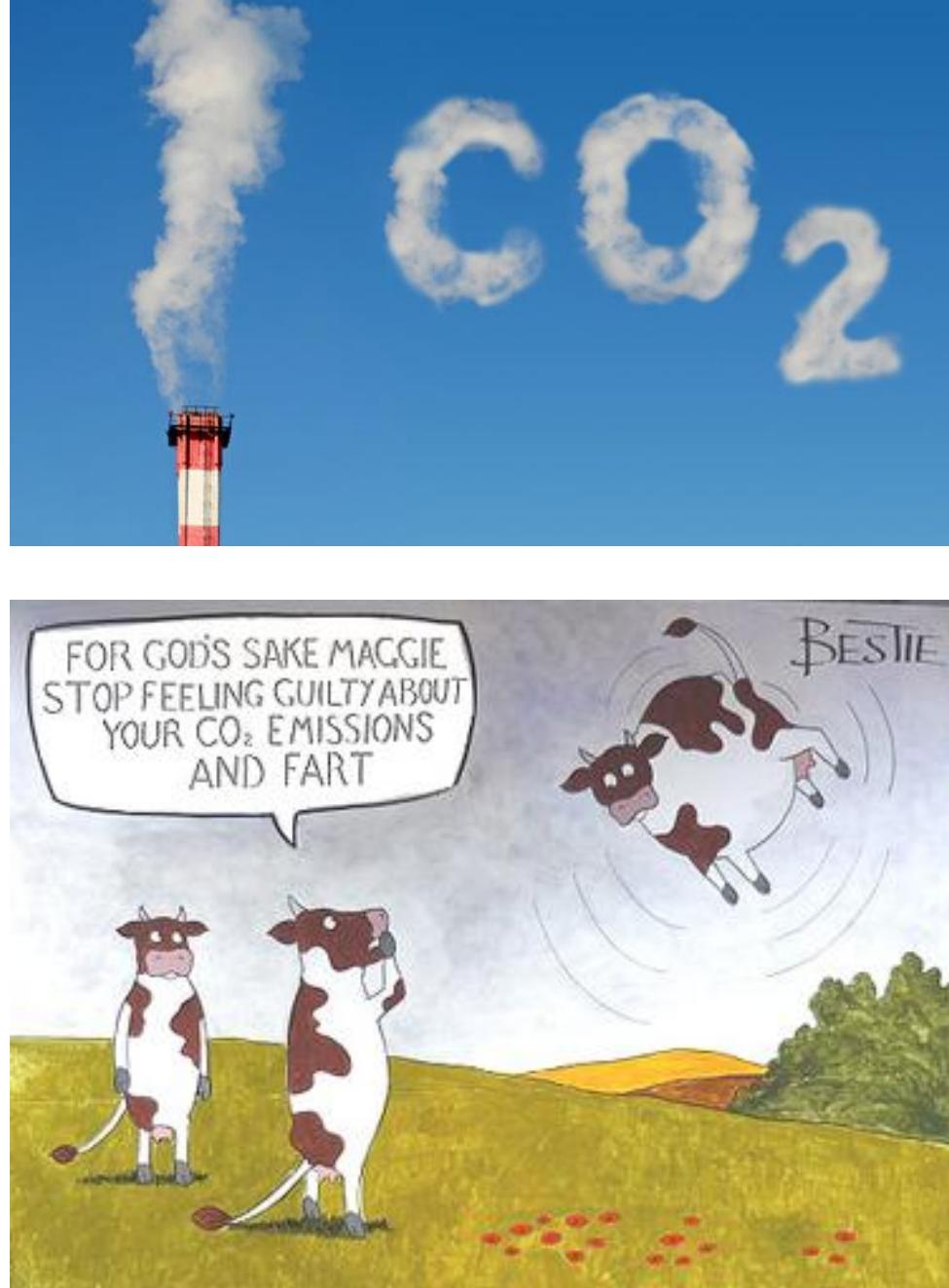
$\text{CO}_2$  is not a *pollutant* in the usual sense, i.e. it does not impact on air *quality*.

Although it is toxic at high concentrations (above 10%), ambient concentration is < 0.05%.

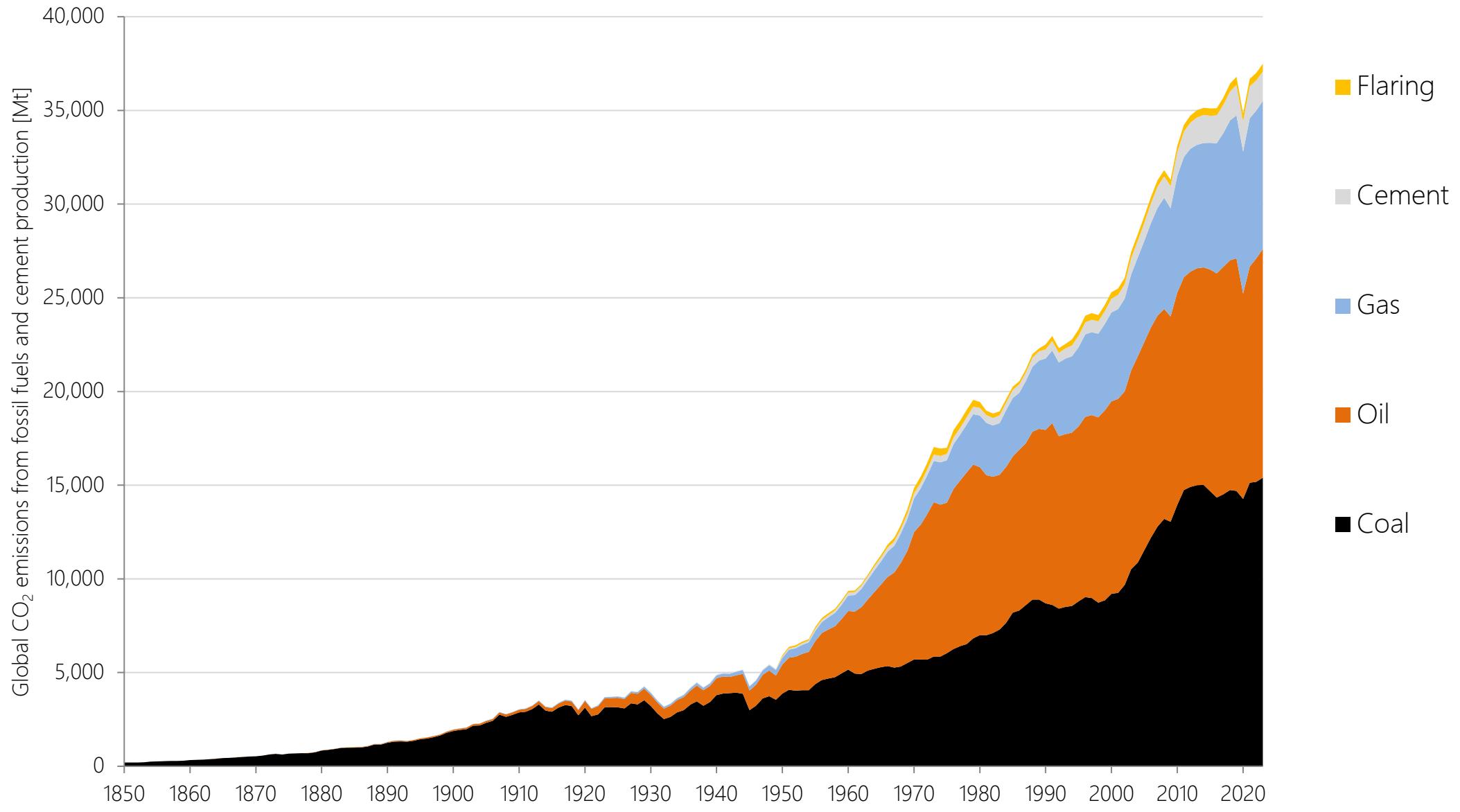
Particulate matter (PM), oxides of nitrogen (NOx), oxides of sulfur (SOx), and some organic molecules (POPs) are much more toxic.

Material covered in this Topic:

- Combustion and CO<sub>2</sub>
- Anthropogenic CO<sub>2</sub> emissions
- CO<sub>2</sub> and the greenhouse effect
- CO<sub>2</sub> accounting, the Carbon cycle, and other GHG



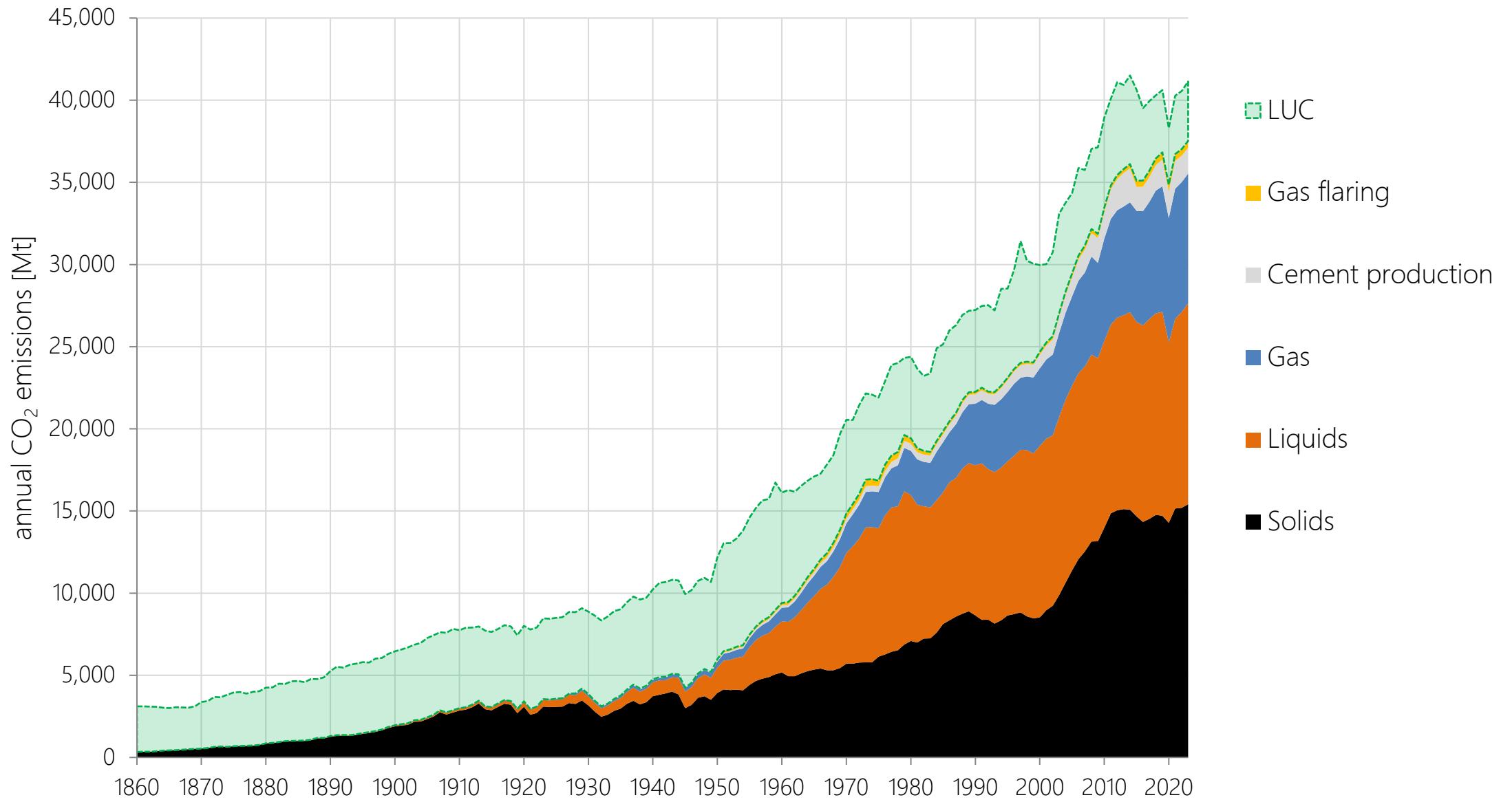
# Global CO<sub>2</sub> emissions



Raw data: Integrated Carbon Observation System <https://www.icos-cp.eu/science-and-impact/global-carbon-budget/2024>

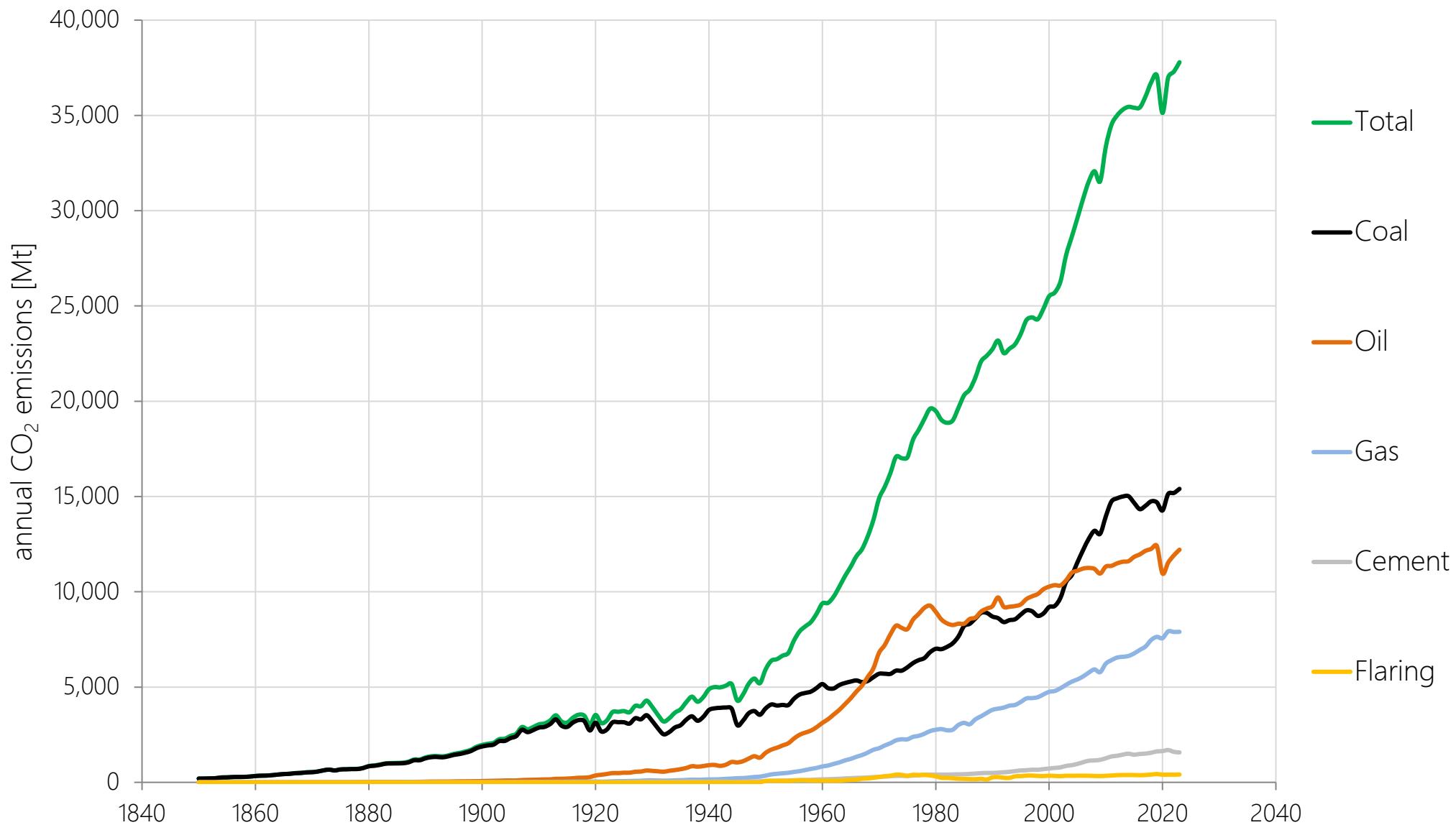


# Global CO<sub>2</sub> emissions



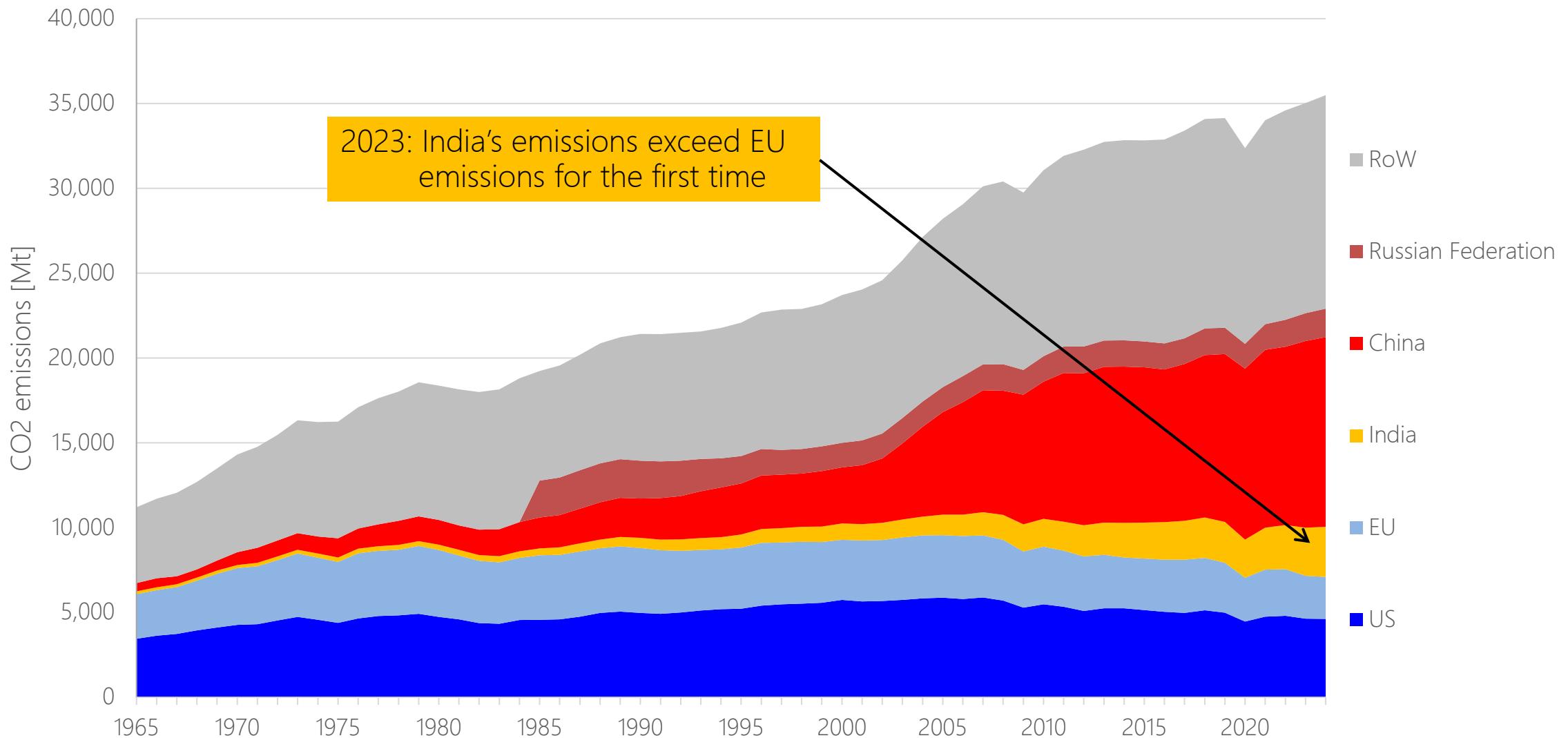
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# Global CO<sub>2</sub> emissions



Raw data: Integrated Carbon Observation System <https://www.icos-cp.eu/science-and-impact/global-carbon-budget/2024>

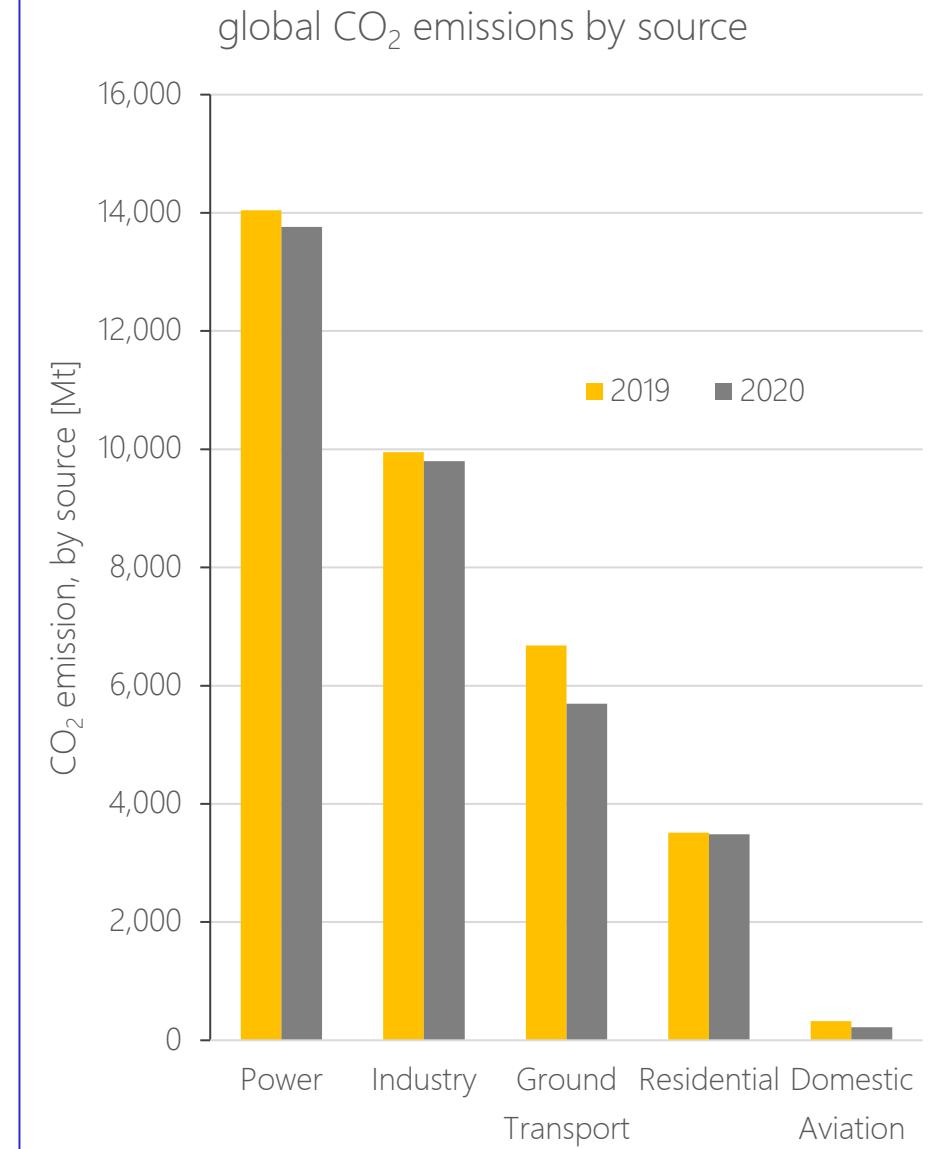
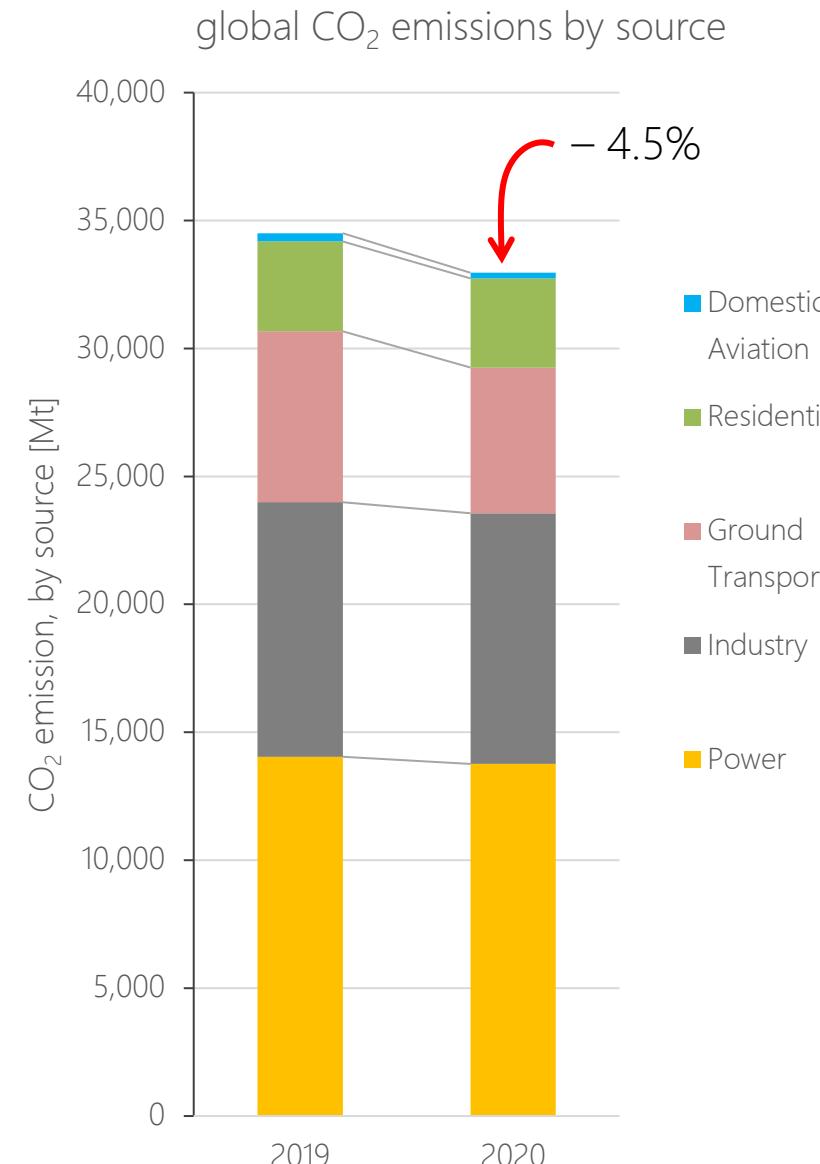
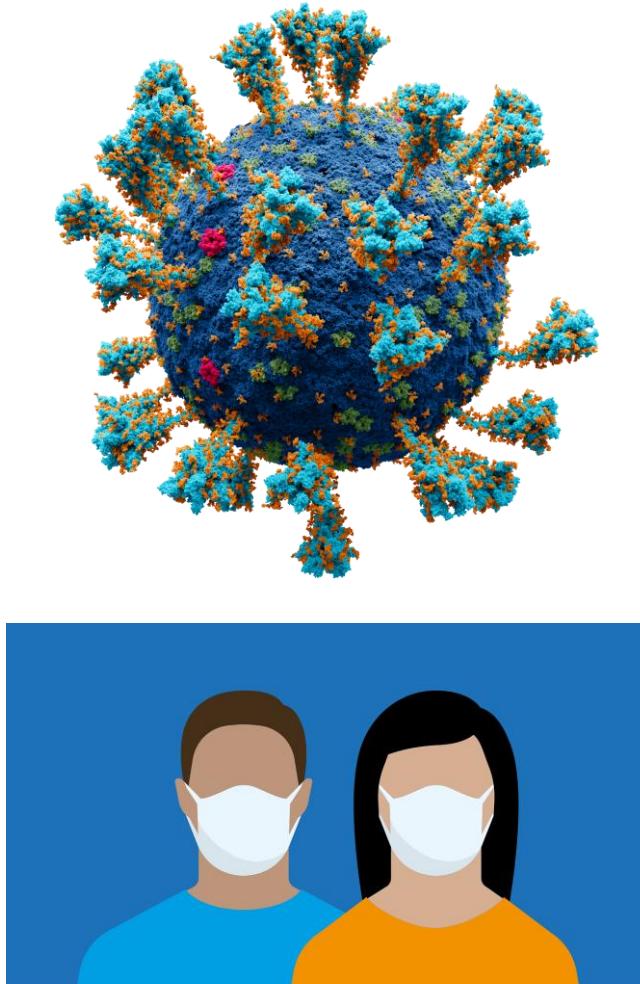
# Global CO<sub>2</sub> emissions



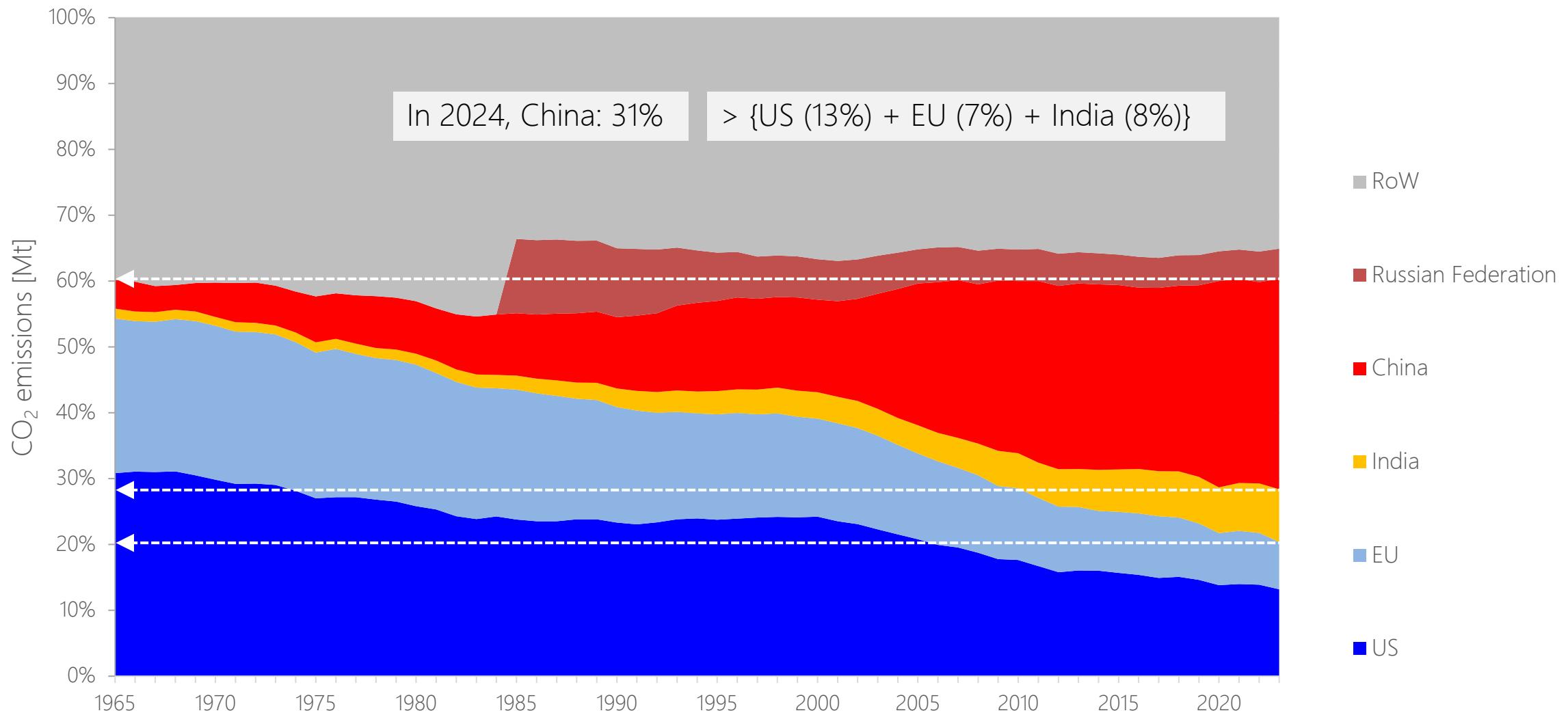
Raw data: Statistical Review of World Energy



# Global CO<sub>2</sub> emissions

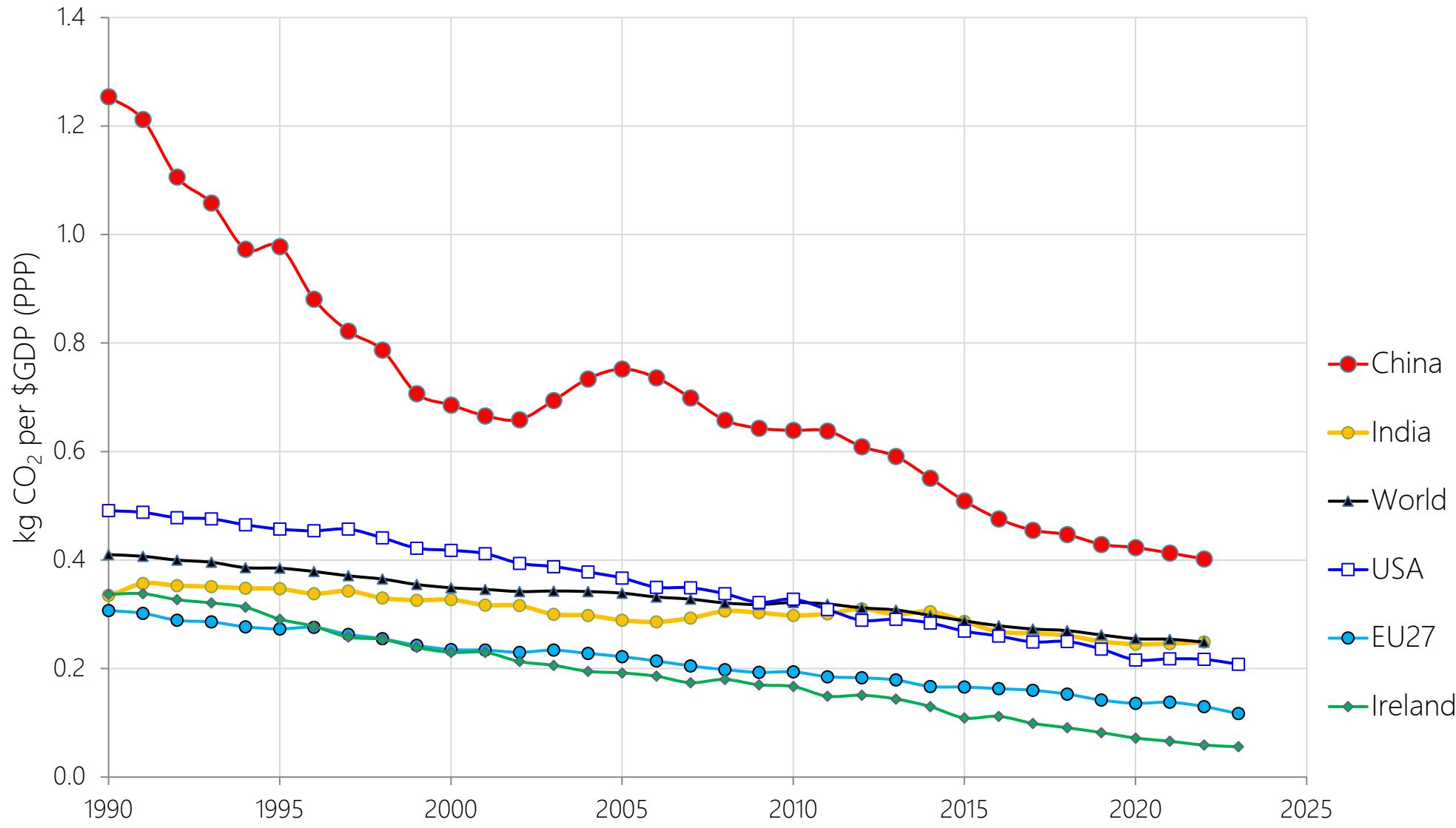


Raw data: <https://carbonmonitor.org/>



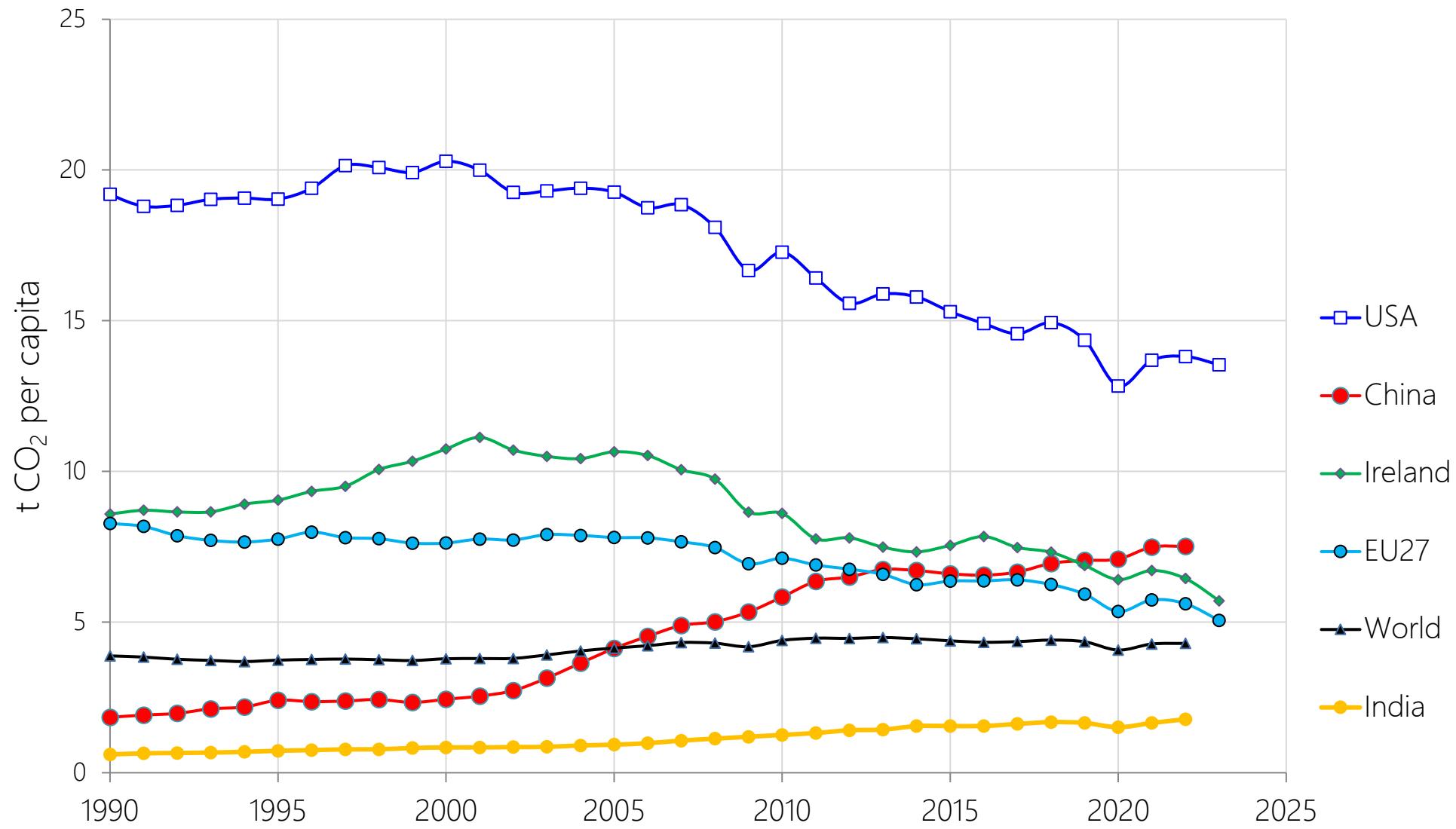
Raw data: BP Statistical Review of World Energy

# Global CO<sub>2</sub> emissions

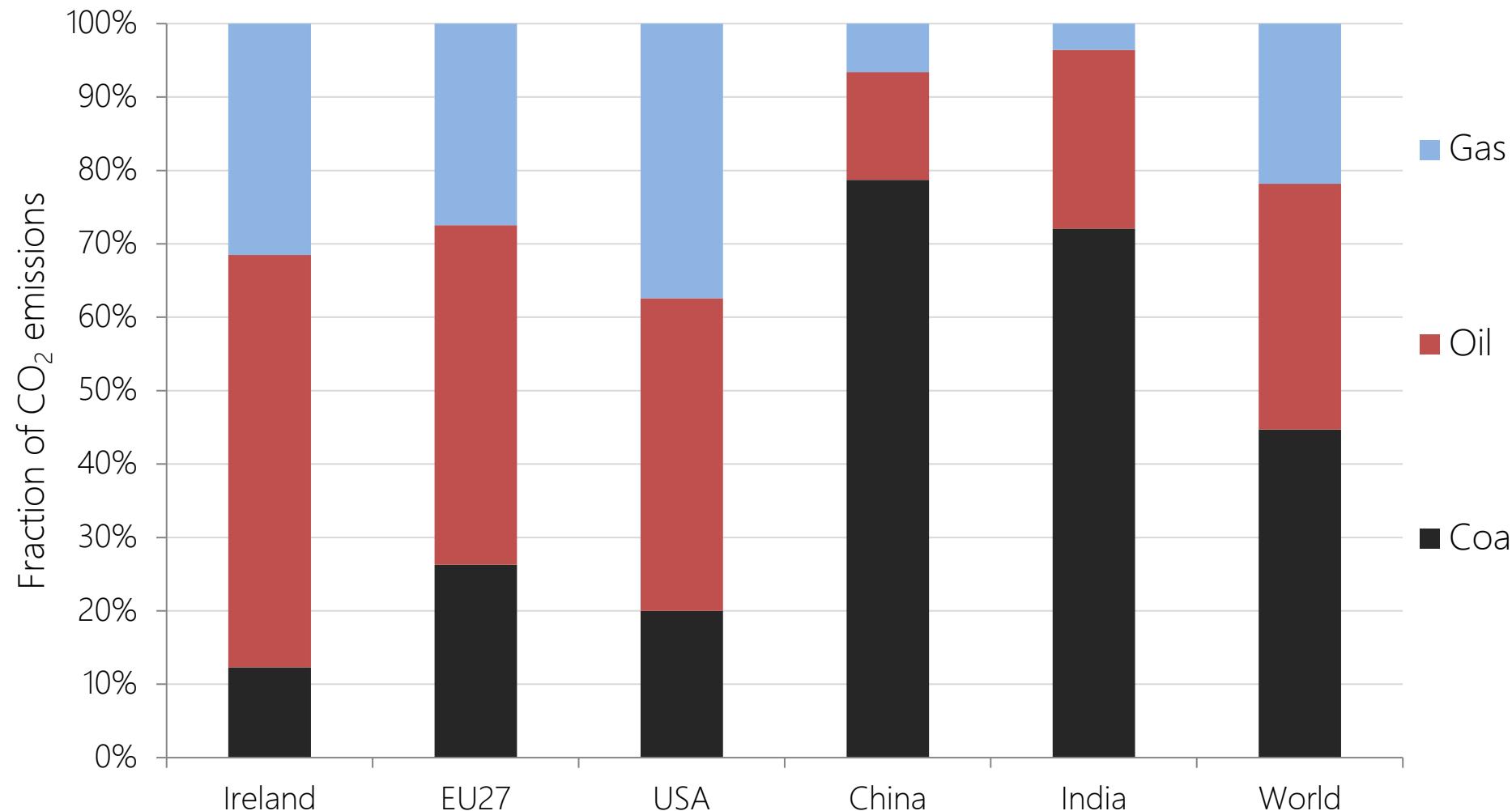


Raw data: GHG emissions from energy – Highlights (IEA)

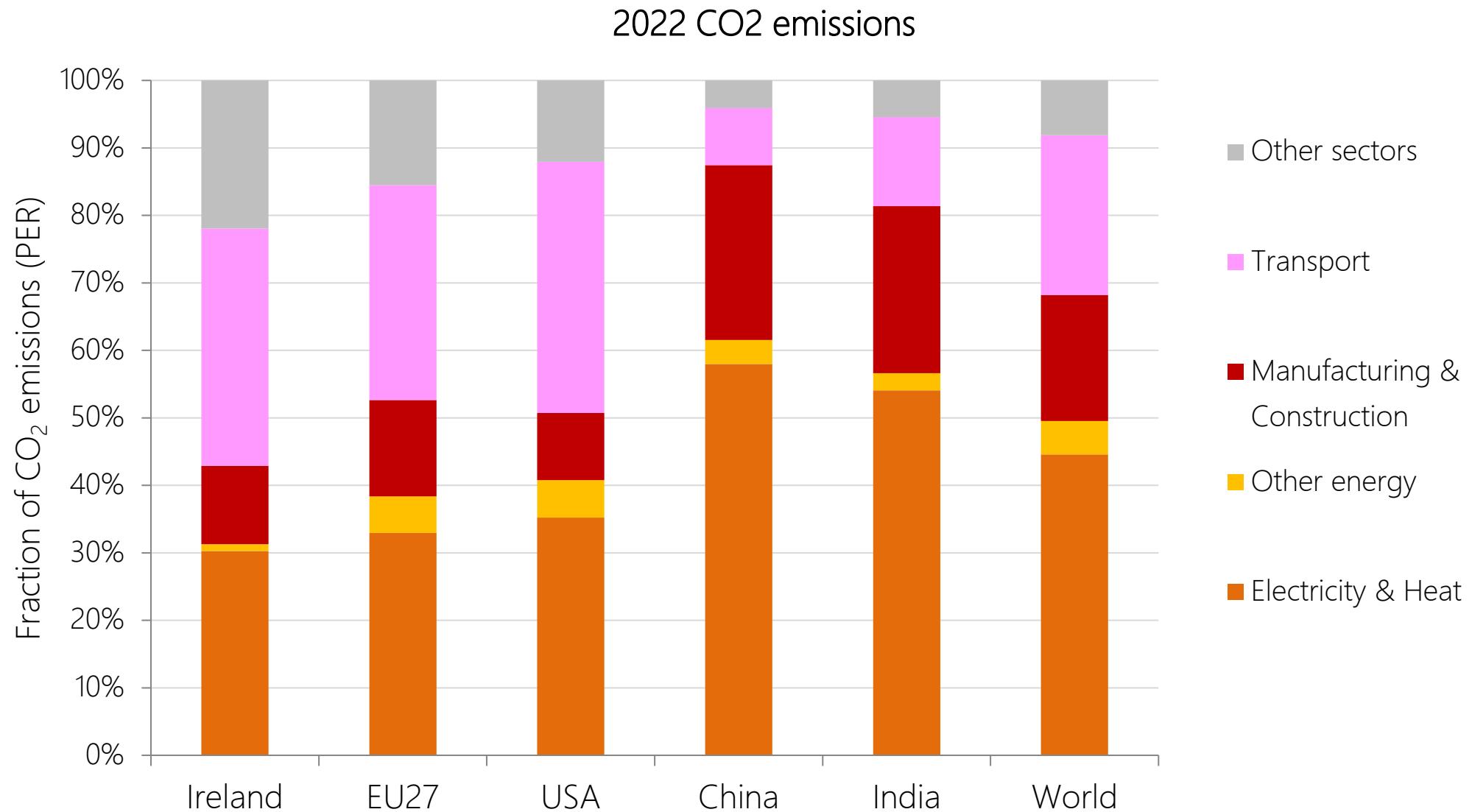
# Global CO<sub>2</sub> emissions



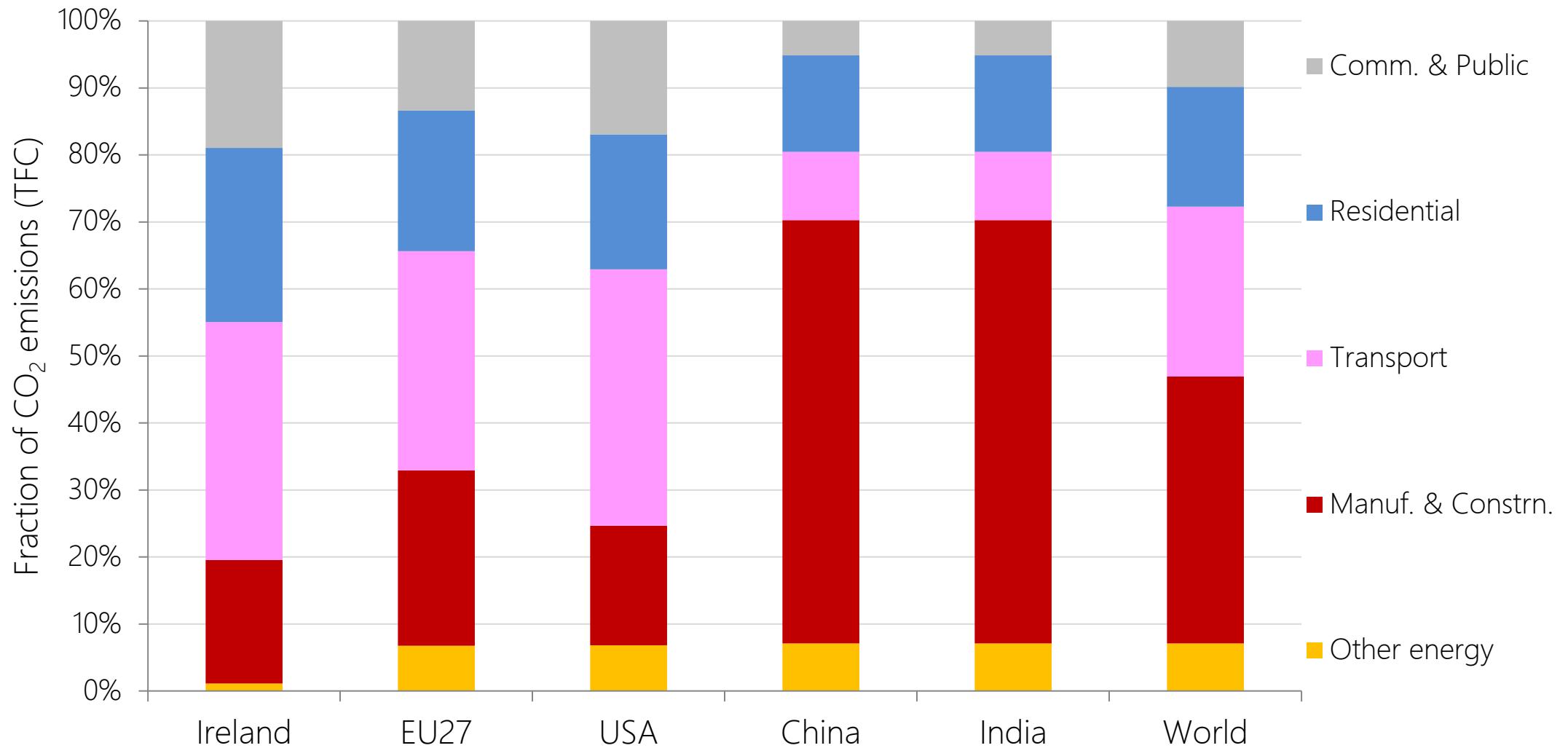
Raw data: GHG emissions from energy – Highlights (IEA)

2022 CO<sub>2</sub> emissions

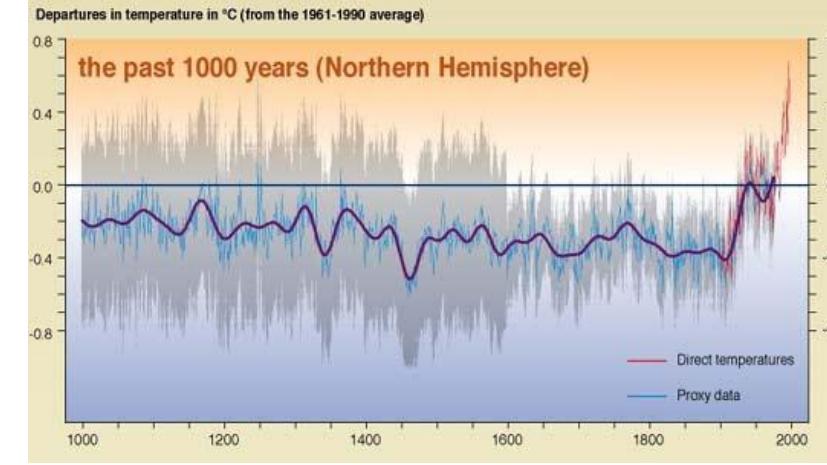
Raw data: GHG emissions from energy – Highlights (IEA)



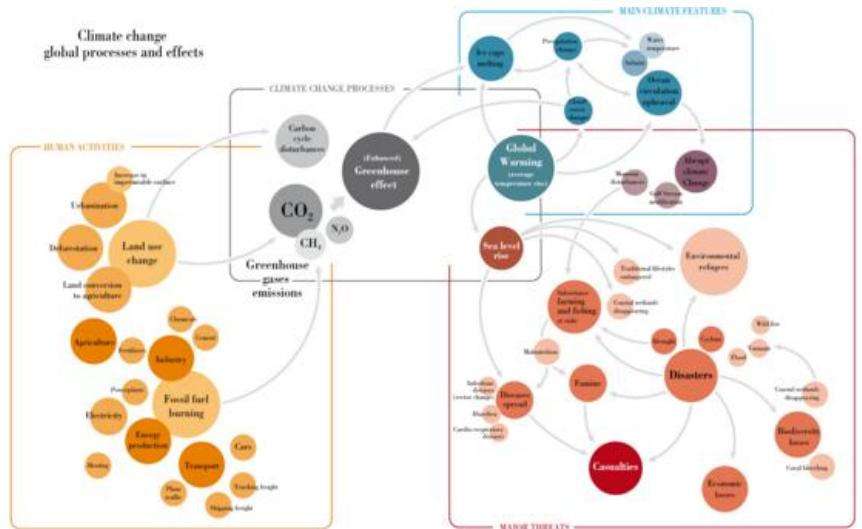
Raw data: GHG emissions from energy – Highlights (IEA)

2022 CO<sub>2</sub> emissions

Raw data: GHG emissions from energy – Highlights (IEA)



# $\text{CO}_2$ and the greenhouse effect

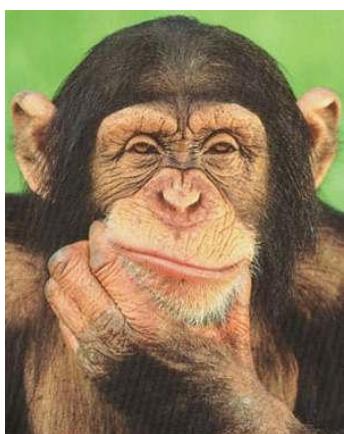
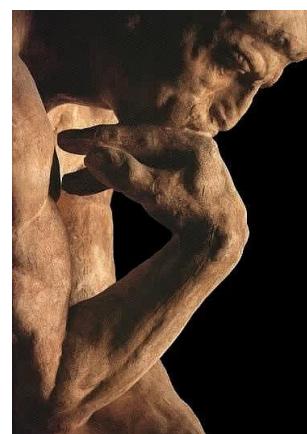


The fundamental question is...

Are anthropogenic emissions to the atmosphere exerting a significant, detrimental, influence on global climate?

To answer that question, we need to address the following issues:

1. Is it physically possible; *i.e.* do we have a plausible mechanism?
2. Is the climate changing?
3. Are the changes driven by anthropogenic emissions?
4. Are the changes detrimental?
5. Are the changes significant?



1. Do we have a plausible mechanism?

Yes! The (enhanced) greenhouse effect

(Really a “better blanket” effect)

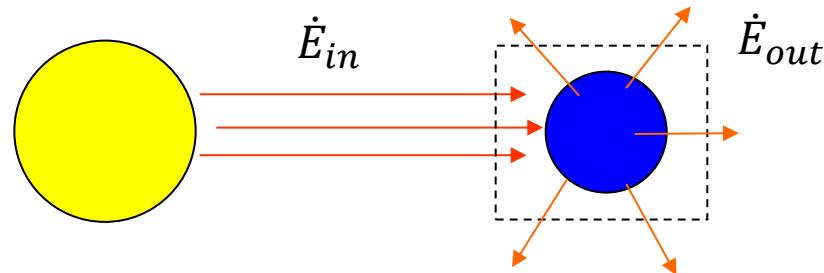
How does it work?

1. Some gases in the atmosphere let the sun’s heat in, but don’t let it out.
2. This causes the earth to heat up.
3. Increasing the concentration of these gases will make the earth even warmer.



First proposed by Svante Arrhenius in 1896

$$1^{\text{st}} \text{ Law of Thermodynamics} \quad \dot{E}_{in} = \dot{E}_{out} + \dot{E}_{cv}$$



The earth is constantly receiving heat input from the sun: why isn't it getting warmer?

Assume earth is in steady-state  $\Rightarrow \dot{E}_{in} = \dot{E}_{out}$

i.e. for thermal equilibrium, heat output rate must equal heat input rate.

Three potential mechanisms for heat output:

Conduction – to a connected solid

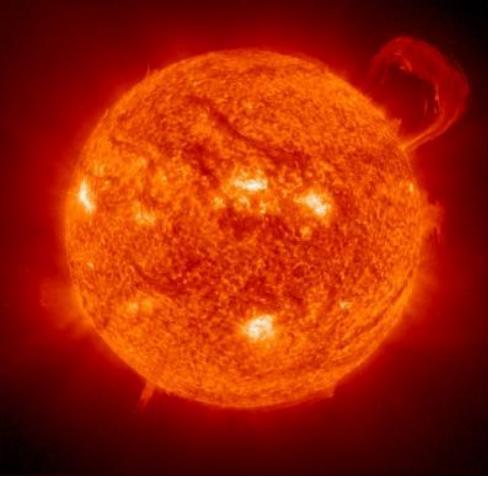
Convection – to a connected fluid

Radiation

}

inter-molecular contact

photon emission



## Thermal radiation

- All bodies radiate energy (emit photons).
- Hot bodies radiate *much* more intensely:
- High-temperature bodies emit high-energy (short-wavelength) photons.



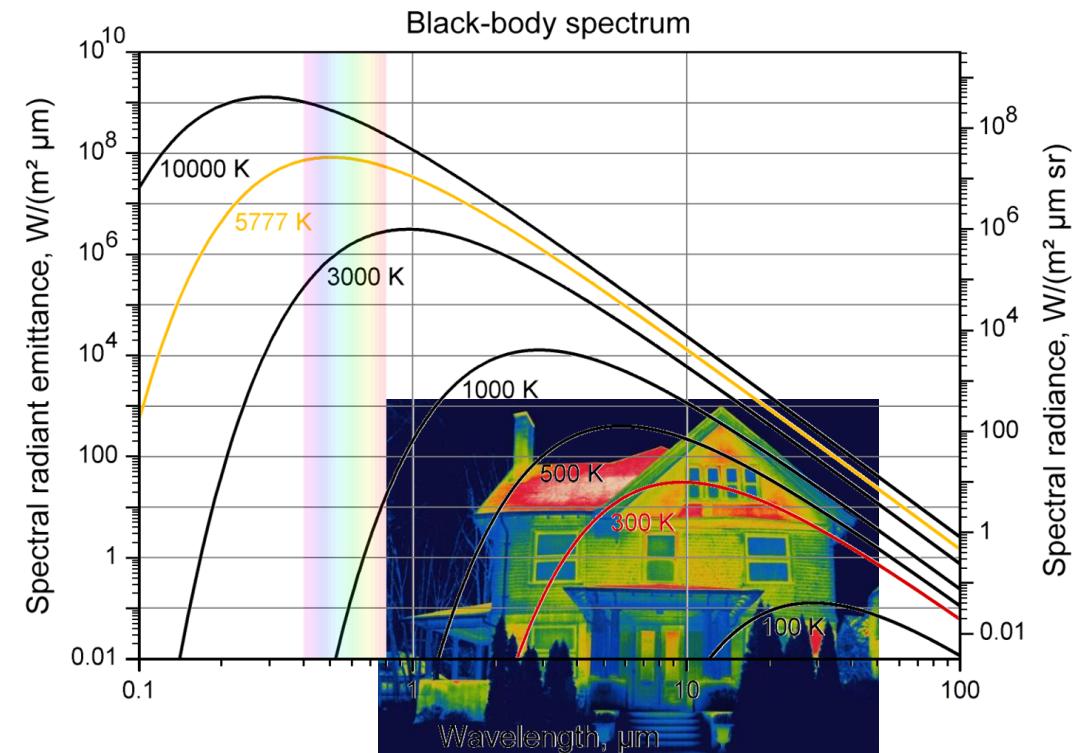
emissivity (surface-dependent)

→ surface area

$$\dot{Q}_{out} = \epsilon \sigma A T^4$$

↓ ↗ surface temperature [K]

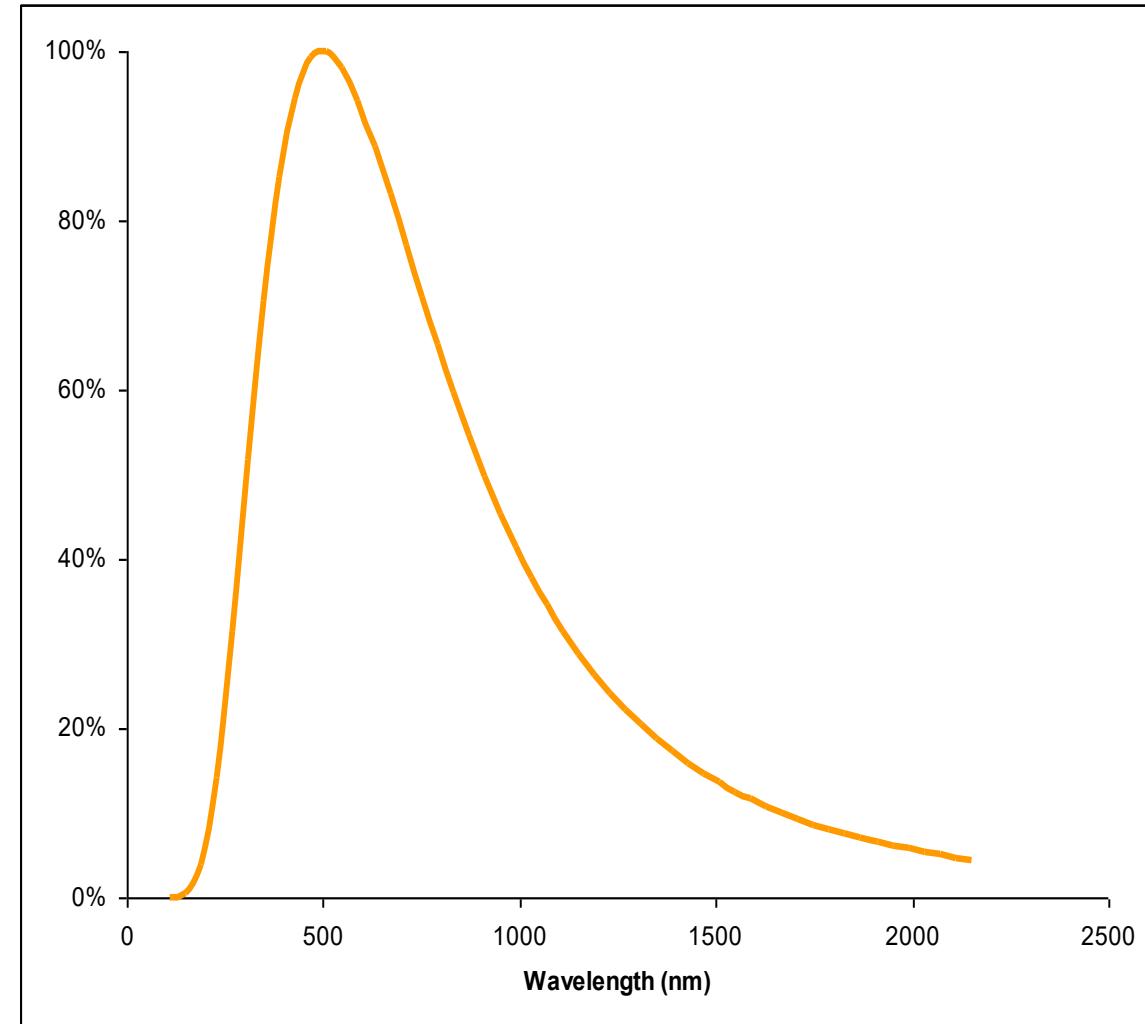
Stefan-Boltzmann constant



## Black body radiation – physical laws

Black body emission spectrum (Max Planck, 1900)

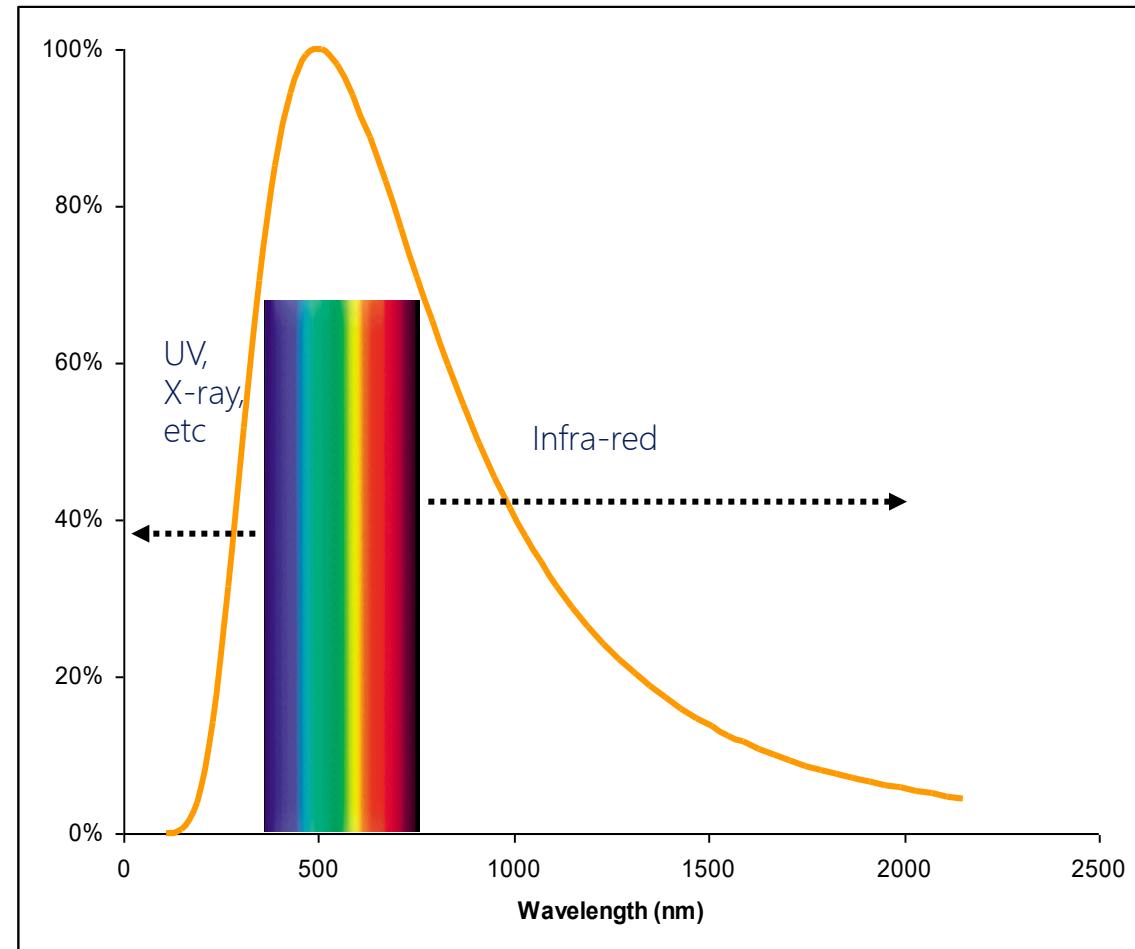
$$I_\lambda(\lambda) = \frac{2\pi hc^2}{\lambda^5 \left( e^{\left( \frac{hc}{\lambda kT} \right)} - 1 \right)}$$



## Black body radiation – physical laws

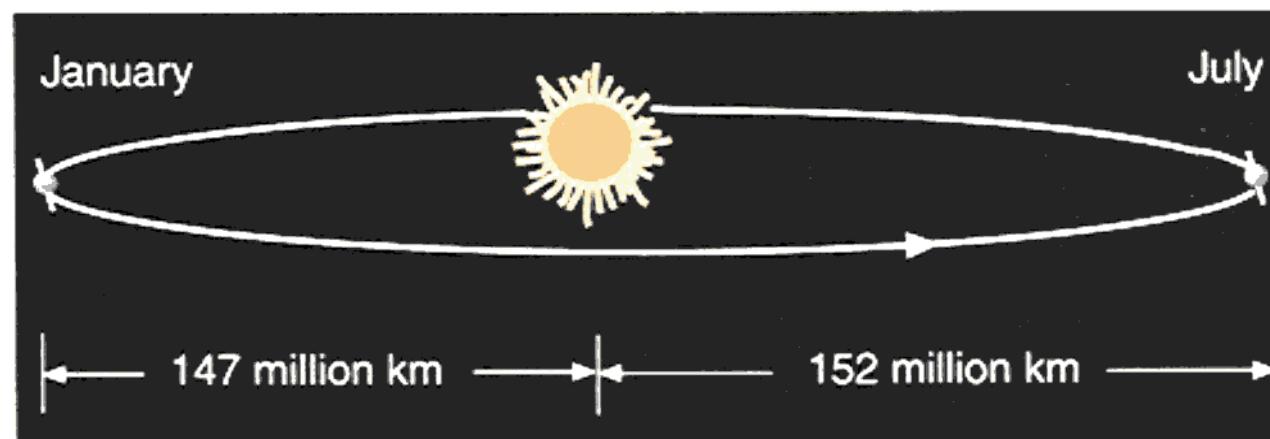
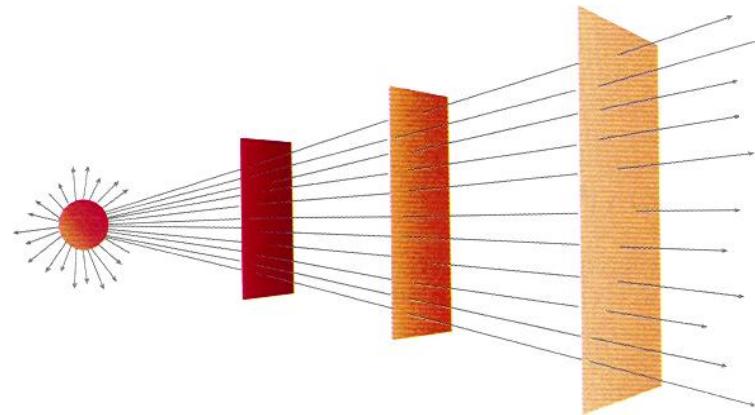
Black body emission spectrum (Max Planck, 1900)

$$I_\lambda(\lambda) = \frac{2\pi hc^2}{\lambda^5 \left( e^{\left( \frac{hc}{\lambda kT} \right)} - 1 \right)}$$



"Solar Constant": the intensity of solar radiation when it reaches Earth

$$\text{Surface area of a sphere} = 4\pi r^2$$



$$I(r) = I_o \frac{r_o^2}{r^2}$$

$$I_o = 6.3 \times 10^7 \text{ W.m}^{-2}$$

$$I_{\text{at earth}} = I_o \frac{r_{\text{sun}}^2}{r^2}$$

$$\approx 6.3 \times 10^7 \left( \frac{6.9 \times 10^8}{1.5 \times 10^{11}} \right)^2$$

$$\approx 1367 \text{ W.m}^{-2}$$

1<sup>st</sup> Law of Thermodynamics  $\dot{E}_{in} = \dot{E}_{out} + \dot{E}_{cv}^0$

Solar constant: ~1,370 W.m<sup>-2</sup>

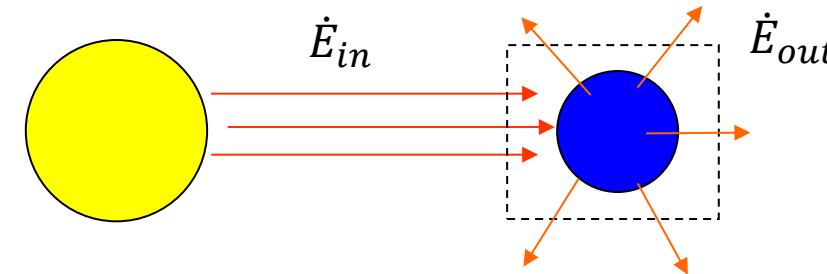
$$\dot{E}_{in} = S(1 - R)\pi r_{earth}^2$$

Reflectivity of earth-atmosphere combination  
(fraction of incoming solar radiation that is reflected, not absorbed)

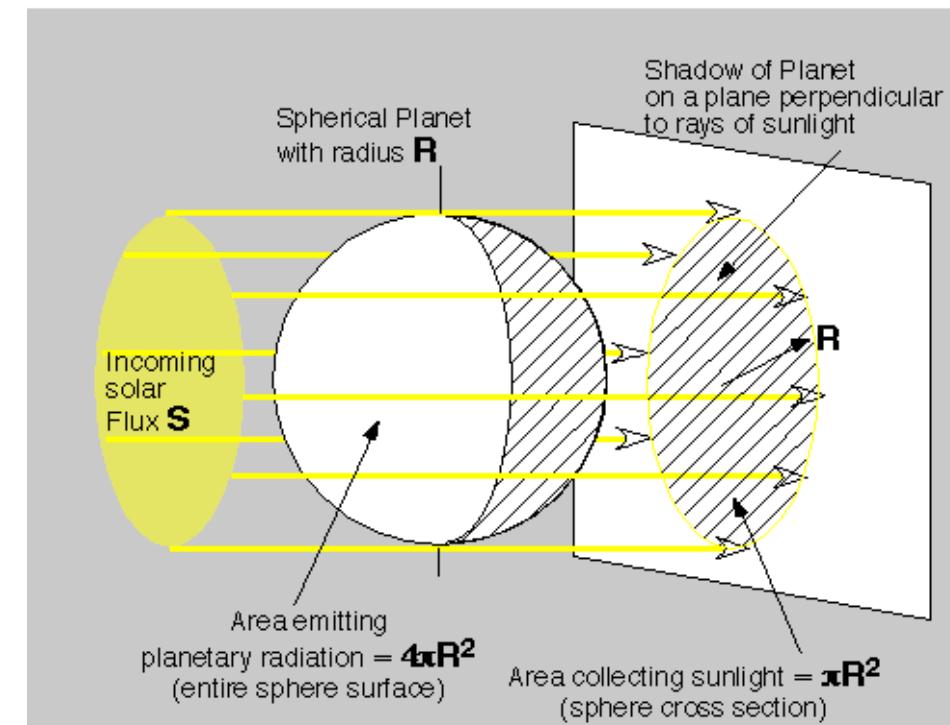
$$\dot{E}_{out} = \epsilon\sigma T_{earth}^4 (4\pi r_{earth}^2)$$

$$T_{earth}^4 = \frac{S(1 - R)}{4\epsilon\sigma} = \frac{1,370(1 - 0.3)}{4(5.67 \times 10^{-8})} = 255 \text{ K } (!?!)$$

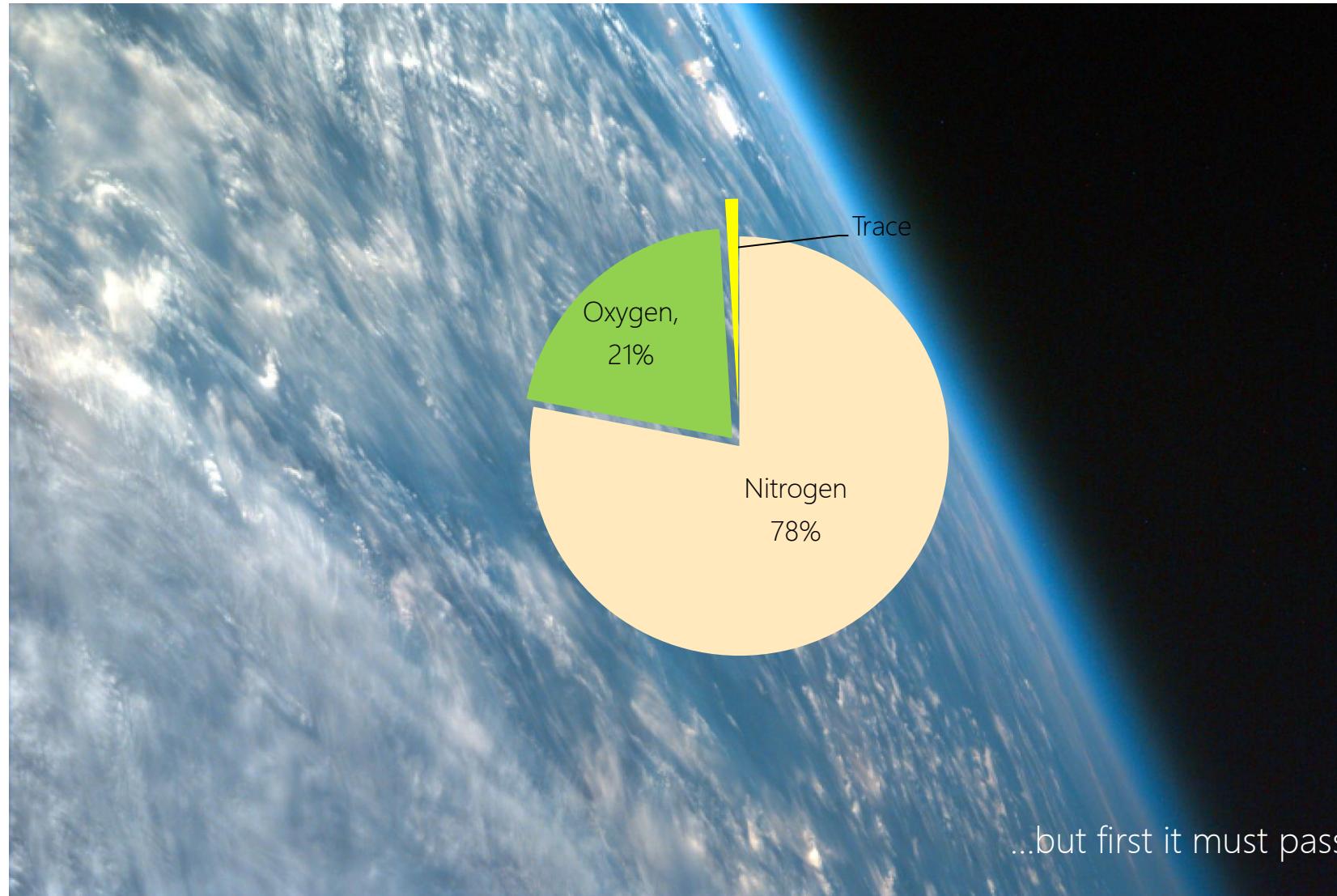
$\sim 30\%$   
 $\approx 1$



A Spherical Planet Receiving the Sun's Radiation



Some of the sun's radiation (0.002%) hits the earth...



Earth's atmosphere

78% nitrogen

21% oxygen

1% trace gases

...but first it must pass through our atmosphere.

## The (radiative) absorption characteristics of gases

Gases may: absorb,

→ (ignore)

transmit,

radiation (photons)

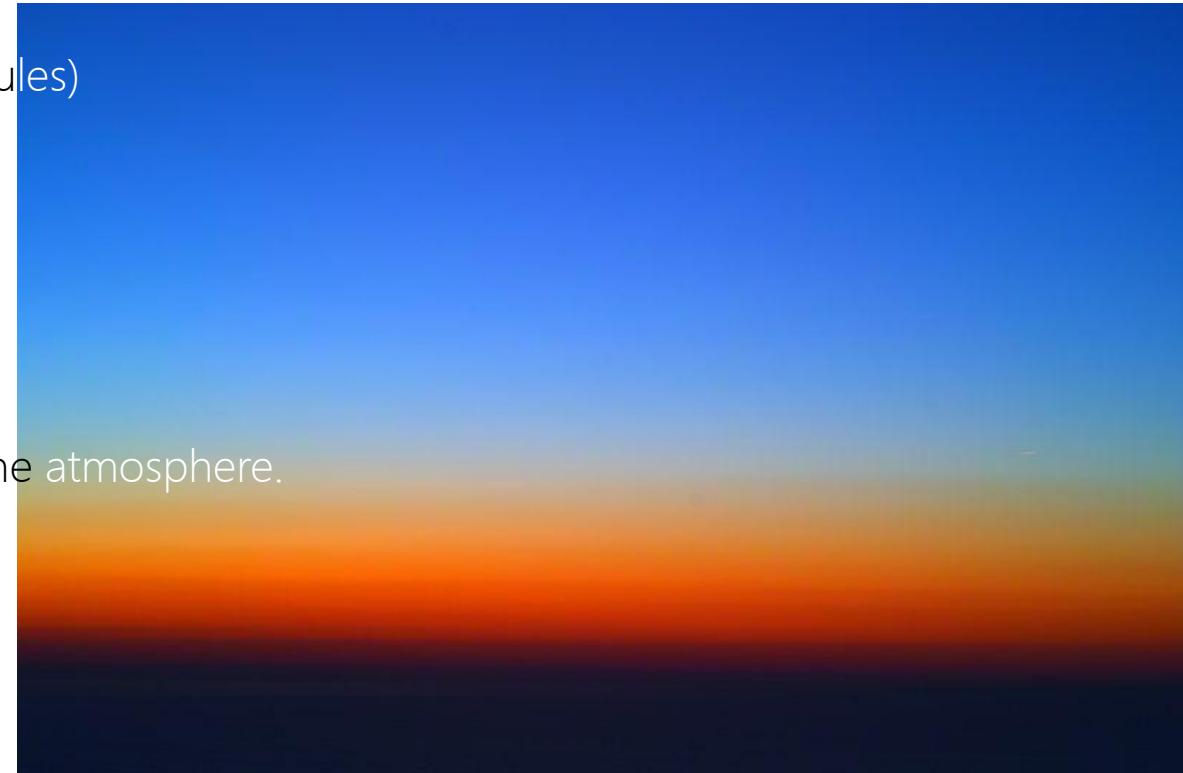
or scatter



Elastic collisions with particles much smaller than  $\lambda$  (e.g. molecules)

Degree of scattering  $\propto \left(\frac{1}{\lambda}\right)^4$  so blue and violet scatter most

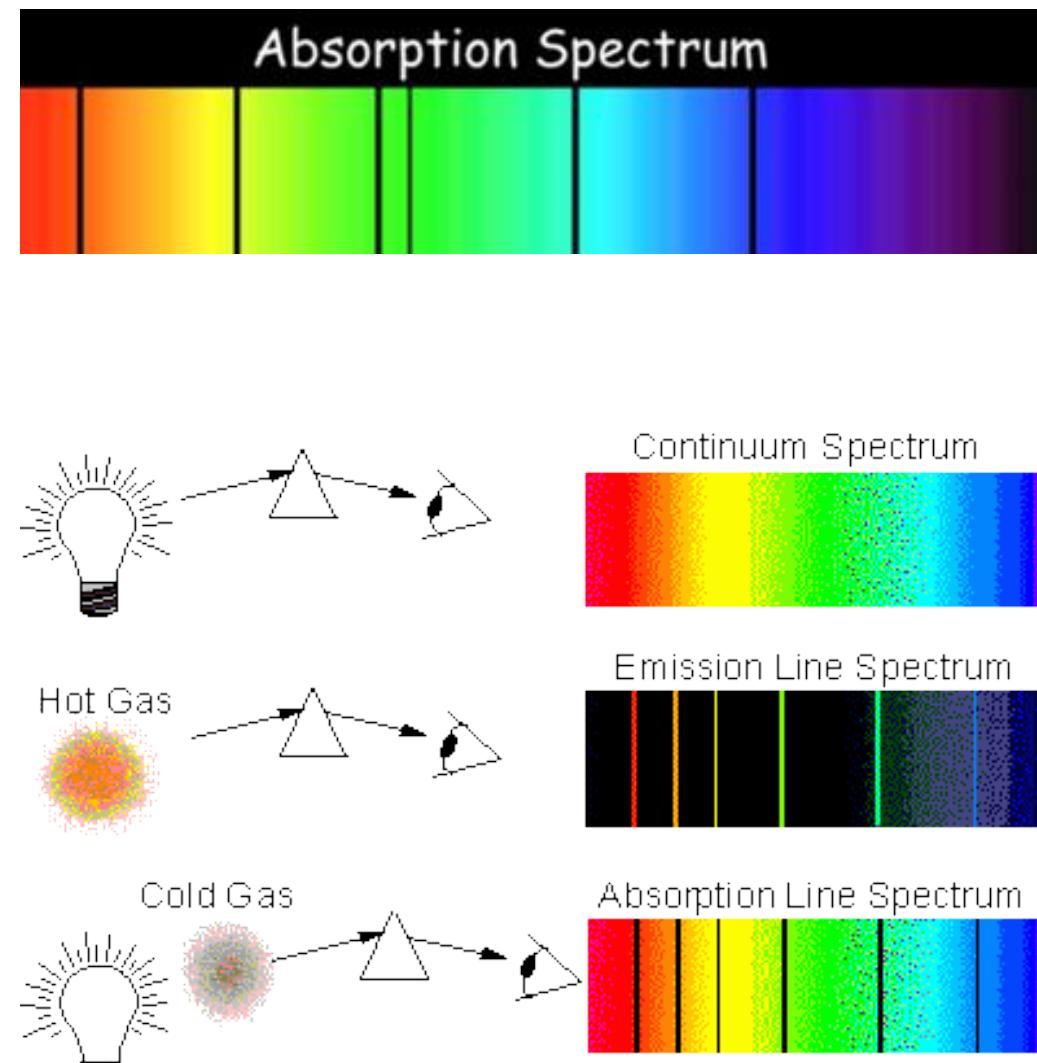
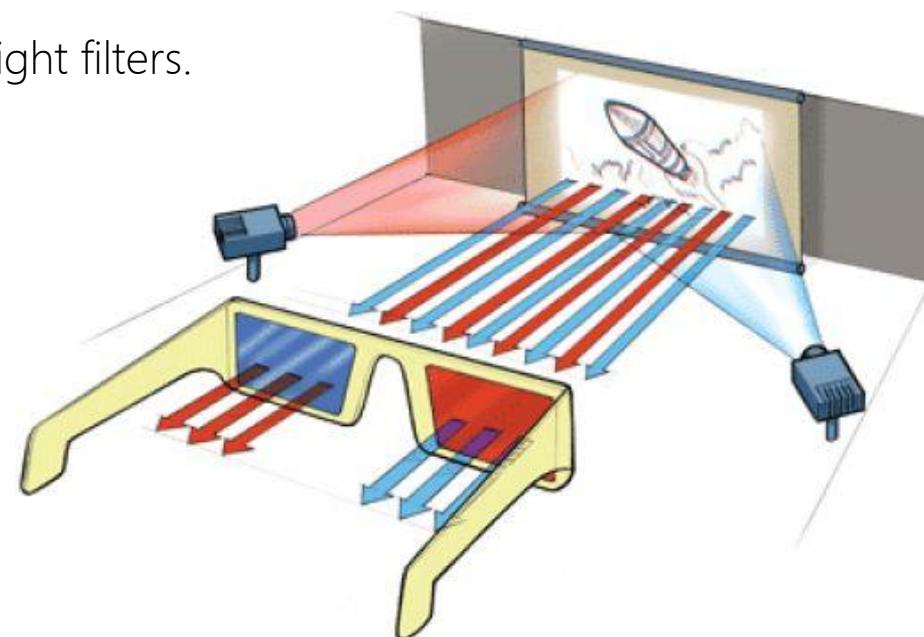
Most obvious at sunset or sunrise, due to long path through the atmosphere.



## The (radiative) absorption characteristics of gases

Gas molecules absorb light only at specific frequencies (photon energies)

- Energies absorbed correspond to differences in energy level for an atom or a molecule.
- This can involve the promotion of an electron between energy levels, or induce the vibration or rotation of a molecule.
- They act as light filters.



## The (radiative) absorption characteristics of gases

After a molecule absorbs a photon, it re-releases that energy by radiation or by convection.

- (2<sup>nd</sup> Law doesn't like to have one very hot molecule in a sea of cooler molecules)
- If the energy is released by convection, then it is shared amongst adjacent molecules (which may or may not be absorbers).
- In a *dry* atmosphere, this leads to an increase in air temperature.
- In a *moist* atmosphere, it may lead to increased evaporation.



Earth's atmosphere is made up of gases:

Nitrogen (N<sub>2</sub>): 77.76%

Oxygen (O<sub>2</sub>): 20.86%

Argon (Ar): 0.93%

Water vapour (H<sub>2</sub>O): 0.40%

Carbon dioxide (CO<sub>2</sub>): 0.05%



Absorb mostly in the UV part of the spectrum

Absorbs mostly in the red and IR part of the spectrum



Absorb mostly in the IR part of the spectrum



The wavelength of visible light is "just right", (mostly) passes through the atmosphere, and hits the earth.

The Earth's atmosphere contains many trace components.

Ozone and oxygen, in the upper atmosphere, absorb short-wavelength (UV) light.

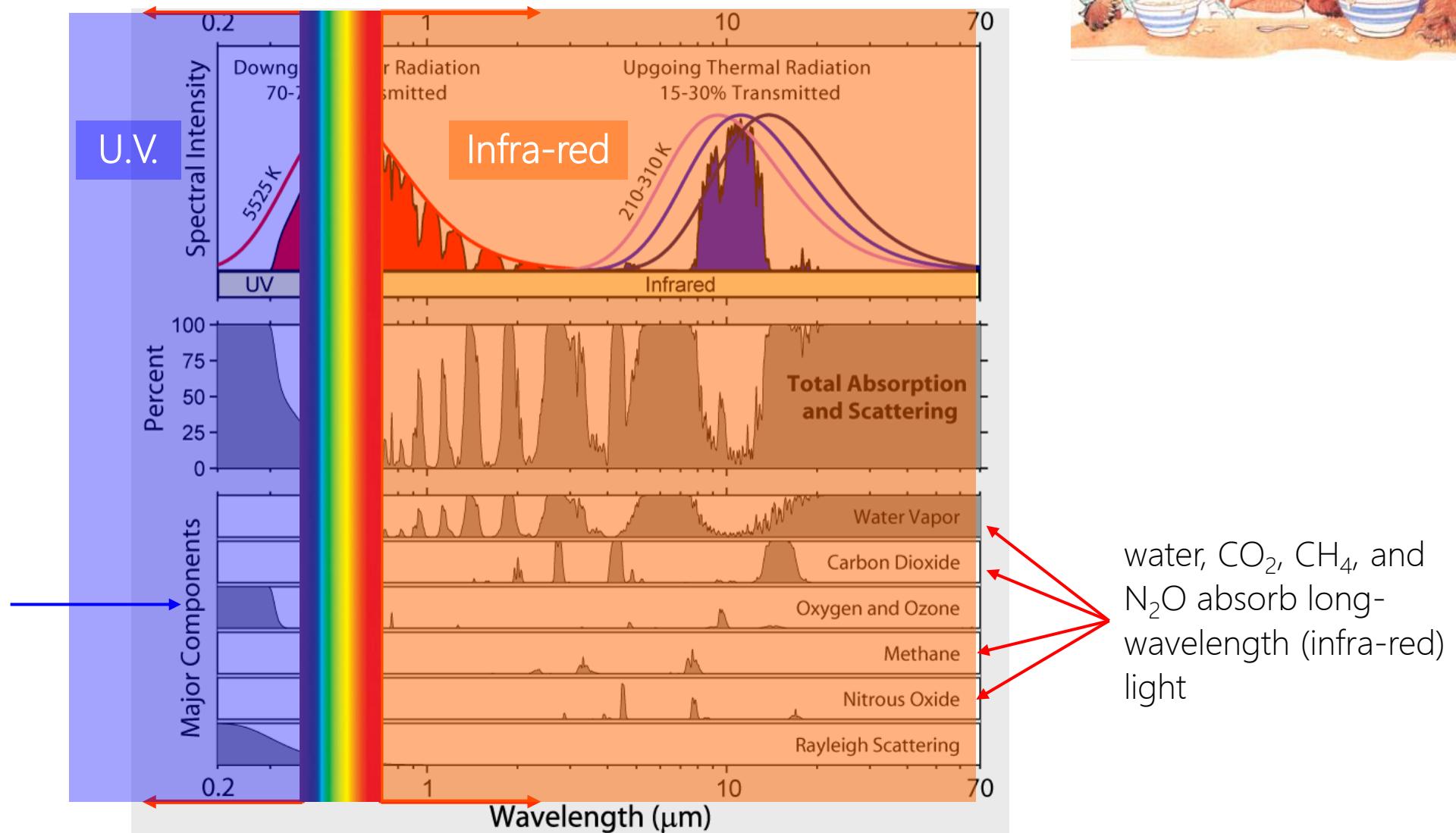


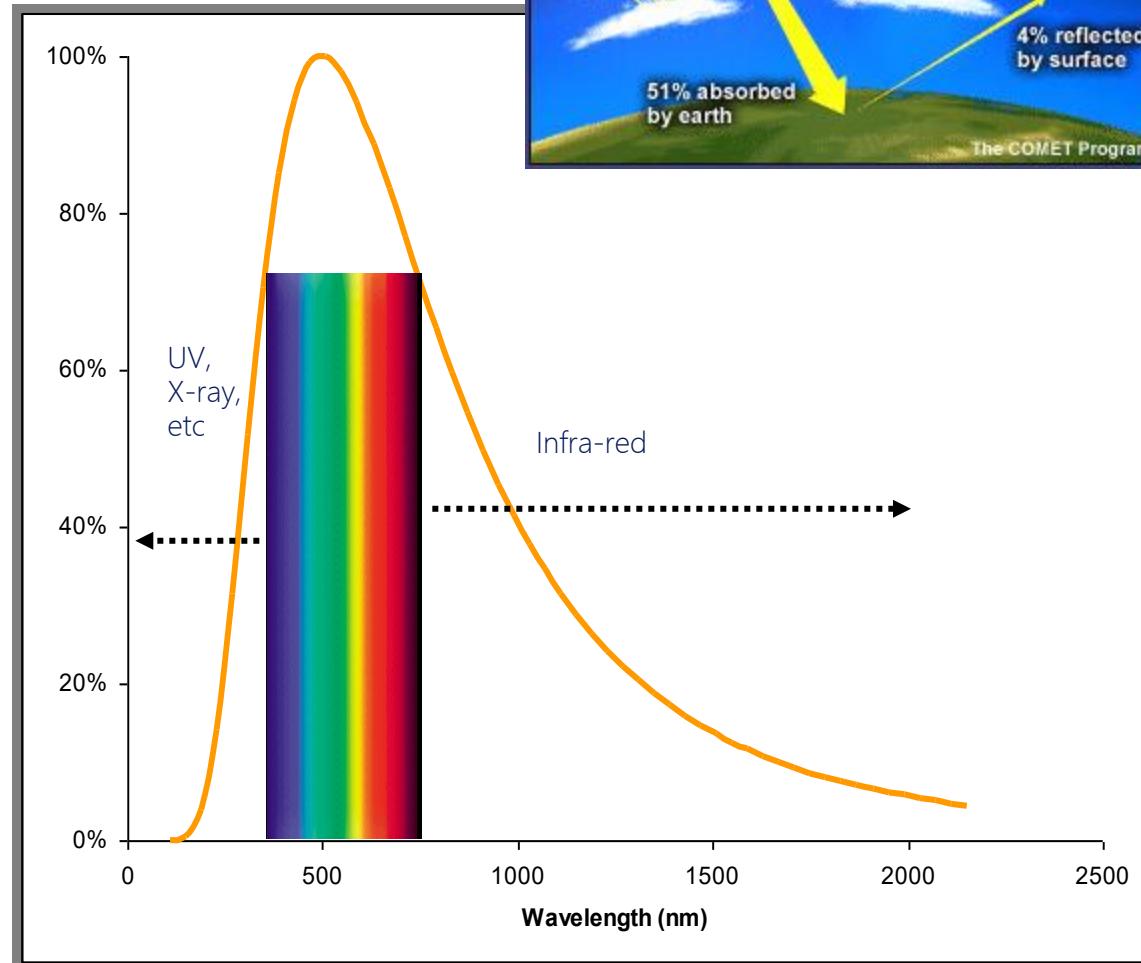
Image source: [https://commons.wikimedia.org/wiki/File:Atmospheric\\_Transmission.png](https://commons.wikimedia.org/wiki/File:Atmospheric_Transmission.png)

## Summary 1:

Trace gases near the top of the atmosphere filter out UV light (and warm up).

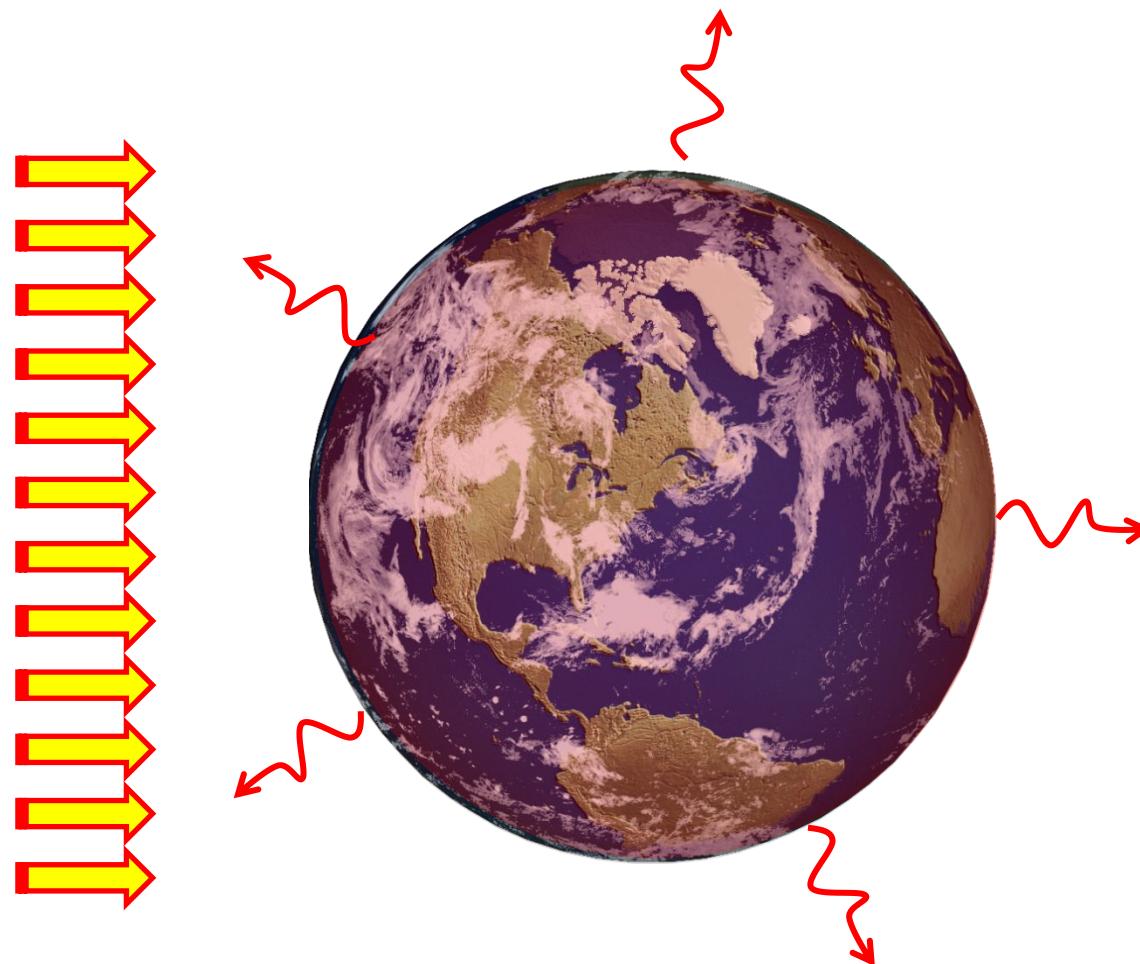
Trace gases lower down filter out IR light (and warm up).

Visible light passes through the atmosphere, and is absorbed by the surface of the earth (which warms up).



What happens?

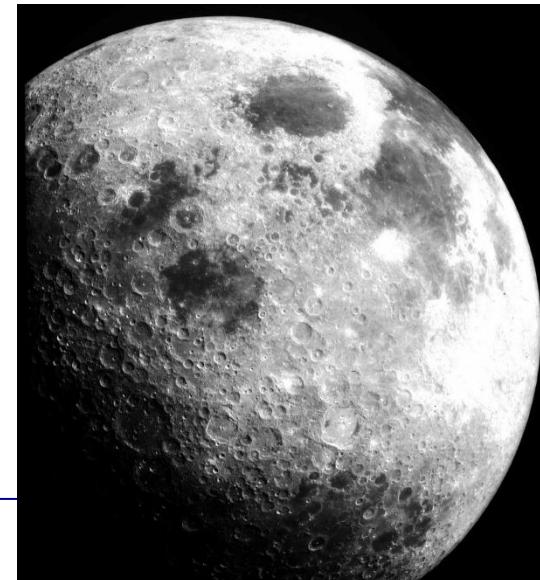
Earth absorbs short-wavelength thermal radiation from the sun.



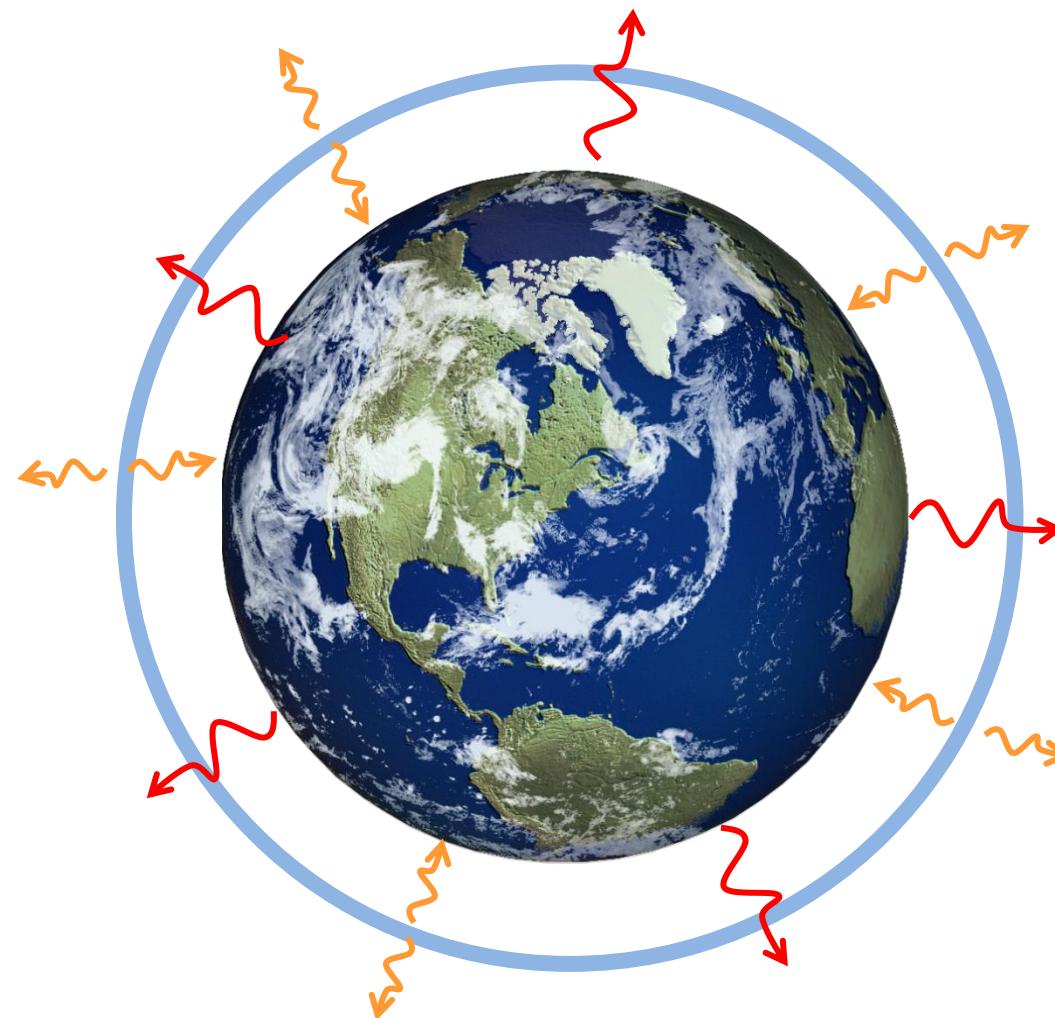
Earth heats up.

Earth radiates heat back out to space at longer wavelengths

That's what happens when a planet  
(or a moon) has no atmosphere.



What happens?

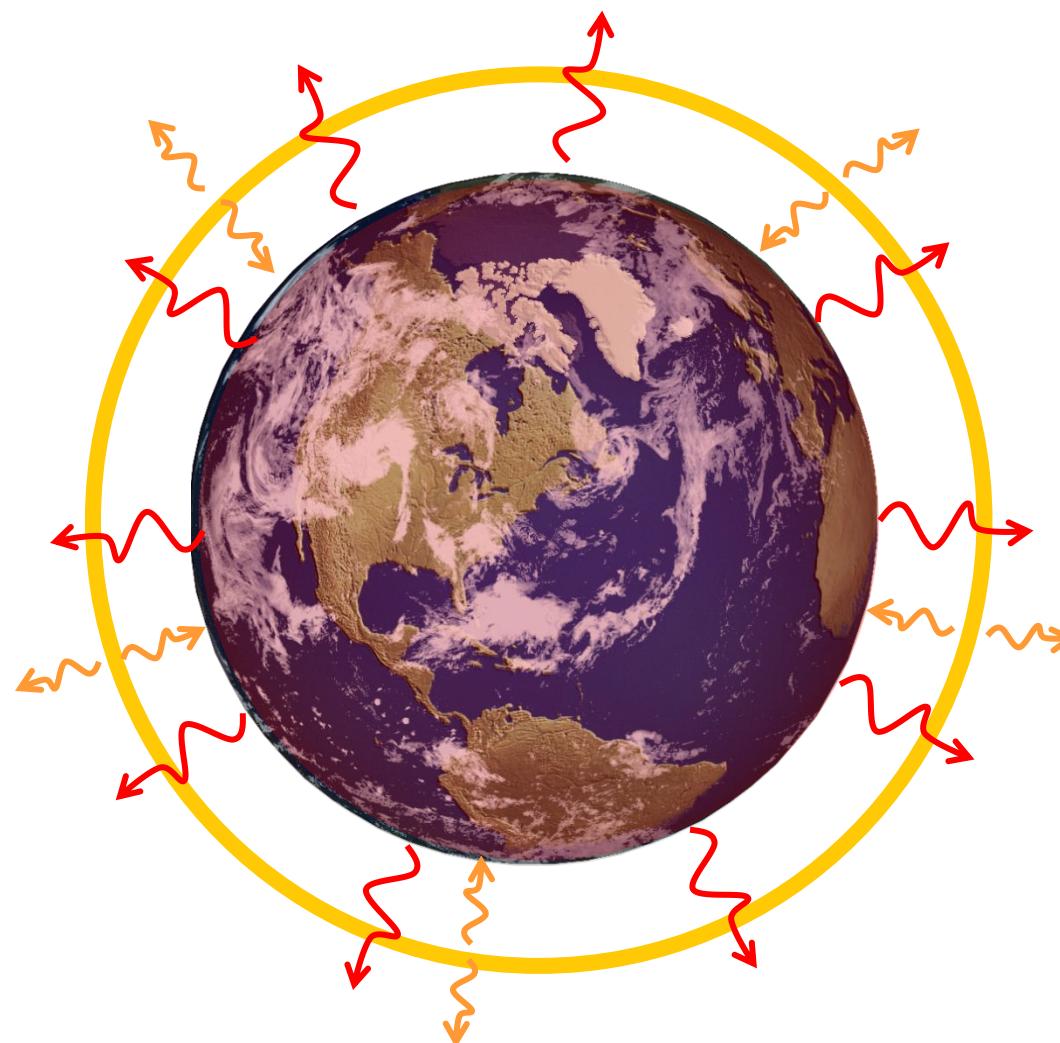


Some of the long-wavelength radiation from Earth is absorbed by “greenhouse gases” (GHG) in the atmosphere .

The GHG (and surrounding air) heat up.

The atmosphere re-radiates that heat uniformly in every direction – so about 50% is radiated back towards Earth’s surface.

What happens?



The downward radiation from the atmosphere heats Earth's surface some more...

...so the rate of photon emission from Earth's surface increases (strongly)...

...until a **new equilibrium** is achieved.

This is the "**greenhouse effect**".

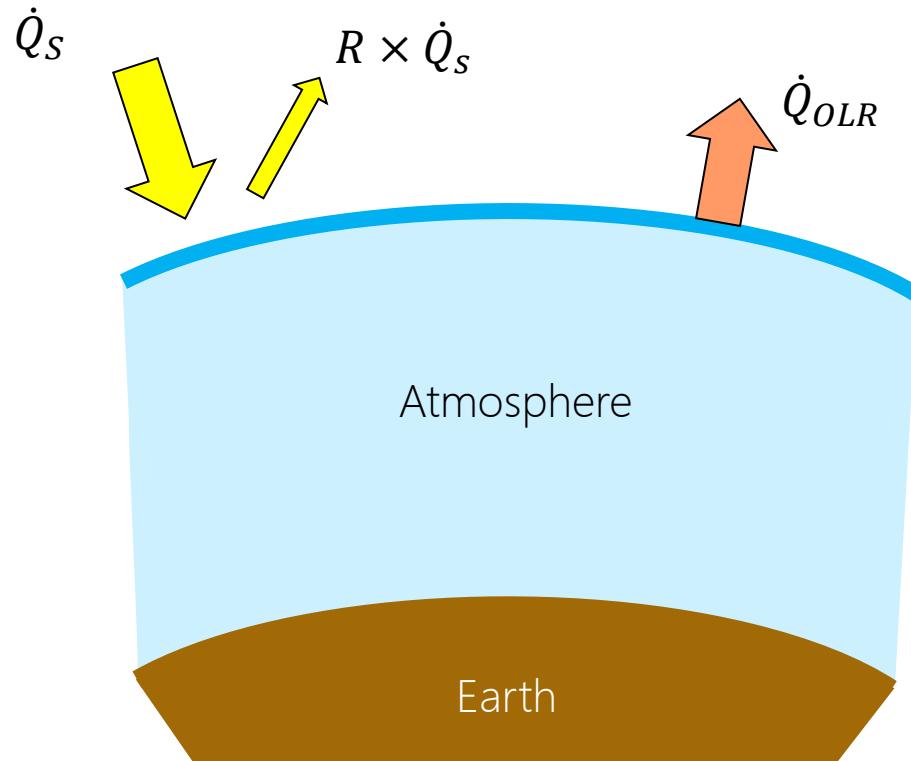
Are anthropogenic emissions to the atmosphere exerting a significant, detrimental, influence on global climate?

1. Is it physically possible; *i.e.* do we have a plausible mechanism? Yes! (GHG)

1b. Is the atmospheric concentration of these GHG increasing?

1c. Is the increased concentration of GHG due to human activity?

1st Law of Thermodynamics: assume thermal equilibrium

 $\dot{Q}_S$  = incoming solar radiation $R$  = reflected fraction (albedo) ~0.3 $\dot{Q}_{OLR}$  = outgoing, longwave radiation $S$  = solar constant ~1,370 W.m<sup>-2</sup>

Energy balance: top of the atmosphere

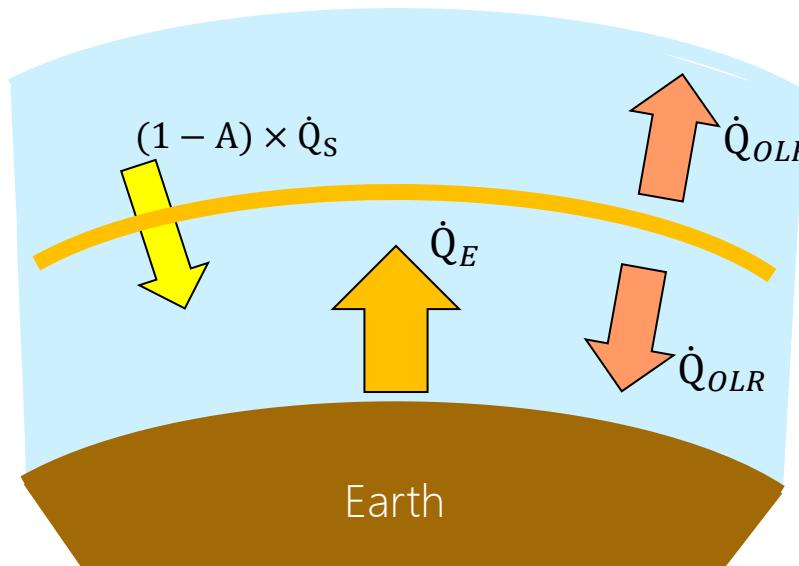
$$\dot{Q}_S = (R \times \dot{Q}_S) + \dot{Q}_{OLR}$$

$$\therefore \dot{Q}_S(1 - R) = \dot{Q}_{OLR}$$

1st Law of Thermodynamics: assume thermal equilibrium

Assume single layer of GHG:

- Absorbs 100% of incident I.R. radiation
- Transmits 100% of other radiation

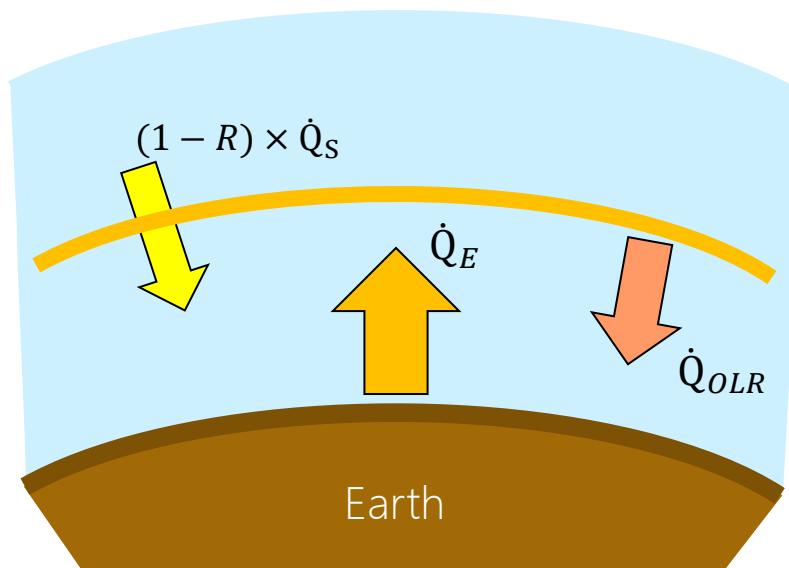


Energy balance: GHG layer

$$\dot{Q}_{GHG\ layer, in} = \dot{Q}_{GHG\ layer, out}$$

$$\therefore \dot{Q}_E = 2\dot{Q}_{OLR}$$

1st Law of Thermodynamics: assume thermal equilibrium

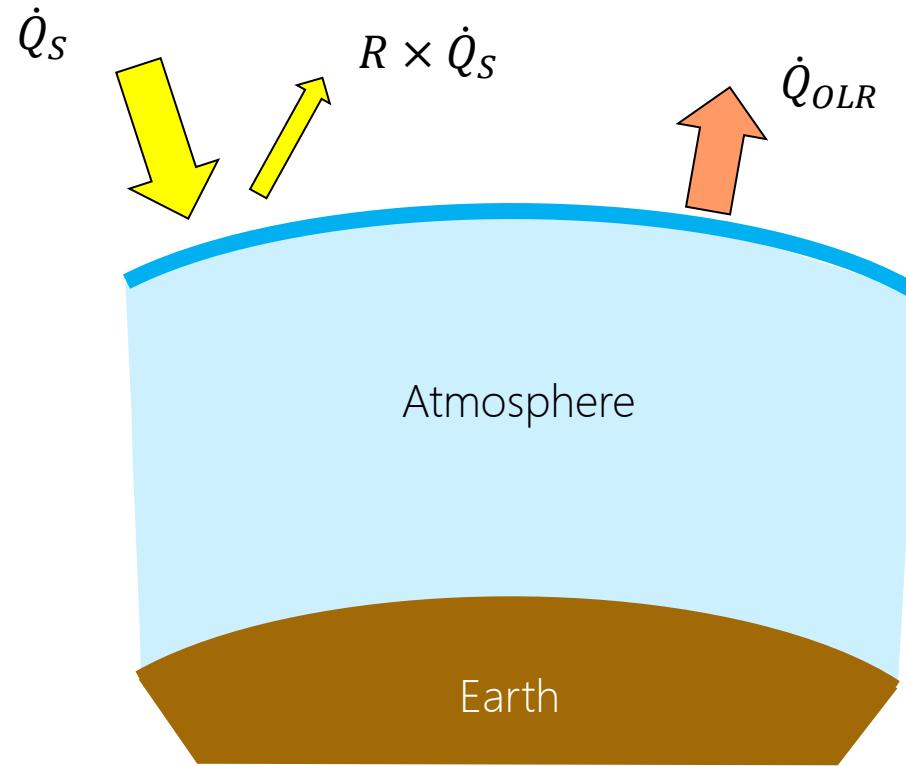


Energy balance: Earth's surface

$$\begin{aligned}\dot{Q}_E &= (1 - R)\dot{Q}_S + \dot{Q}_{OLR} \\ &= 2\dot{Q}_{OLR}\end{aligned}$$

1st Law of Thermodynamics: assume thermal equilibrium

Energy balance: top of the atmosphere



$$\dot{Q}_S(1 - R) = \dot{Q}_{OLR}$$

$$\dot{Q}_S = S(\pi r_{atmosphere}^2) \approx S(\pi r_{earth}^2)$$

$$\dot{Q}_{OLR} = \varepsilon\sigma(4\pi r_{GHG}^2)T_{GHG}^4 \approx \varepsilon\sigma(4\pi r_{earth}^2)T_{GHG}^4$$

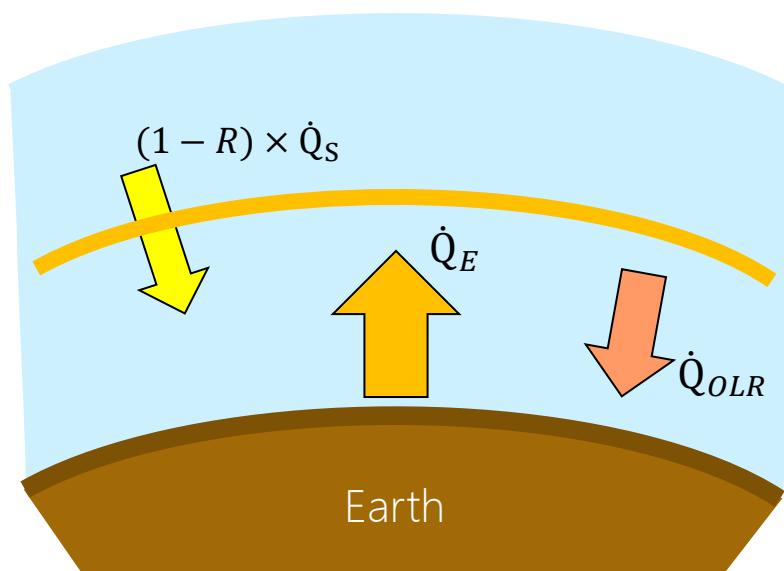
$$S(1 - R)\pi r_{earth}^2 = \varepsilon\sigma(4\pi r_{earth}^2)T_{GHG}^4 \therefore T_{GHG}^4 = \frac{S(1 - R)}{4\varepsilon\sigma}$$

$$\therefore T_{GHG} = \left( \frac{1,370 \times 0.7}{4 \times 1 \times (5.67 \times 10^{-8})} \right)^{\frac{1}{4}} = 255 \text{ K}$$

1st Law of Thermodynamics: assume thermal equilibrium

Assume earth is a perfect blackbody:

- Uniform surface temperature
- Heat loss by radiation only



Energy balance: Earth's surface

$$\dot{Q}_E = (1 - R)\dot{Q}_S + \dot{Q}_{OLR} = 2\dot{Q}_{OLR}$$

$$\dot{Q}_E = \varepsilon\sigma(4\pi r_{earth}^2)T_{earth}^4 \approx 2\varepsilon\sigma(4\pi r_{earth}^2)T_{GHG}^4$$

$$T_{earth}^4 = 2 \times T_{GHG}^4 \quad \therefore T_{earth} = T_{GHG} \times 2^{1/4} \approx 1.19 T_{GHG}$$

$$T_{earth} = 1.19 \times 255 = 303 \text{ K}$$

$$\frac{\dot{Q}_E}{4\pi r_{earth}^2} = \varepsilon\sigma T_{earth}^4 = 1 \times (5.67 \times 10^{-8}) \times 303^4 \approx 480 \text{ W.m}^{-2}$$

## Why the greenhouse effect is good

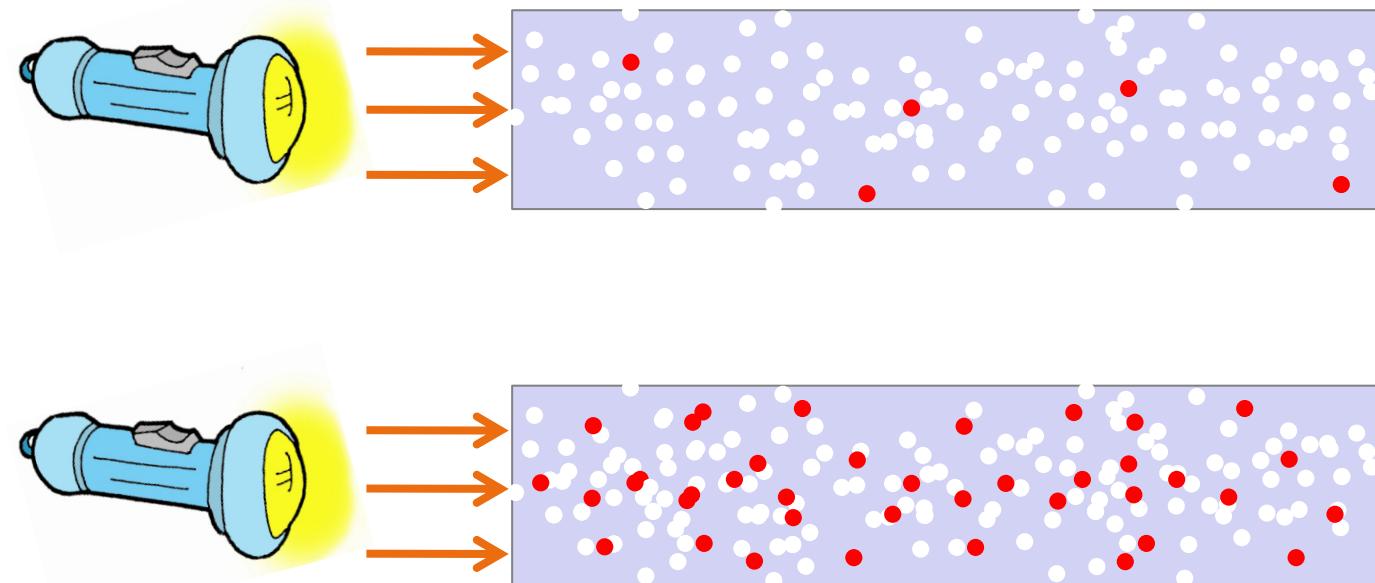


However...



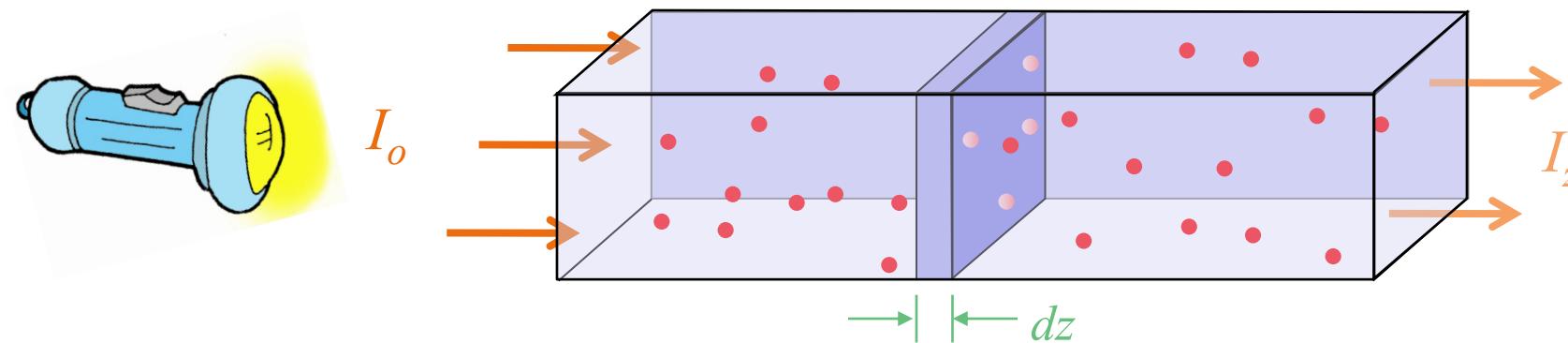
## Absorption:

The probability of a photon being absorbed (as it passes through a gas mixture) is proportional to the concentration of absorbing molecules.



NB: A consequence of the above is that absorption is a logarithmic function of concentration (Beer-Lambert Law).

Consider a beam of parallel, monochromatic light, with intensity  $I_o$ , passing through a column of gas that contains some light-absorbing molecules.



Suppose that each of these molecules has an **absorption cross-sectional area  $\sigma$** , for light of this wavelength.

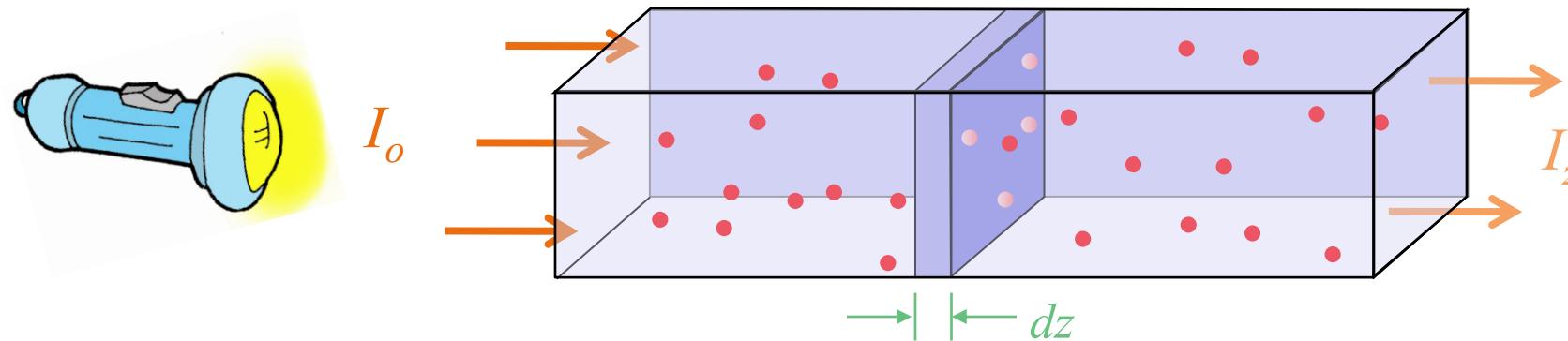
Now consider a thin slice of this column, of area  $A$  and thickness  $dz$ :

As the light passes through our infinitesimal volume, its intensity decreases by an amount  $dI$ .

The fractional reduction in light intensity is therefore:

$$F_{\text{absorbed}} = \frac{dI}{I(z)}$$

Consider a beam of parallel, monochromatic light, with intensity  $I_o$ , passing through a column of gas that contains some light-absorbing molecules.



If the concentration of absorber molecules in the column is  $N$  molecules.m<sup>-3</sup>, then the number in our thin slice is given by:

$$n^* = N \times dV = N \times A \times dz$$

The fraction of the area blocked by light-absorbing molecules in our infinitesimal volume is therefore:

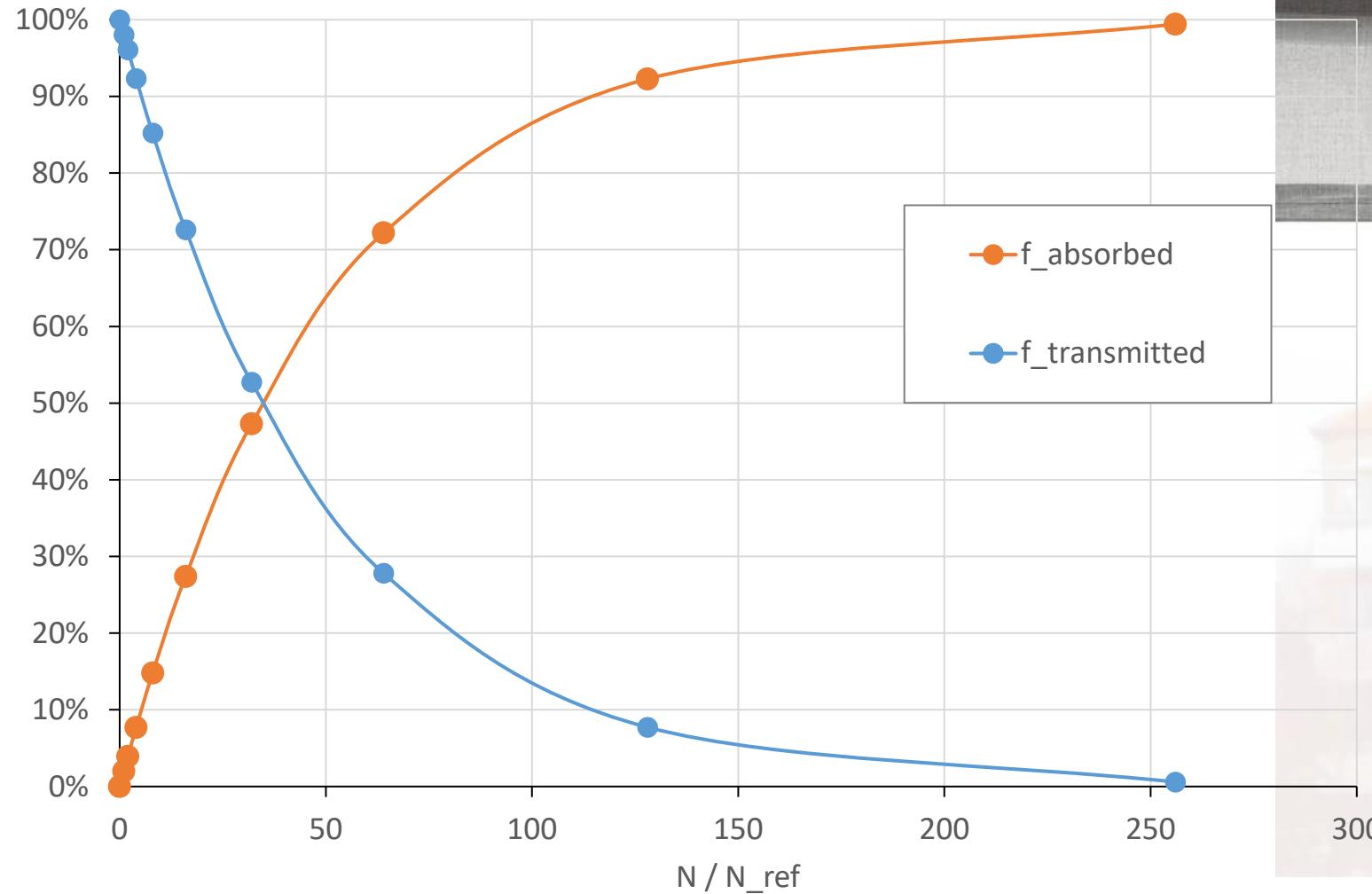
$$F_{\text{blocked}} = \frac{A_{\text{absorbers}}}{A} = \frac{n^* \times \sigma}{A} = N \times \sigma \times dz$$

Since  $F_{\text{absorbed}}$  is equal to the probability of a photon being blocked:  $\frac{dI}{I(z)} = -N\sigma dz$

Integrating over the entire column:

$$\int_0^z \frac{dI}{I(z)} = \ln \left( \frac{I_z}{I_o} \right) = -N\sigma z$$

If we assume  $\sigma$  and  $z$  are fixed, and vary the concentration of light-absorbing molecules in the column:



## Interim summary (important)

- The absorption of outgoing longwave radiation (OLR), by GHG in the atmosphere, increases the temperature of the atmosphere.
- That leads to increased back radiation towards earth – radiative forcing.
- The intensity of the radiative forcing (RF) is proportional to ln of the concentration of the GHG:  $RF = A \times \ln\left(\frac{C}{C_o}\right)$
- For CO<sub>2</sub>,  $A$  has the value of 5.67 W.m<sup>-2</sup>, so a doubling of atmospheric CO<sub>2</sub> would lead to\* radiative forcing (RF) of:

$$RF_{CO_2} = 5.67 \times \ln(2) = 3.93 \text{ W.m}^{-2} \quad \dots(\text{IPCC AR6, Section 7.5.1.1})$$

\* Note that this [assumes zero absorption overlap](#) between CO<sub>2</sub> and other GHG (*e.g.* water vapour)

- Modelling [earth as a grey body](#), with emissivity ( $\epsilon$ ) = 0.9 and a surface [temperature of 288 K](#), OLR = 351 W.m<sup>-2</sup>.
- To increase OLR by 4 W.m<sup>-2</sup>, to balance the RF from a doubling of atmospheric CO<sub>2</sub>, would require surface temperature to increase by ~0.8 K.
- A surface temperature increase of 1.5 K, the aspirational target of the Paris Climate Agreement, corresponds to an atmospheric CO<sub>2</sub> concentration of ~ 1,000 ppm...(!?!)

Are anthropogenic emissions to the atmosphere exerting a significant, detrimental, influence on global climate?

1. Is it physically possible; *i.e.* do we have a plausible mechanism? Yes! (GHG)  
...but there's (a lot of) other stuff happening as well
- 1b. Is the atmospheric concentration of these GHG increasing?
- 1c. Is the increased concentration of GHG due to human activity?

Absorption of radiation in earth's atmosphere

What happens?

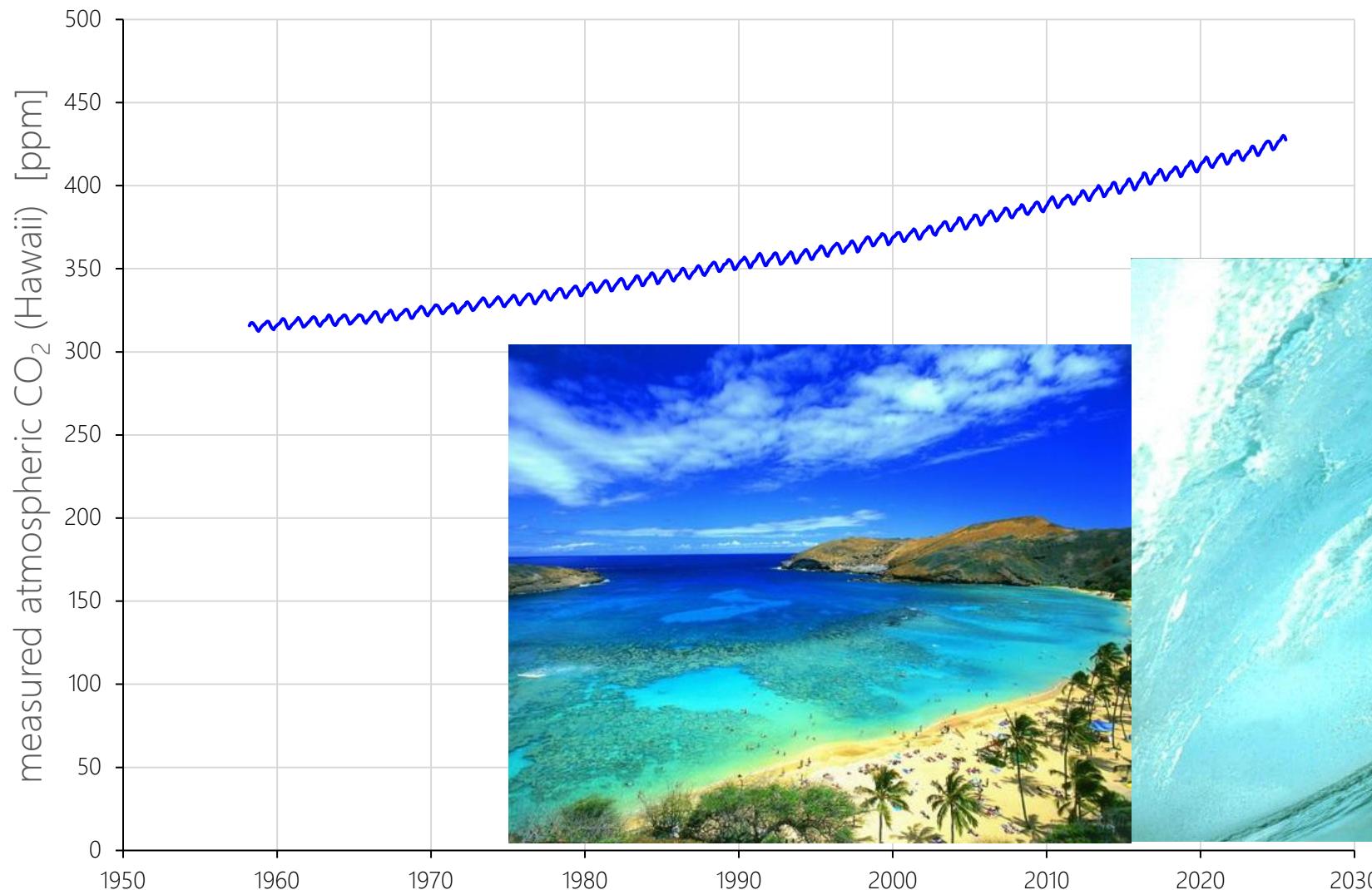
Temperature rise on earth depends on level of absorption by GHG.

That depends on concentration of GHG.



1b. Is the atmospheric concentration of these GHG increasing?

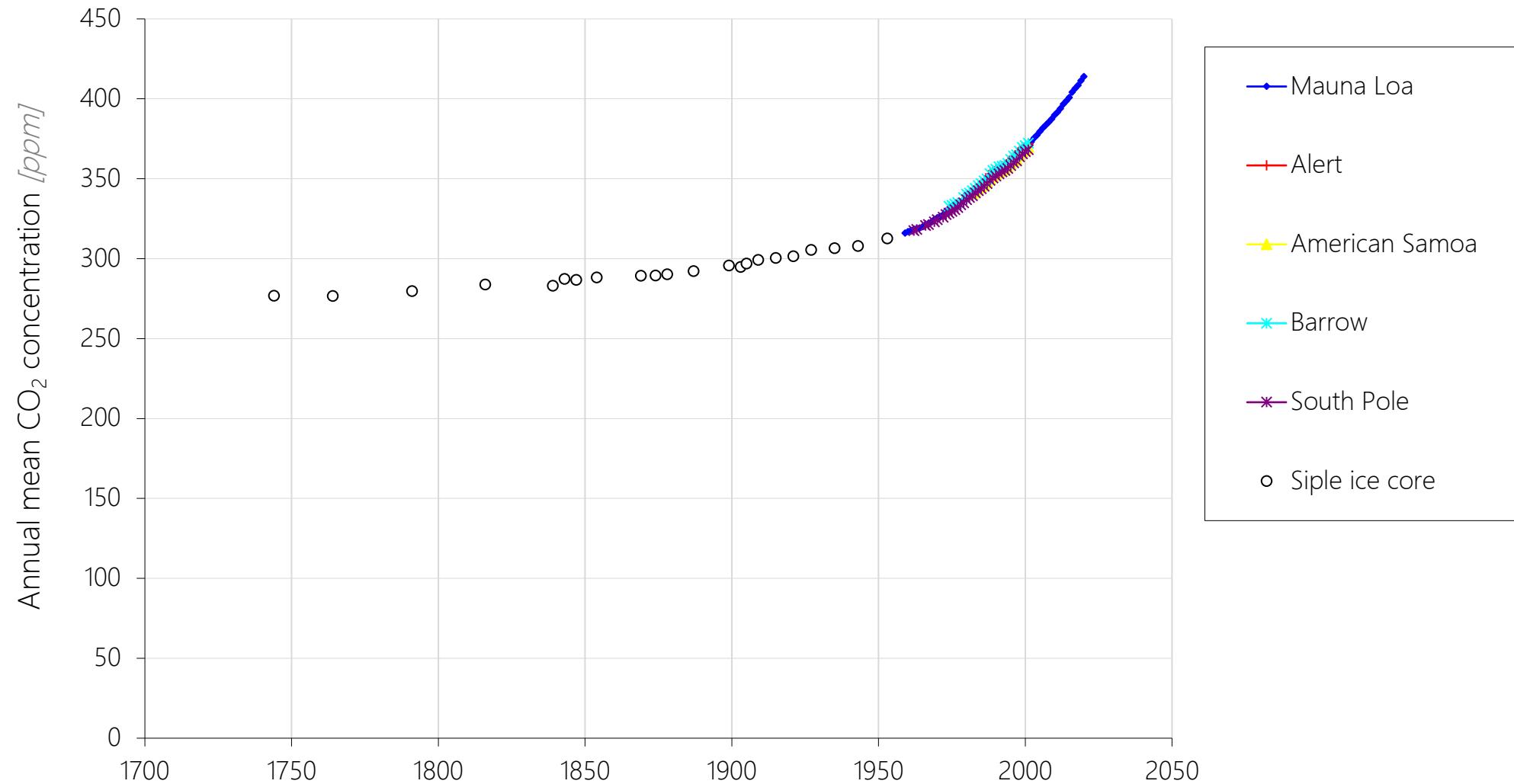
Yes!



Raw data: [http://scrippsco2.ucsd.edu/data/atmospheric\\_co2/primary\\_mlo\\_co2\\_record.html](http://scrippsco2.ucsd.edu/data/atmospheric_co2/primary_mlo_co2_record.html)

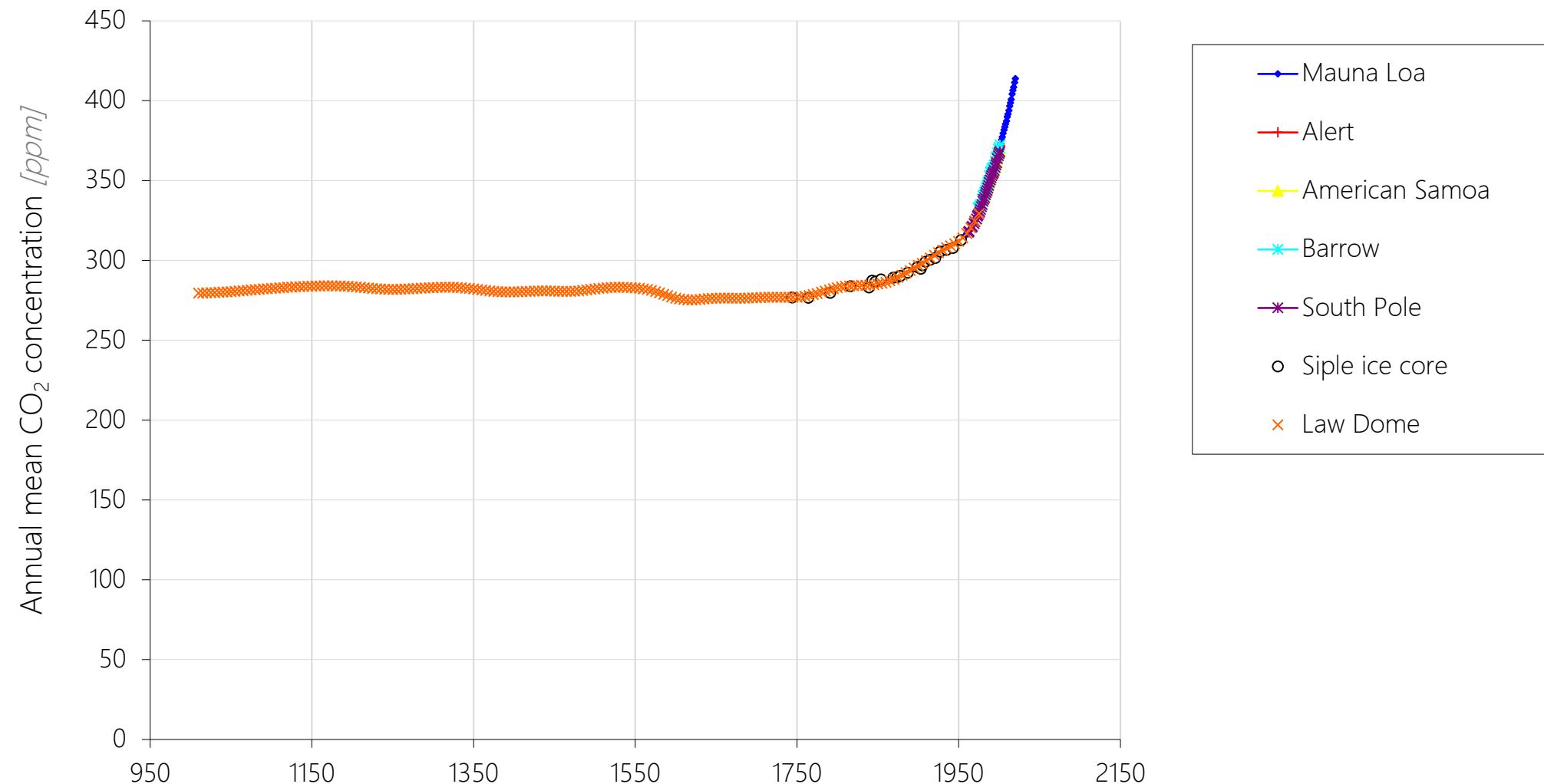
1b. Is the atmospheric concentration of these GHG increasing?

Yes!



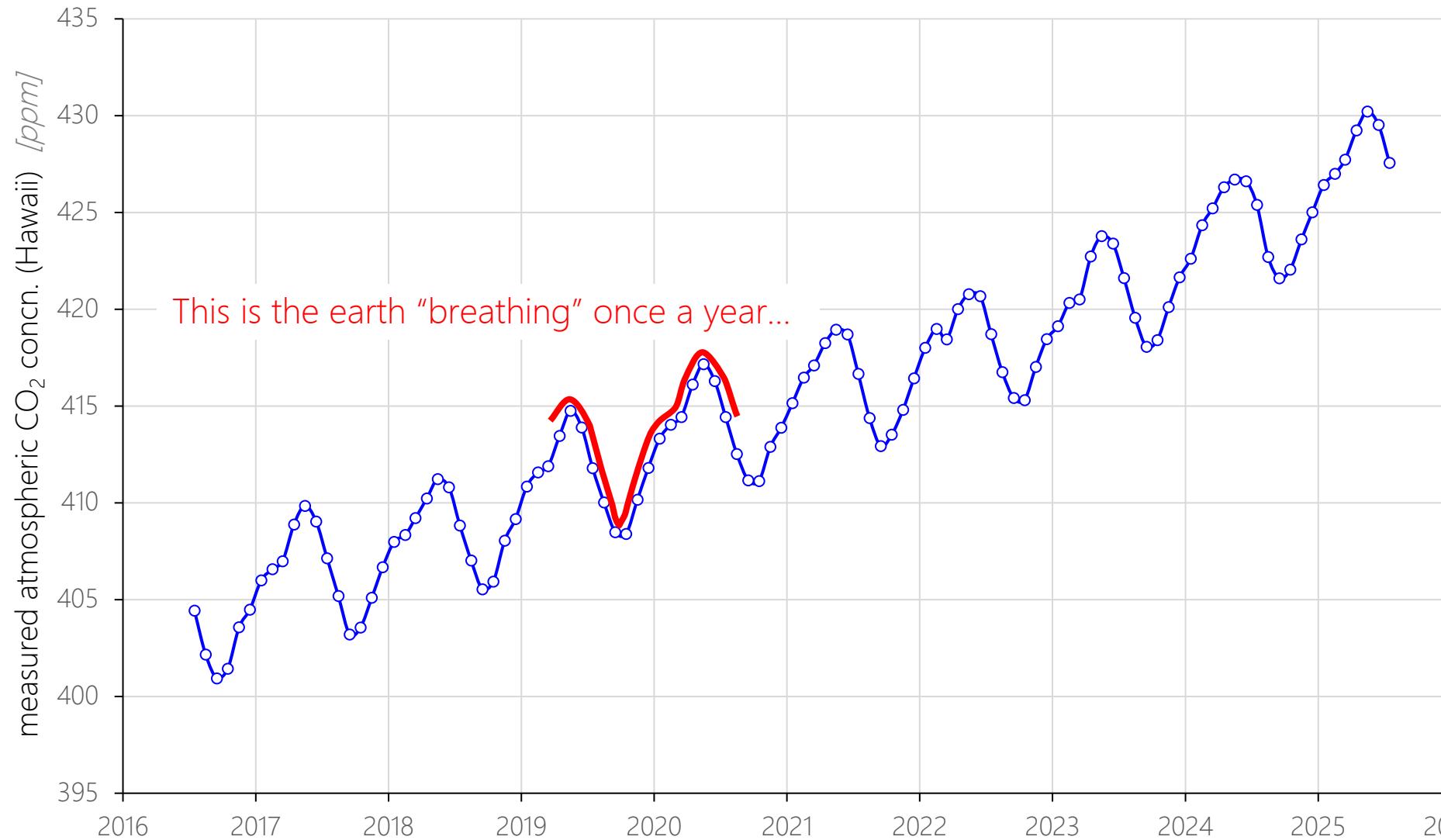
1b. Is the atmospheric concentration of these GHG increasing?

Yes!



1b. Is the atmospheric concentration of these GHG increasing?

Yes!

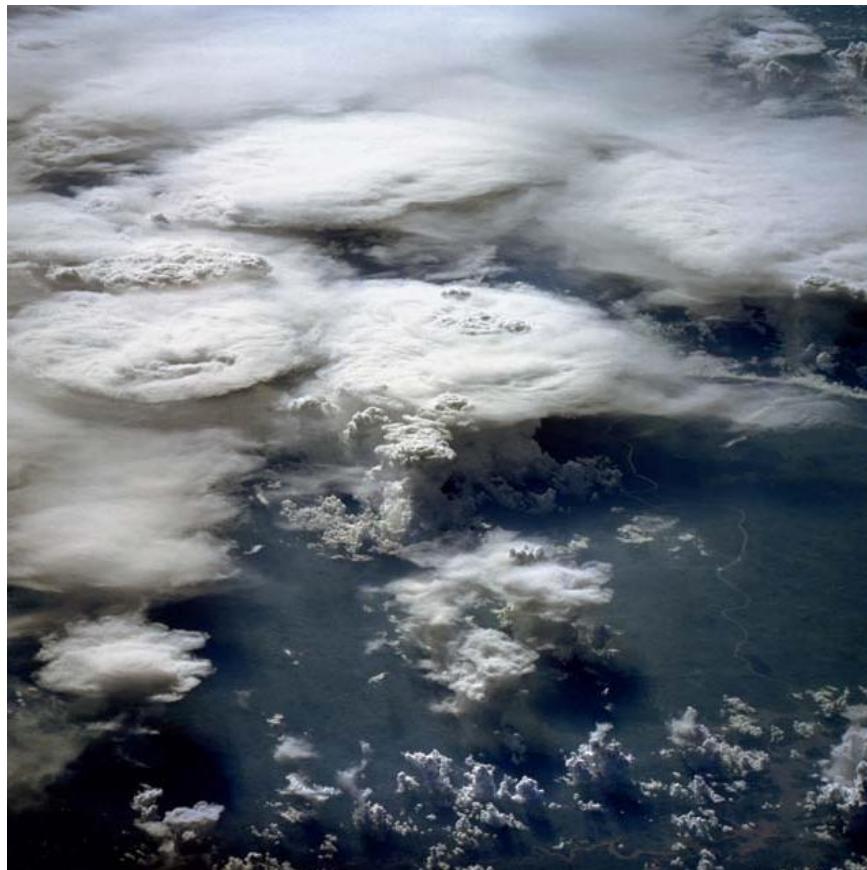


Raw data: [http://scrippsco2.ucsd.edu/data/atmospheric\\_co2/primary\\_mlo\\_co2\\_record.html](http://scrippsco2.ucsd.edu/data/atmospheric_co2/primary_mlo_co2_record.html)

## Calculating expected changes in atmospheric CO<sub>2</sub> concentration

The concentration is measured on a *molar* basis:

i.e. the number of moles (or molecules) of CO<sub>2</sub> in the atmosphere, relative to the total number of moles (or molecules) in the atmosphere.



Calculating expected changes in atmospheric CO<sub>2</sub> concentration

Really, what we're interested in is the mass of the *troposphere*. That's the region where almost all the CO<sub>2</sub> "lives", and it constitutes ~80% of the total mass of the atmosphere.



Calculating expected changes in atmospheric CO<sub>2</sub> concentration

We know that the troposphere is ~79% Nitrogen (N<sub>2</sub>), and ~21% Oxygen (O<sub>2</sub>), so we can easily calculate the mass of one mol of "troposphere":

$$M_{tropo} = (0.79 \times M_{N_2}) + (0.21 \times M_{O_2}) = (0.79 \times 28) + (0.21 \times 32) = 28.84 \text{ kg.kmol}^{-1}$$

If we can estimate the total mass of the troposphere, then we can calculate the total number of mols:



$$m_{tropo} = N_{tropo} \times M_{tropo} \therefore N_{tropo} = \frac{m_{tropo}}{M_{tropo}}$$

First, weigh the atmosphere:

This may require a cunning plan...

Calculating expected changes in atmospheric CO<sub>2</sub> concentration

Atmospheric pressure at sea level is approximately 0.101325 MPa (MN.m<sup>-2</sup>).

Pressure = Force  
Area



The force is due to the *weight* of the atmosphere:  $F_{atm} = m_{atm} \times g$      $\therefore m_{atm} = \frac{P_{atm} \times A}{g}$

The surface area of the earth is given by:  $A_{earth} = 4\pi r_{earth}^2$

Inserting the relevant numbers:  $m_{atm} = \frac{(1.01325 \times 10^5) \times 4 \times \pi \times (6.37 \times 10^6)^2}{9.81} = 5.267 \times 10^{18} \text{ kg}$

$$m_{tropo} = 0.8 \times m_{atm} = 4.21 \times 10^{18} \text{ kg}$$

Calculating expected changes in atmospheric CO<sub>2</sub> concentration

So, the number of kmol in the troposphere is...

$$N_{tropo} = \frac{m_{tropo}}{M_{tropo}} = \frac{4.21 \times 10^{18}}{28.84} = 1.37 \times 10^{17} \text{ kmol}$$



Anthropogenic CO<sub>2</sub> is about 40 Gt.year<sup>-1</sup>. How many kmol is that?

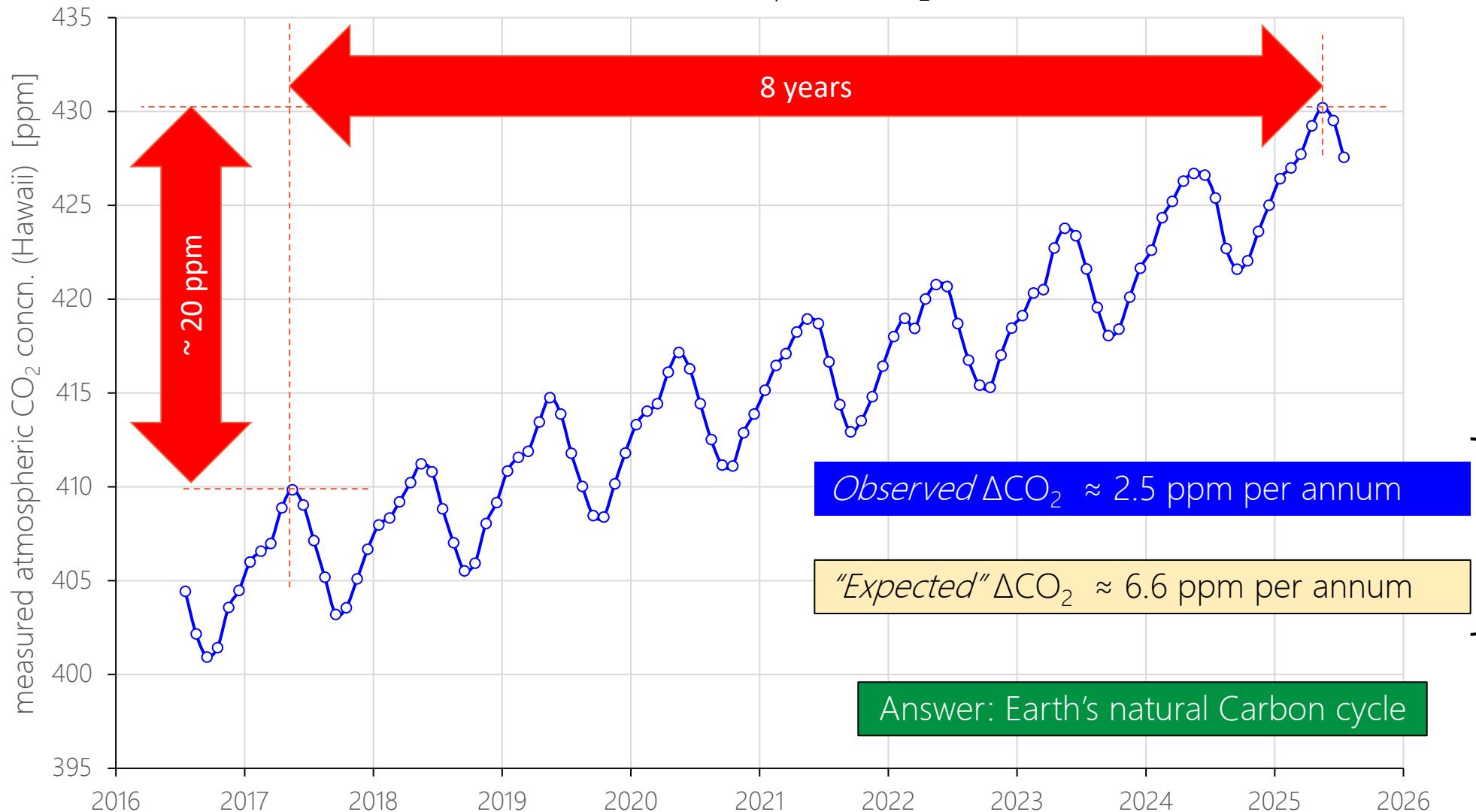
$$N_{CO_2} = \frac{m_{CO_2}}{M_{CO_2}} = \frac{40 \times 10^{12}}{44} = 9.1 \times 10^{11} \text{ kmol.year}^{-1}$$

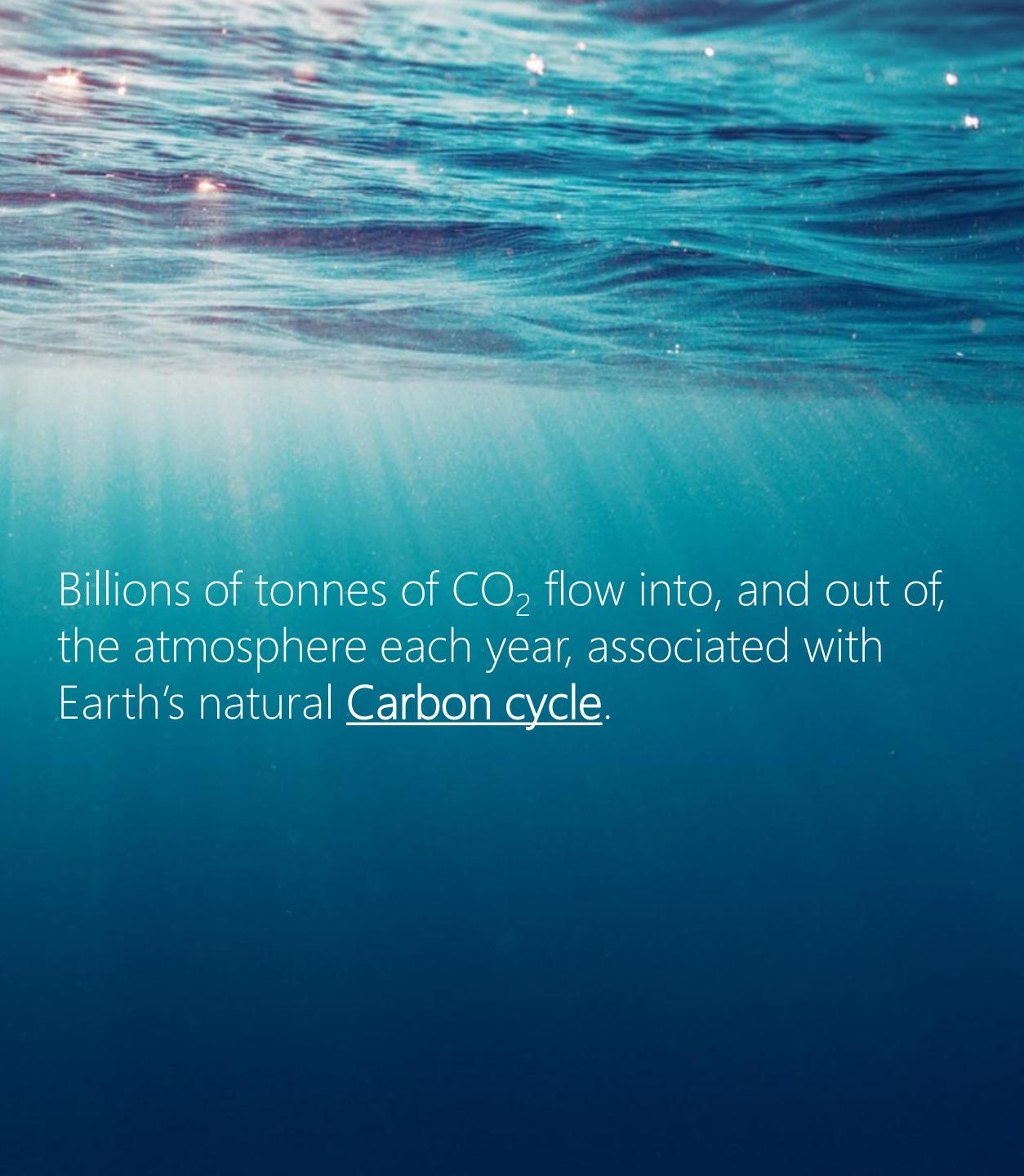
So the mol fraction added per year is:

$$\frac{N_{CO_2}}{N_{tropo}} = \frac{9.1 \times 10^{11}}{1.37 \times 10^{17}} = 6.6 \times 10^{-6}$$

$$= 6.6 \text{ ppm}$$

Note: This is equivalent to 0.166 ppm per Gt of CO<sub>2</sub> added to the troposphere.

Global atmospheric CO<sub>2</sub> concentration



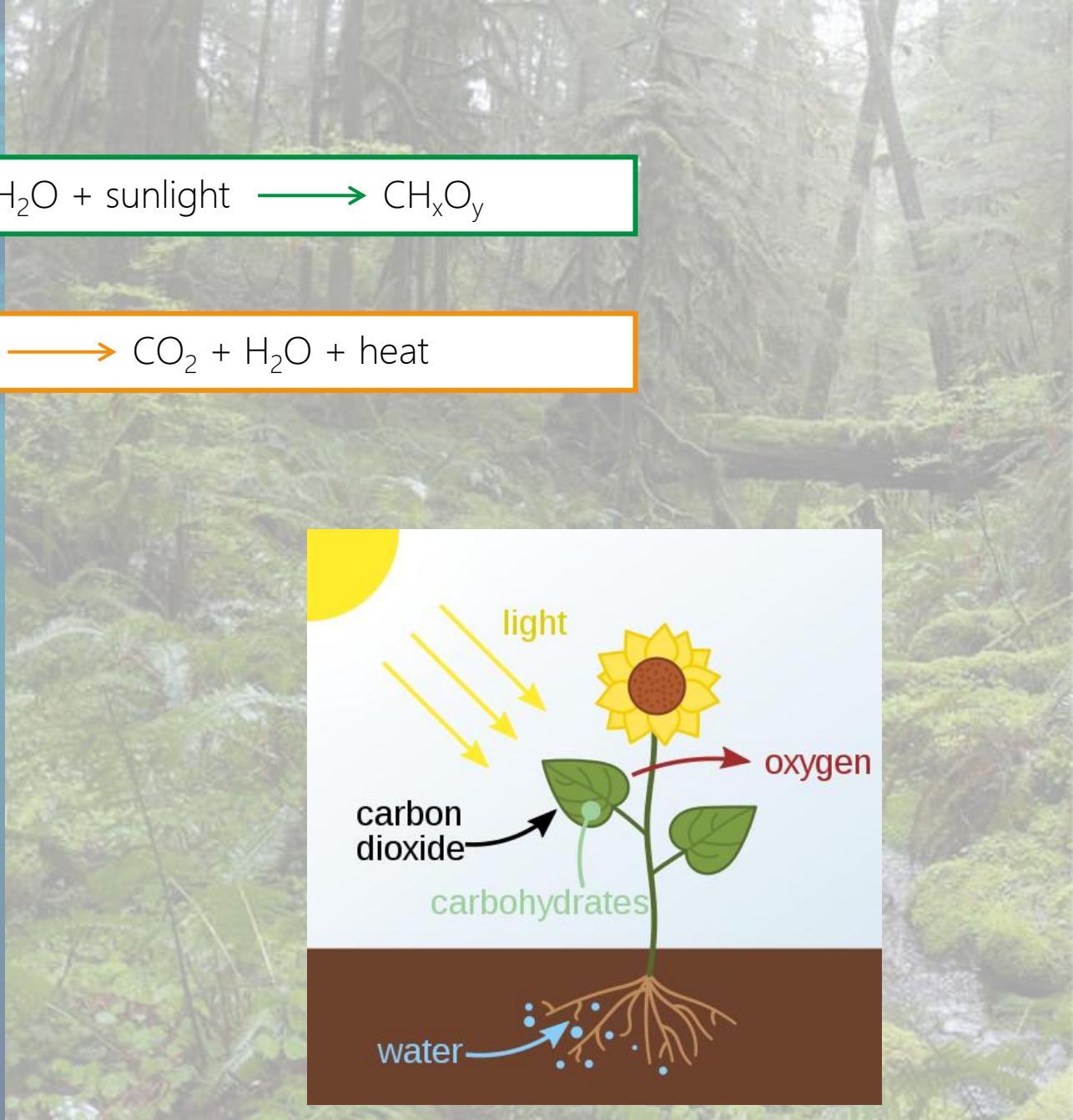
Billions of tonnes of CO<sub>2</sub> flow into, and out of, the atmosphere each year, associated with Earth's natural Carbon cycle.

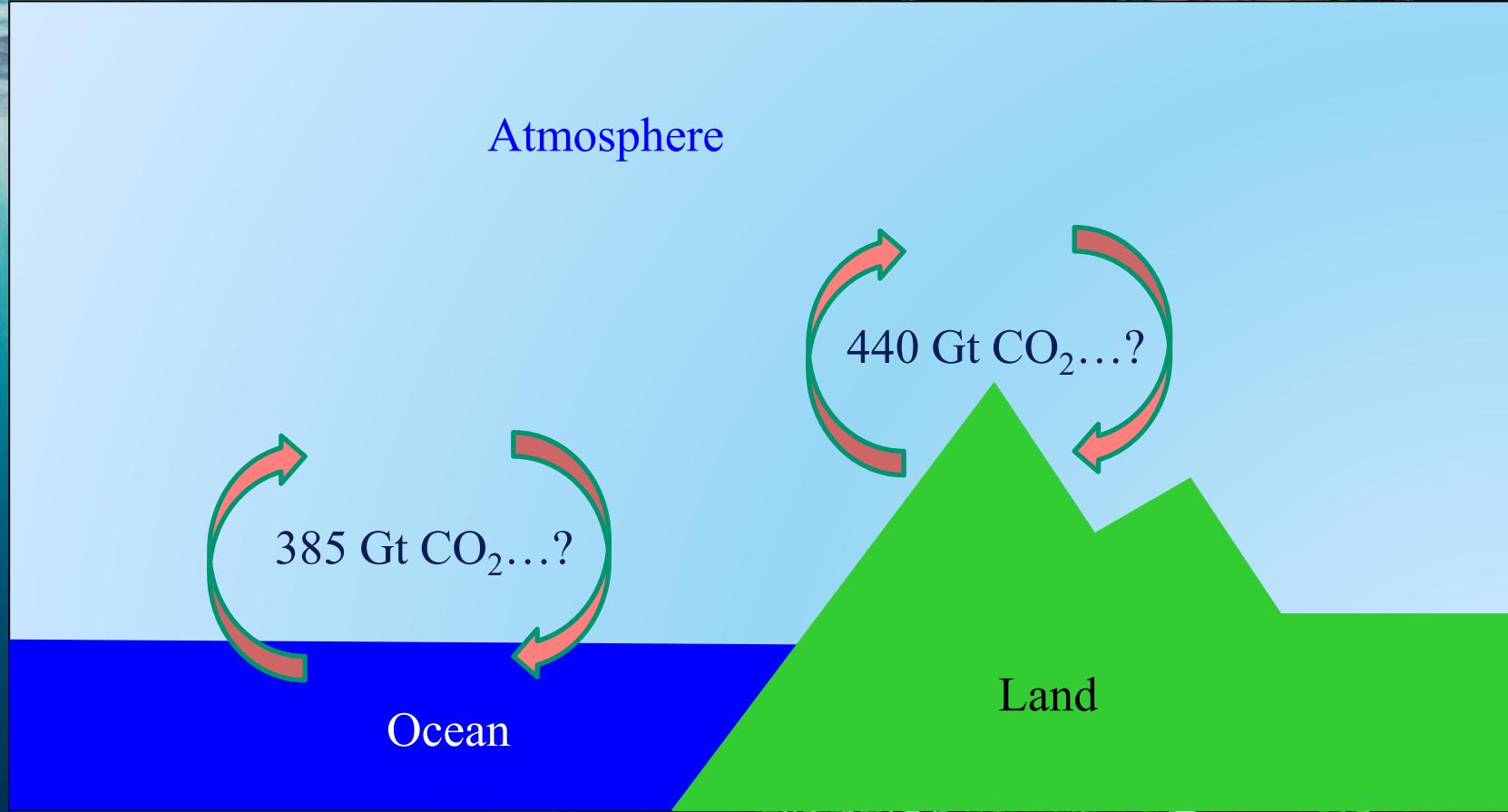


# The global Carbon cycle

During growth:  $\text{CO}_2 + \text{H}_2\text{O} + \text{sunlight} \longrightarrow \text{CH}_x\text{O}_y$

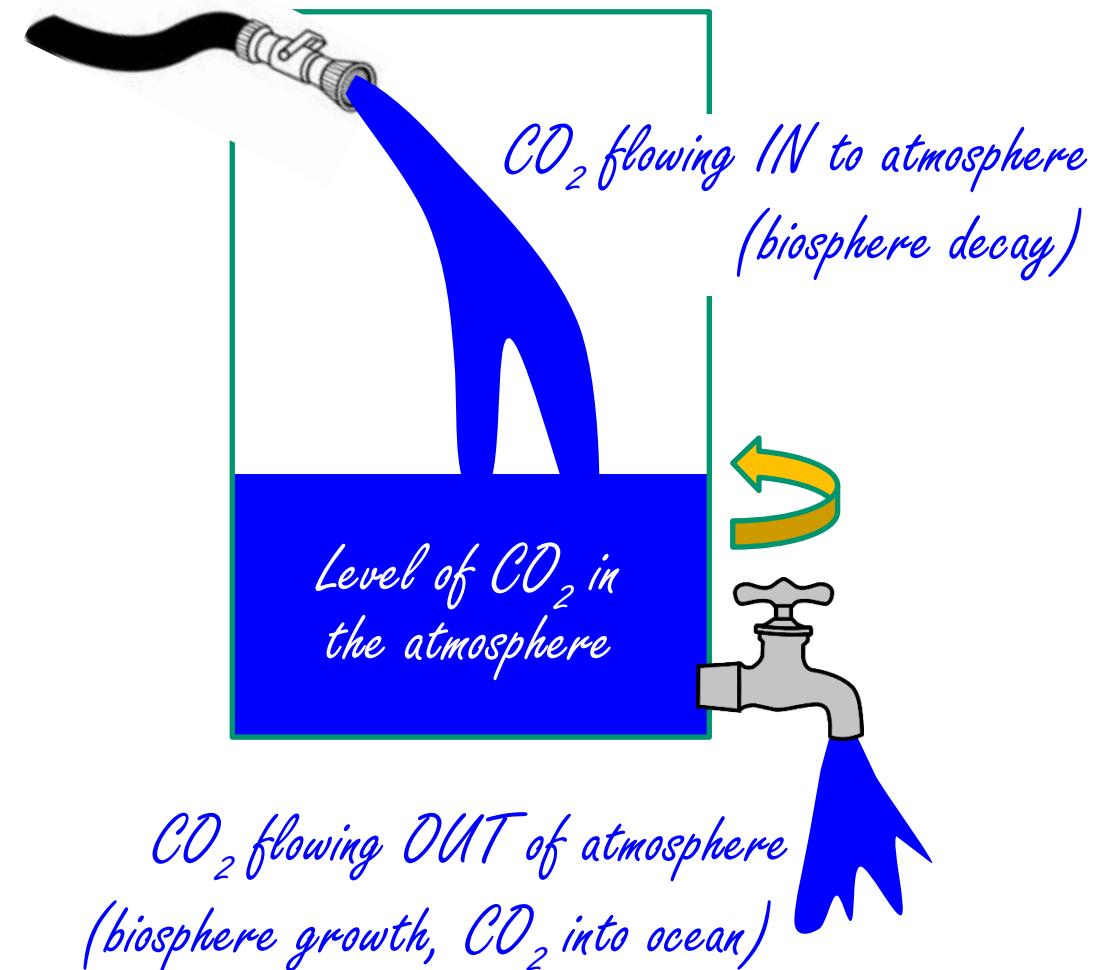
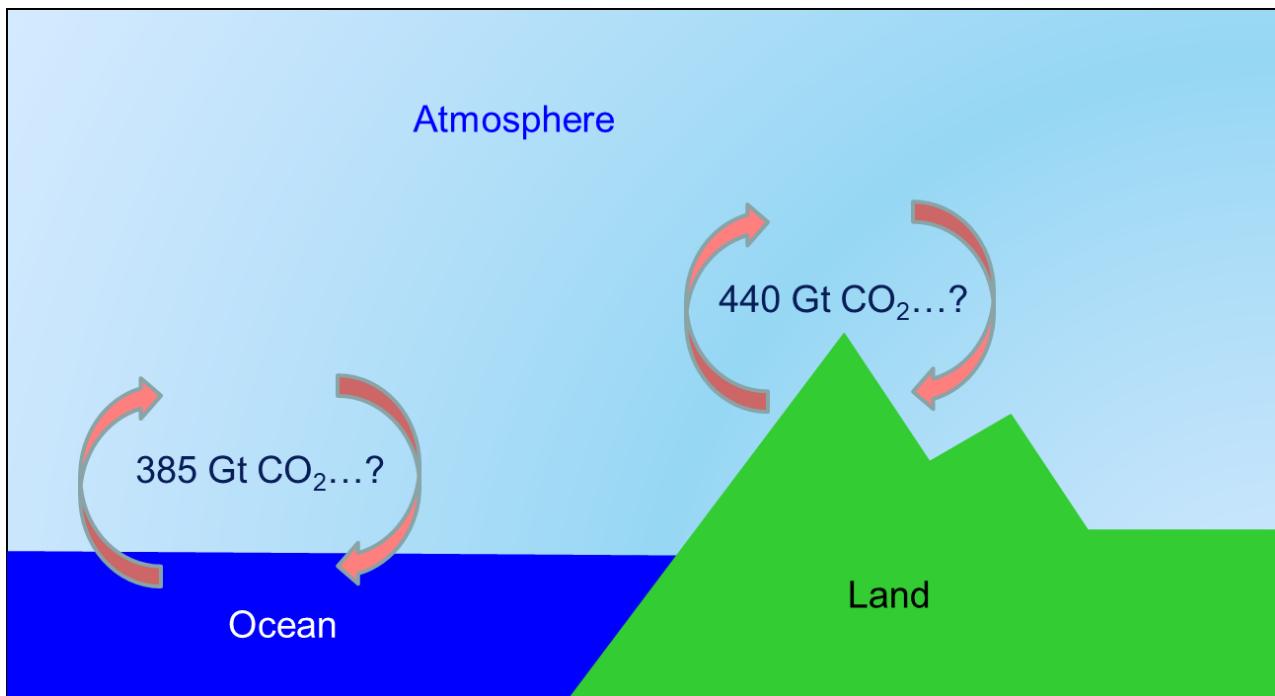
During decay:  $\text{CH}_x\text{O}_y \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{heat}$





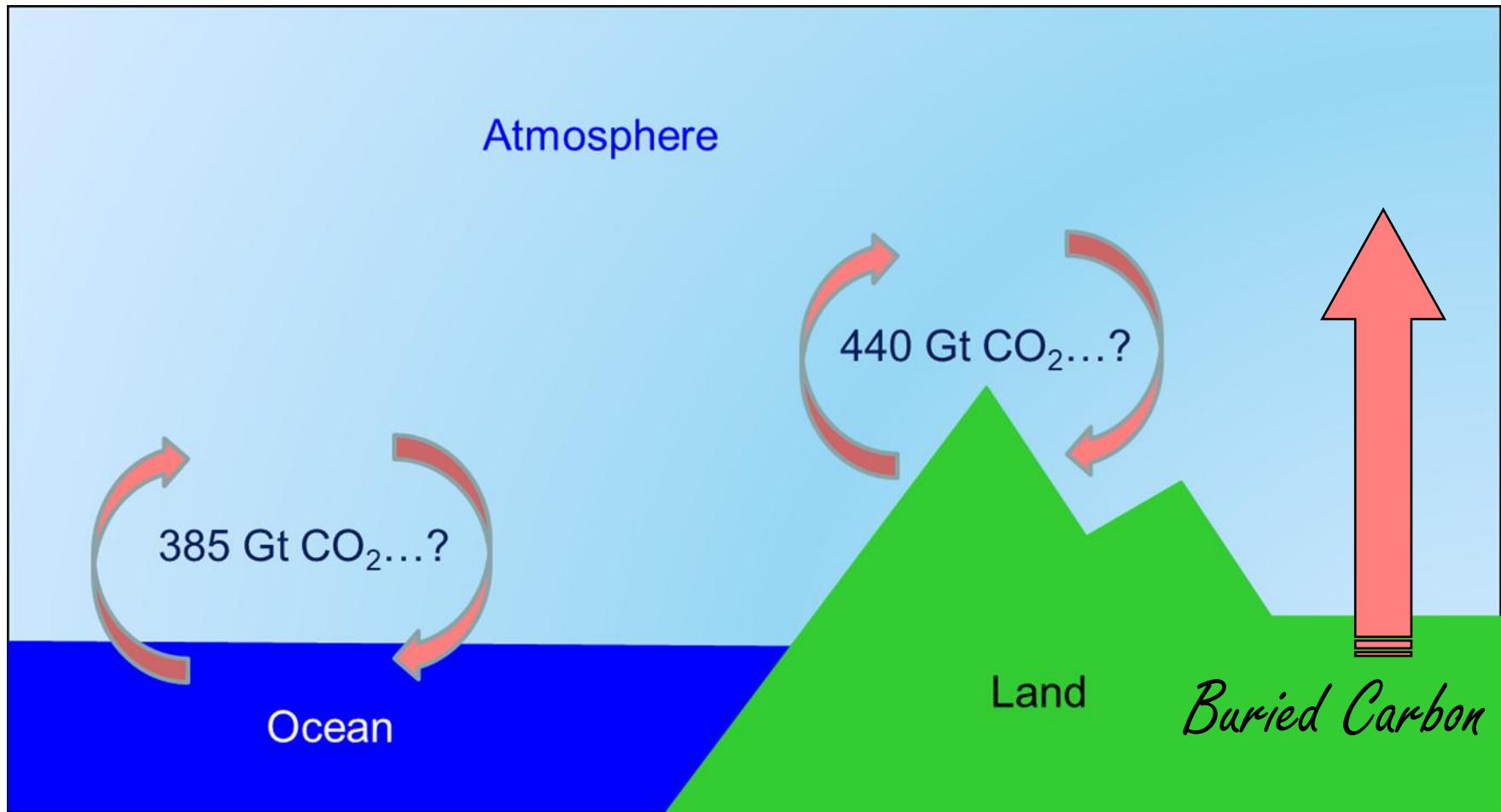
# The global Carbon cycle – CO<sub>2</sub> concentration in the atmosphere

The observed CO<sub>2</sub> concentration in the atmosphere reflects a **dynamic balance** between these inflows and outflows.



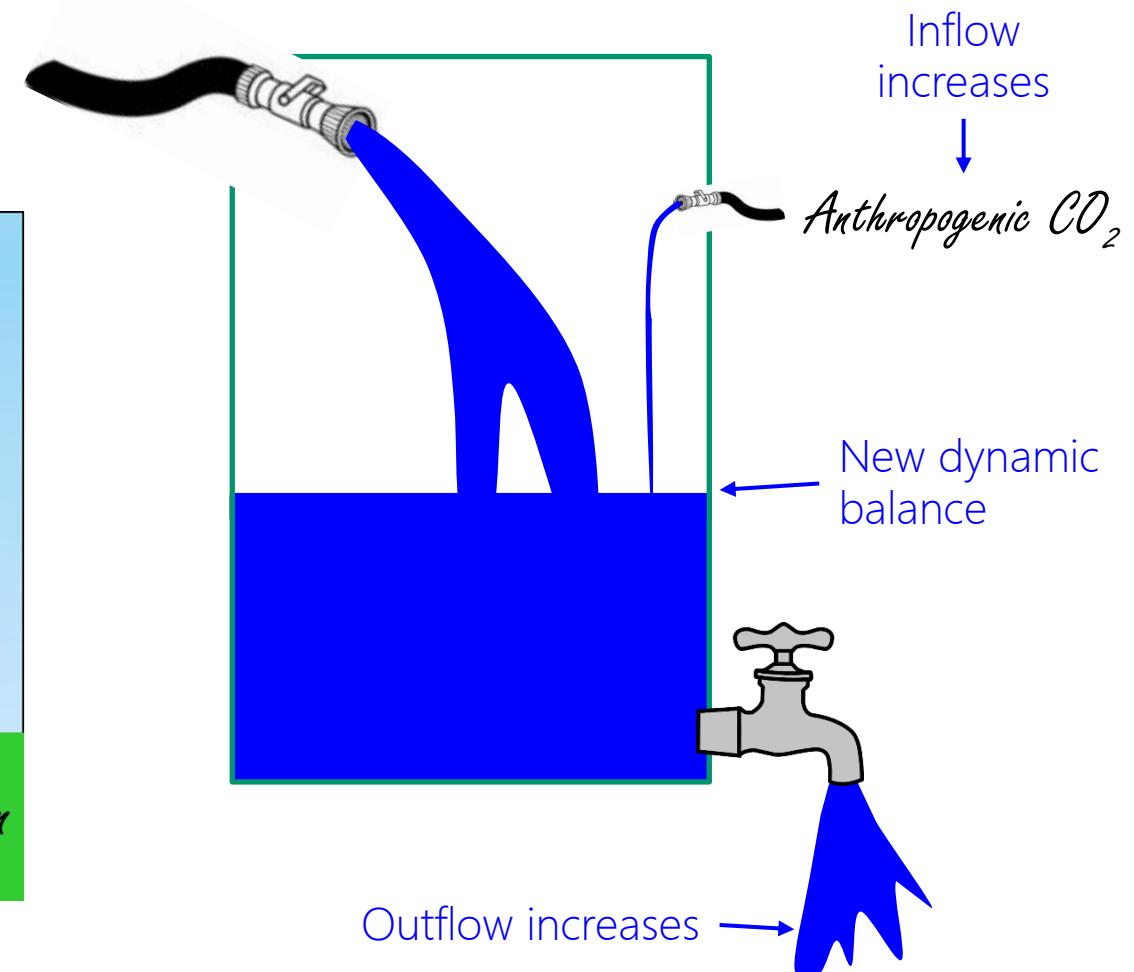
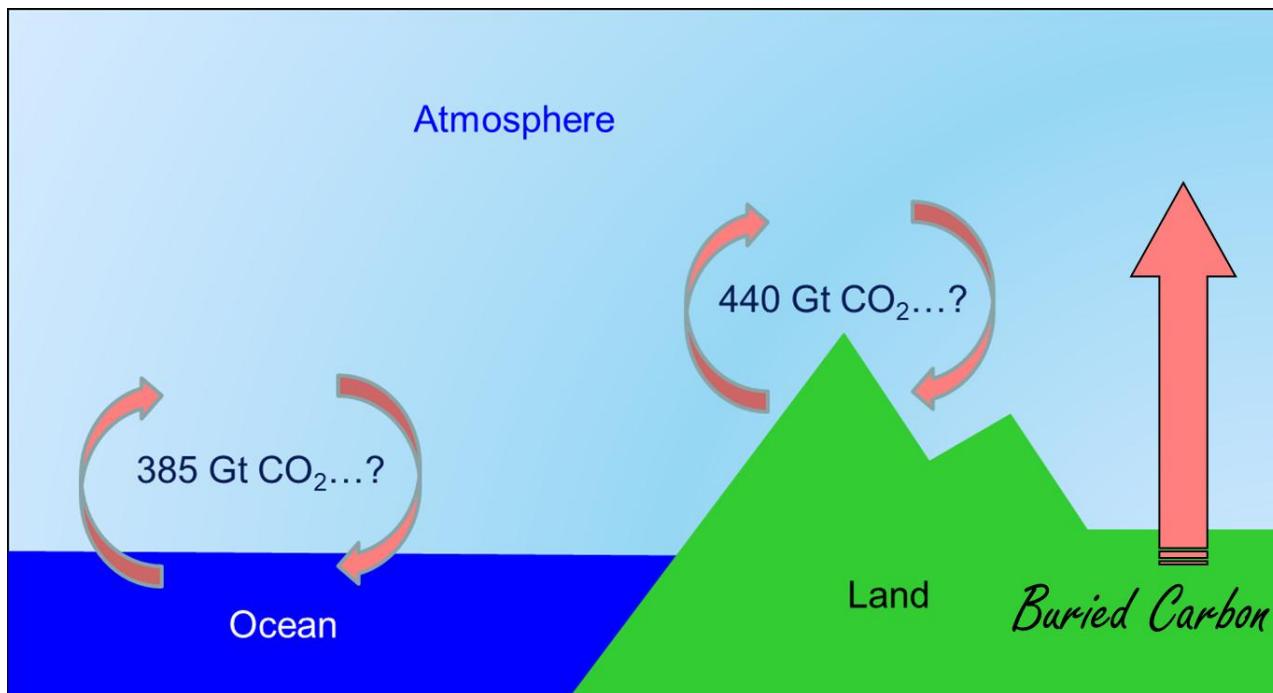
# The global Carbon cycle

Human activities – including fossil-fuel combustion and land-use change – are injecting additional CO<sub>2</sub> into the atmosphere. This additional CO<sub>2</sub> comes from carbon that has been locked in the ground for thousands or millions of years.



# The global Carbon cycle – CO<sub>2</sub> concentration in the atmosphere

The observed CO<sub>2</sub> concentration in the atmosphere increases as a result of these anthropogenic emissions – until a new **dynamic balance** is achieved.



# The global Carbon cycle

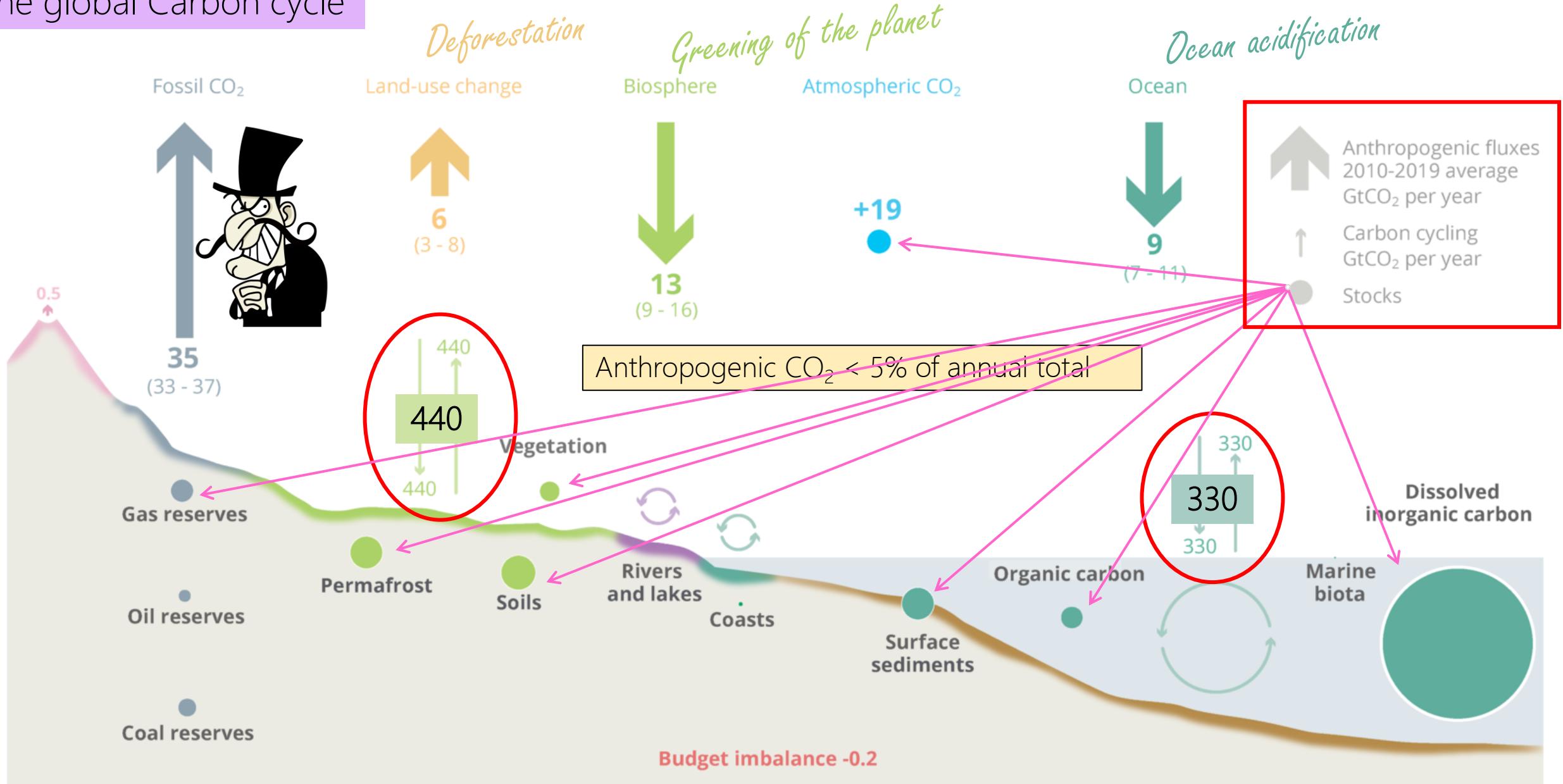


Image source: <https://www.icos-cp.eu/science-and-impact/global-carbon-budget/2020>

# The global Carbon cycle

## Fate of anthropogenic CO<sub>2</sub> Emissions (2004-2013 average)

$32.4 \pm 1.6$  Gt CO<sub>2</sub>/yr      91%



$15.8 \pm 0.4$  Gt CO<sub>2</sub>/yr

44%

Measurements



$3.3 \pm 1.8$  Gt CO<sub>2</sub>/yr      9%



$10.6 \pm 2.9$  Gt CO<sub>2</sub>/yr

29%

Calculated as the residual  
of all other flux components



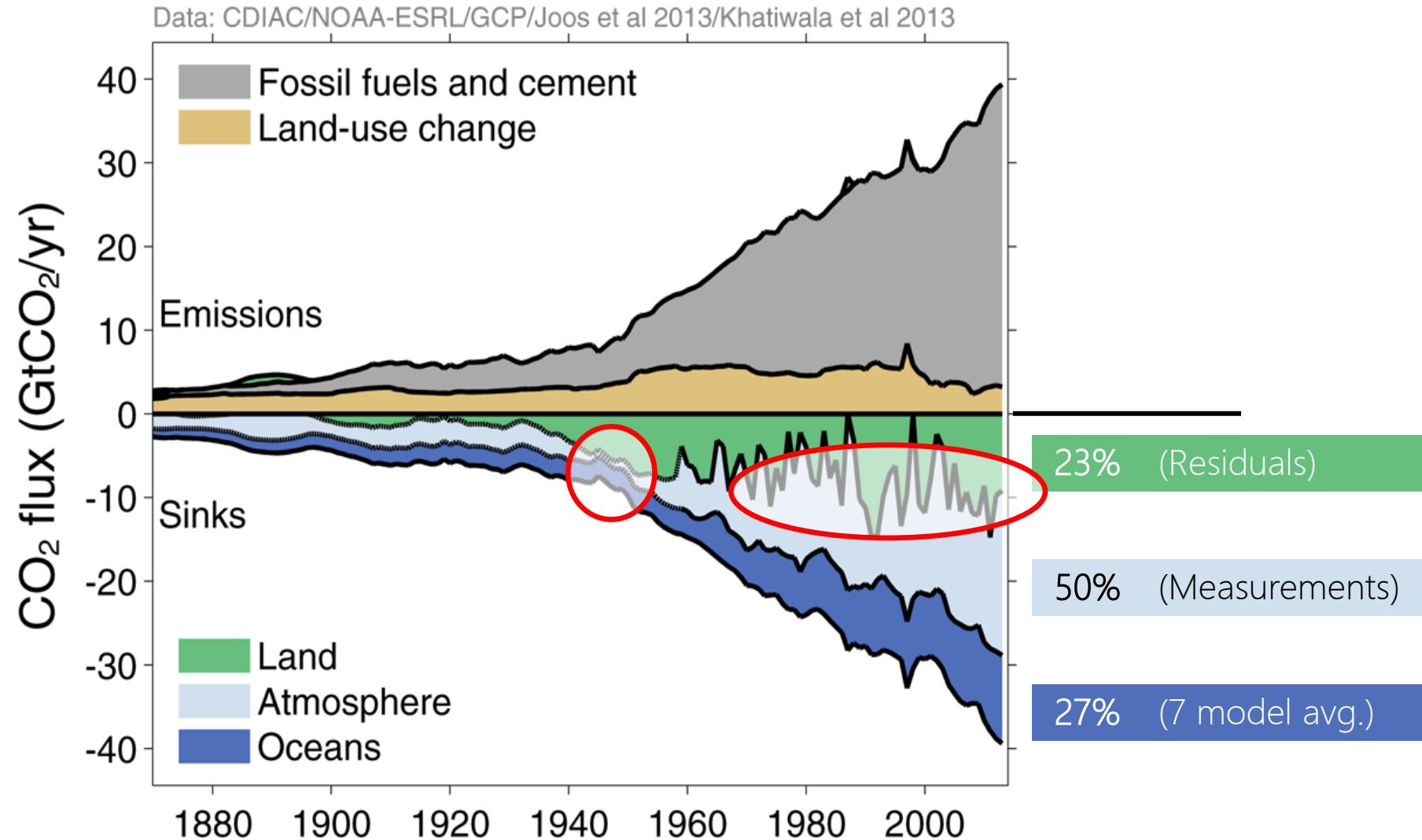
26%

$9.4 \pm 1.8$  Gt CO<sub>2</sub>/yr

Average from models

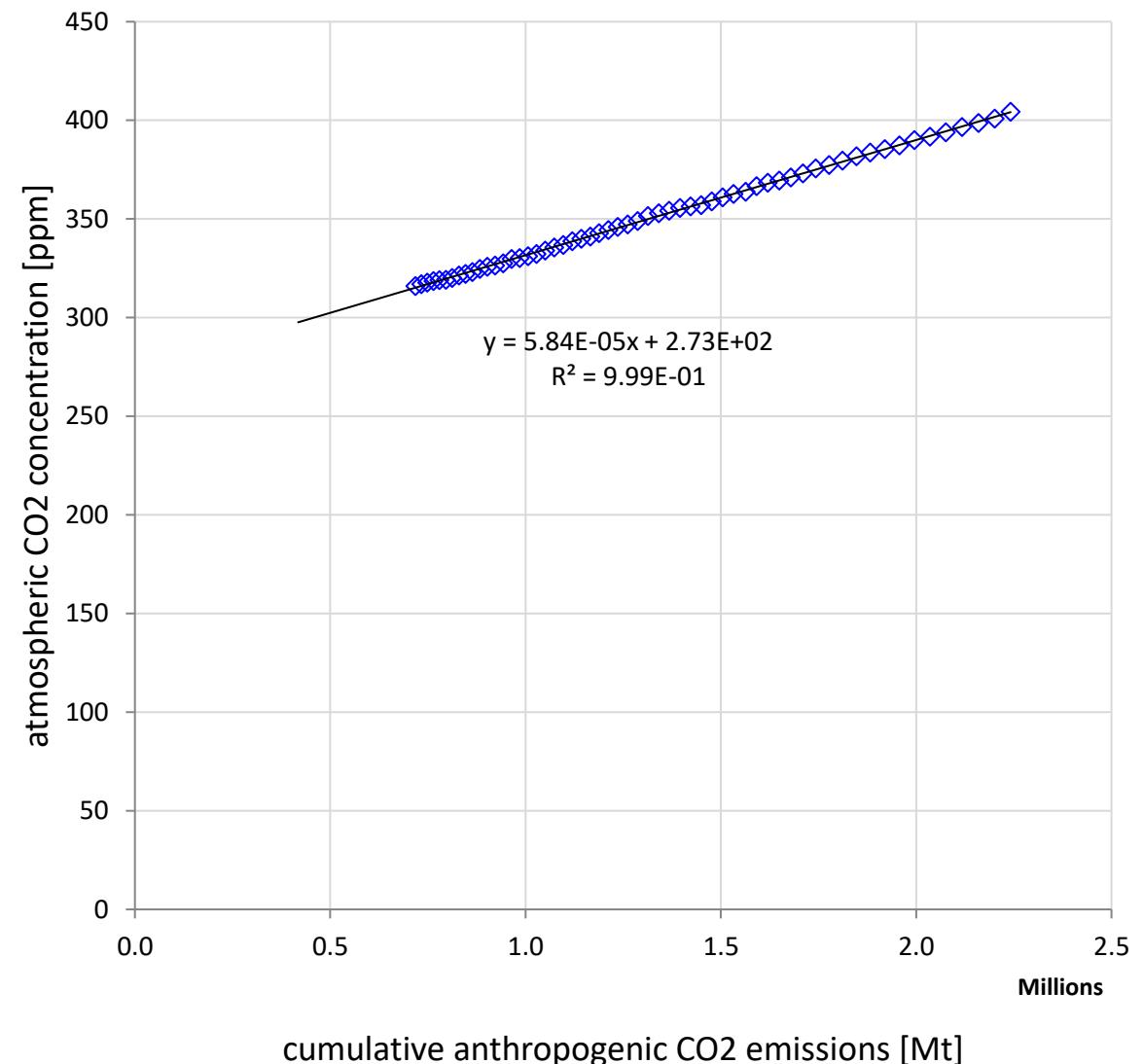
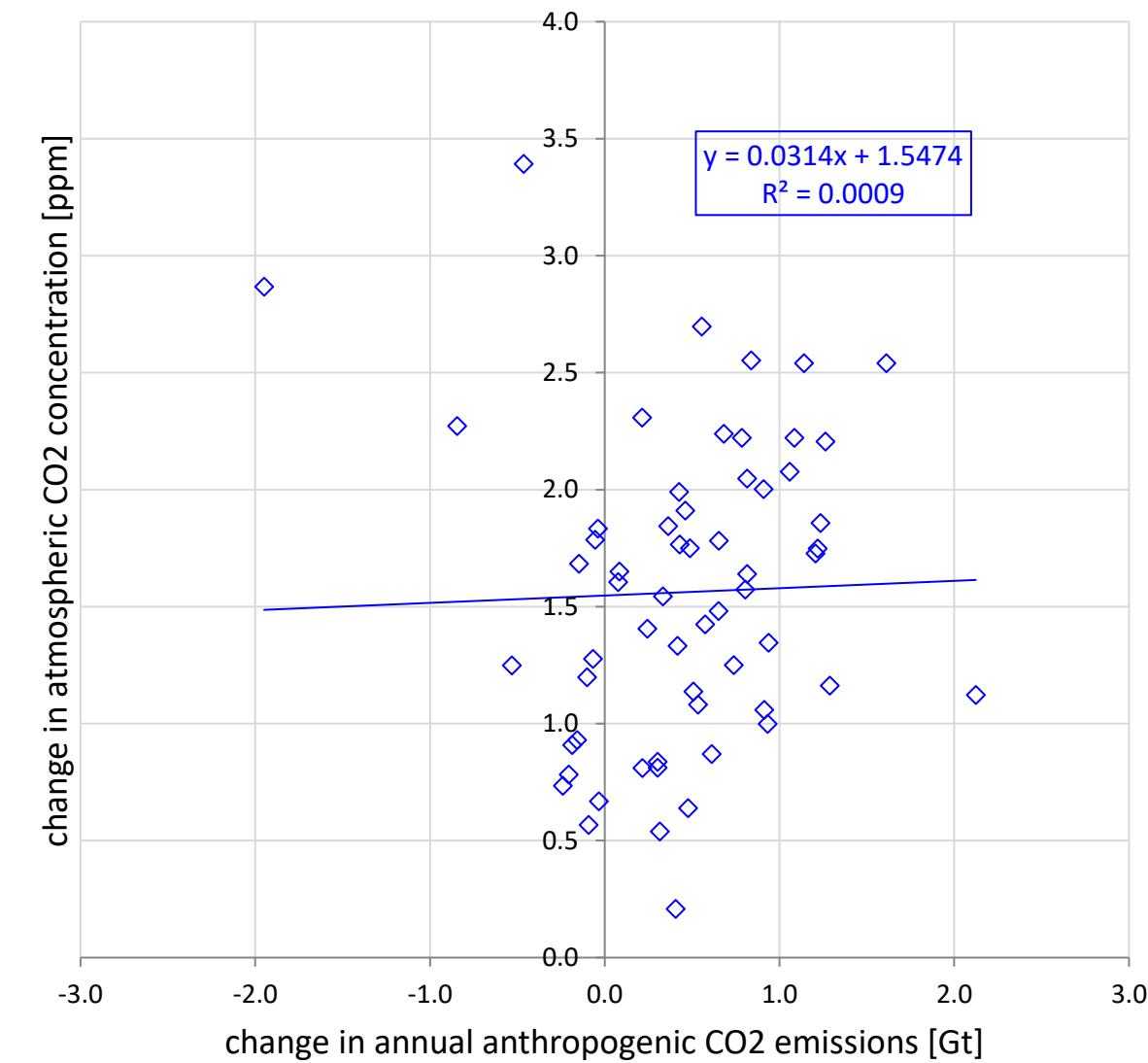


# The global Carbon cycle



Source: Carbon Budget 2012, (Global Carbon Project, 2014)

# The global Carbon cycle

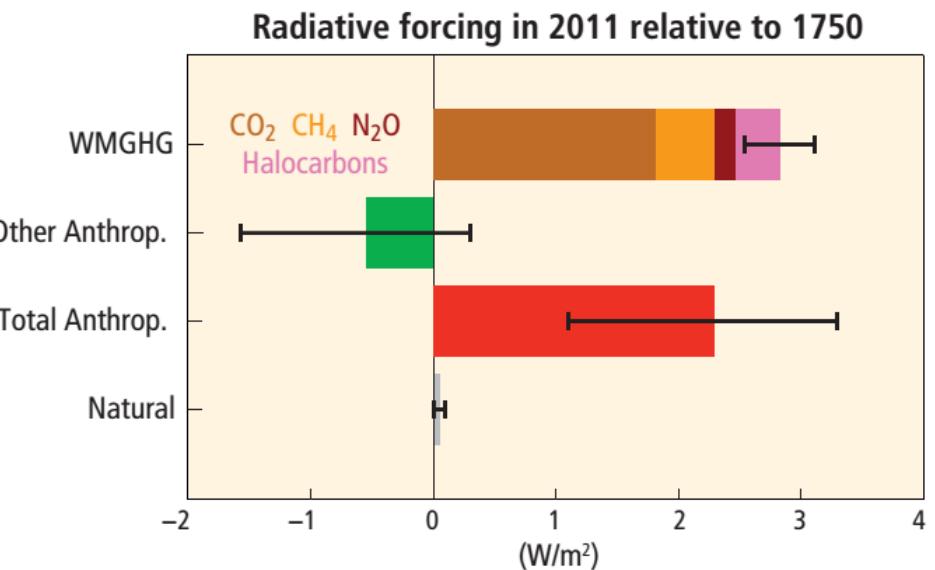
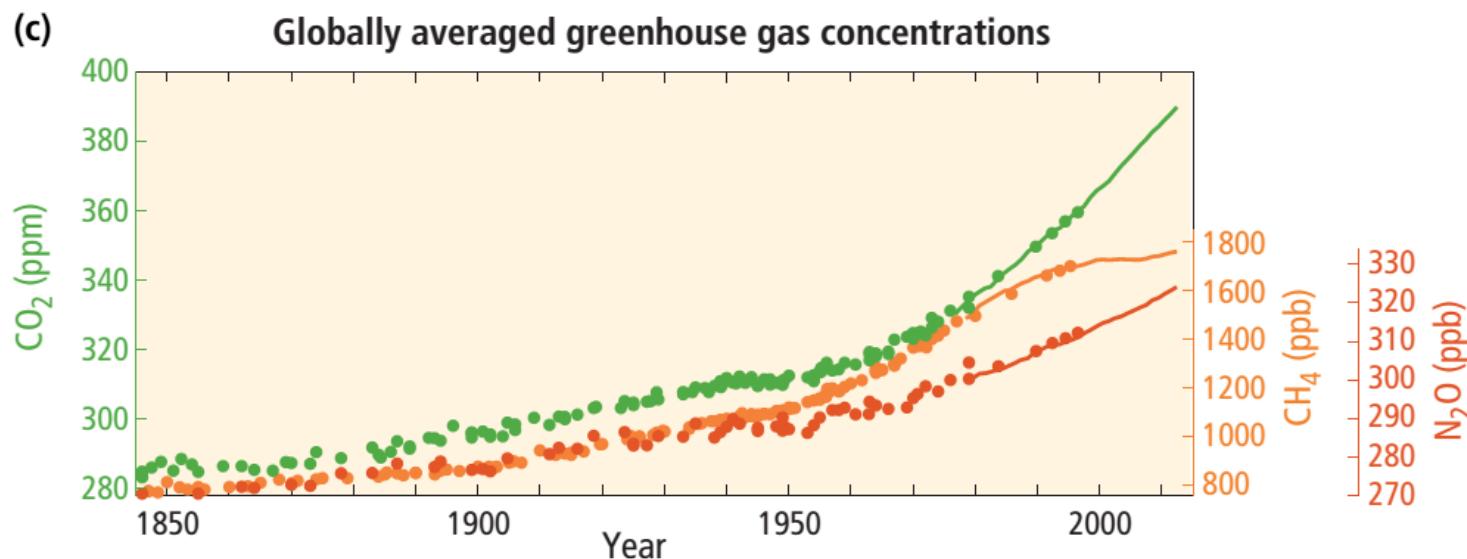


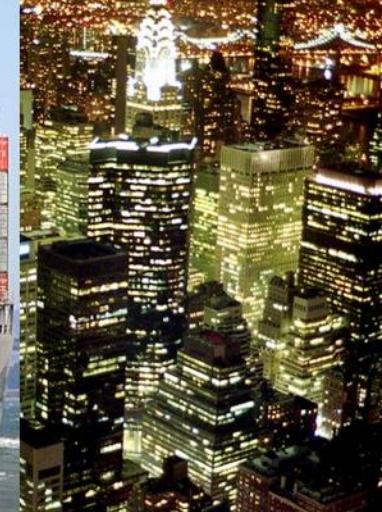
Source: Carbon Budget 2019, (Global Carbon Project, 2020)

Are anthropogenic emissions to the atmosphere exerting a significant, detrimental, influence on global climate?

1. Is it physically possible; *i.e.* do we have a plausible mechanism? Yes! (GHG)  
...but there's (a lot of) other stuff happening as well
- 1b. Is the atmospheric concentration of these GHG increasing? Yes!
- 1c. Is the increased concentration of GHG due to human activity? Yes!  
...but there's (a lot of) other stuff happening as well

- What other GHG are important?
- How do they compare, in terms of concentration, and radiative forcing?
- What are the principal sources?
- Judith Curry presentation, June 2018 (Brightspace)





# Energy Systems & Climate Change

