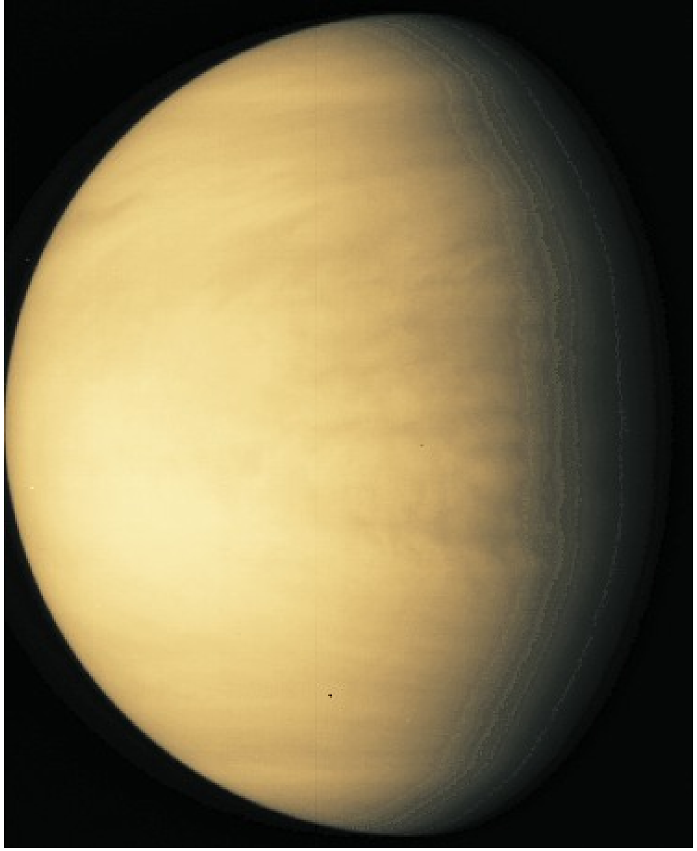
Chemistry 471/671

Global Climate Change

The Greenhouse Effect and Global Warming

These are NOT the same thing!

To begin with, let's make the distinction



Earth
Average temperature 15°C
Average pressure: 1 atm
Atmosphere 78% N_2
Clouds of Water
(-18°C)

Venus
Average temperature 450°C
Average pressure: 90 atm
Atmosphere 96% CO_2
Clouds of Sulfuric Acid
(100 °C)

The Greenhouse Effect

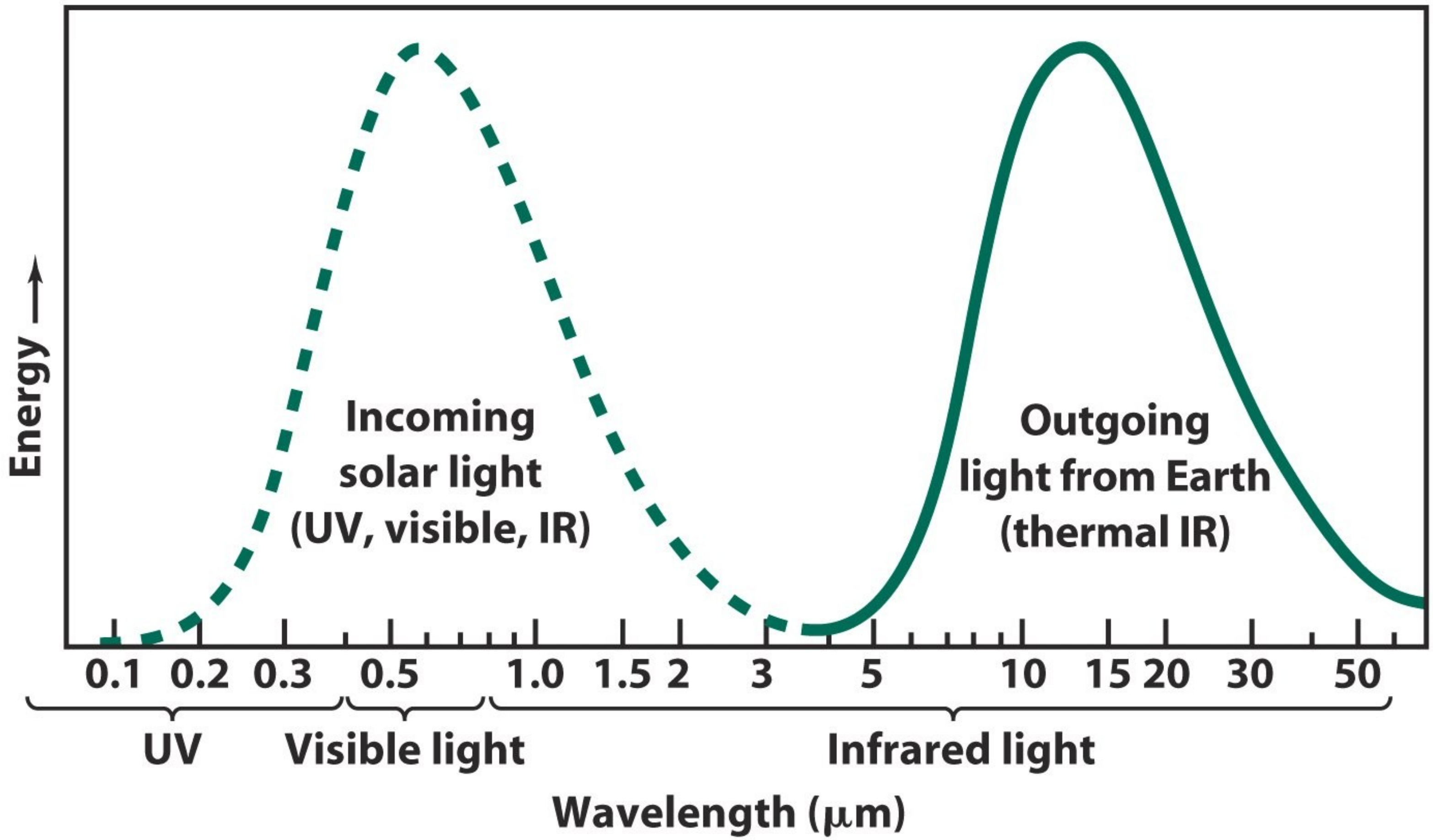


Figure 4-1
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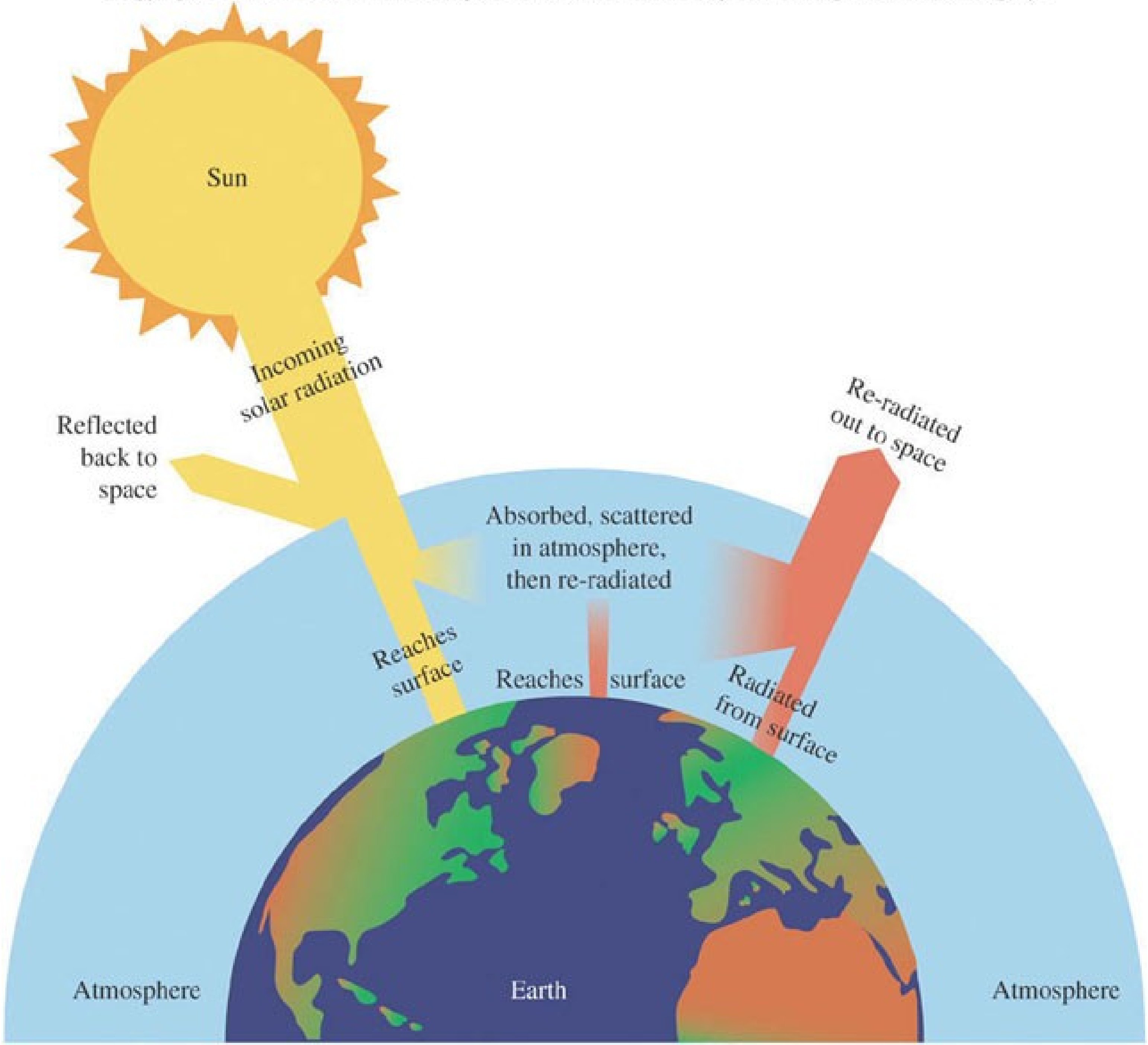
Blackbodies emit a broad spectrum centered around λ_{max} = 2897/T

λ_{max}(sun) = λ_{max}(5800K) = 0.50 μm **λ_{max}(earth) = λ_{max}(300K) = 10 μm**


Sun
Incoming solar radiation
Reflected back to space
Re-radiated out to space
Absorbed, scattered in atmosphere, then re-radiated
Reaches surface
Reaches surface
Radiated from surface
Atmosphere
Earth
Atmosphere

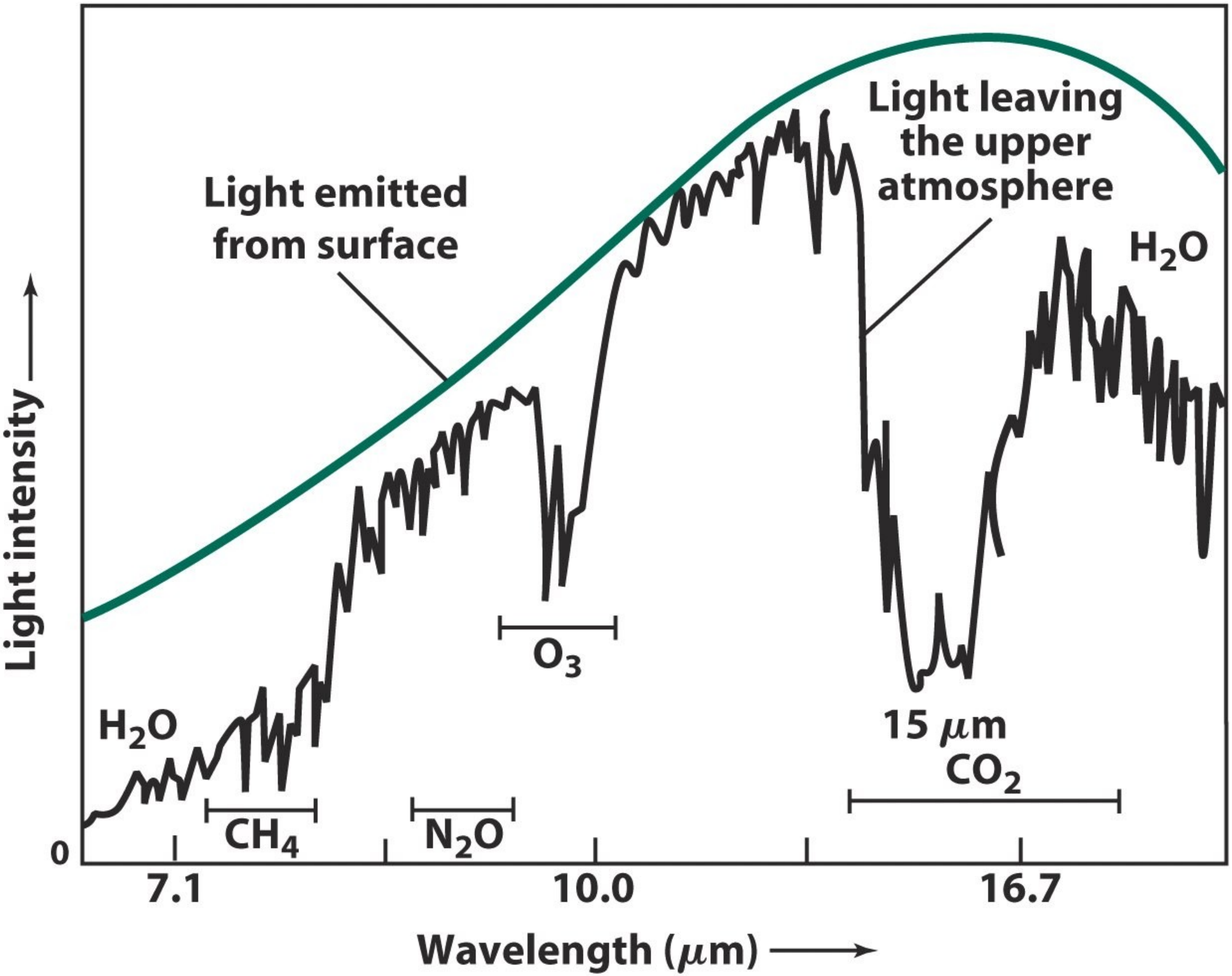


Figure 4-6
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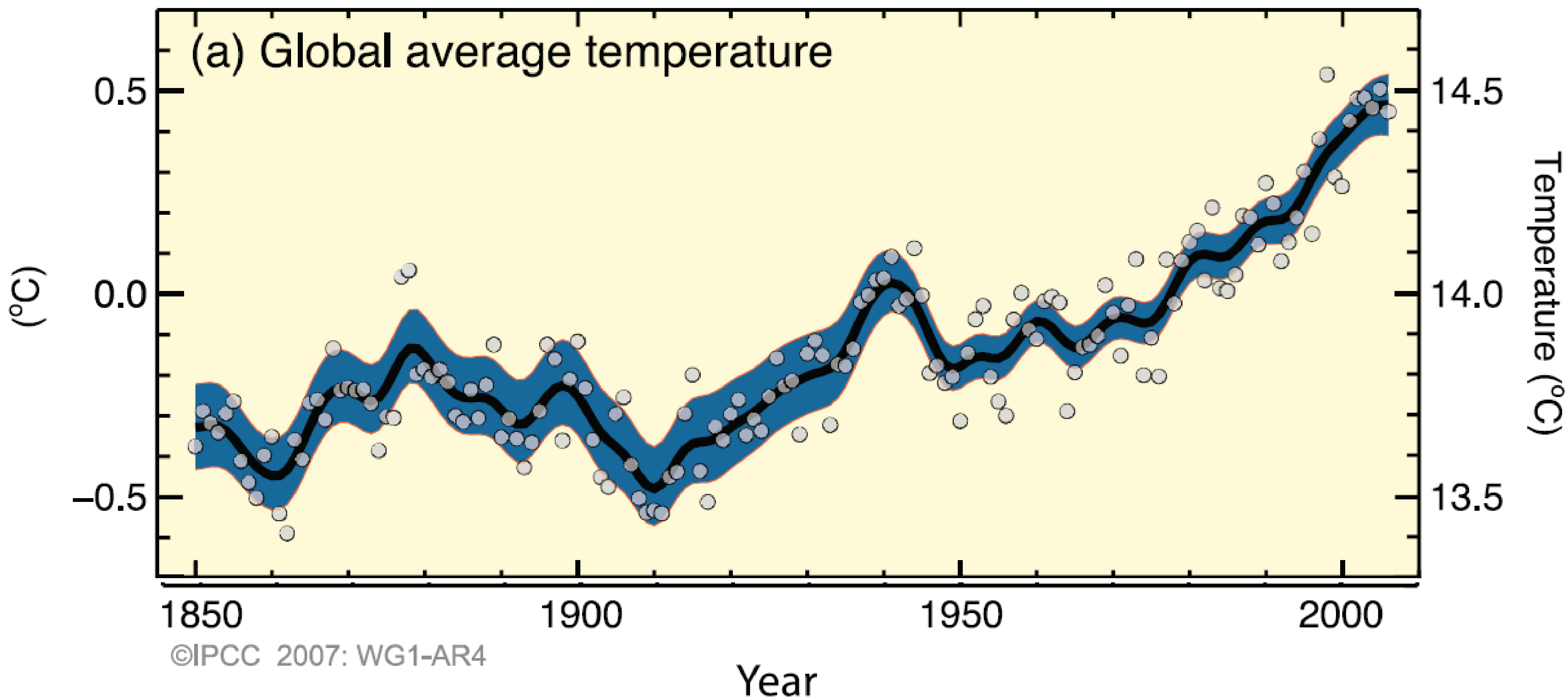
Ok, that's the Greenhouse Effect.

So what's global warming?

Changes in Temperature, Sea Level and Northern Hemisphere Snow Cover



This is global warming

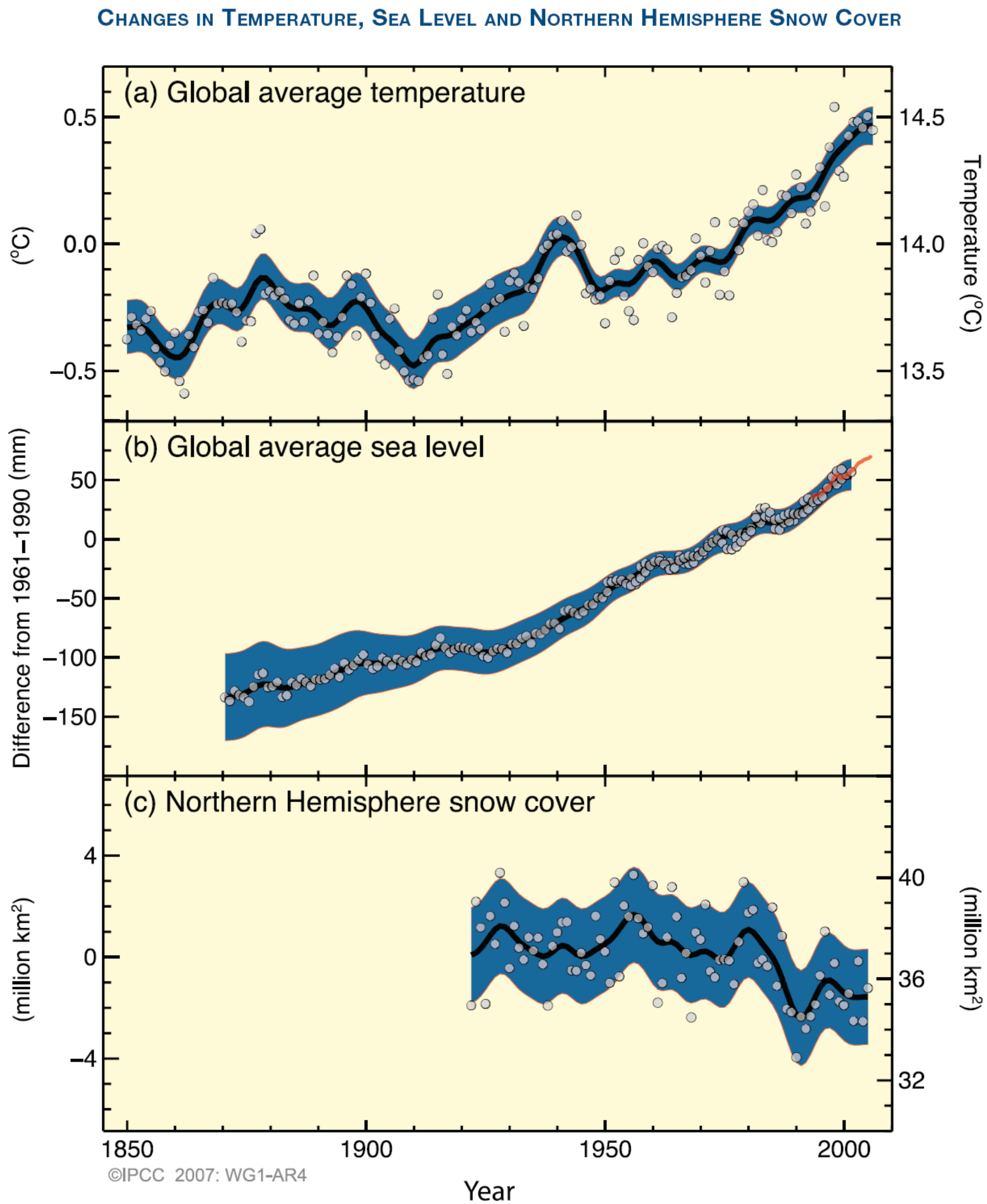
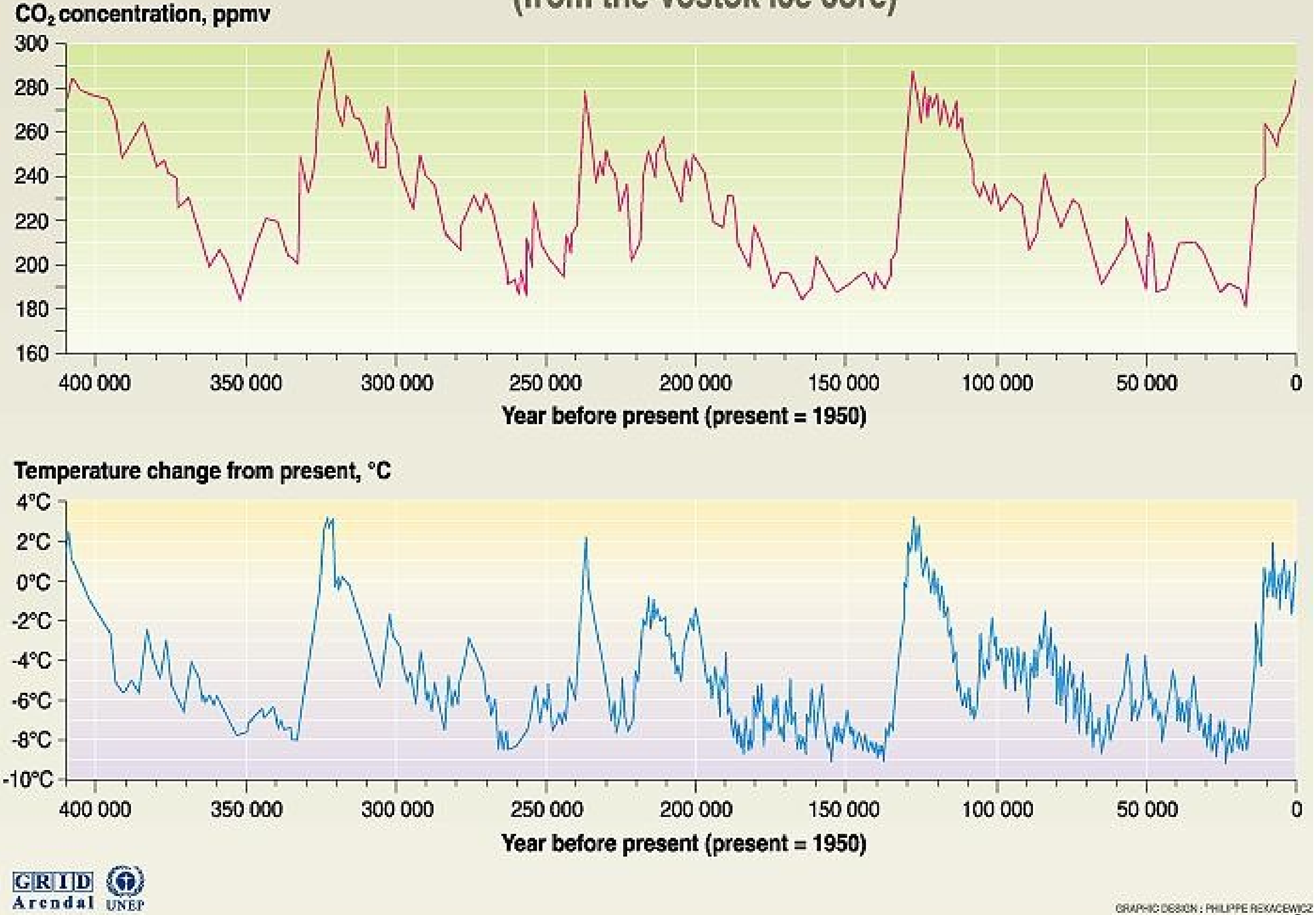


Figure SPM.3. *Observed changes in (a) global average surface temperature, (b) global average sea level from tide gauge (blue) and satellite (red) data and (c) Northern Hemisphere snow cover for March-April. All changes are relative to corresponding averages for the period 1961–1990. Smoothed curves represent decadal average values while circles show yearly values. The shaded areas are the uncertainty intervals estimated from a comprehensive analysis of known uncertainties (a and b) and from the time series (c). {FAQ 3.1, Figure 1, Figure 4.2, Figure 5.13}*

Among the explanations offered for this remarkable temperature increase is an *Enhanced Greenhouse Effect* due to an increase in the steady state concentration of Greenhouse Gases.

So, just how remarkable IS this temperature change? And what makes for an effective Greenhouse Gas?

Temperature and CO_2 concentration in the atmosphere over the past 400 000 years (from the Vostok ice core)



Source: J.R. Petit, J. Jouzel, et al. Climate and atmospheric history of the past 420 000 years from the Vostok ice core in Antarctica, Nature 399 (3JUne), pp 429-436, 1999.

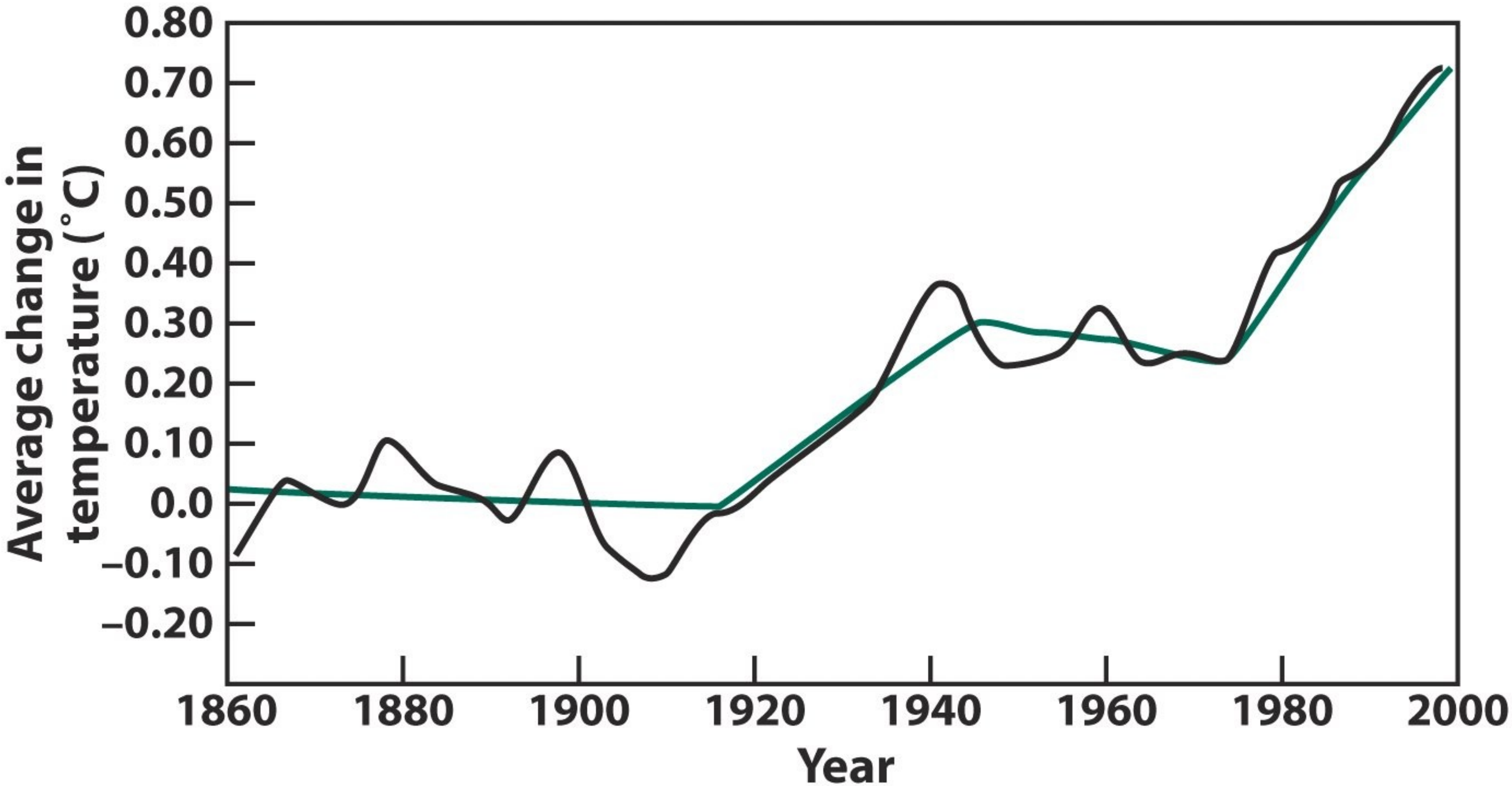


Figure 4-2b
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Greenhouse Gases: CO_2

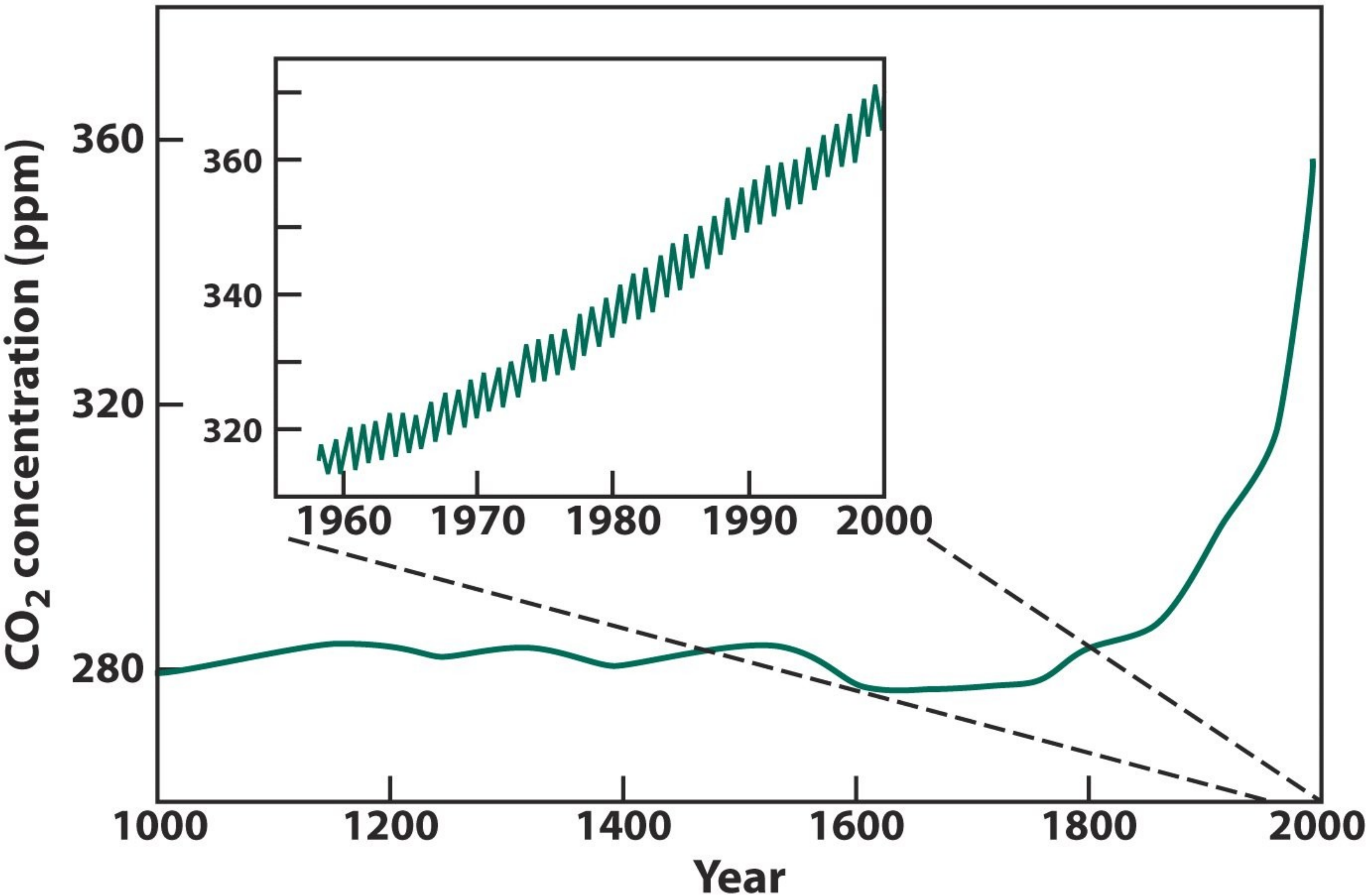

Figure 4-7
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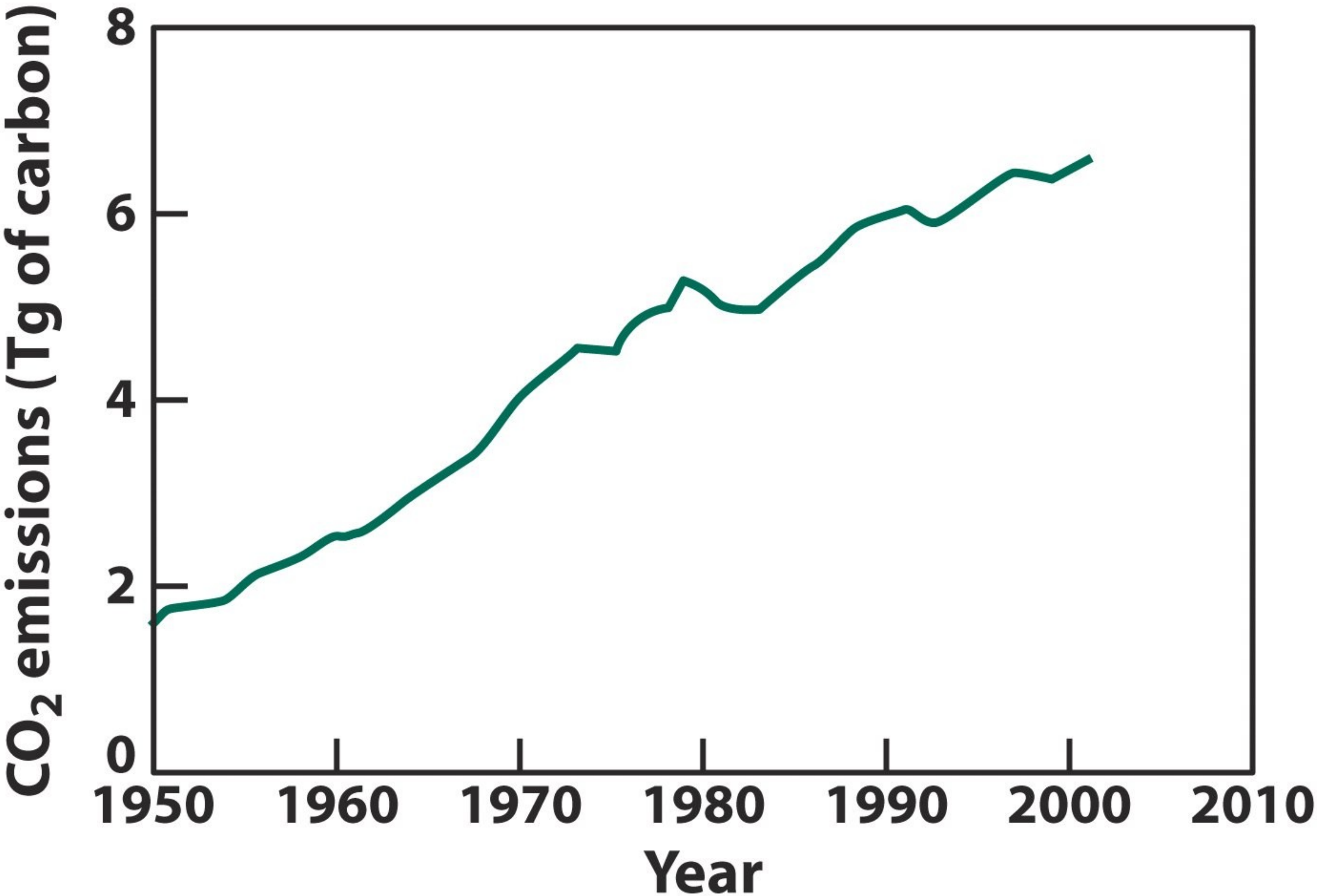

Figure 4-8
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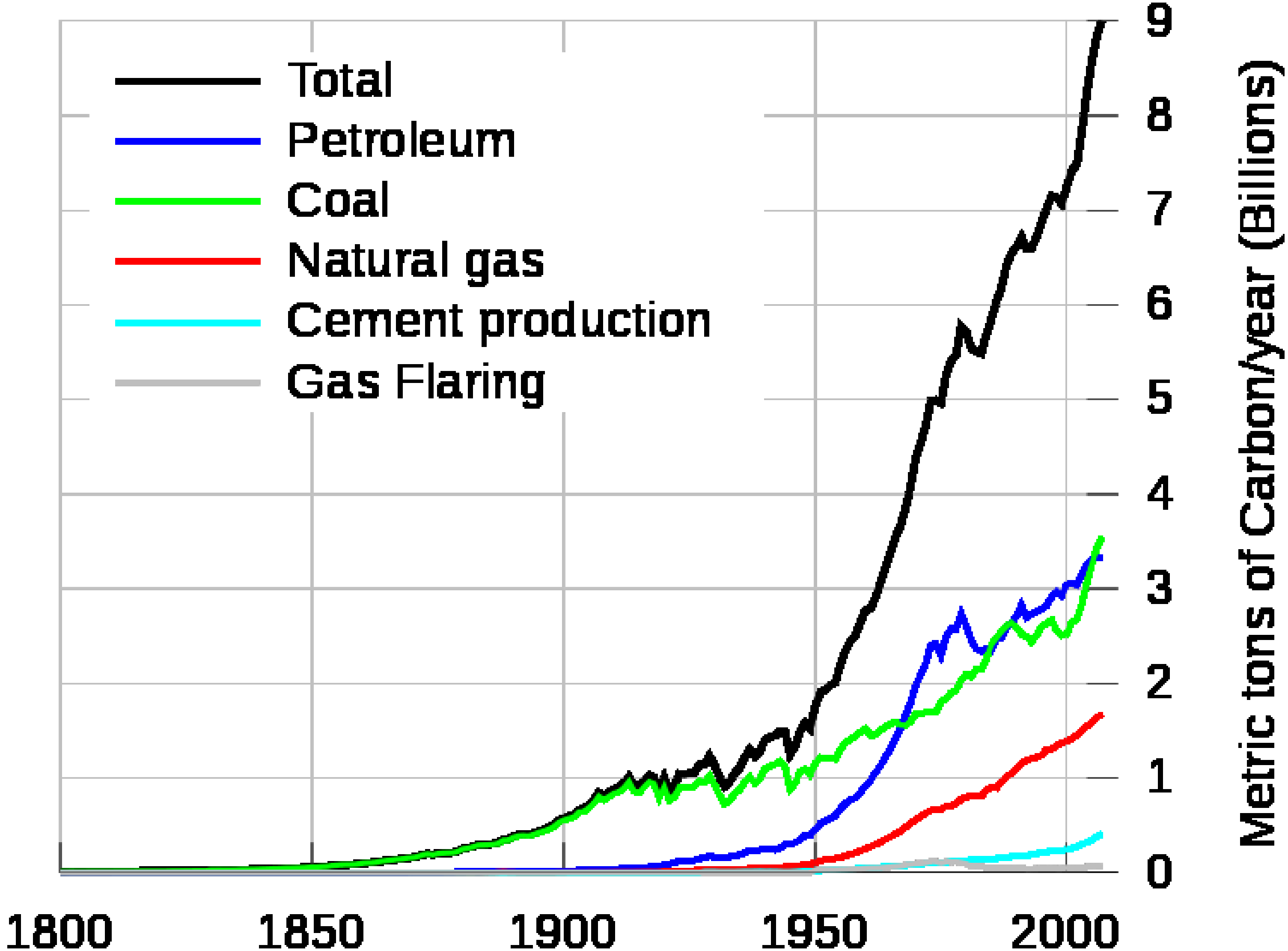
CO_2 emissions from fossil fuel combustion

Anthropogenic carbon dioxide emissions over time



Source: Wikimedia Commons

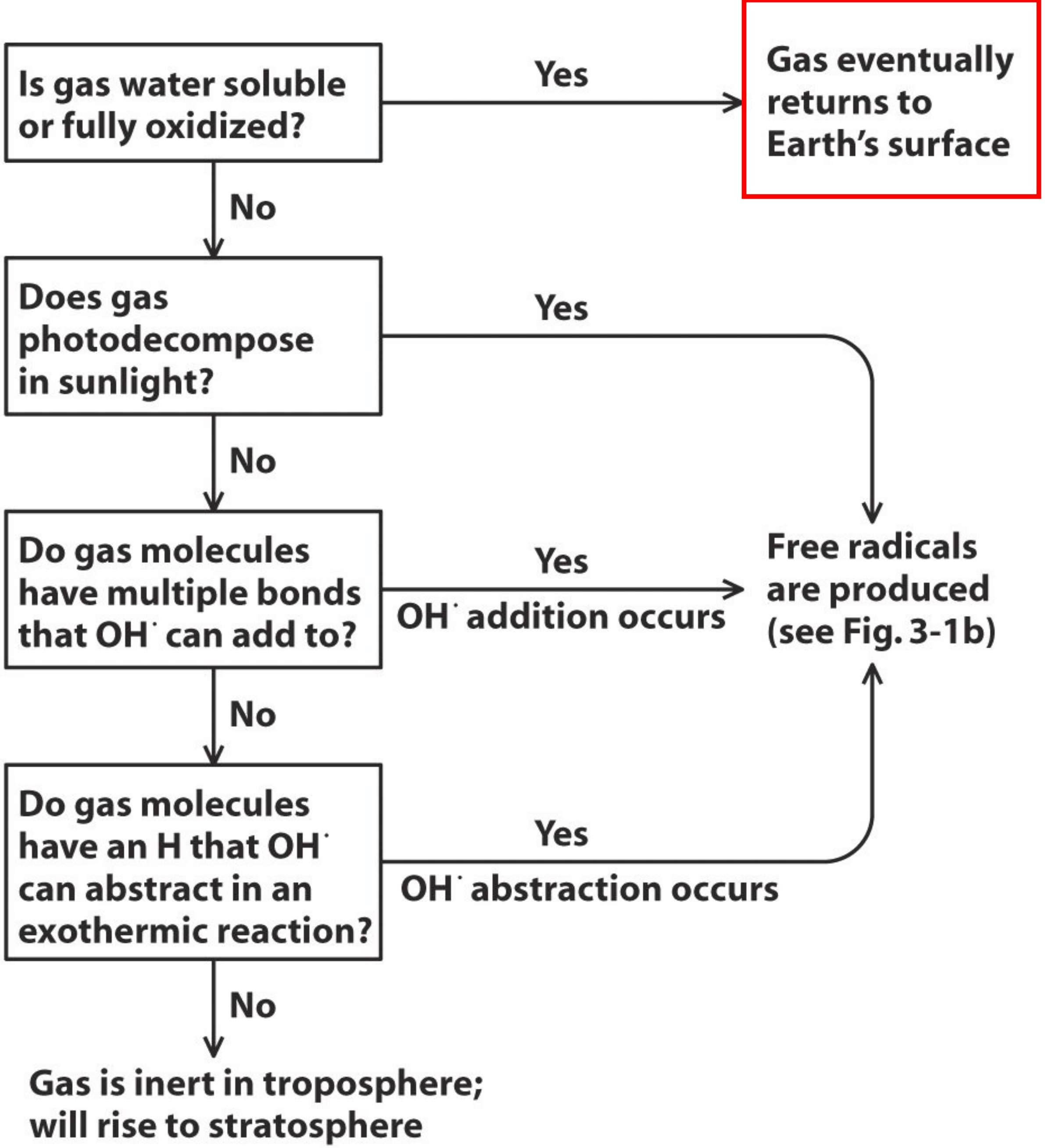


Figure 3-1a
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Indicators of the human influence on the atmosphere during the Industrial Era

(a) Global atmospheric concentrations of three well mixed greenhouse gases

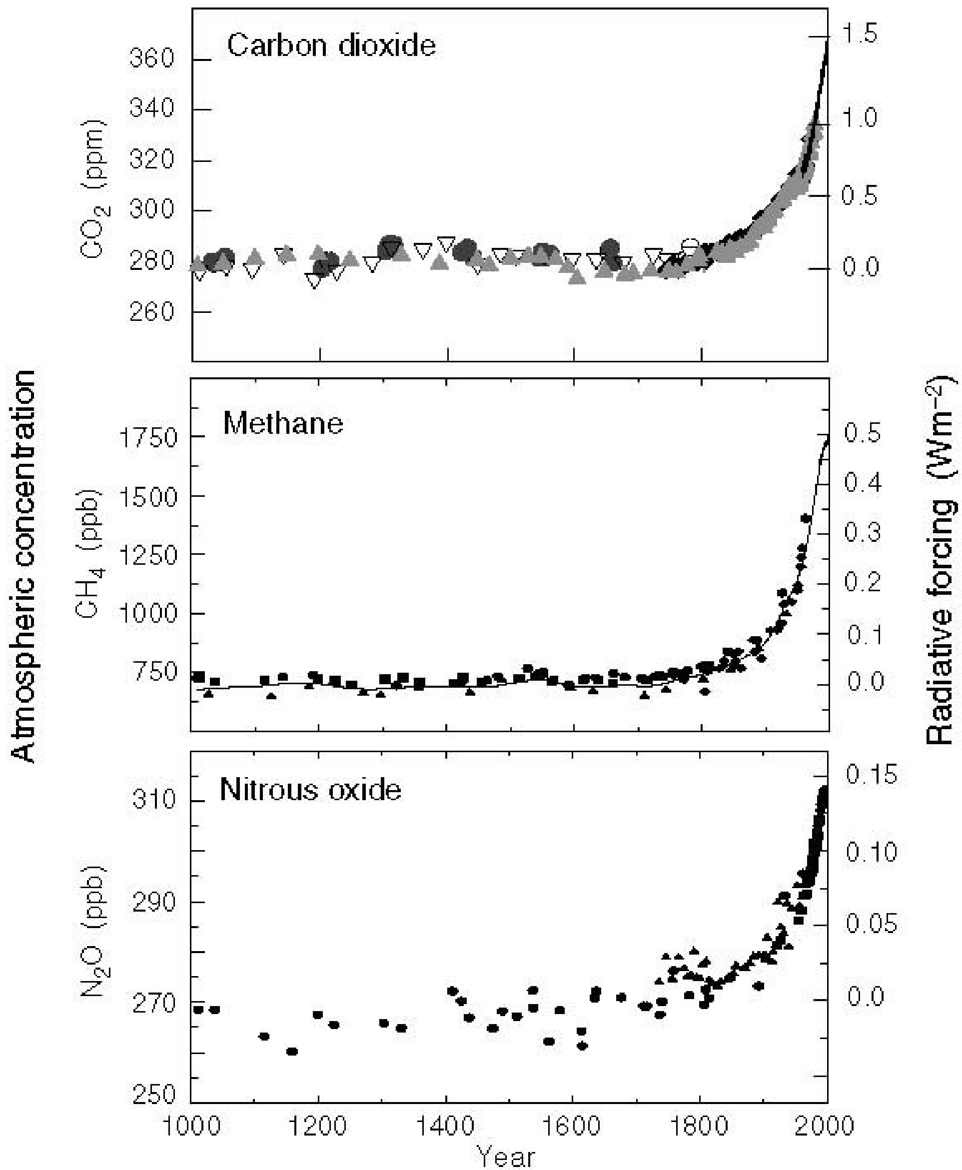

TABLE 4-1 Summary of Information About Some Greenhouse Gases

Gas	Current concentration	Residence time, in years	Relative global warming efficiency, 100-year horizon
CO_2	373 ppm	50–200	1
CH_4	1.77 ppm	12	23
N_2O	316 ppb	120	296
CFC-11	0.26 ppb	45	4600
HCFC-22	0.15 ppb	12	1700
HFC-134a	0.01 ppb	14	1300
Halon-1301	0.003 ppb	65	6900

Table 4-1
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?

What makes for an effective Greenhouse Gas?

1) **The gas must absorb IR radiation**

This requires the vibrations of the molecule to induce a change in dipole moment

Homonuclear diatomics (N_2, O_2) cannot absorb IR

The greater the change in the dipole, the greater the IR absorption

What makes for an effective Greenhouse Gas?

2) The gas must absorb IR radiation **that isn't already being absorbed!**

The absorption of species which are currently in low concentrations are more impacted by new emissions

Species which absorb at the same wavelengths as CO_2 and H_2O are quite inefficient

"The Atmospheric Window" from 8 to 13 μm

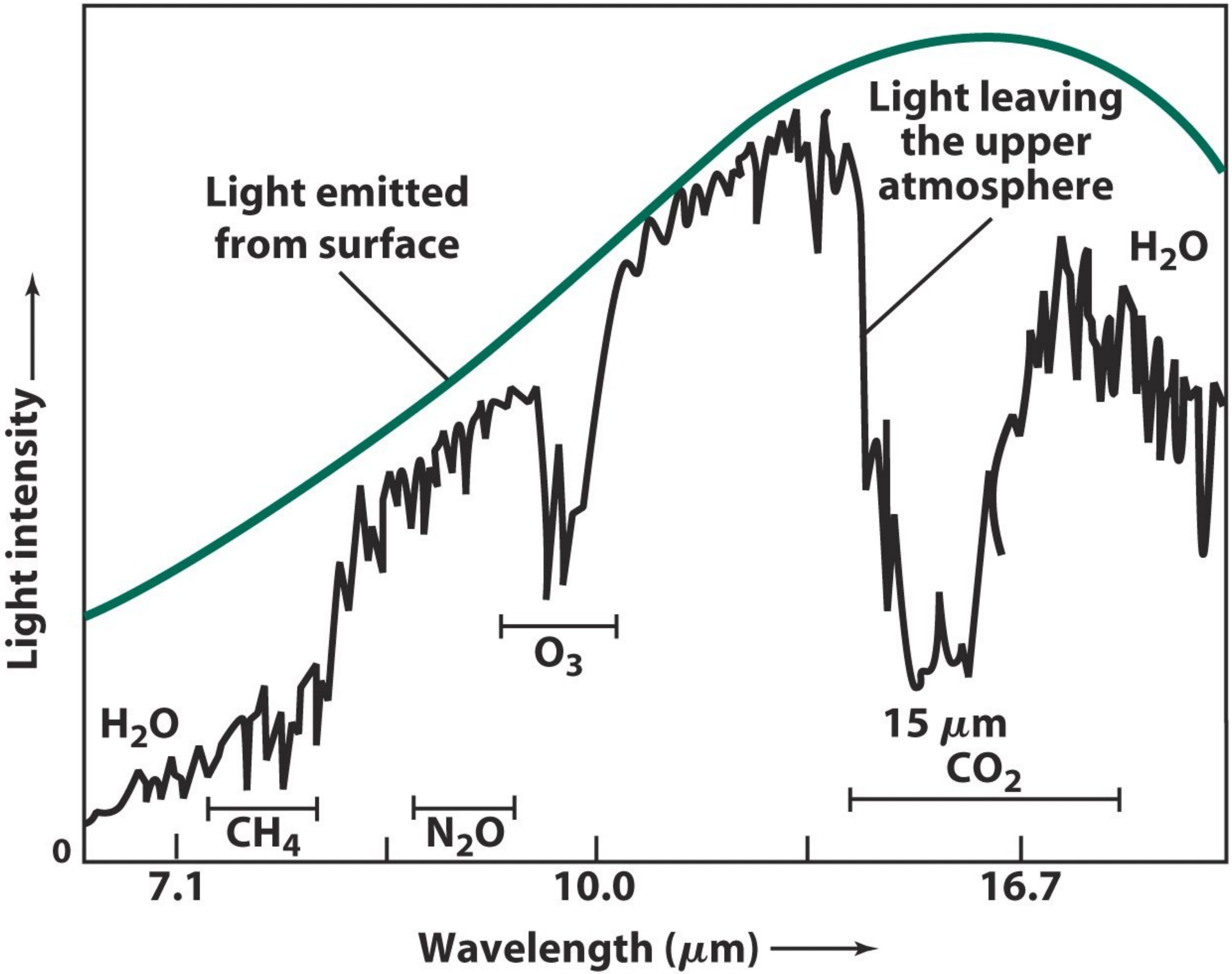

Figure 4-6
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What makes for an effective Greenhouse Gas?

3) The gas must have a significant lifetime in the atmosphere

How can we calculate the residence time of a species?

Residence Time and Steady State

The extent to which a substance accumulates in the atmosphere depends on two factors:

The rate at which it is released (source), and

The rate at which it is consumed (sink)

In general the release rate is constant and independent of concentration. Let's call it R

The rate at which it is consumed depends on chemical loss processes. If we *assume* a single first-order reaction as a sink, we can call the loss rate kC.

At some time before we start to emit any of this compound into the atmosphere, $C_0=0$.

Thus, the initial loss rate is also 0, but increases as C(t) increases

Residence Time and Steady-State

- The loss rate increases as the concentration increases, but the release rate is constant
- Eventually, the loss rate increases to the point where it equals the release rate, and steady state concentration is achieved
- At steady state, sources = sinks

  $kC_{SS} = R$

  $C_{SS} = R/k$

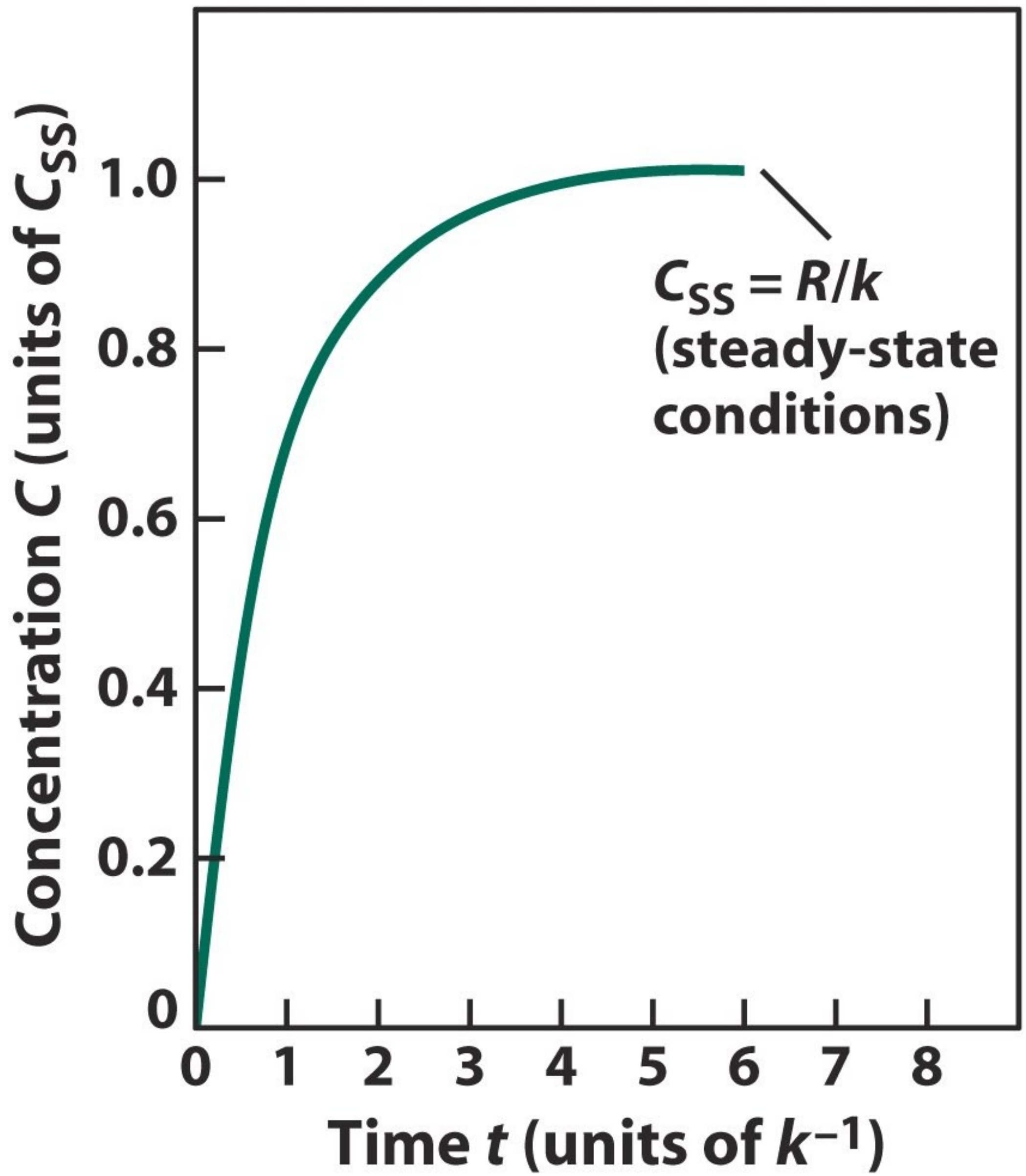

Figure 4-13
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Residence Time and Steady-State

If we somehow eliminate the source term, C will decrease exponentially as a first-order reaction

If we go through the (simple) calculus starting from $dC/dt = -kC$, we can obtain an expression for C(t) relative to C_{SS}

$$C(t) = C_{SS}e^{-kt} \qquad C(t)/C_{SS} = e^{-kt}$$

It is useful (read: traditional) to define "residence time" as the time it takes for the concentration of a species to fall to 1/e of its original value

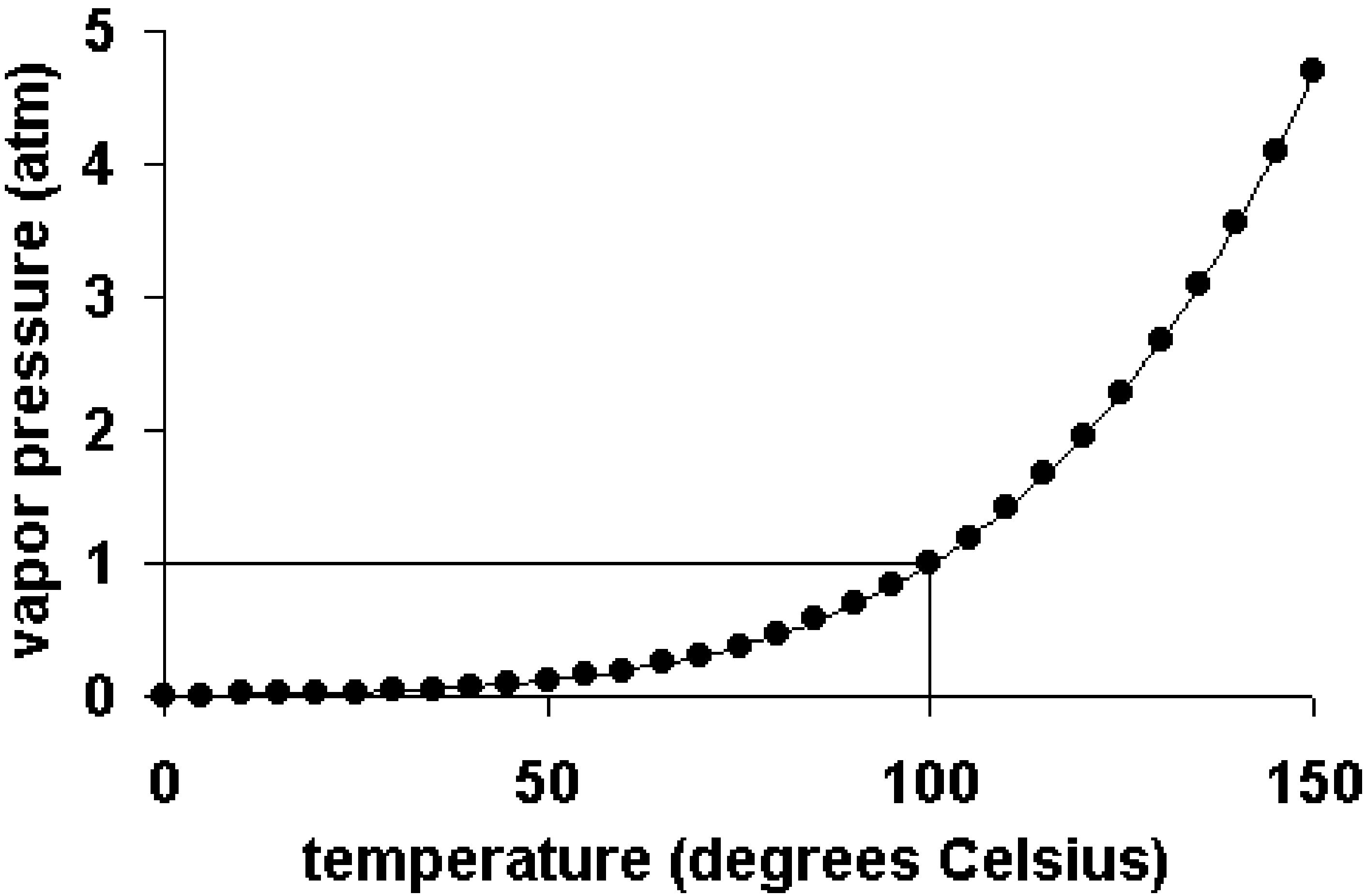
$$1/e = e^{-kt}$$

$$\ln(e^{-1}) = -kt_{avg}$$

$$t_{avg} = 1/k$$

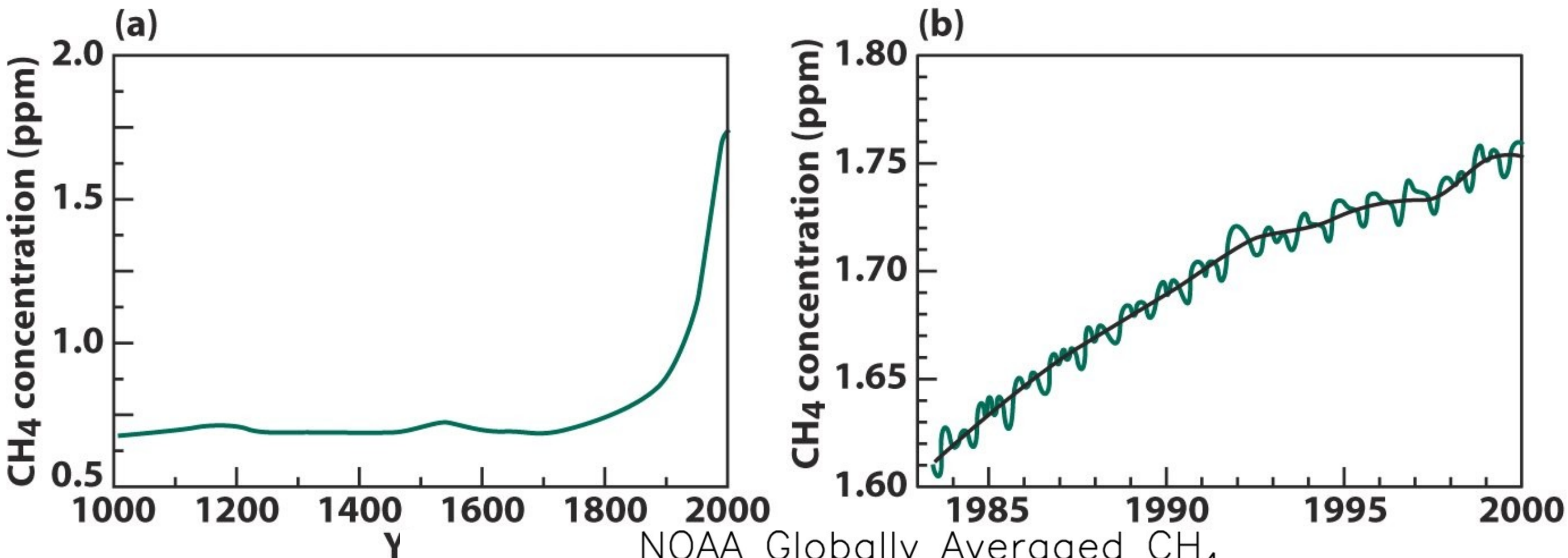
And thus, $C_{SS} = R^*t_{avg}$ or $t_{avg} = C_{SS}/R$

Greenhouse Gases: Water Vapor



Positive feedback

Greenhouse Gases: Methane



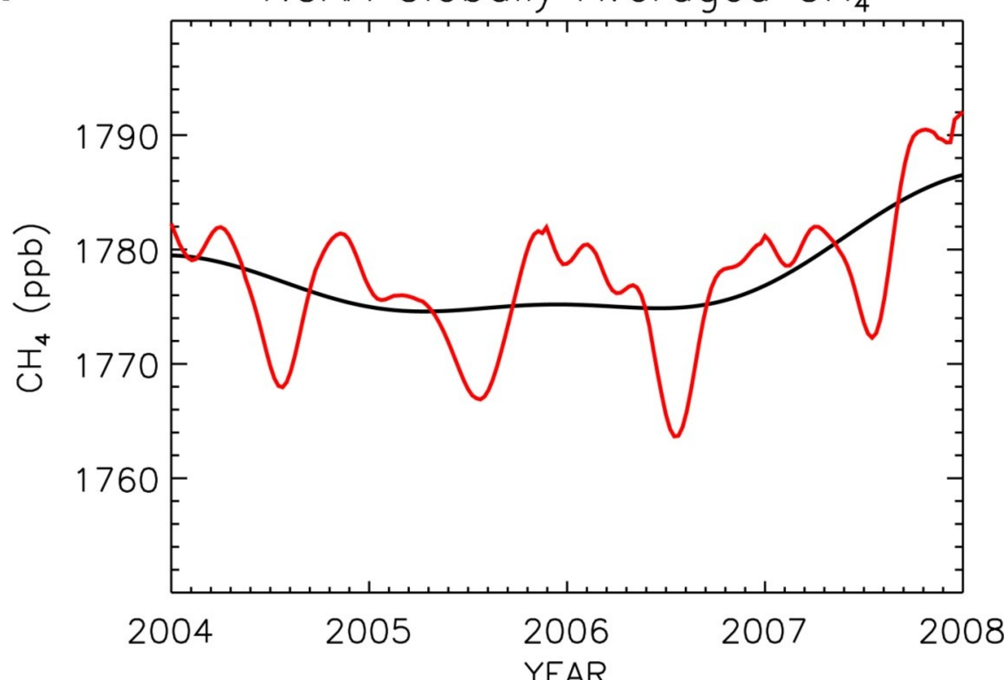


Figure 4-15
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Greenhouse Gases: Methane

Emissions:

- 70% of current emissions are anthropogenic
- Natural gas leaks
- Coal mines
- Oil refineries
- Ruminants
- Anaerobic decomposition of plant matter
  - natural and created wetlands, landfills
- Burning of biomass
- Rice production

The Future:

- Positive feedback? From increased rates, but also thawing permafrost

Greenhouse Gases: N_2O

Emissions:

- <40% of current emissions are anthropogenic
- Release from oceans
- Nitrification/denitrification of plants
  - including that induced by fertilizer
- Growth of new grasslands
  - including that induced by deforestation
- Fabrication of nylon
- Consumption of coal, biomass
- Consumption of gasoline without catalytic converters

No tropospheric sinks

The Future:

- Positive feedback again? From increased rates, but also thawing permafrost

Greenhouse Gases: SF_6

Emissions:

Almost entirely anthropogenic

Used as an insulating gas in electrical industry

Exceedingly long-lived

Very strong absorber

The Future:

Emissions have largely ceased, but concentrations remain

Greenhouse Gases: O_3

Emissions:

Largely anthropogenic, from polluted urban air

Also from forest fires, grass fires, lightning

Perhaps 10% of all global warming is induced by ozone

The Future:

Unknown – unlikely to change significantly in the short term

Greenhouse Gases: CFCs

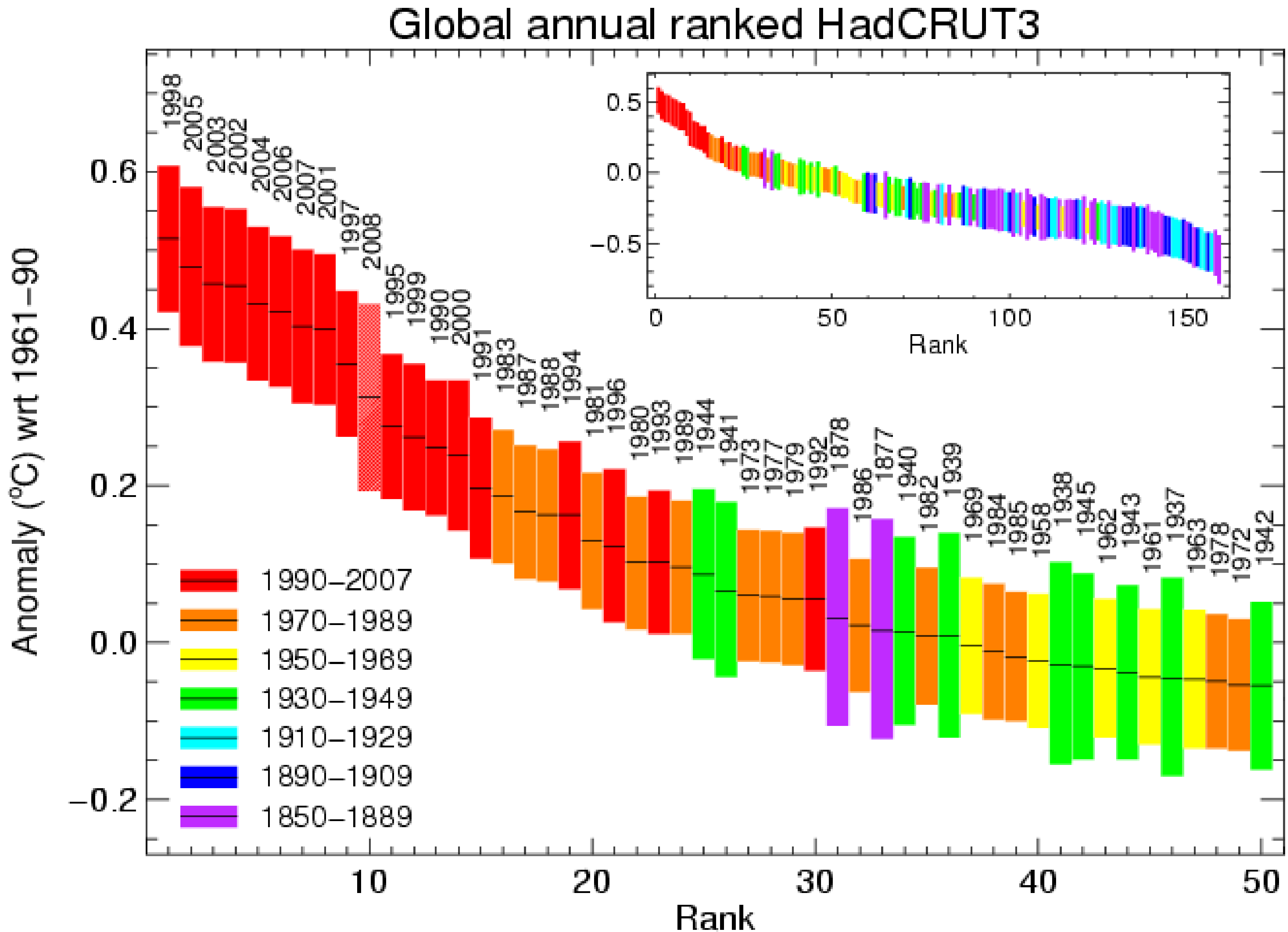
Sources have been discussed

Net effect is small: while they absorb IR themselves, they also cool the stratosphere by hindering the Chapman mechanism

Use of CFCs in refrigerants reduced the energy requirements of those machines, reducing CO_2 emissions

The Future:

- CFCs themselves will clearly decline in importance
- How important will HCFCs and HFCs be?



Global annual ranked HadCRUT3
Anomaly (°C) wrt 1961–90
Rank
1990–2007
1970–1989
1950–1969
1930–1949
1910–1929
1890–1909
1850–1889

Additional Signs of Climate Change over the last 100 years

- **The 12 hottest years on record have all occurred since 1995**
- Winters (first frost to last) have become shorter by about 11 days
  - Fewer “frost days” endanger permafrost
- The Earth’s ice cover is rapidly shrinking
  - About 10% of winter snow cover and sea ice is gone
- Warming water is killing coral reefs and other sea life
  - 95% of coral bleached in Seychelles, now spreading to Caribbean
- Mosquito-borne diseases have spread to higher altitudes
  - Dengue fever in Central America
  - Malaria in Texas, Florida, Michigan, New York, New Jersey, *Ontario*
- Rising sea levels threaten Pacific islands
  - Average level has risen more than 10 cm since 1940
- Extreme weather is becoming more common – both in frequency and in intensity
  - Hurricanes, blizzards, heat waves, drought
- What does the future hold?