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An introduction to atmospheric chemistry

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An introduction to atmospheric chemistry

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Lecture outline

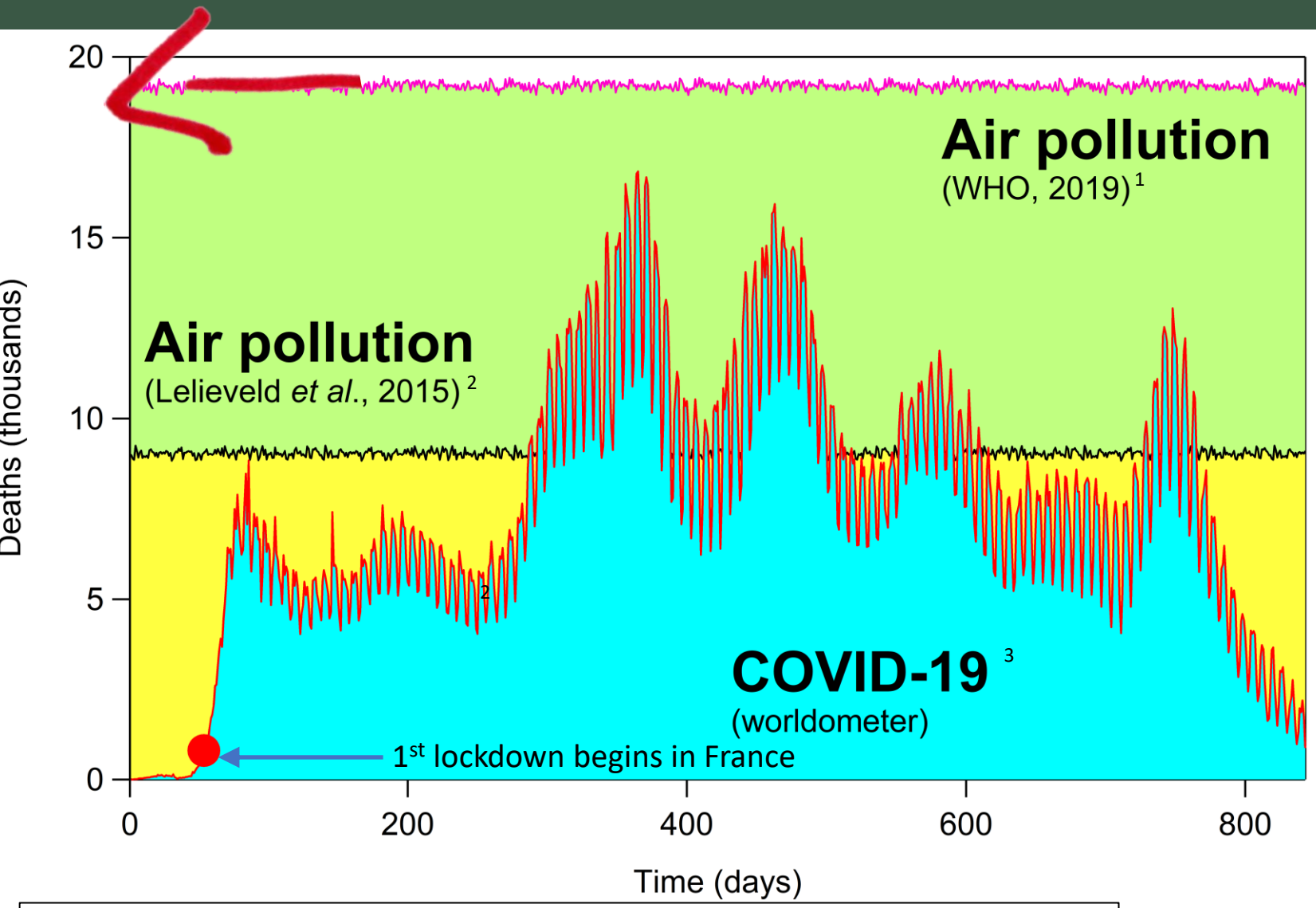
- Why does chemical composition matter?
  - Air quality
  - Climate
- Getting to know the atmosphere
  - Physical attributes (structure, temperature, pressure)
  - Chemical composition
- Chemical reactions in the troposphere
- Chemical reactions in the stratosphere
- Approaches to studying the atmosphere

Part 1 – Why does chemical composition matter?

"the simple act of breathing is killing 7 million people a year and harming billions more"

Dr. T.A. Ghebreyesus, head of the World Health Organization

Air pollution: an invisible pandemic?



Time-series showing the global daily fatalities due to air pollution/ COVID-19

- Impact of our emissions is defined by atmospheric chemistry
- Air pollution is atmospheric chemistry
- Air pollution is an urgent problem
- And it will get worse in the future[2]
- The only vaccine is to understand it and legislate against it
- **But there is still so much that we don't yet understand**

[1] https://www.who.int/news-room/detail/02-05-2018-9-out-of-10-people-worldwide-breathe-polluted-air-but-more-countries-are-taking-action

[2] Lelieveld, J. *et al*. The Contribution of Outdoor Air Pollution Sources to Premature Mortality on a Global Scale. Nature 2015, 525 (7569), 367–371

[3] https://www.worldometers.info/coronavirus/coronavirus-death-toll/

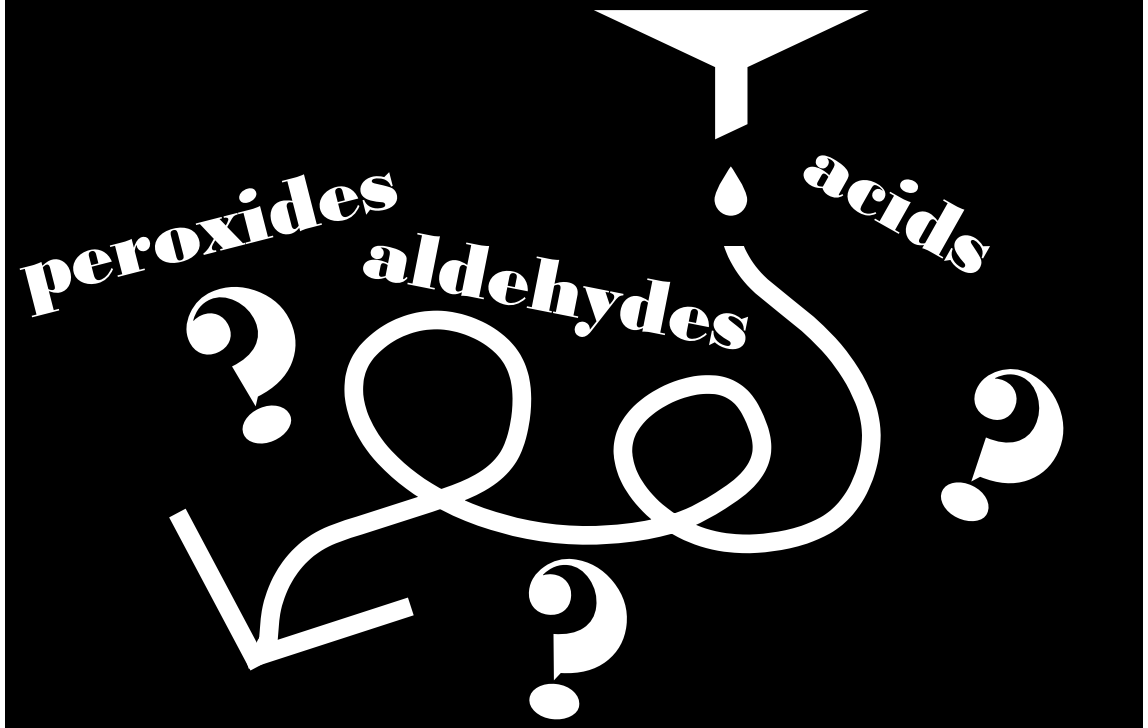
Air pollution: an old problem

Air pollution episode	Date	Cause	Consequences
Meuse River Valley, Belgium	1930	High concentrations of SO_2 in the atmosphere during a temperature inversion	63 people died and thousand sick
Donora, Pennsylvania, USA	1948	High concentrations of SO_2 coupled with temperature inversion and foggy weather	20 people died due to cardiac respiratory disease and about half of town's 12,000 residents complained of cough, respiratory tract irritation, chest pain, headaches, nausea, and vomiting
Poza Rica, Mexico	1950	Natural gas plant inadvertently released hydrogen sulphide coupled with temperature inversion and foggy weather	22 people died and 320 were hospitalized
London, England	1952	A five day temperature inversion trapped deadly acid aerosols in the atmosphere	8000 deaths. Over 4000 succumbed to bronchitis, pneumonia, and respiratory and cardiac disease

Air pollution: a brief history

What we knew in the 1950s:

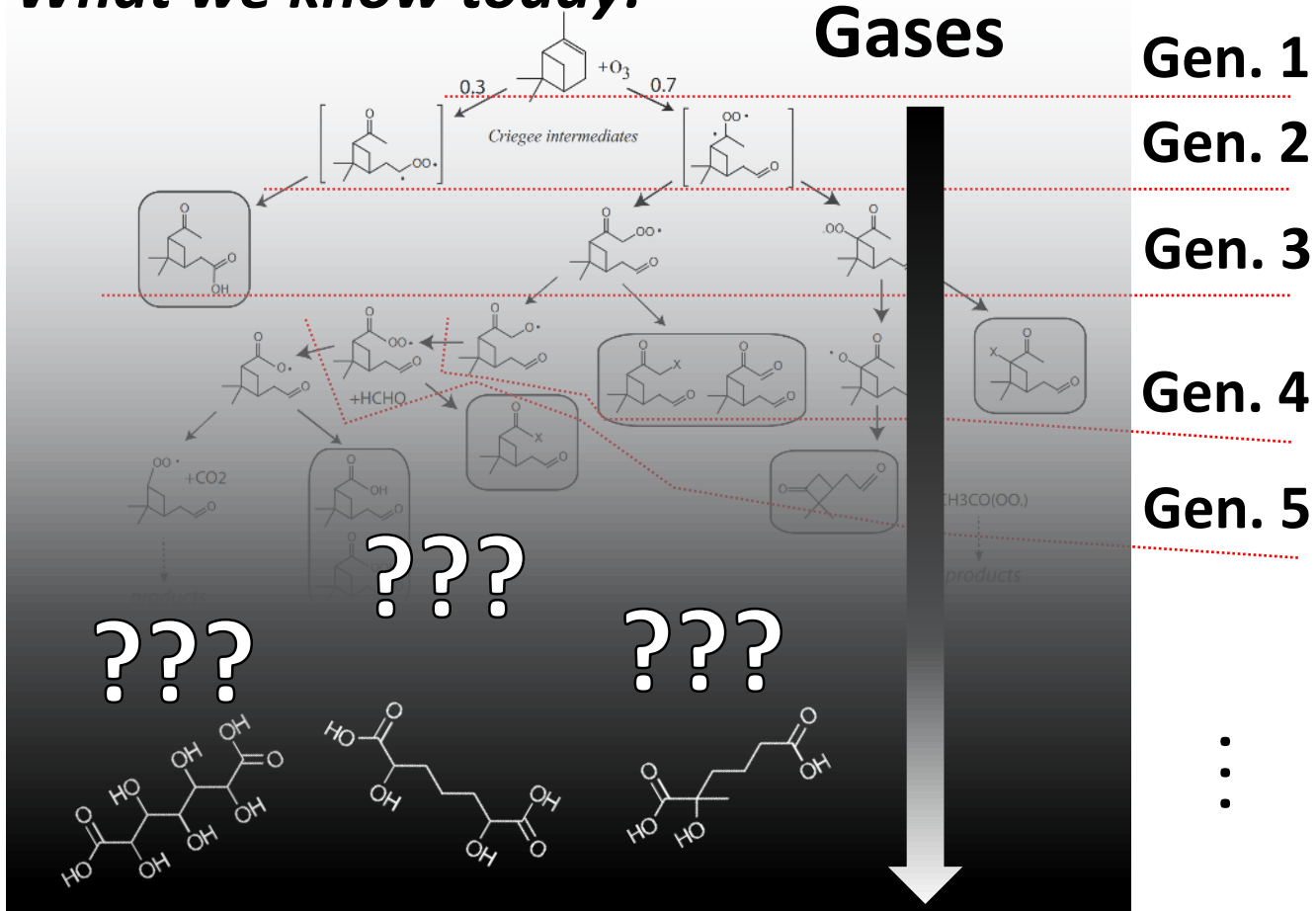
Hydrocarbons + NO_x + sunlight + SO_2



SMOG/Aerosols

Adapted (radically) from: Haagen-Smit (1952)

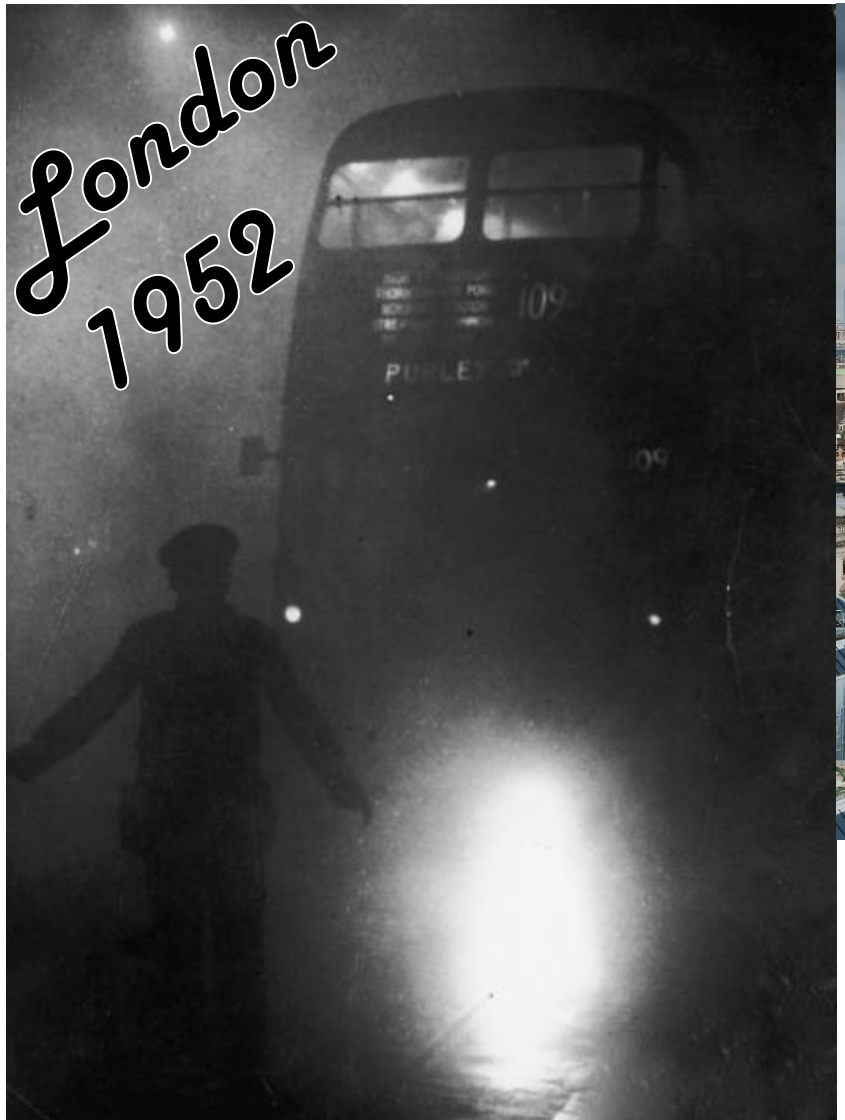
What we know today:



+ H_2SO_4, + HNO_3, + … = Aerosols

Sources: Valorso et al. (2011), Gao et al. (2004)

Is air pollution a thing of history?

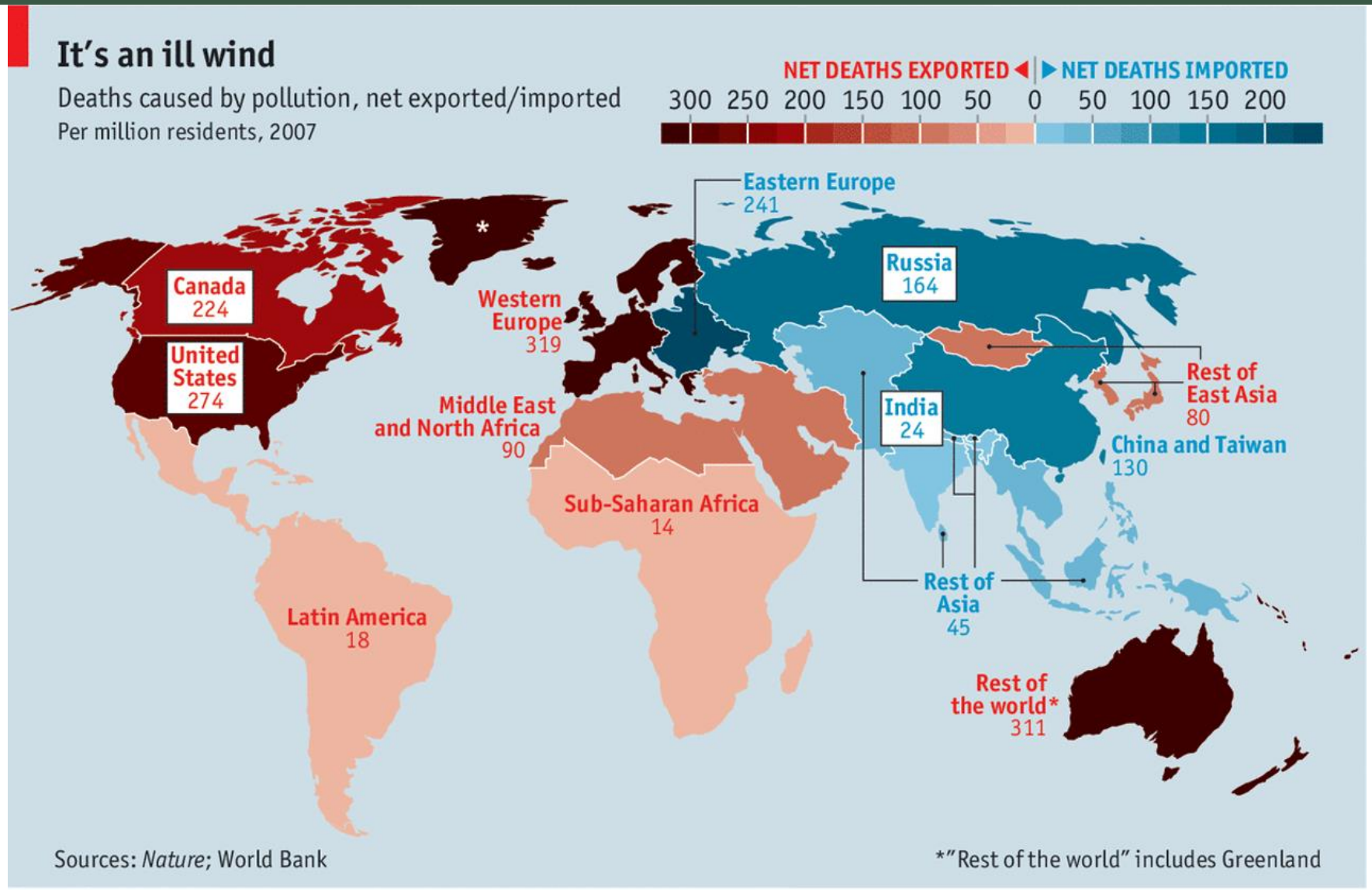


It depends on your perspective

Is air pollution a thing of history?

Clearly not

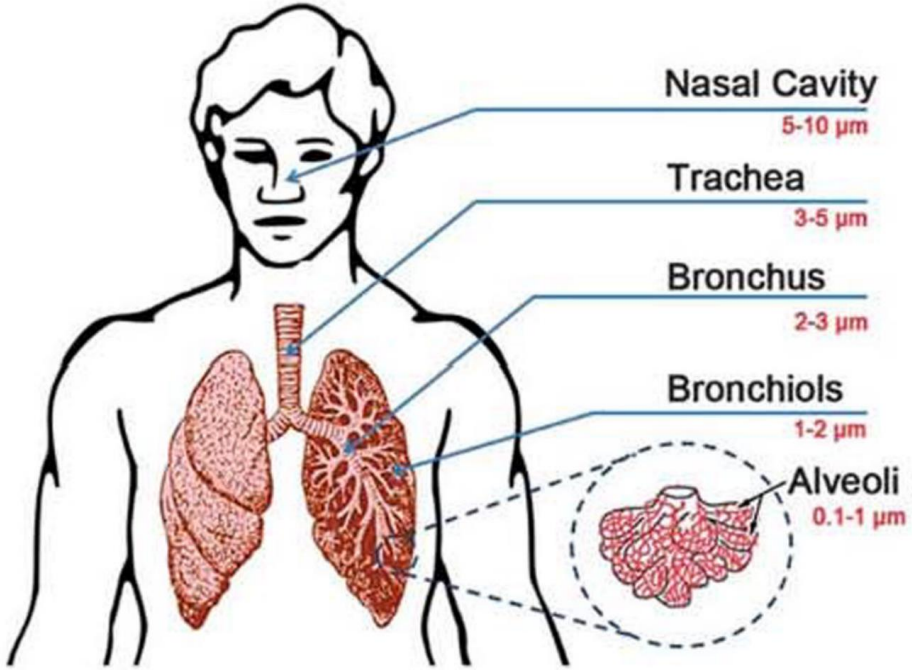
The export of pollution



Economist.com

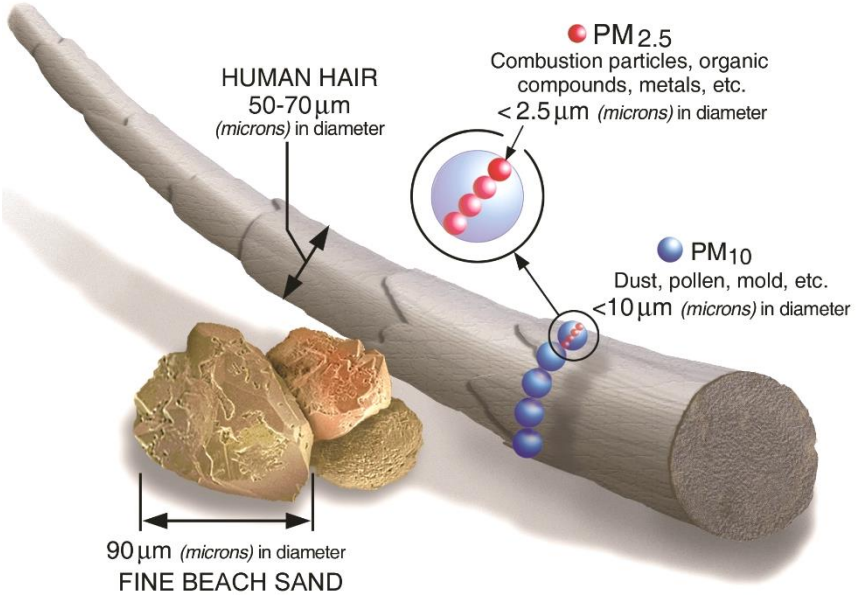
- The Global North is transitioning away from industrialization
- But our appetite for consumer goods and resources has increased
- As a consequence, we are seeing an explosion of pollution in the developing world
- Note: this figure is from 2007, the geopolitical picture is changing fast
- What about Africa?

The health effects of air pollution



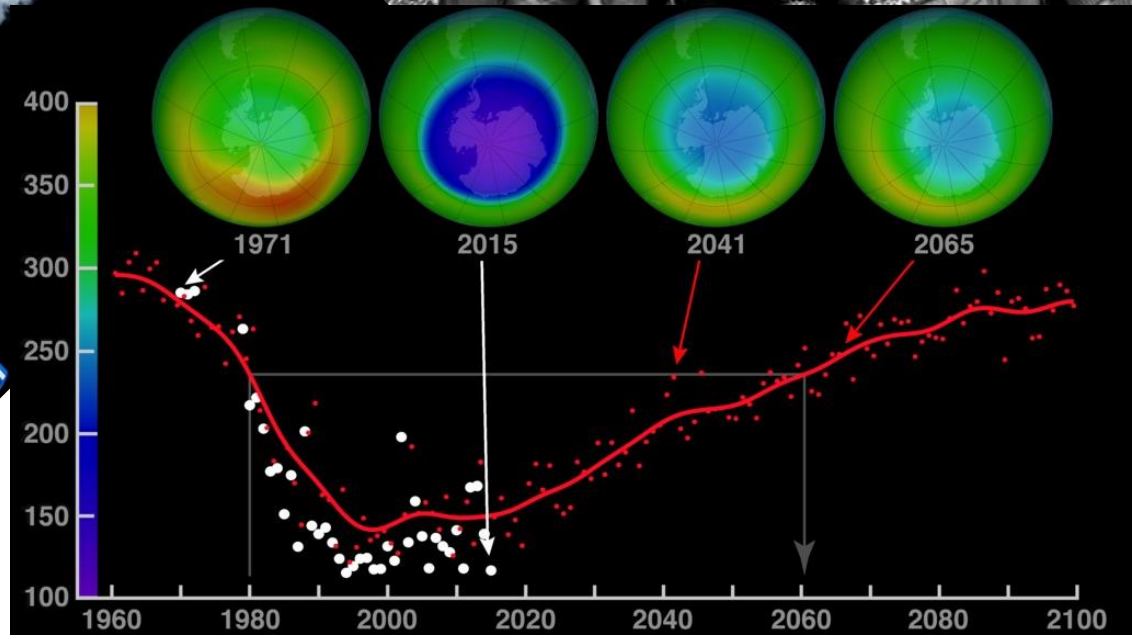
- Fine particulate matter is considered be the most dangerous component of air pollution
- These are the most aerodynamic/ mobile particles and they can reach the alveoli
- It is suspected that chemical composition may play a role in toxicity of particulates

- Lung cancer and chronic obstructive pulmonary disease are very bad outcomes
- But many other conditions are correlated with air pollution: asthma, dementia, COVID deaths
- Even behavioural patterns and cognitive ability



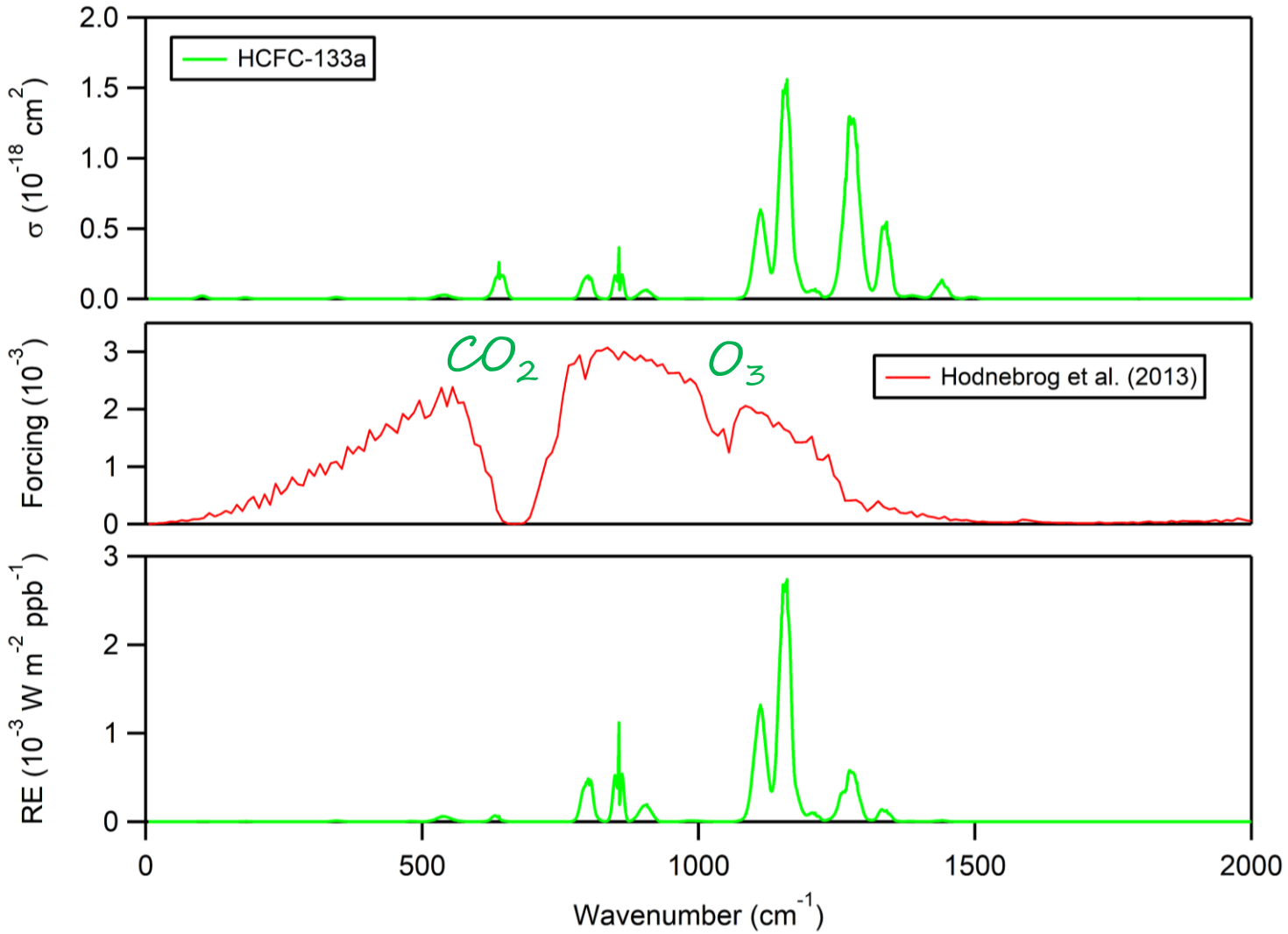
The ozone hole

- The use of ozone-depleting substances starting in the 1960s has had a profound effect on the upper atmosphere
- These chemicals were used in a large variety of applications (not only hairspray!)
- This can be viewed as stratospheric air pollution



Climatic effects

- Many pollutants (such as CO_2) absorb infrared radiation
- Some pollutants absorb strongly in the atmospheric "window" → radiative efficiency (RE)
- Some pollutants are highly persistent in the atmosphere, leading to a high global warming potential (GWP)
- Some of the worst greenhouse gases can have a GWP 1000s of times higher than CO_2

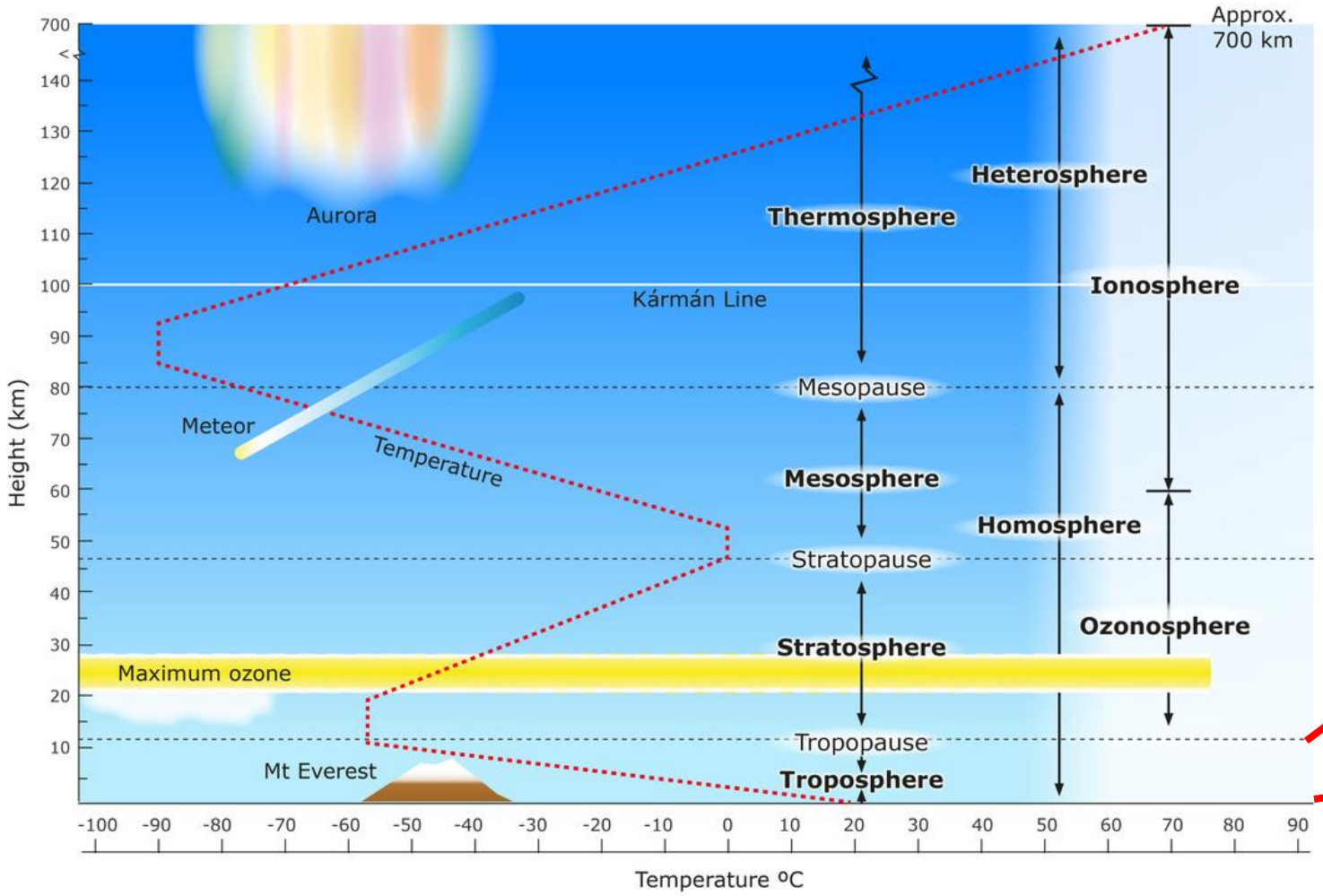


Conclusions:
Part 1 – Why does air pollution matter?

- Air pollution is estimated to kill millions of people each year
- It impacts the lives of billions
- It's less problematic now than it was (in the developed world)
- But it's becoming worse (in the developing world)
- Air pollution now kills more people than tobacco (a lifestyle choice)
- Breathing is not a lifestyle choice, it is a necessity!
- + we should not forget the climatic effects that will impact the whole world

Part 2 – Getting to know the atmosphere

Physical attributes (structure)



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- The atmosphere is categorized as a set of layers
- We spend almost all of our time in the planetary boundary layer

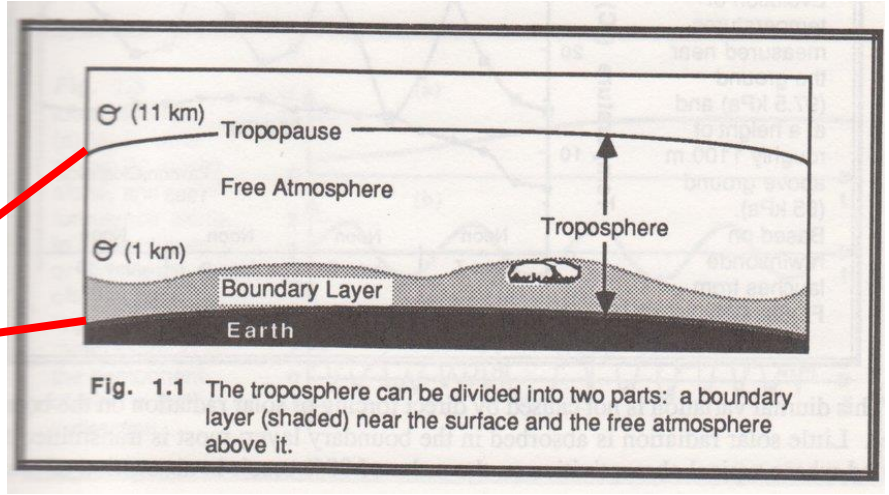
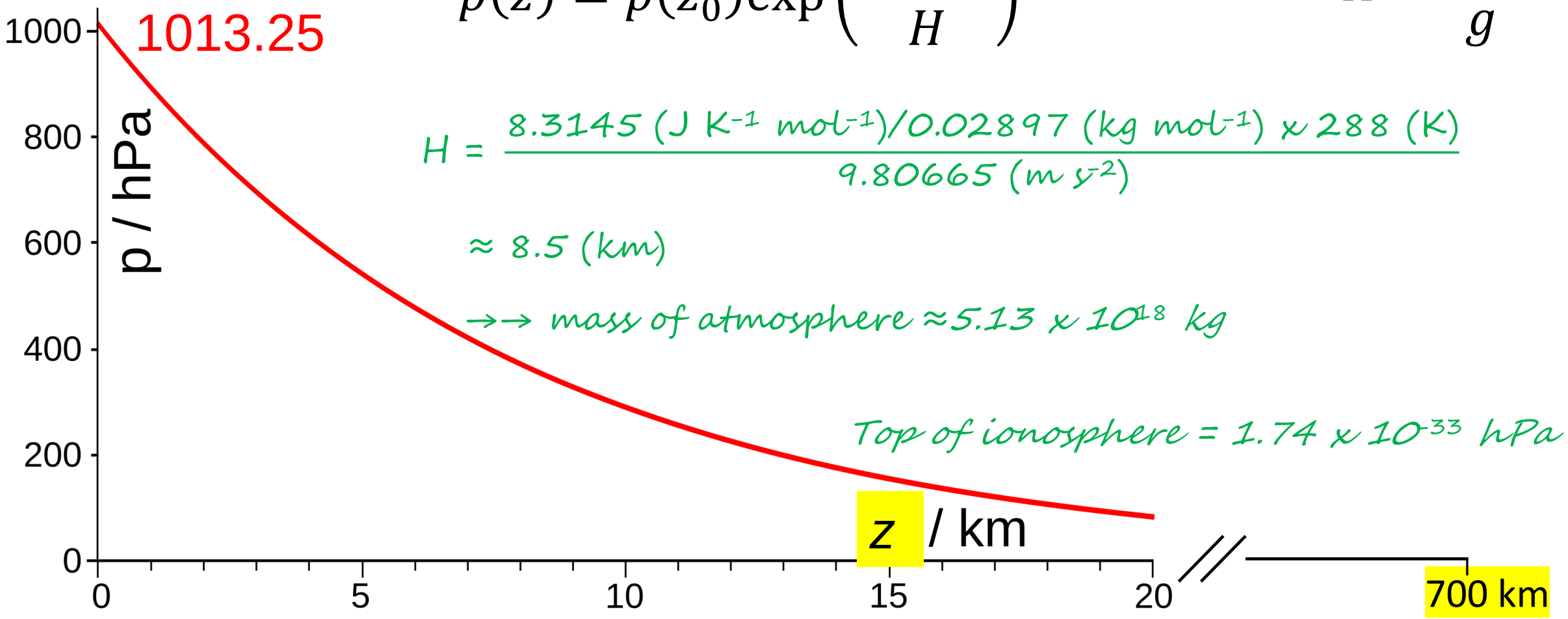


Fig. 1.1 The troposphere can be divided into two parts: a boundary layer (shaded) near the surface and the free atmosphere above it.

Physical attributes (atmospheric pressure)

$$p(z) = p(z_0)\exp\left(\frac{z - z_0}{H}\right) \quad \textit{where:} \quad H = \frac{RT}{g}$$



$$H = \frac{8.3145\ (\mathrm{J\ K^{-1}\ mol^{-1}})/0.02897\ (\mathrm{kg\ mol^{-1}}) \times 288\ (\mathrm{K})}{9.80665\ (\mathrm{m\ s^{-2}})}$$

≈ 8.5 (km)

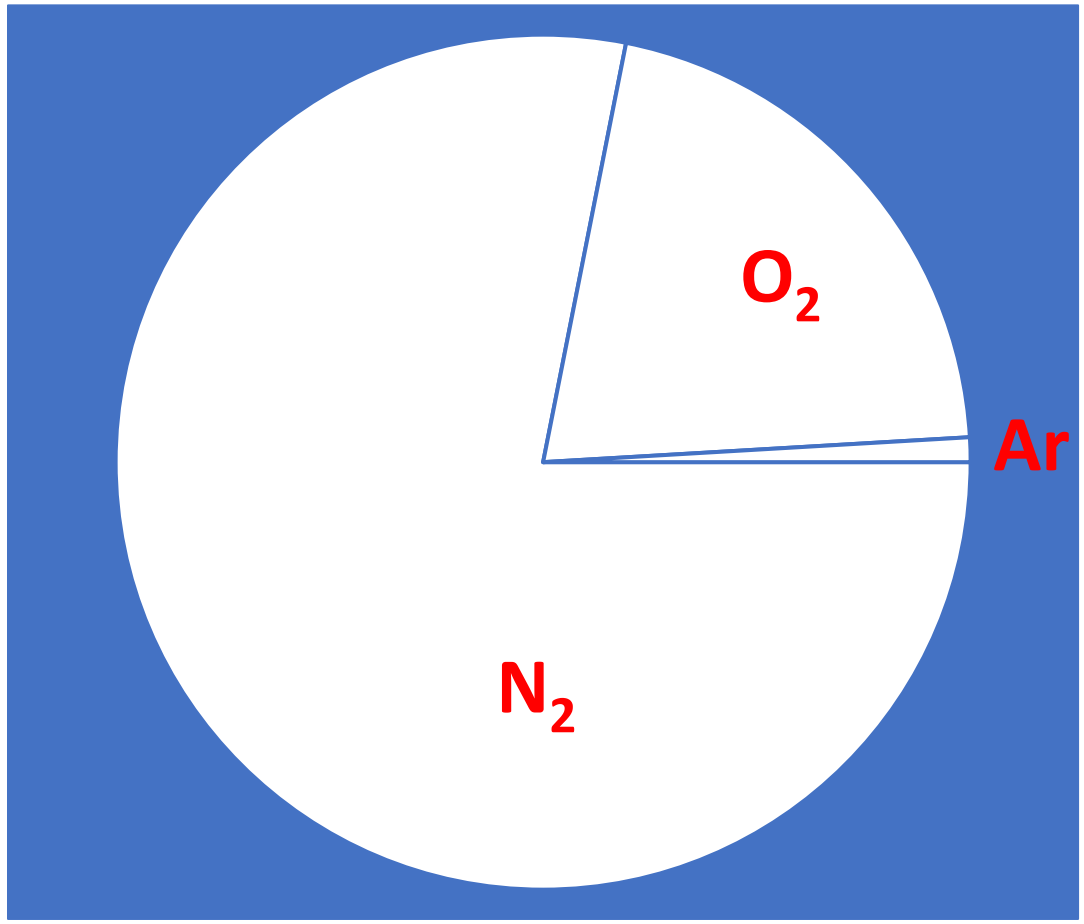
→→ mass of atmosphere $\approx 5.13 \times 10^{18}$ kg

Top of ionosphere = 1.74×10^{-33} hPa

Physical attributes (in context)

- In terms of spatial extent: the atmosphere is to the solid Earth, what an apple's skin is to its diameter
- In terms of mass: it is a single eyelash lying next to the apple…
- From a physical point of view, the atmosphere is therefore a thin, insubstantial layer

Chemical composition (major components)



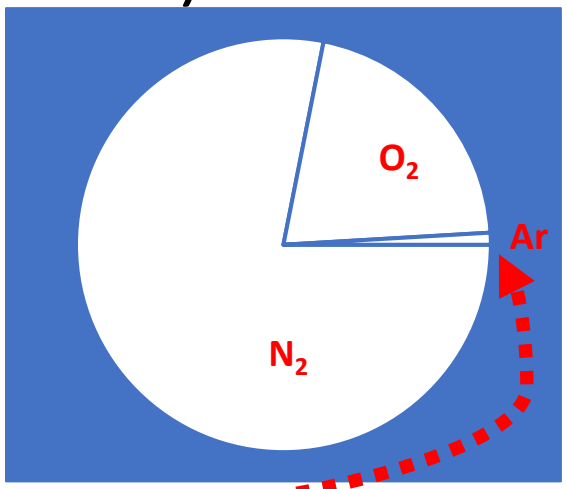
N_2 = 78.08%
O_2 = 20.95%
Ar = 0.93%

$\boxed{99.96\%}$

Most of the atmosphere is very boring!

Chemical composition (trace components)

Gas	Mixing ratio	Source(s)
Carbon dioxide	420 (ppm)	Combustion, ocean, biosphere
Methane	1.7 (ppm)	Biogenic, anthropogenic
Helium	5.2 (ppm)	Radioactive decay, anthropogenic
Nitrous oxide	0.31 (ppm)	Biogenic, anthropogenic
Ozone (stratosphere)	0.5–10 (ppm)	Photochemical
Ozone (troposphere)	10–500 (ppb)	Photochemical
Carbon monoxide	50–200 (ppb)	Photochemical, combustion
Formaldehyde	0.1–1 (ppb)	Photochemical, anthropogenic
NMHCs	ppqs–ppbs	Photochemical, anthropogenic, biogenic
Hydroxyl radical (daytime)	~ 40 (ppq)	Photochemical



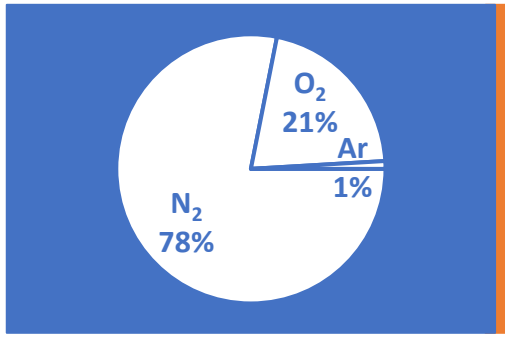
Total = 0.0438% (+99.96%) = 100.0038%

How has Earth's atmosphere changed?

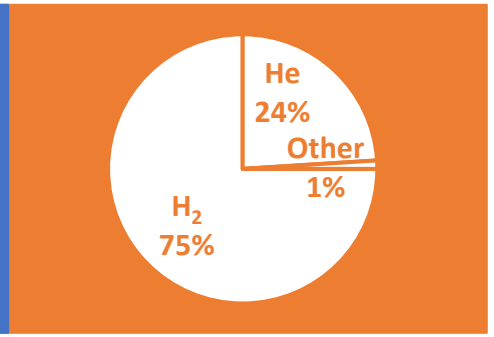
- Earth's atmosphere was very different millions/ billions of years ago
- The evolution of photosynthetic organisms transformed much of the CO_2 into O_2
- Further back in time, Earth's atmosphere would have contained much more of the most abundant components of the solar system: hydrogen and helium
- Because of atmospheric escape, most has been lost to space

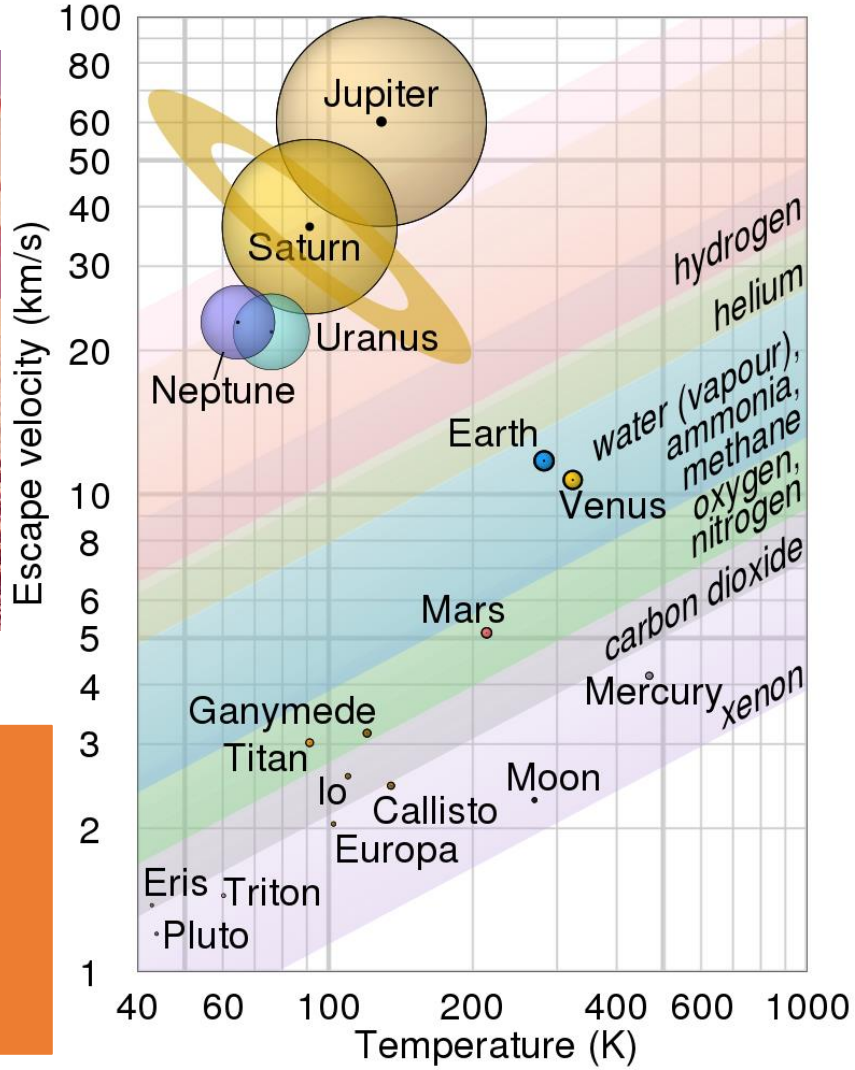
Prebiotic Earth

Earth

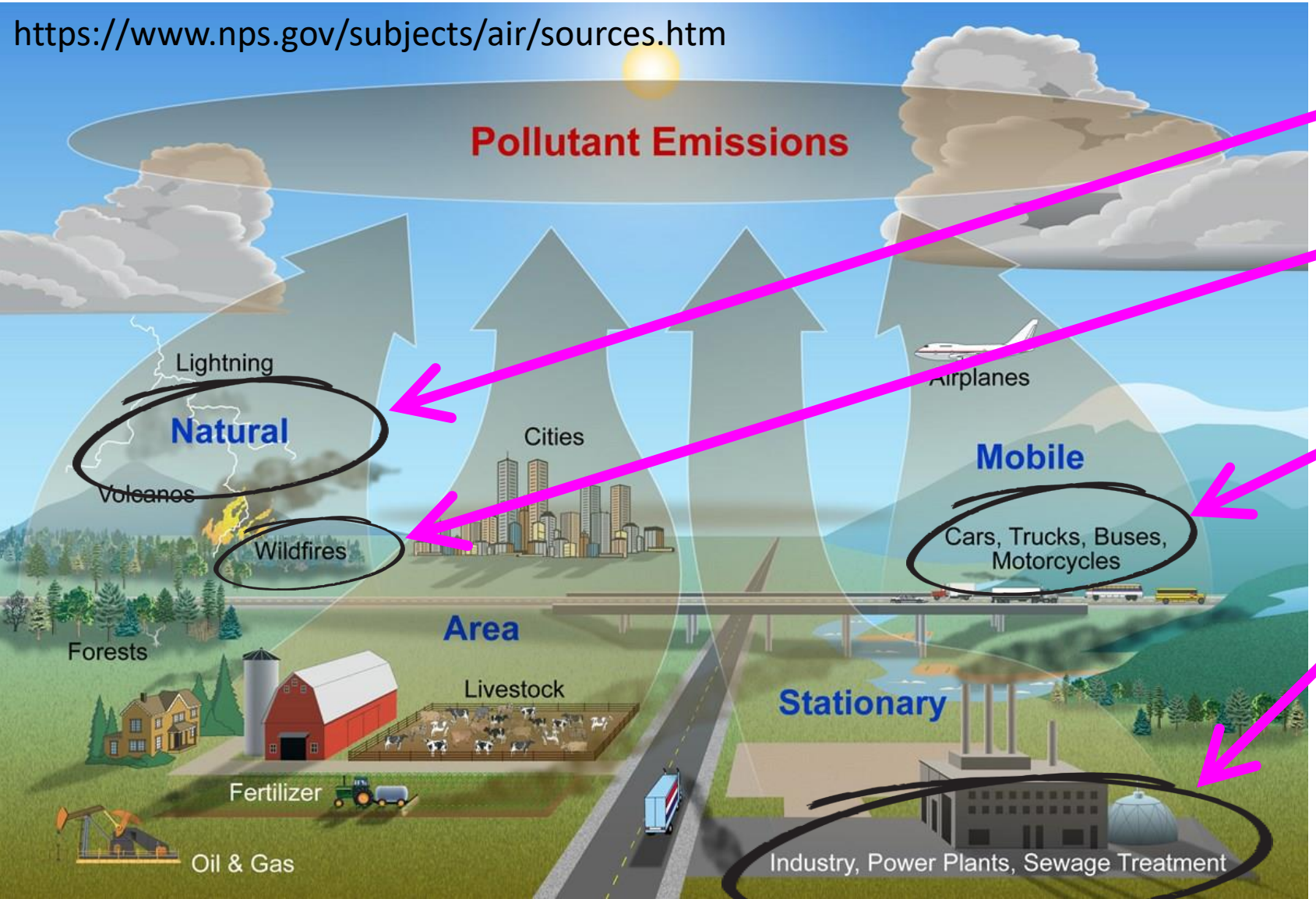


Jupiter





Atmospheric emissions



- 55,000 different terpenoid species known to science
- Wildfires, >10,000 species identified in the tar-ball component of a single burning plume
- Hydrocarbon fuels are complex mixtures, containing 10^3–10^4 species (maybe more)
- >75,000 industrial chemicals registered in environmental monitoring networks (US EPA CPDAT)

A paradox: low concentration, big effect

- How can things at such low concentrations be so important?
- **Possibility 1:** the mass flux is high

Field concentration: ppts

Atmospheric emission: 5–7.5 x 10^6 tons yr^{-1}

sources → [isoprene] → sinks

- **Possibility 2:** a molecule has a catalytic effect

e.g. stratospheric chlorine sources (see later)

- **Possibility 3:** high toxicity

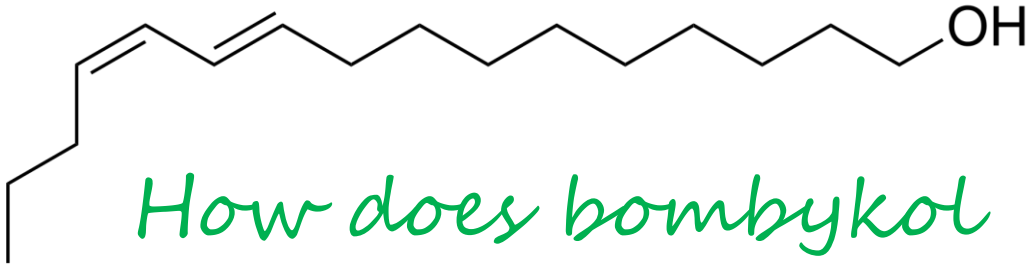
high specific toxicity / high collective toxicity

- **Possibility 4:** extremely sensitive effect

aerosol nucleation / infrared absorption / catalytic behaviour / biological role

VOCs and ecosystems

- The most sensitive VOC detectors on Earth are not in our laboratories
- Certain species of insect are hypothesized to be able to detect single molecules
- We are capable of measuring 10s of ppq levels with certain mass spectrometric and fluorescence techniques (if we are lucky)
- For a sample volume of 1 cm^3 at atmospheric pressure and room temperature, this is >2.5 x 10^5 molecules



How does bombykol behave in the atmosphere?

Conclusions
Part 2 – Getting to know the atmosphere

- We live in a thin, fragile and insubstantial part of the Earth system
- Most of the atmosphere is relatively inert
- Earth's atmosphere has changed a lot since it was formed
- Trace components affect air quality, climate, ecosystems
- These are the things that react…

Part 3 – Chemical reactions in the troposphere

The atmosphere as a combustion engine

- Much like an engine, the atmosphere is an oxidizing environment
- The volatile organic compounds (VOCs) emitted to the atmosphere represent the fuel
- What we learned at school:

$$Fuel + O_2 \rightarrow \rightarrow CO_2 + H_2O$$

- However, under ambient (and most other) conditions, these things don’t react together…

Getting things started…

- Atmospheric chemistry is a complex set of cycles, and it's difficult to choose a starting point!
- Remember, the atmosphere is mostly N_2, O_2 and Ar with trace VOCs
- But none of these things react together…
- We need some extra ingredients: NO_x, sunlight, O_3, organic molecules

Reactive nitrogen

Energy source

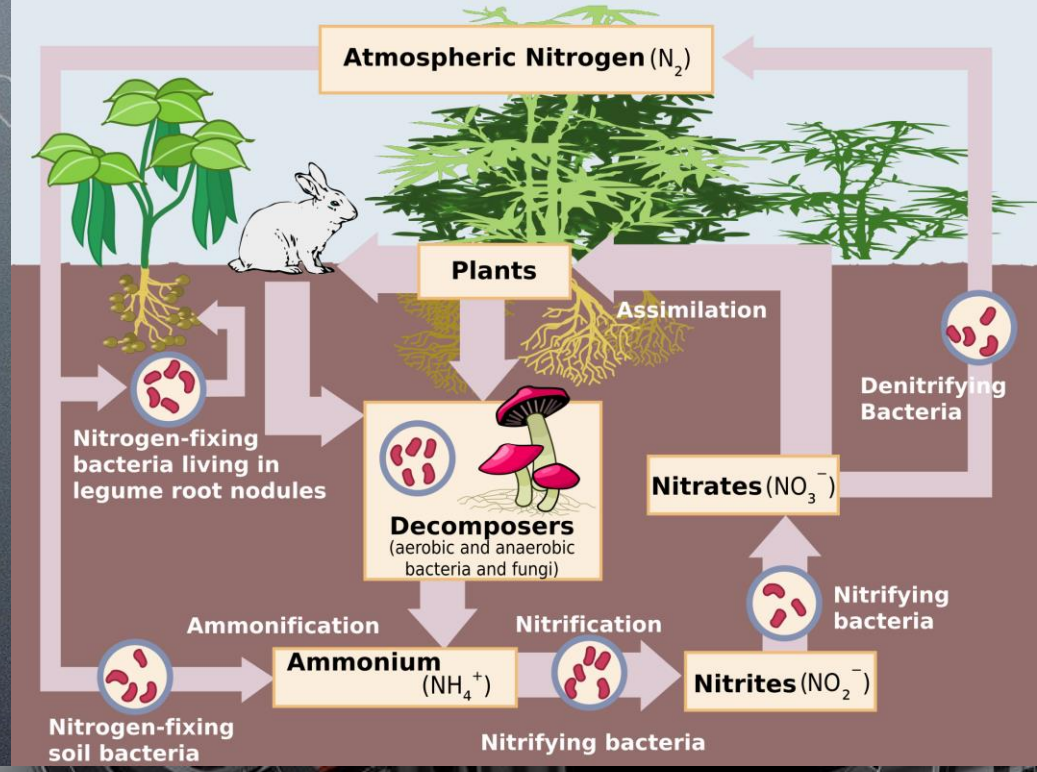
Ozone

Fuel

- These create the conditions for the autocatalytic oxidizing environment of the troposphere

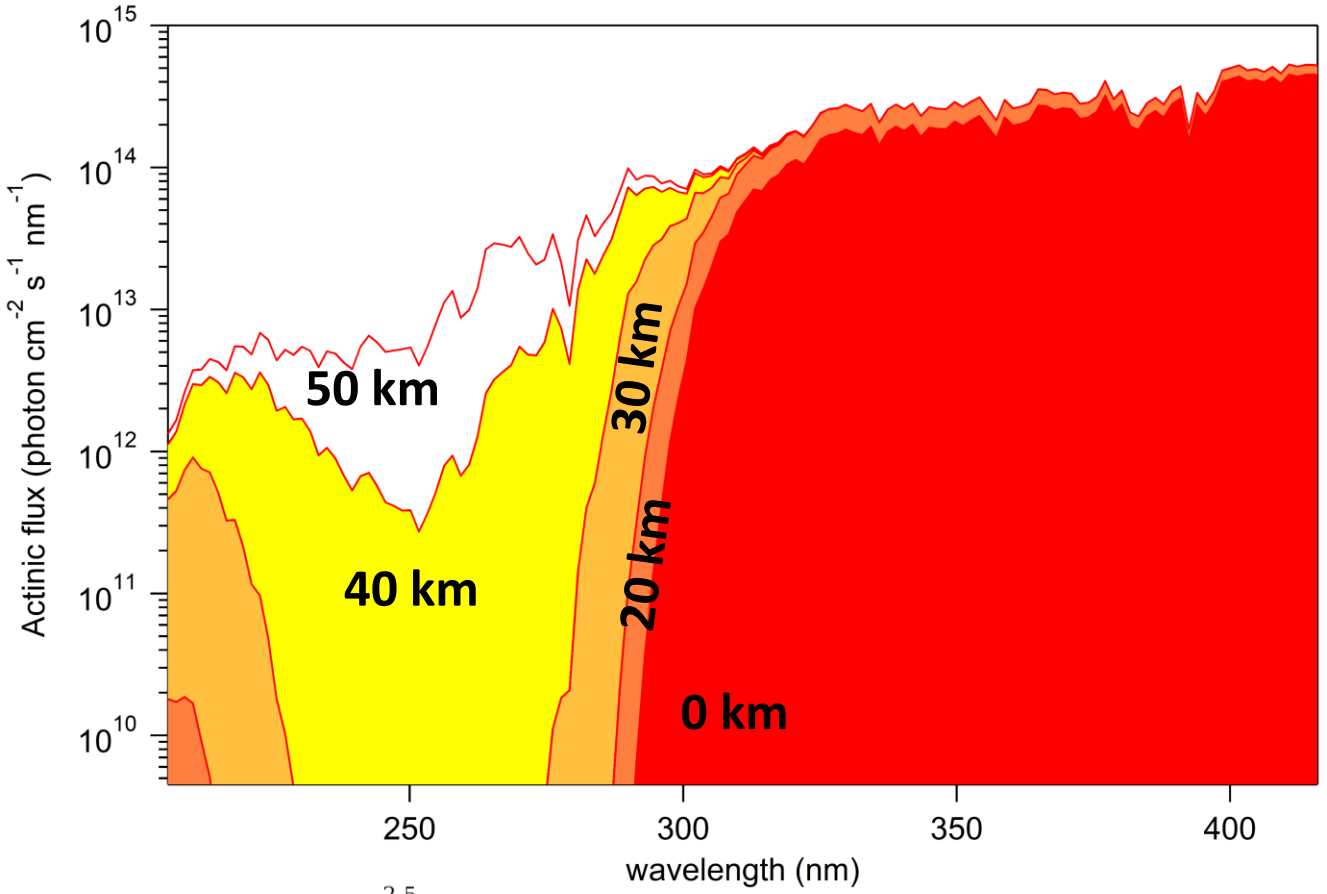
Ingredient 1: fixed nitrogen

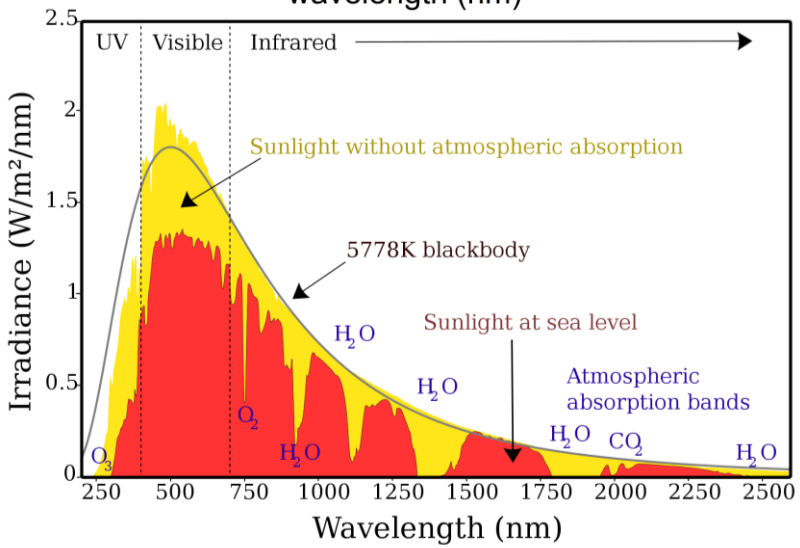
- Most nitrogen is present in a highly unreactive form: N≡N (BDE = 226 kcal mol^{-1})
- Nitrogen "fixation" may be biotic or abiotic
- Biotic: biochemical reactions involving the nitrogenase enzyme
- Abiotic: generally involves extreme heat (the core of lightning bolt/ a high-temperature combustion engine)



Ingredient 2: sunlight

- The sun is the energy source
- Top of the atmosphere: solar irradiance resembles 5778K black body
- Ground-level: the layers above act as a filter
- If a molecule absorbs enough energy it can transform…





Photodissociation

- Reaction AB + *hv* ⟶ A + B
- Rate of reaction is given by:

$$-\frac{d[AB]}{dt} = J \times [AB]$$

- *J*, the photolysis frequency, is described as follows:

$$J = \int_{\lambda_1}^{\lambda_2} F(\lambda) \times \Phi(\lambda) \times \sigma(\lambda)$$

Where: $F(\lambda)$ = actinic flux

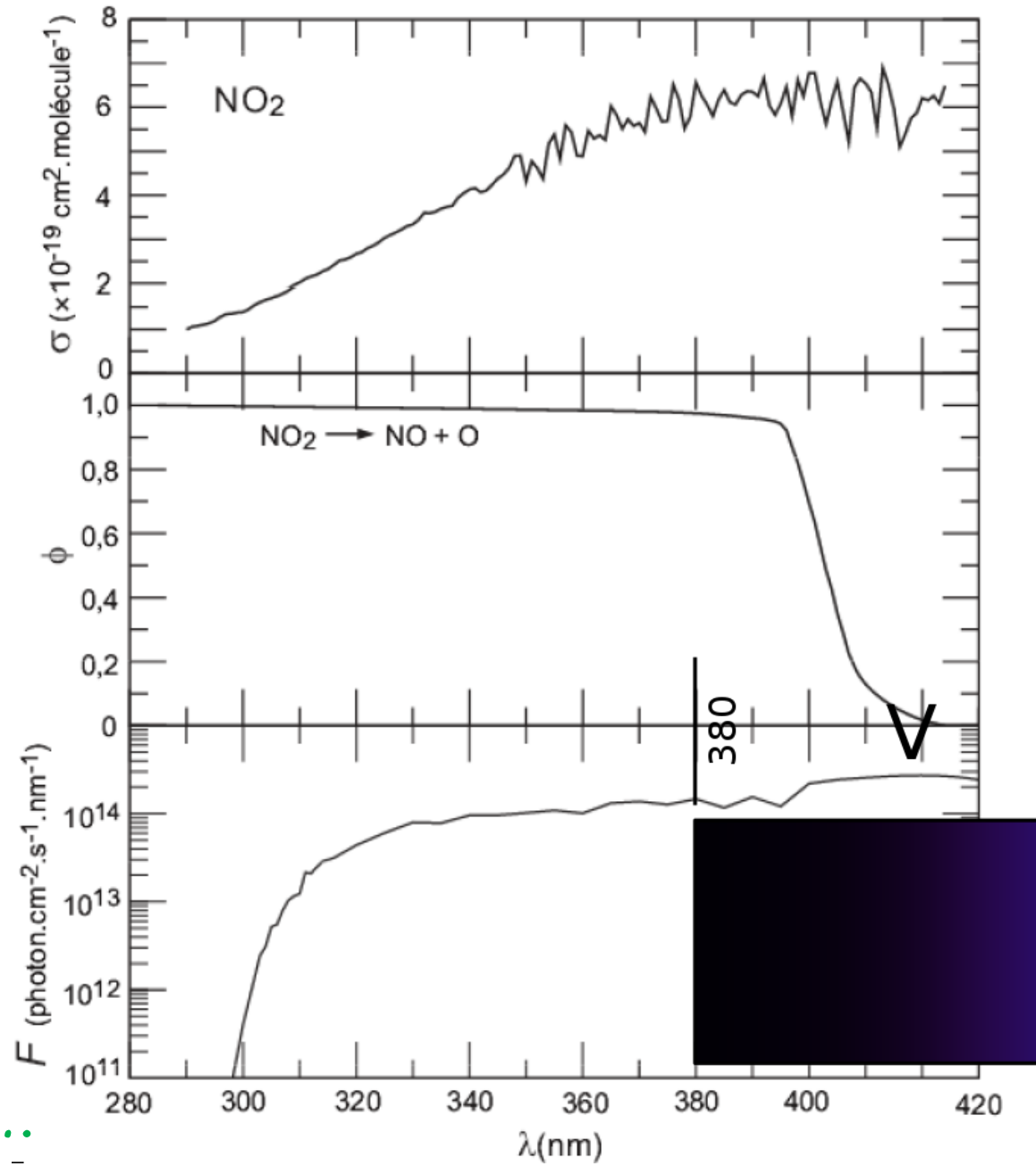
$\sigma(\lambda)$ = absorption cross section

$\Phi(\lambda)$ = quantum yield

$$\Phi(\lambda) = \frac{\#photons\ leading\ to\ reaction}{\#photons\ absorbed}$$

- Example:

$NO_2 + hv \longrightarrow NO + O(^3P)$ $\qquad J(NO_2)$



However, there are other processes besides dissociation...

Ingredient 3: ozone

- Now we have some fixed nitrogen and some sunlight:

$NO_2 + h\nu \longrightarrow NO + O(^3P)$

$O(^3P) + O_2 \longrightarrow O_3$

$O_3 + h\nu \longrightarrow O(^1D) + O_2$

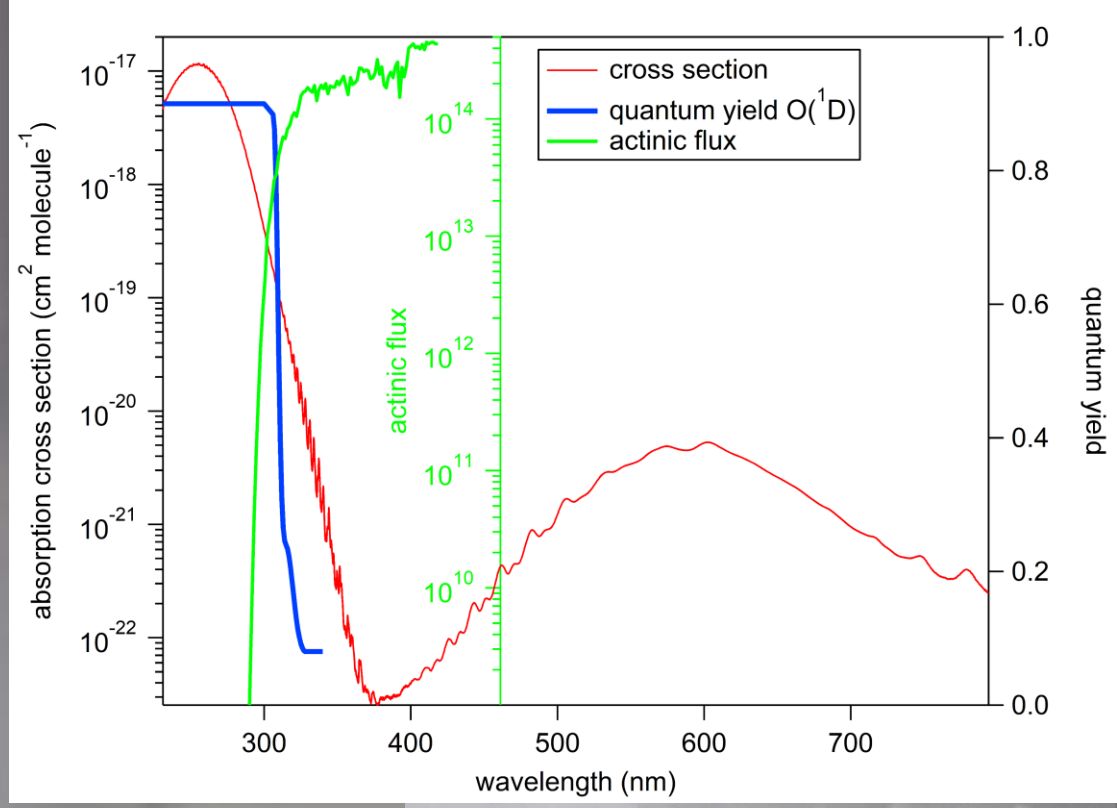
$O_3 + h\nu \longrightarrow O(^3P) + O_2$

$O(^1D) + H_2O \longrightarrow 2OH$

$RCHO + h\nu \longrightarrow R + CHO$

$CHO + O_2 \longrightarrow HO_2$

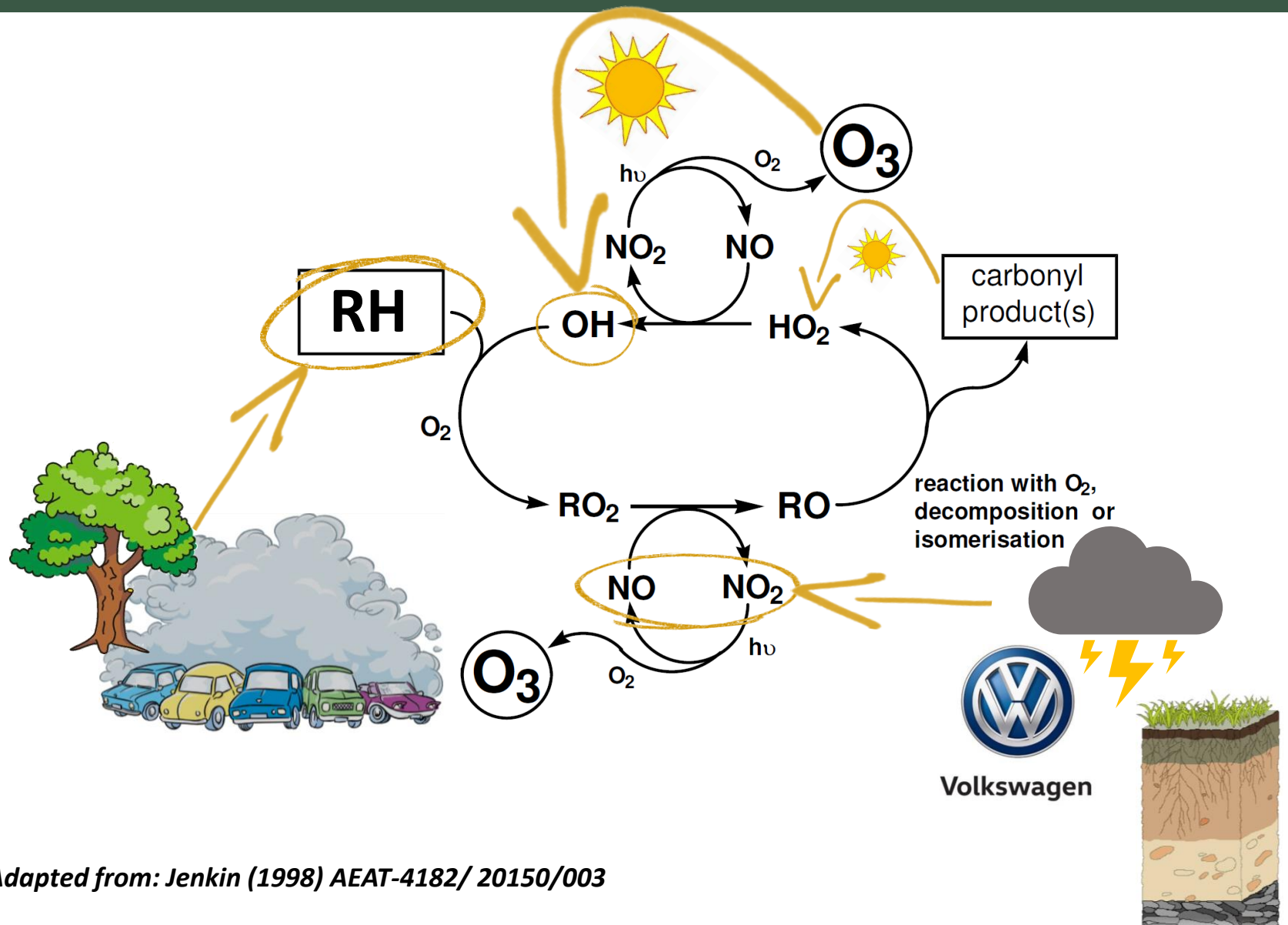
$HO_2 + NO \longrightarrow OH + NO_2$



Ingredient 4: fuel

- Finally, we need the fuel
- In principle, this can be any VOC
- Some fuels are more reactive than others
- This leads to differences in local and regional effects
- Some fuels are “cleaner” than others
- i.e. contain more carbon → longer chemical chain length
- → more efficient aerosol precursors

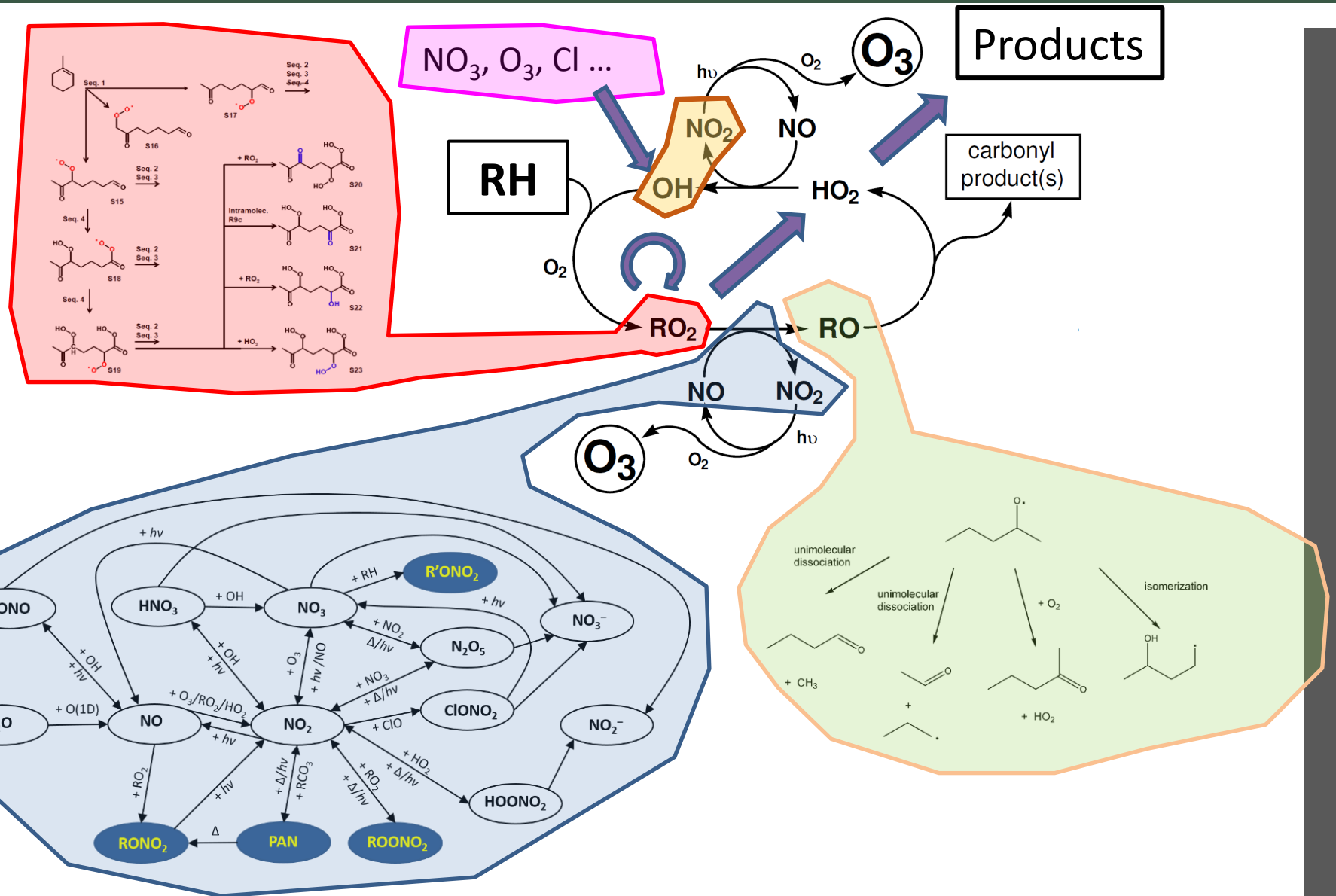
Oxidation in the troposphere



Adapted from: Jenkin (1998) AEAT-4182/ 20150/003

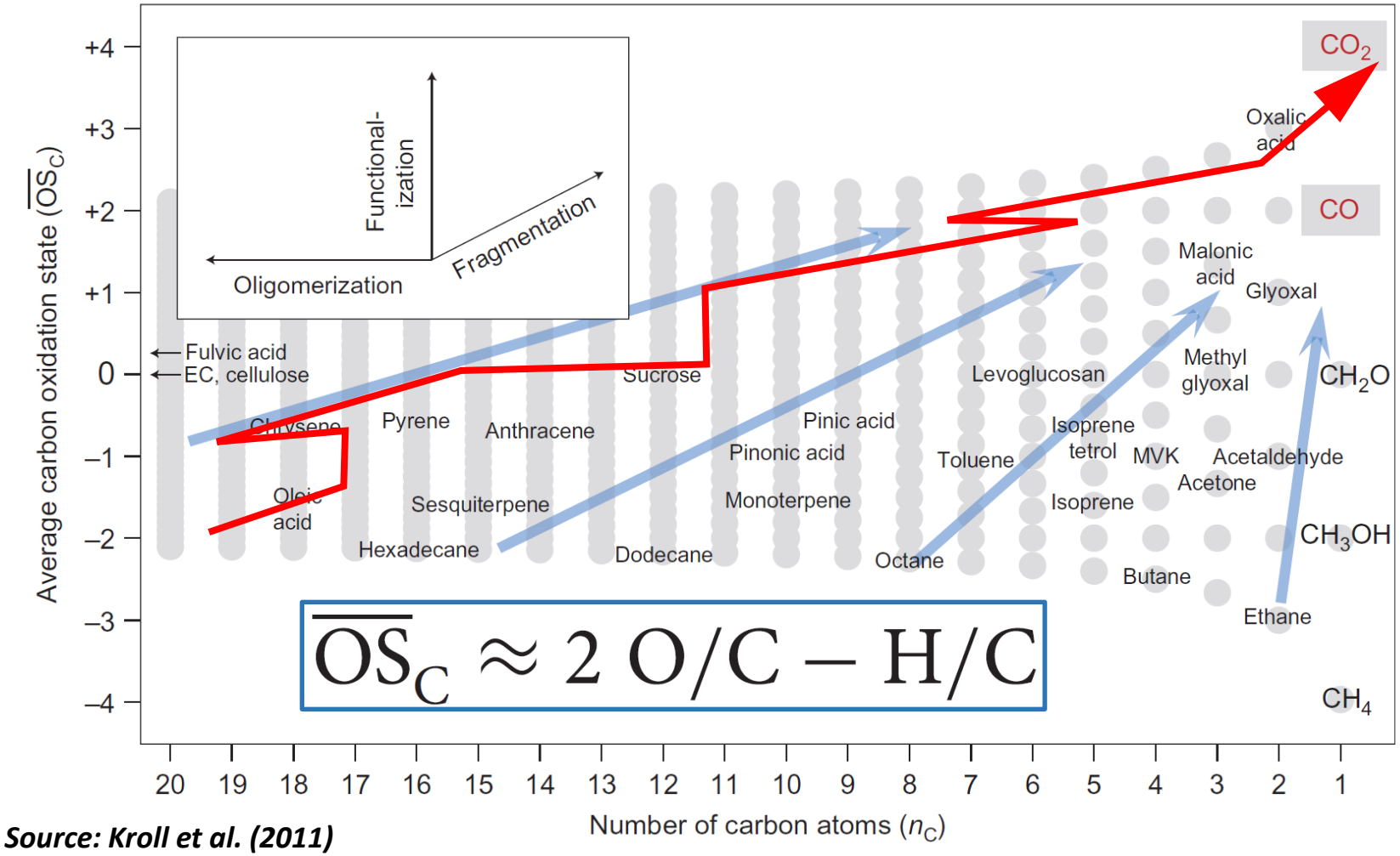
- VOCs are emitted from many sources: trees, vehicles, industries, etc.
- They are consumed by OH, but other oxidants are important (NO_3, O_3, Cl)
- **Oxidants are produced in a collectively autocatalytic set**
- Here, VOCs are transformed into a sequence of carbonyls of diminishing size → CO_2 However…

But life is never that easy…



- **There are many branching channels to consider**
- RO_2 and RO have a high capacity for isomerization and fragmentation
- Separate chemical cycles involving nitrogen and sulphur are important
- What if R contains a heteroatom?

Meandering through oxidation space



$$\overline{OS}_C \approx 2\,O/C - H/C$$

Source: Kroll et al. (2011)

- Atmospheric chemistry is a very cold, very slow combustion
- Eventually, a "fuel" may be converted to CO_2 and H_2O
- **But the path through this space is not simple or direct**
- At what point is atmospheric chemistry unknowable/ unpredictable?

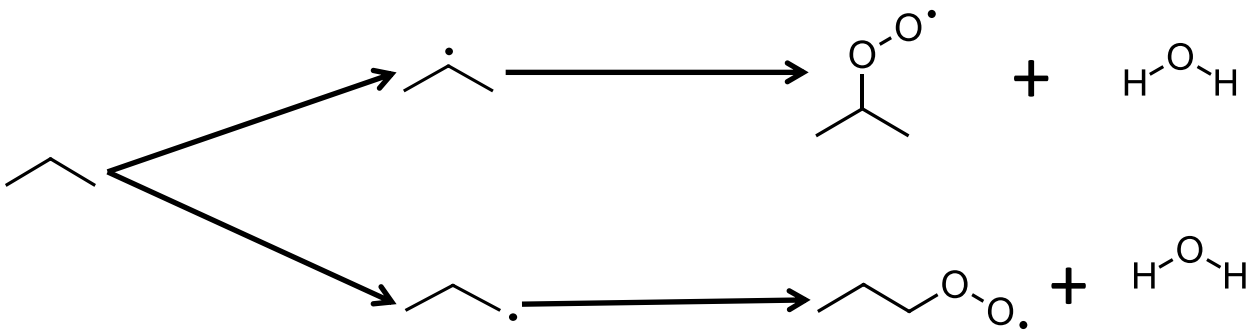
The hydroxyl radical

·O–H

- Also known as the “detergent of the atmosphere”
- Daytime sources: O_3 + *hv*, HONO + *hv*, RCHO + *hv*
- Nighttime source (minor): alkene ozonolysis
- Sinks: reactions with VOCs, reaction with NO_2
- Ambient concentration: ~1×10^6 molecule cm^{-3}
- OH has the balance between high reactivity and high enough concentration to be an effective cleaner of the atmopshere

Hydroxyl radical reactions

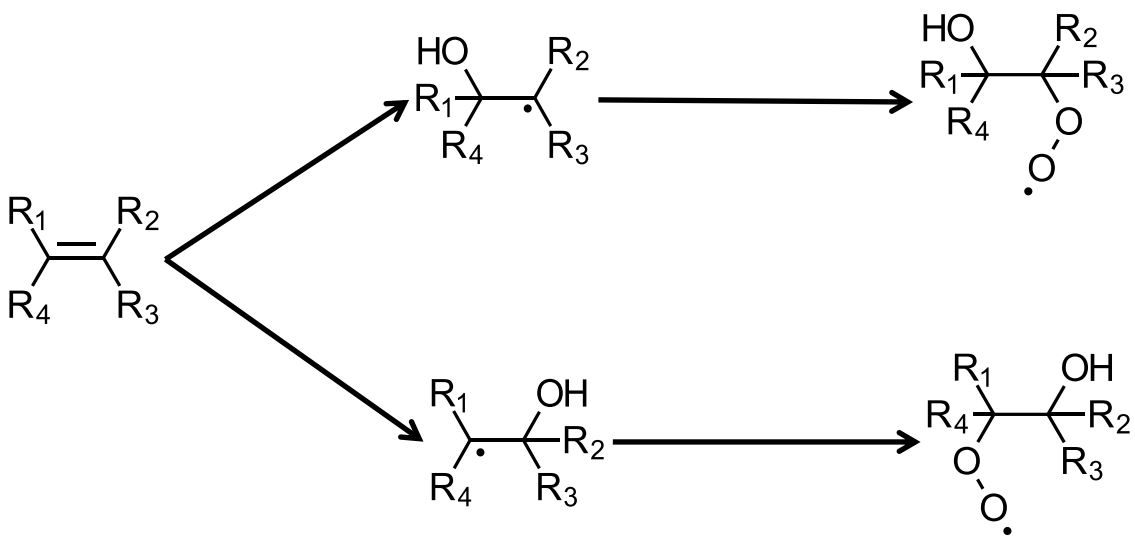
- Hydrogen abstraction



- Comparatively high reactivity with alkanes and other unsaturated species

Hydroxyl radical reactions ·O–H

- Hydroxyl addition



- High reactivity towards alkenes and aromatics
- Add alcohol functionality to alkenes

The nitrate radical

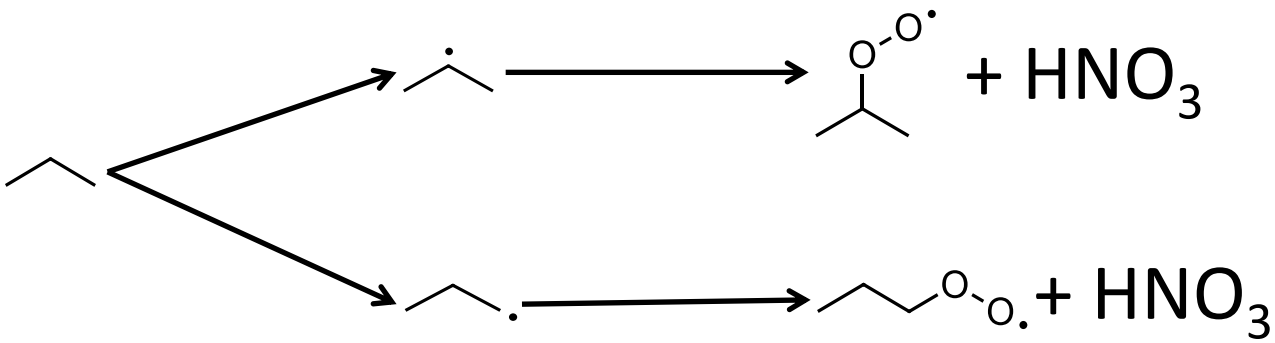
NO_3

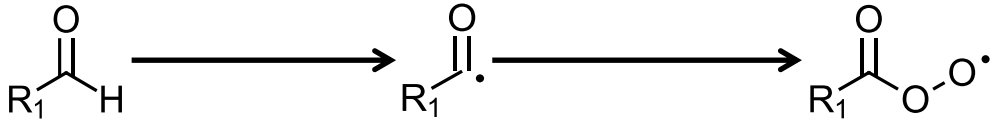
- The nitrate radical can be the most effective oxidant at night
- Nitrate is part of the following equilibrium: $NO_2 + NO_3 \rightleftharpoons N_2O_5$
- NO_3 is most important in areas that are affected by anthropogenic NO_x and ozone
- Sinks: photolysis, reactions with alkenes and NO
- Ambient concentration: ~5×10^8 molecule cm^{-3}
- NO_3 has a very high photolysis cross section in the actinic region, so it is effectively lost during the day

Nitrate radical reactions

NO_3

- Hydrogen abstraction



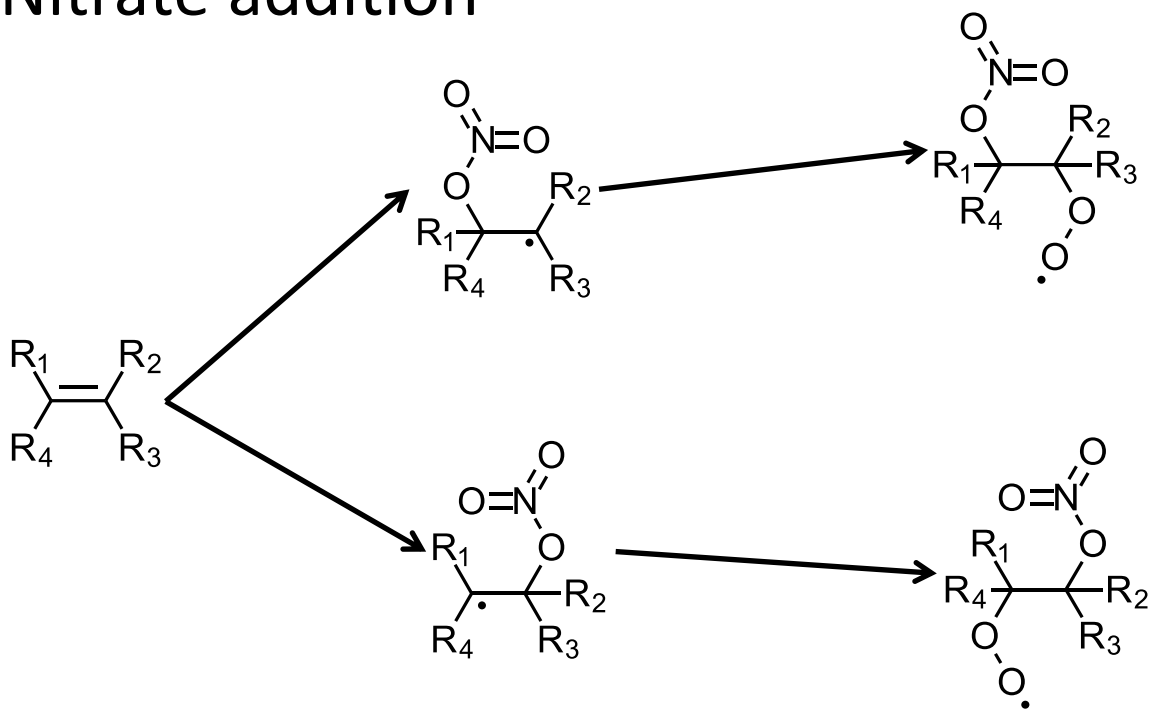


- Generally very low reactivity towards hydrogen abstraction
- Aldehydic C–H bonds are an exception to this rule

Nitrate radical reactions

NO_3

- Nitrate addition



- High reactivity towards activated alkenes
- Adds nitrate and epoxy functionality to alkenes

Atomic chlorine

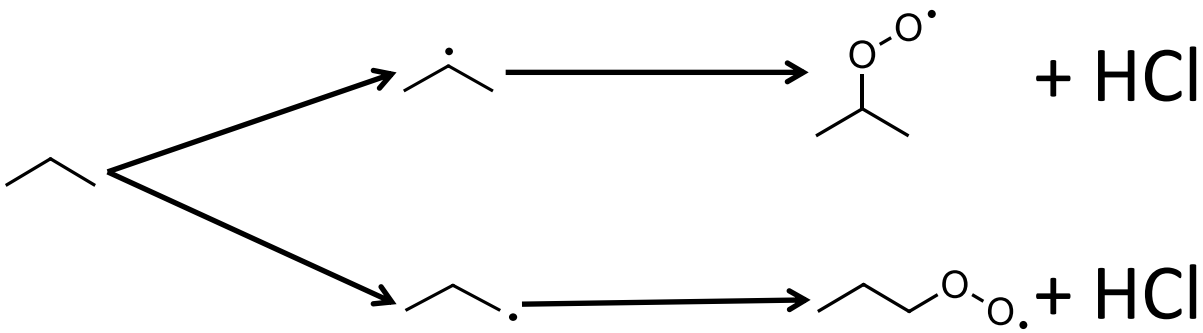
$\cdot Cl$

- Atomic chlorine is one of the most reactive oxidants known
- Typically, higher concentrations are seen in coastal environments
- This is not always the case with longer-lived precursors such as $ClNO_2$
- Sinks: rapid reactions with organic compounds
- Ambient concentration: ~1×10^4 molecule cm^{-3}

Atomic chlorine reactions

·Cl

- Hydrogen abstraction

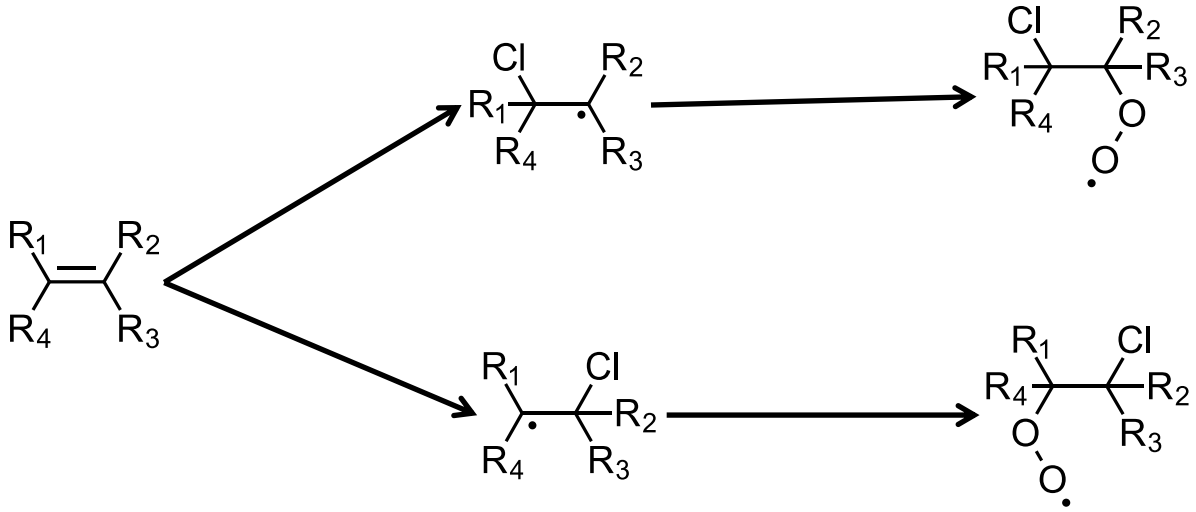


- Generally very rapid reactions with most types of C–H bonds

Atomic chlorine reactions

·Cl

- Chlorine addition



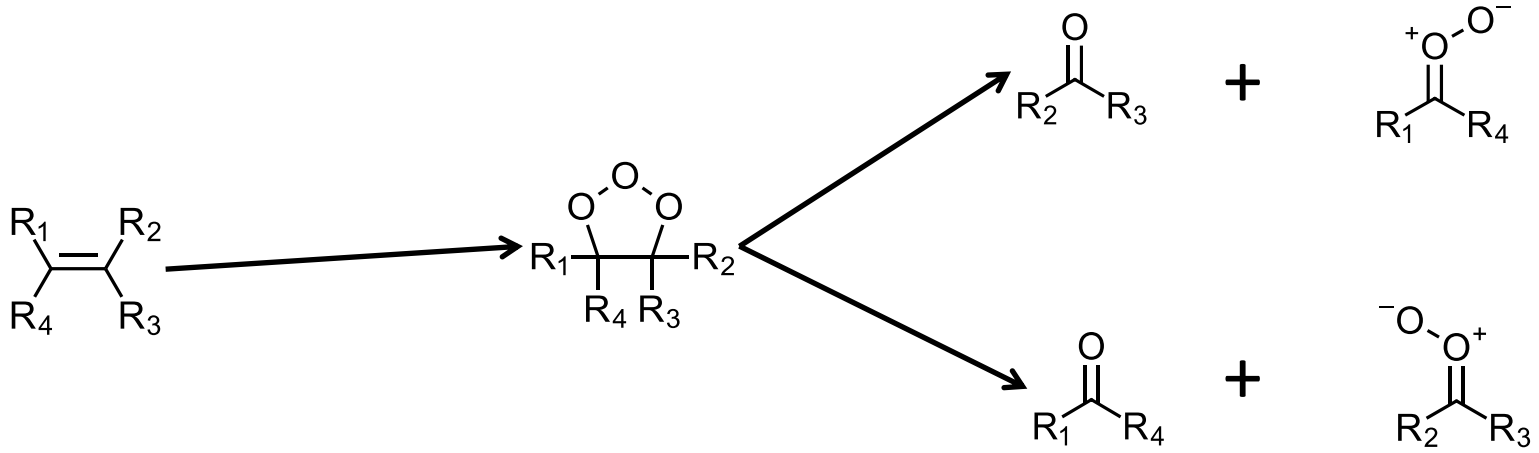
- Very rapid reactions with alkenes, less so with aromatics
- Adds chlorine functionality to alkenes structures

Ozone

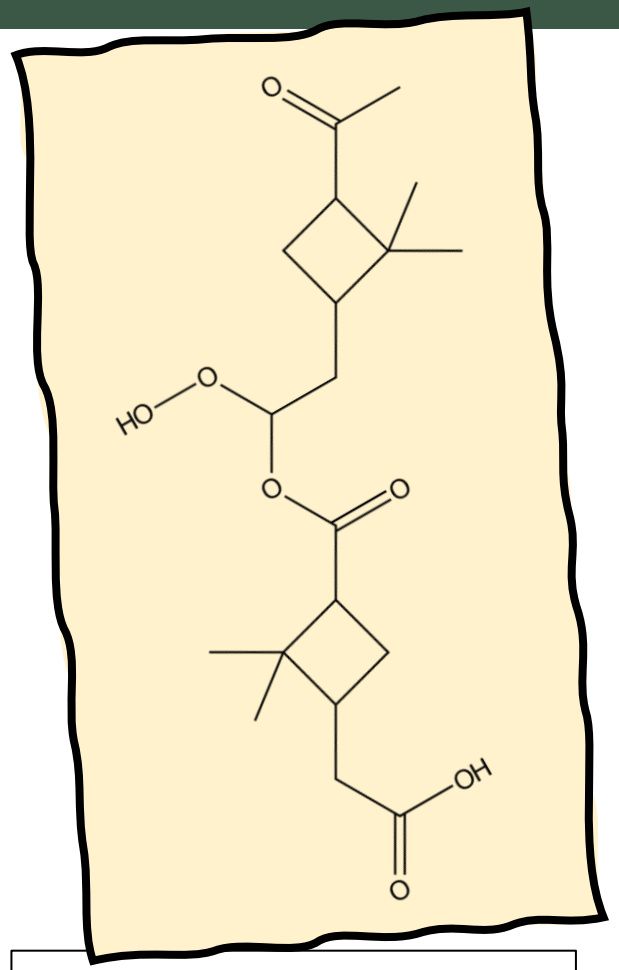
- Ozone is less reactive than other oxidants
- It is produced from the photochemical oxidation cycles in the atmosphere
- As a consequence, $[O_3]$ can be much higher, especially in urban environments
- This means that reaction rates can be competitive with other oxidants
- Sinks: reactions with alkenes and NO
- Ambient concentration: ~7×10^{11} molecule cm^{-3}

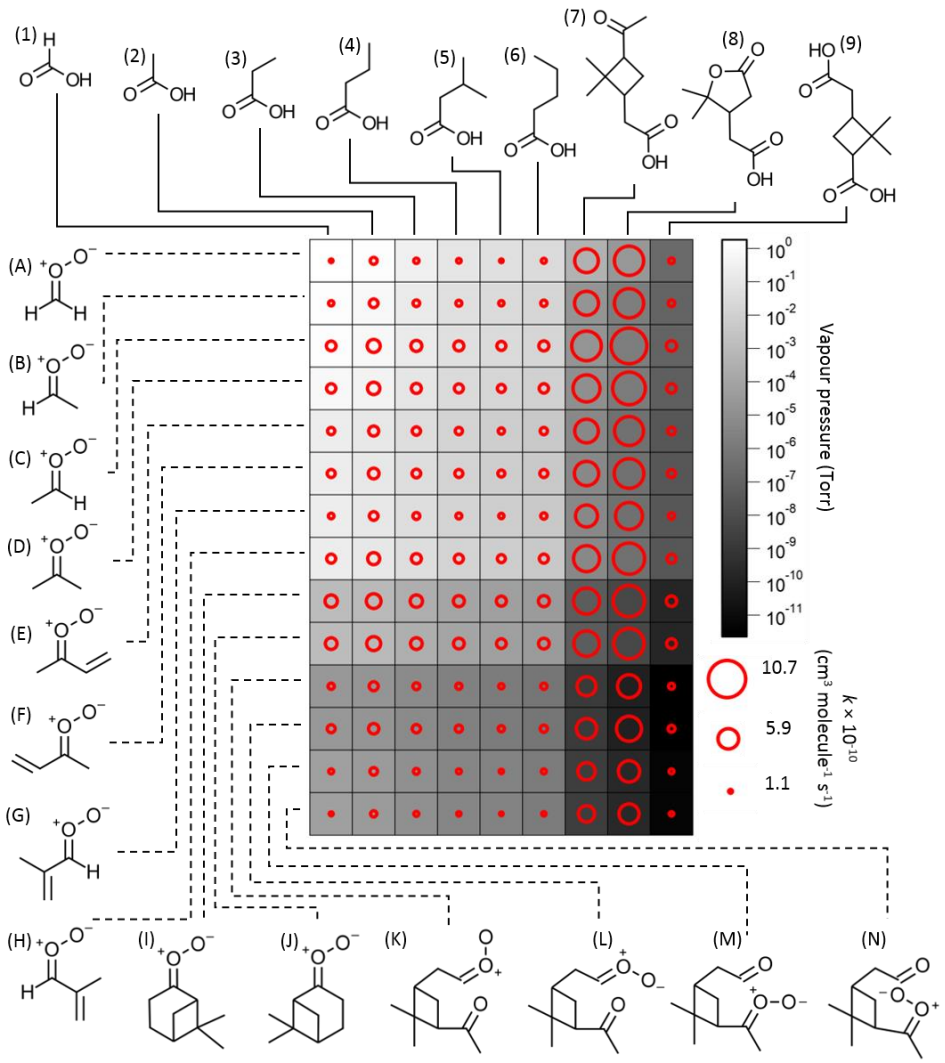
Ozone reactions

- Ozonolysis



Criegee intermediates





Source: Chhantyal-Pun et al. (2018)

Above: A low-vapour pressure hydroperoxide
Right: A matrix of different CI and acid combinations

- There are potentially lots of different Criegee intermediates and R(O)OH in the atmosphere
- These rate constants are really big
- It's a way of adding carbon and oxygen in one step
- **This could be a source of particles in the atmosphere**

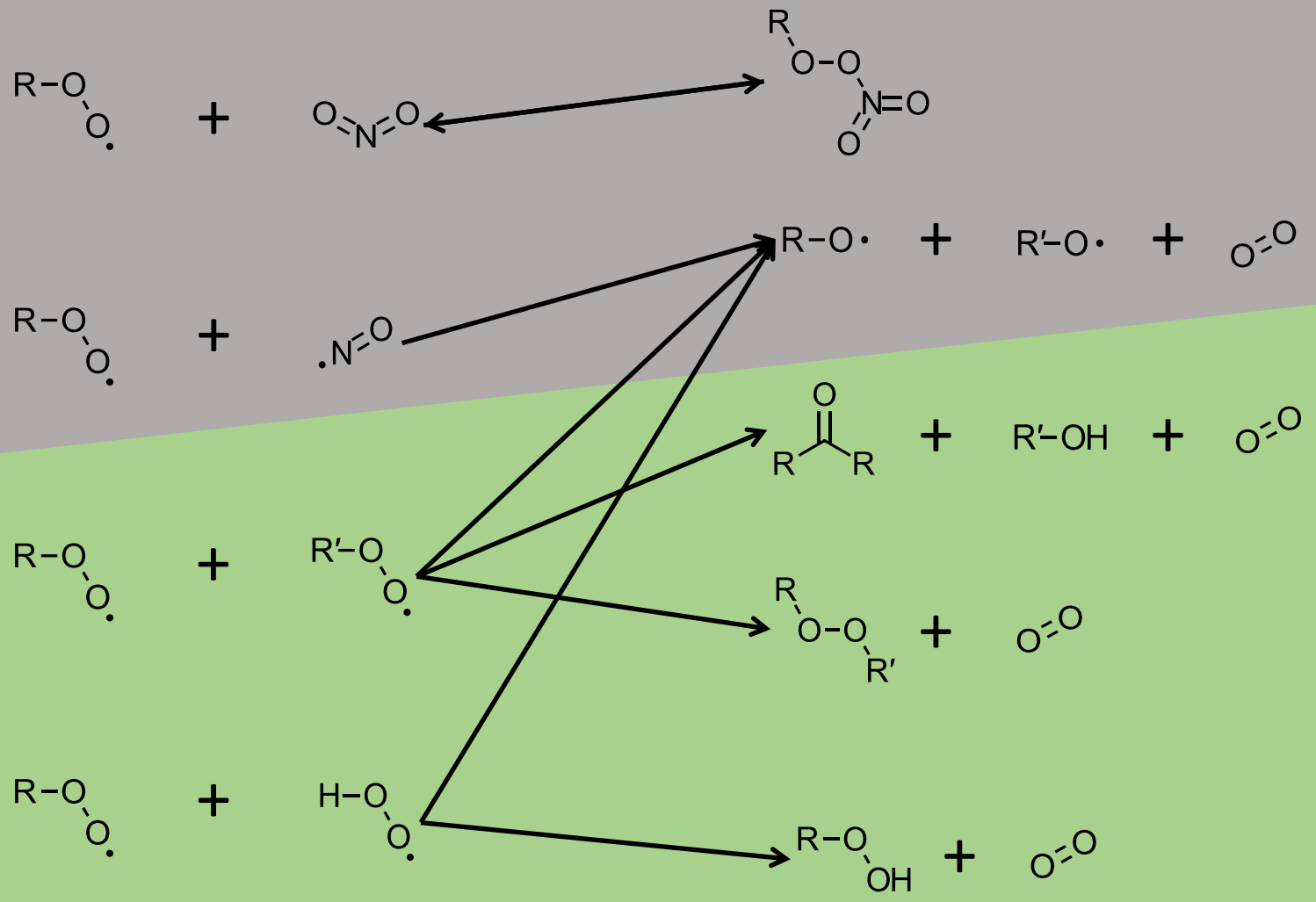
Peroxy radicals (RO_2)

- Peroxy radicals are produced from the reaction of carbon-centred radicals with O_2

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

- Carbon-centred radicals are produced during hydrogen abstraction and addition reaction mentioned earlier
- In urban environments, the sinks with NO_x are very important
- In more remote environments reactions with other peroxy radicals become important
- For certain RO_2, hydrogen shifts are very important

Peroxy radical reactions



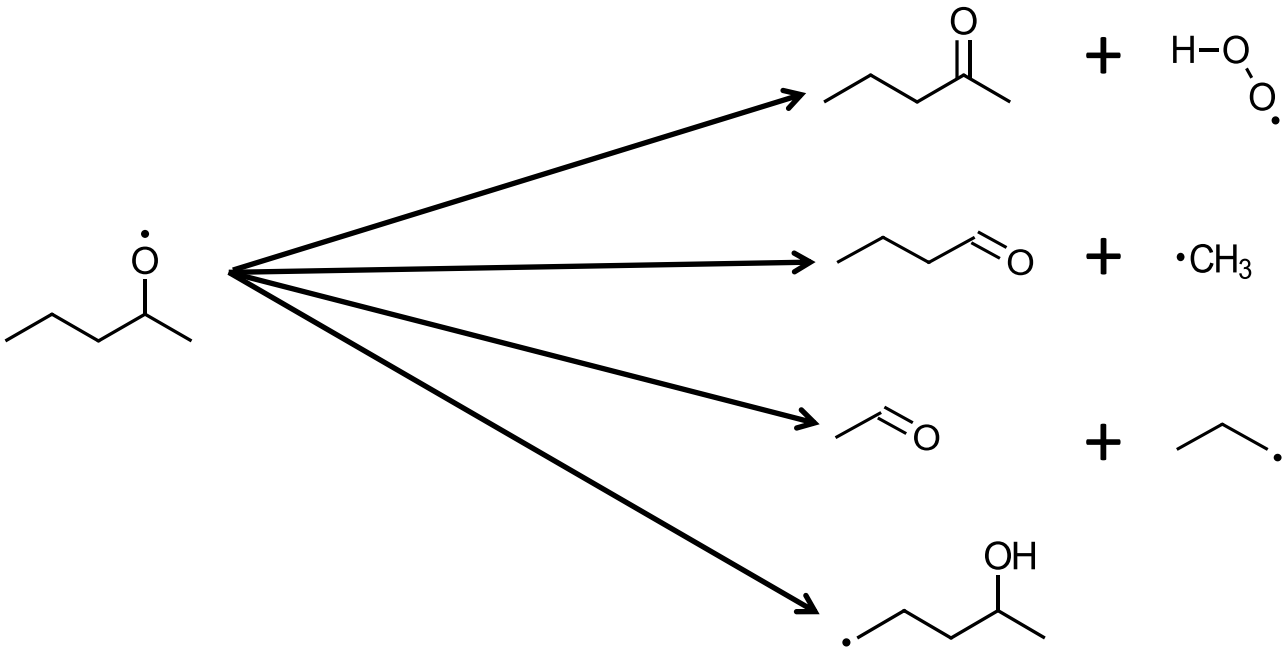
URBAN

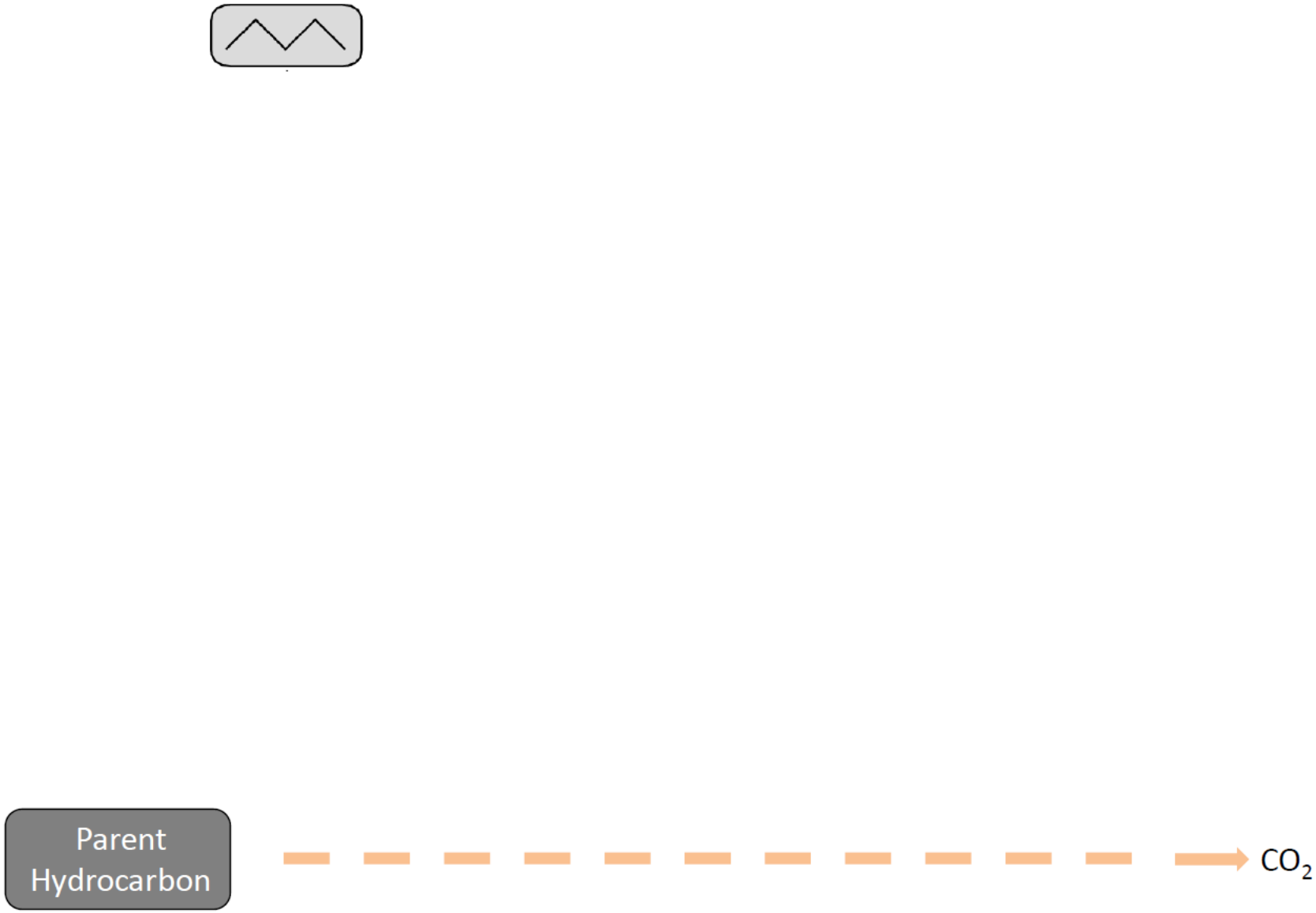
REMOTE

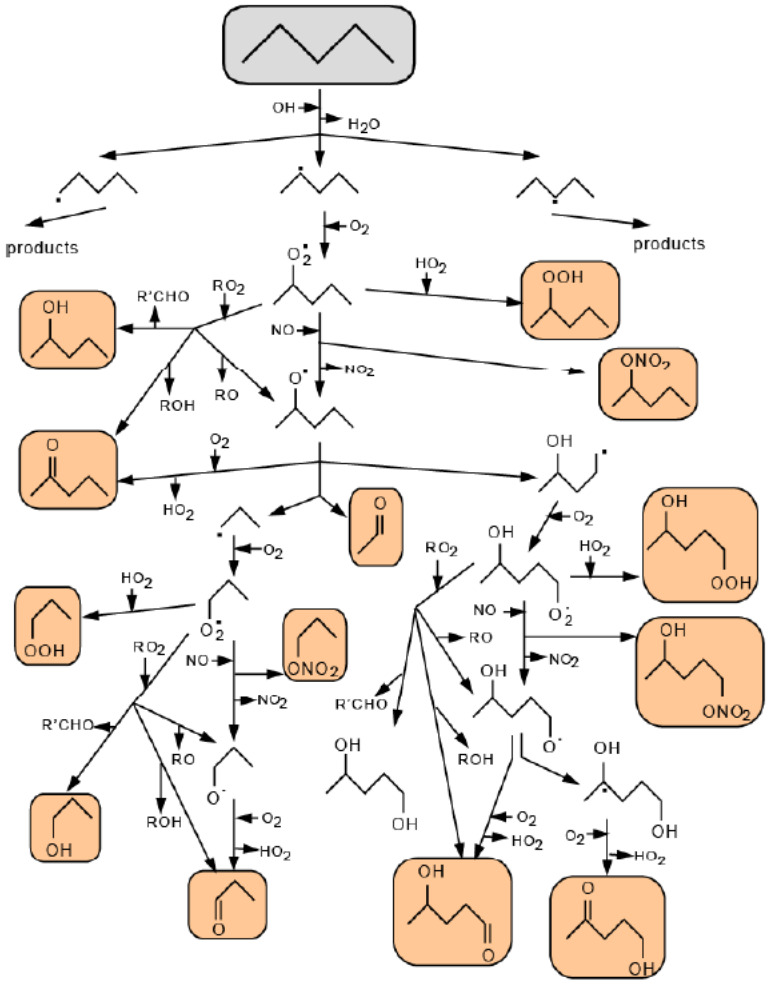
Alkoxy radicals

- Alkoxy radicals are short-lived intermediates that are produced from the reactions of RO_2
- Because of their high reactivity towards O_2, their propensity for decomposition and rearrangement, their concentrations in the atmosphere are low
- Because of their ubiquity and the branching pathways available to alkoxy radicals, they are a major source of atmospheric complexity

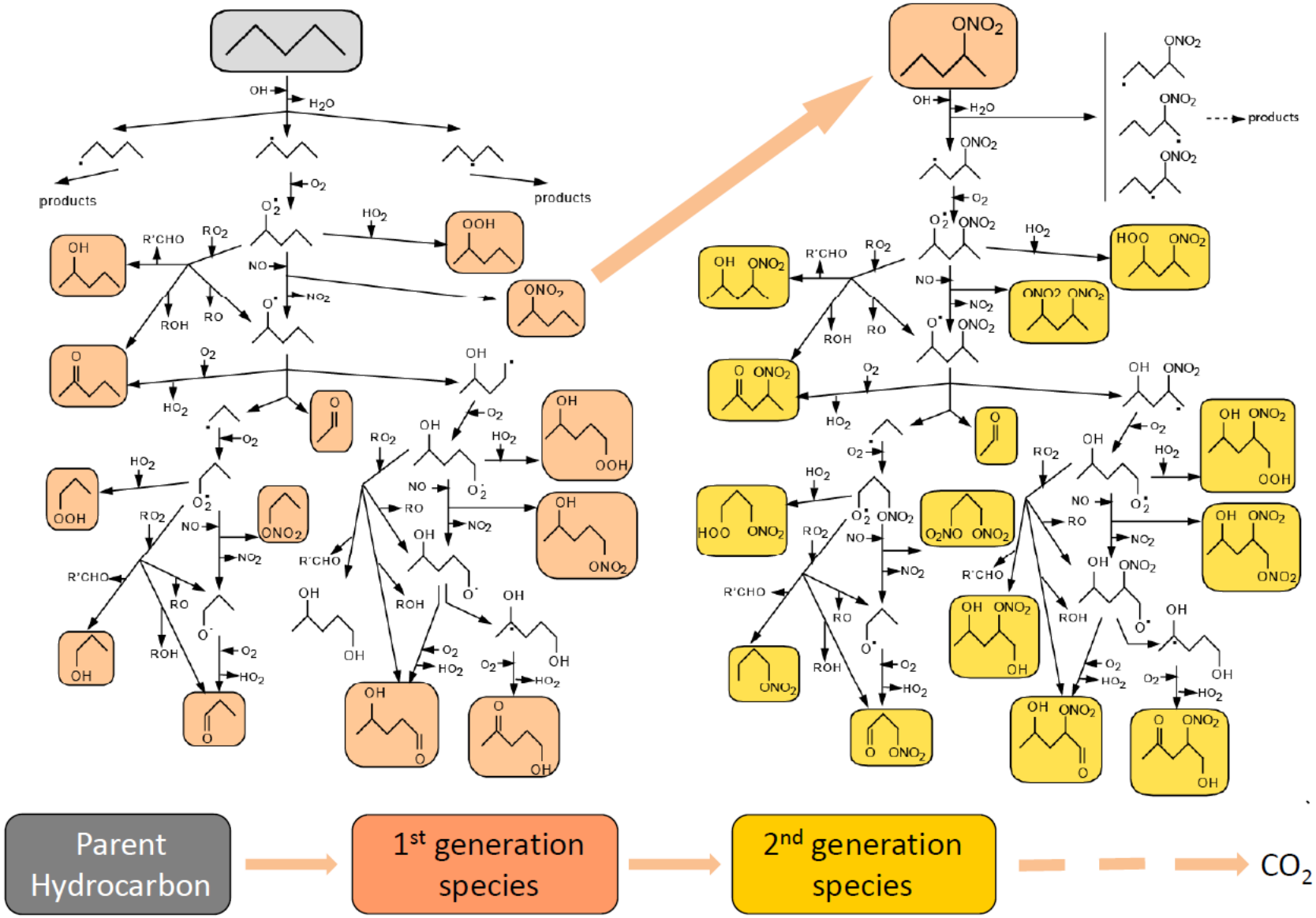
Alkoxy radical reactions




Parent Hydrocarbon
CO_2

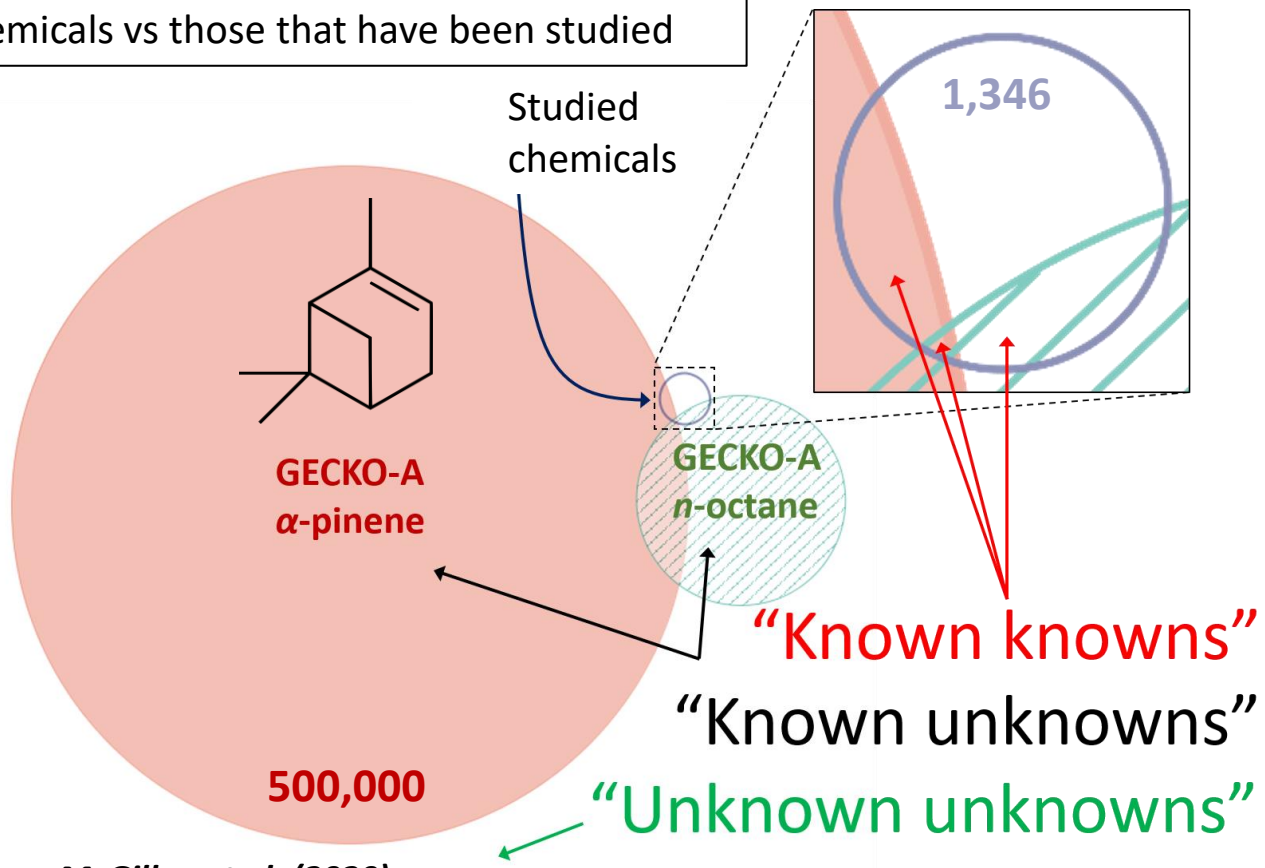


Parent Hydrocarbon → 1st generation species → CO_2


Parent Hydrocarbon
1st generation species
2nd generation species
CO2

The many unknowns of tropospheric chemistry

Area-proportional Venn diagram: number of products formed from two atmospheric chemicals vs those that have been studied



Source: McGillen et al. (2020)

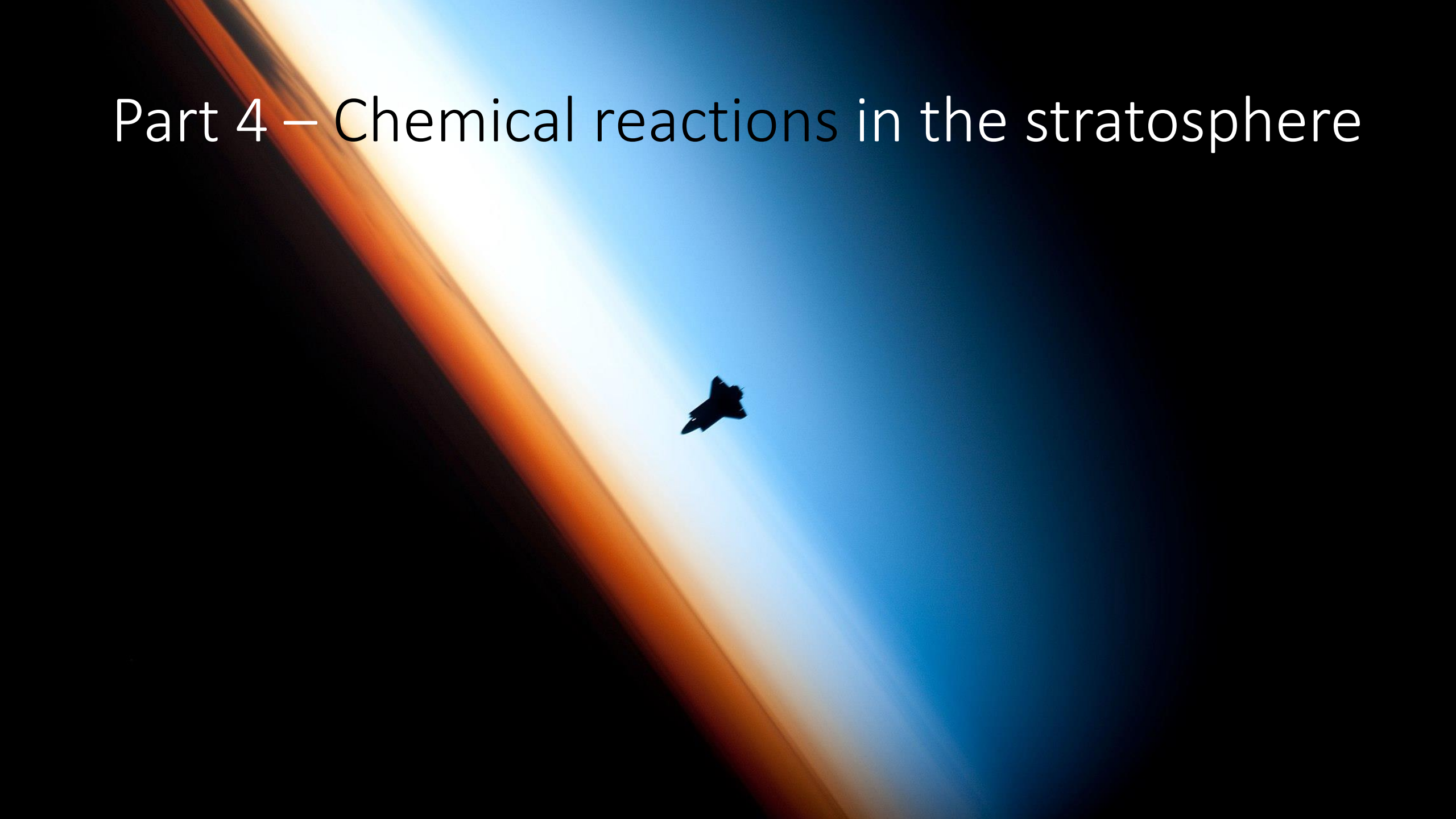
- Far more chemicals expected to form in the atmosphere[1] than have been studied[2]
- Remember: these are just two primary emissions, what about the 1000s of others?[3]
- **It is surprising how much we don't know yet (reactivity, products, multiphase)**
- Why? Partly because of the huge numbers, partly because of the types of chemicals formed…

[1] Aumont, B. et al. Modelling the Evolution of Organic Carbon during Its Gas-Phase Tropospheric Oxidation: Development of an Explicit Model Based on a Self Generating Approach. Atmospheric Chem. Phys. 2005, 5 (9), 2497–2517.
[2] McGillen, M. R. et al. Database for the Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds. Earth Syst. Sci. Data, 2020, 12, 1203–1216.
[3] Goldstein, A. H.; Galbally, I. E. Known and Unexplored Organic Constituents in the Earth's Atmosphere. Environ. Sci. Technol. 2007, 41 (5), 1514–1521.

Conclusions:
Part 3 – Chemical reactions in the troposphere

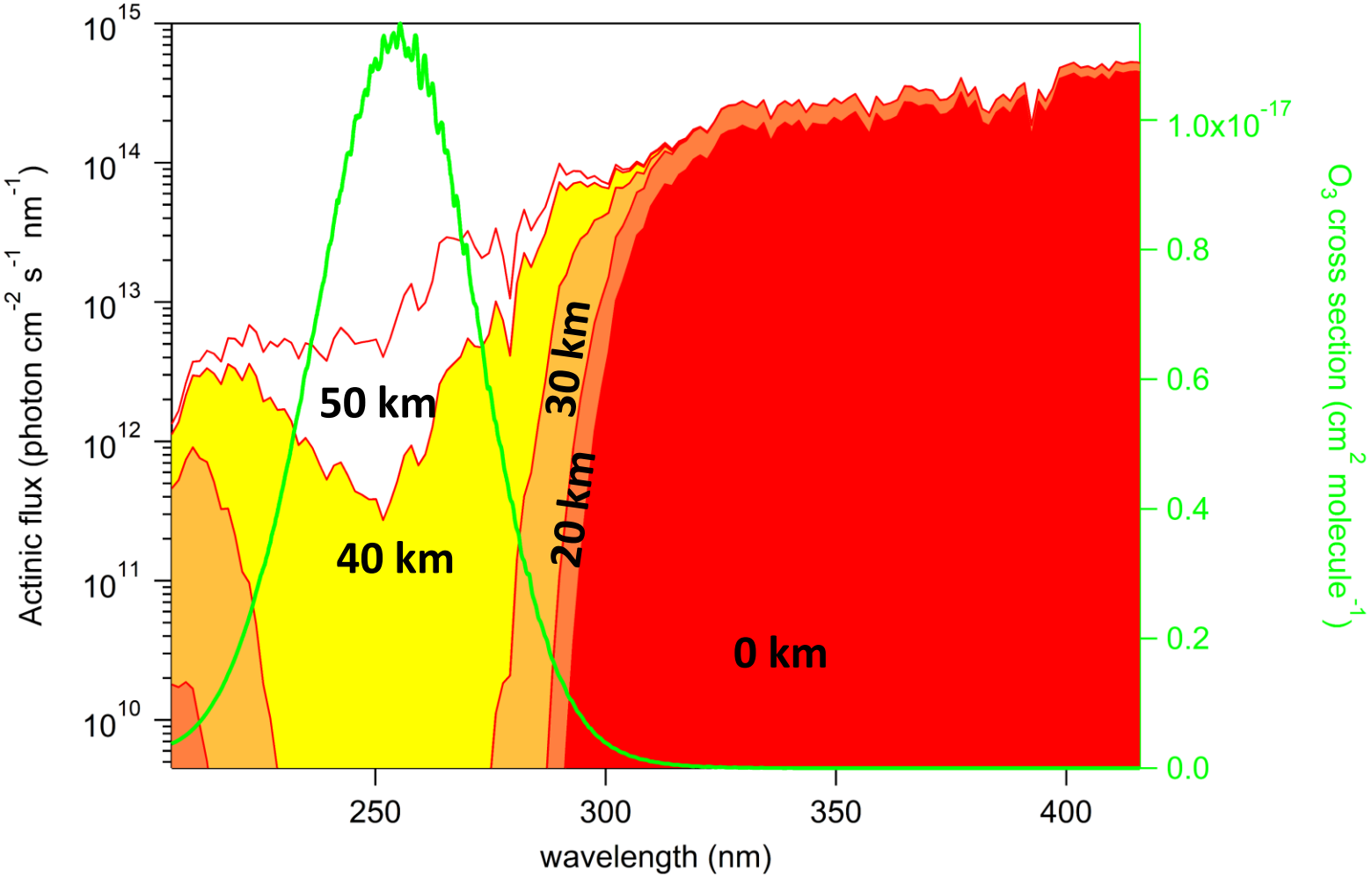
- The troposphere contains the largest variety of chemical reactions in the atmosphere
- It is an auto-catalytic cycle involving sunlight, NO_x, O_3 and VOCs
- These reactions clean the atmosphere, but they also produce harmful degradation products along the way
- The level of complexity that is generated from tropospheric chemistry is an example of a combinatorial explosion

Part 4 – Chemical reactions in the stratosphere

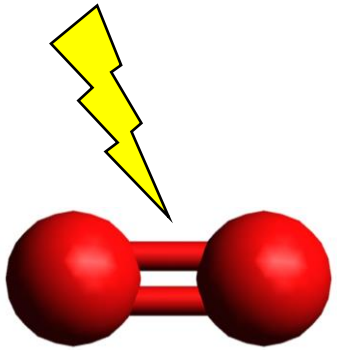


Stratospheric ozone

- The ozone layer is one of the most important features of the atmosphere
- It is what attenuates most of the UV wavelengths in the troposphere
- Going above the ozone layer opens up the Herzberg continuum…



$h\nu$ <240nm



$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$

$O \rightarrow 249 \times 2 \text{ kJ mol}^{-1}$

From Hess's law:

$\Delta H_{rxn} = \nu(p)\Delta H_{f(p)} - \nu(r)\Delta H_{f(r)}$

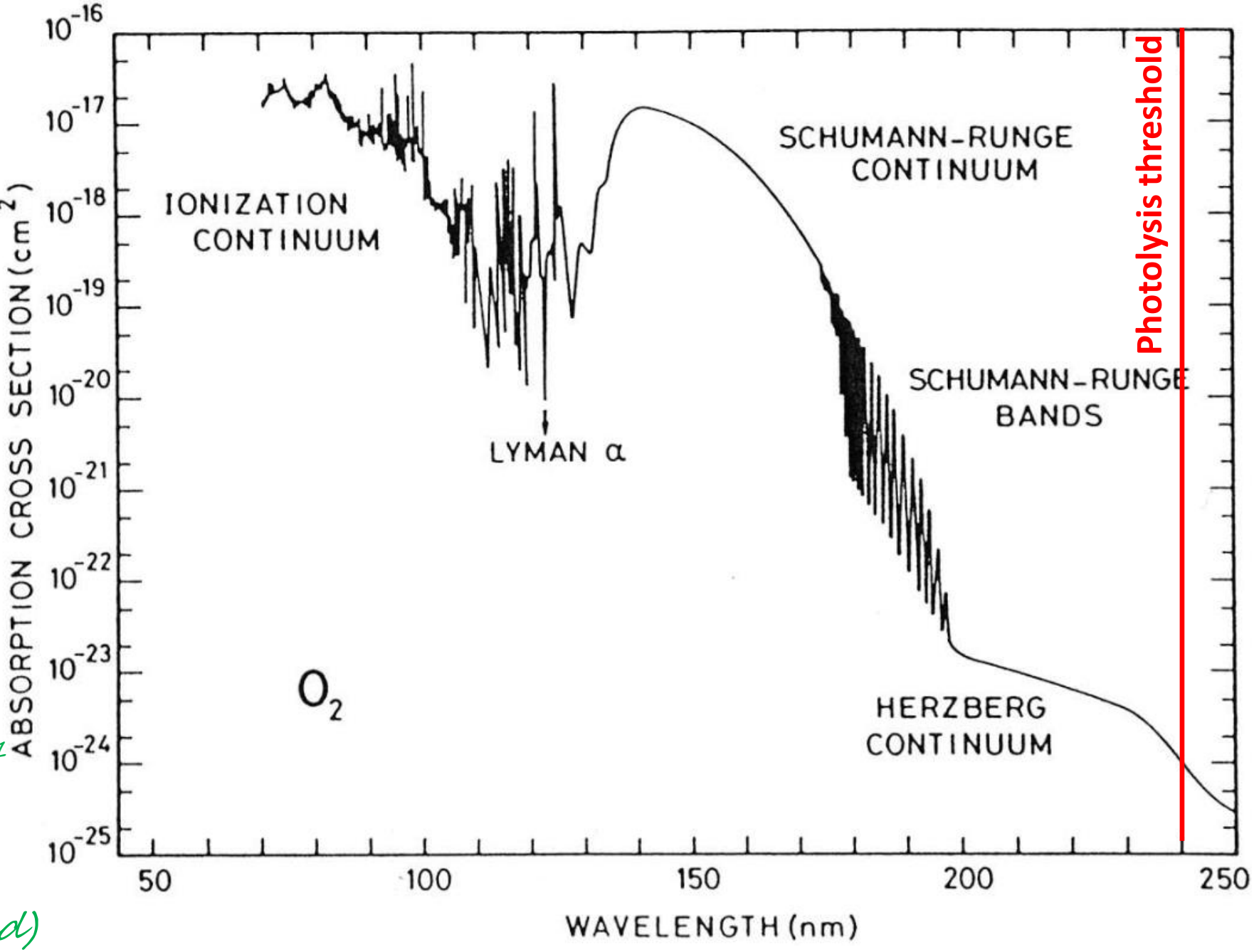
$= 498 \text{ kJ mol}^{-1}$

$= \frac{498{,}000 \text{ J mol}^{-1}}{N_A}$

$= \frac{8.27 \times 10^{-19} \text{ J photon}^{-1}}{h \times c}$

$= 240 \text{ nm}$

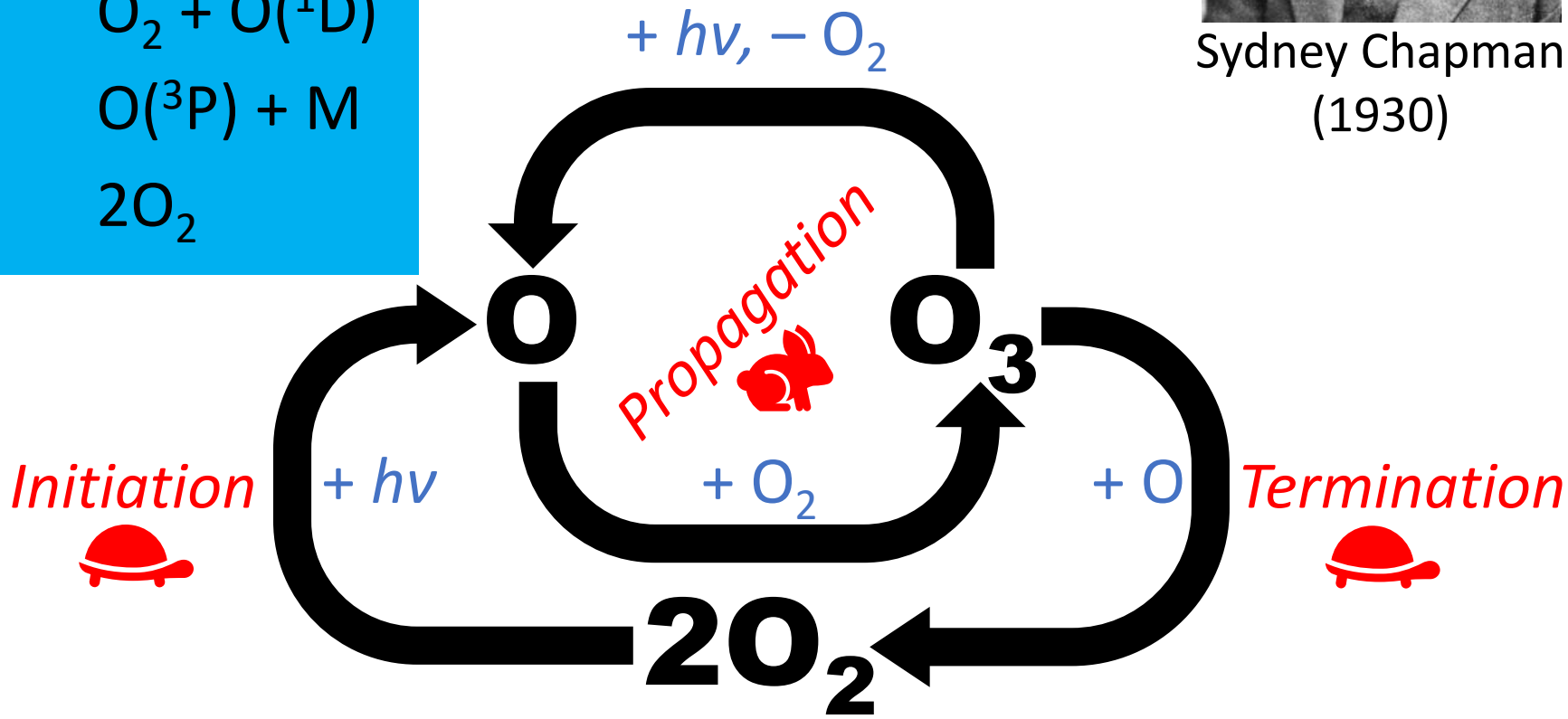
(the photolysis threshold)



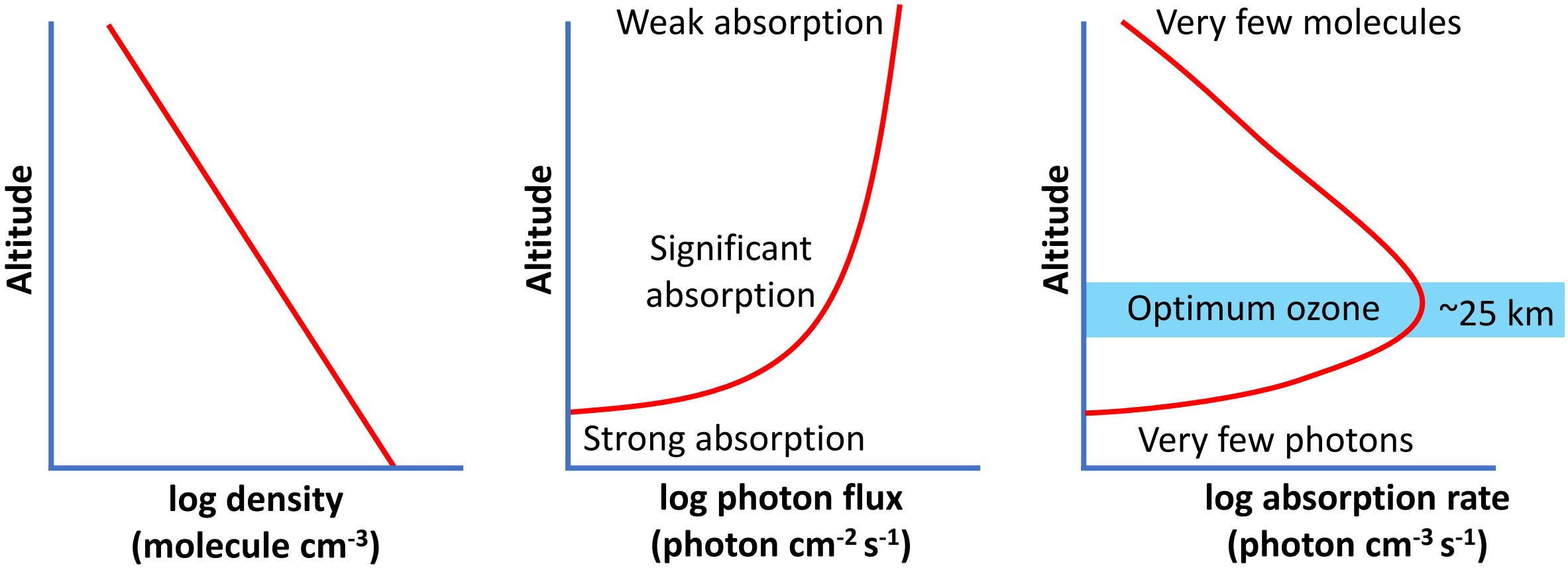
The Chapman Cycle

- $O_2 + h\nu \rightarrow 2O(^3P)$
- $O_2 + O(^3P) + M \rightarrow O_3 + M$
- $O_3 + h\nu \rightarrow O_2 + O(^1D)$
- $O(^1D) + M \rightarrow O(^3P) + M$
- $O(^3P) + O_3 \rightarrow 2O_2$

Sydney Chapman (1930)



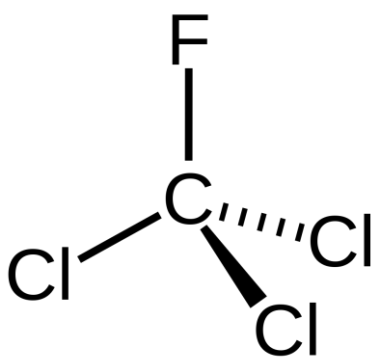
The Chapman profile



Ozone production is a balance between number density, photon flux and absorption cross sections of O_2 and O_3

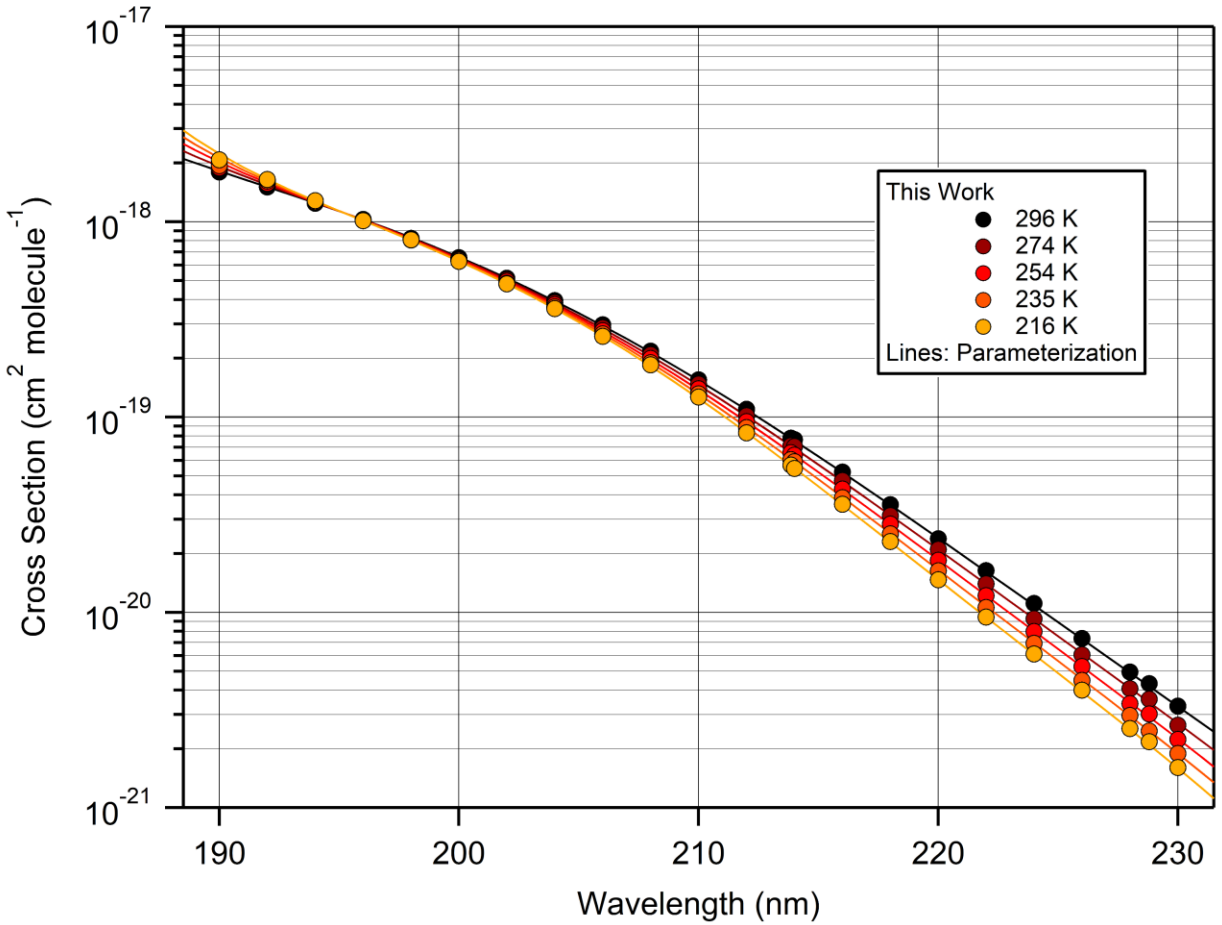
– Quiz –

- Remember all those reactions that are available to oxidize chemicals in the troposphere?
- What happens to this molecule?

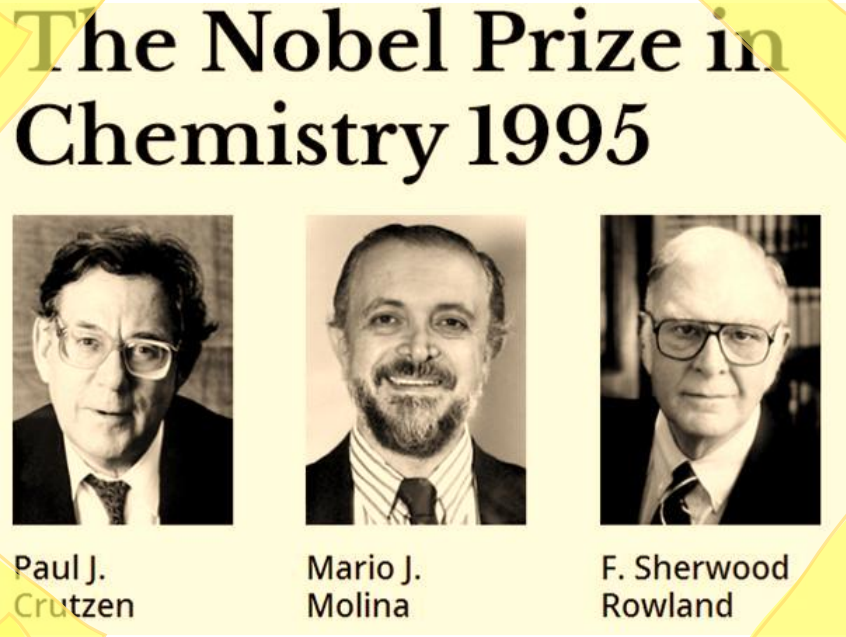


CFC-11

  - No reaction with any of the tropospheric oxidants
  - No significant absorption in the actinic range



James Lovelock (1972)



- CFC-11 ($CFCl_3$) was observed in the air samples of James Lovelock in 1972
- Molina and Rowland determined that these molecules survive for decades/ centuries
- This indicates upward transport
- Together with Crutzen they anticipated the threat that this presents to the stratosphere…

Catalytic ozone destruction

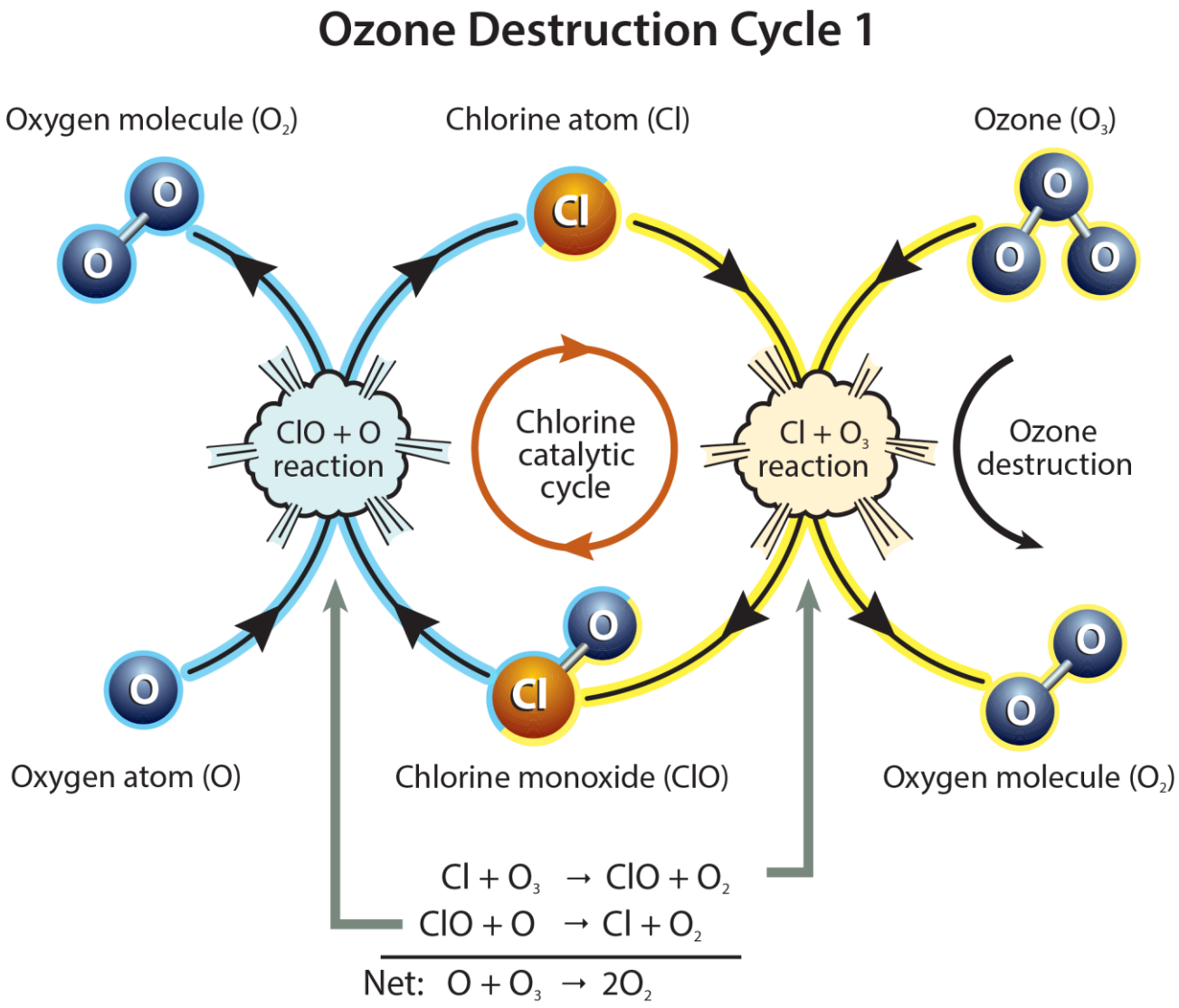
Initiation:

e.g. $CFCl_3 + h\nu \longrightarrow Cl + CFCl_2$

Propagation:

$Cl + O_3 \longrightarrow ClO + O_2$
$O + ClO \longrightarrow Cl + O_2$
Net: $\mathbf{O_3 + O \longrightarrow 2O_2}$

$Cl + O_3 \longrightarrow ClO + O_2$
$NO + ClO \longrightarrow Cl + NO_2$
$NO_2 + h\nu \longrightarrow NO + O$
$NO_2 + O \longrightarrow NO + O_2$
$NO + O_3 \longrightarrow NO_2 + O_2$
Net: $\mathbf{2O_3 \longrightarrow 3O_2}$



Catalytic ozone destruction

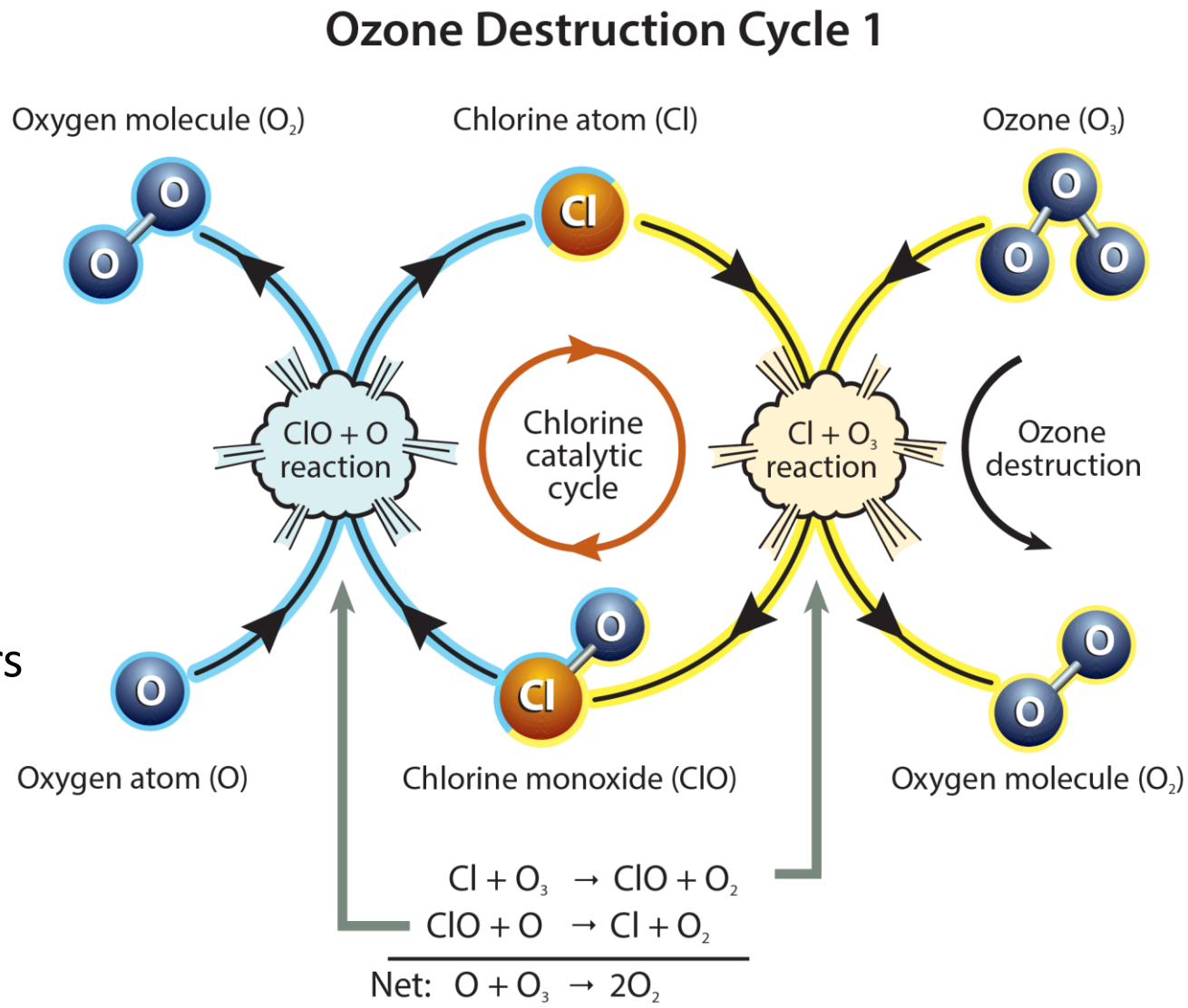
Termination:

$$\mathbf{ClO} + NO_2 + M \longrightarrow \mathbf{ClONO_2} + M$$
$$\mathbf{Cl} + HO_2 \longrightarrow \mathbf{HCl} + O_2$$
$$\mathbf{Cl} + CH_4 \longrightarrow \mathbf{HCl} + CH_3$$
$$\mathbf{ClO} + CH_3OO \longrightarrow \mathbf{CH_3OCl} + O_2$$
$$\mathbf{ClO} + HO_2 \longrightarrow \mathbf{HOCl} + O_2$$

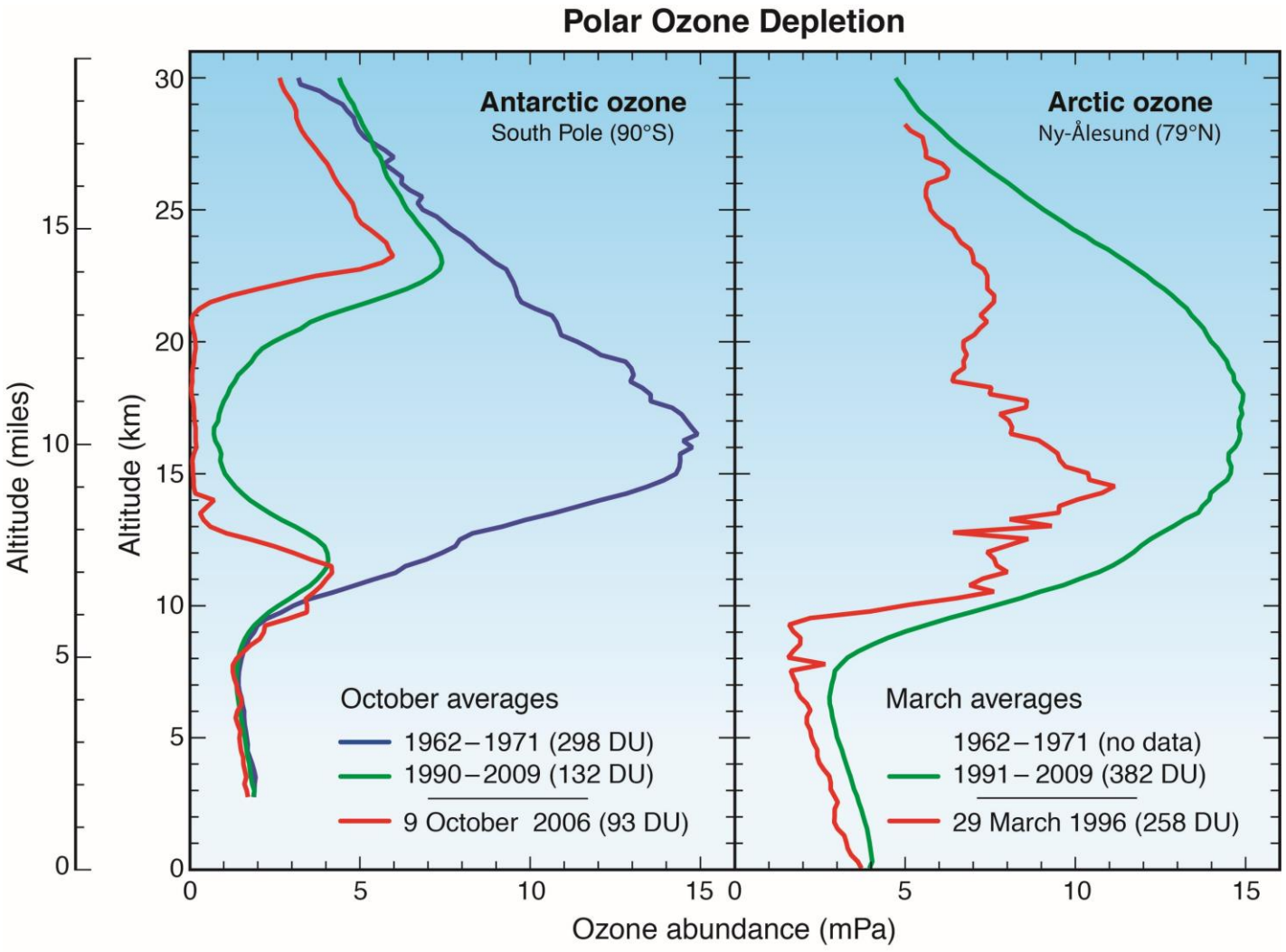
Cl and ClO: active chlorine

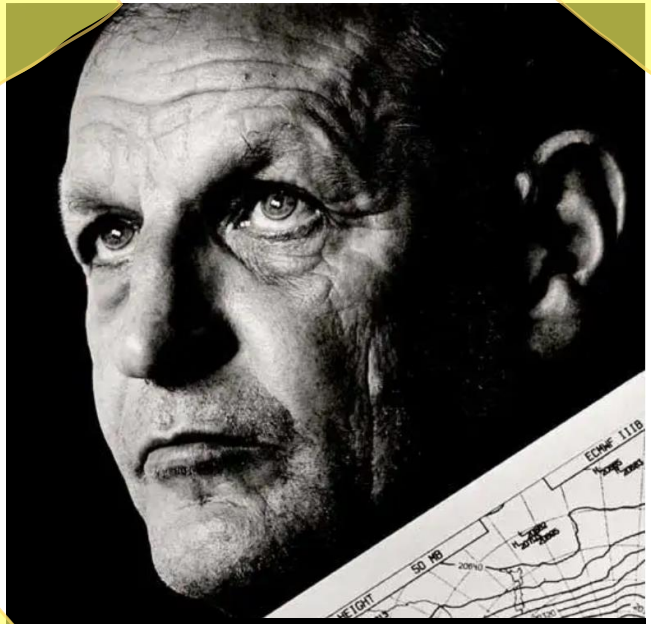
HCl and $ClONO_2$: important Cl reservoirs

HOCl and CH_3OCl: less important Cl reservoirs



The ozone hole





Joe Farman
(1985)

- Observation of the ozone hole was very sudden and unexpected
- This led to a rapid international effort to understand this process further

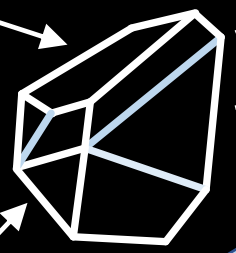
In the polar night

1

Formation of polar stratospheric clouds:

2

Activation of Cl_x:



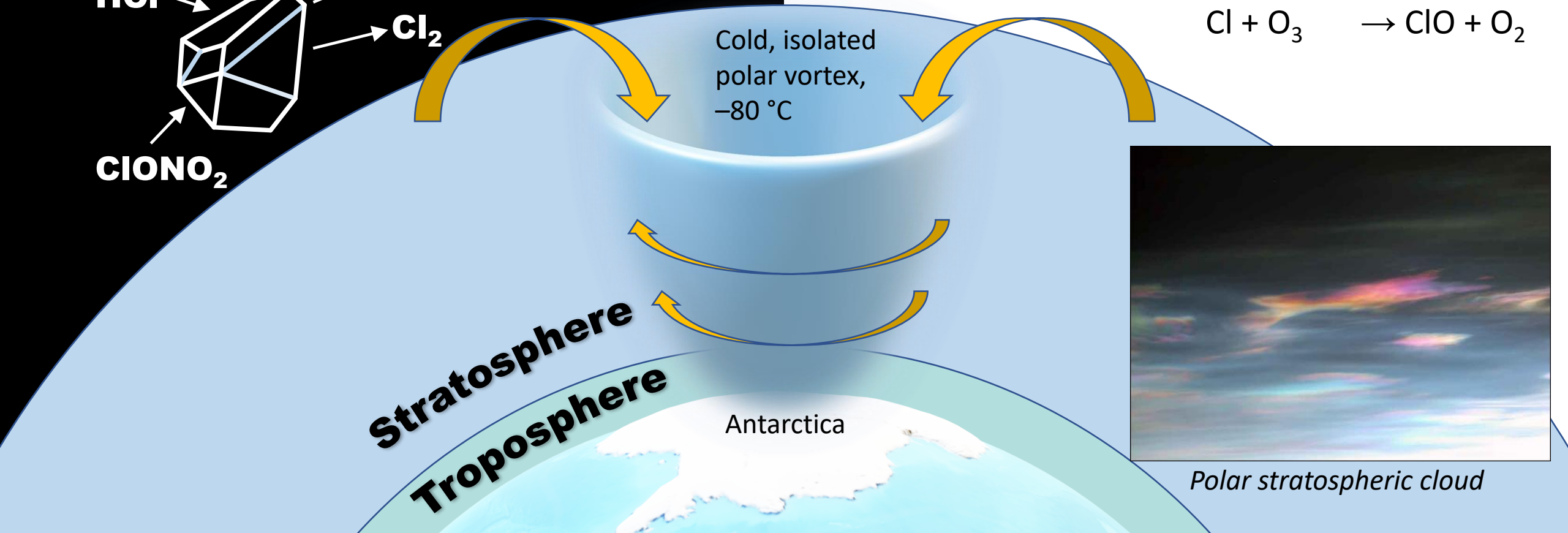
In the polar spring

3 Formation of ClO_x:

$$Cl_2 + h\nu \longrightarrow 2Cl$$
$$HOCl + h\nu \longrightarrow OH + Cl$$
$$Cl + O_3 \longrightarrow ClO + O_2$$

4 Catalytic O_3 depletion:

$$ClO + ClO \longrightarrow Cl_2O_2$$
$$Cl_2O_2 + h\nu \longrightarrow 2Cl + O_2$$
$$Cl + O_3 \longrightarrow ClO + O_2$$



Polar stratospheric cloud

Conclusions:
Part 3 – Chemical reactions in the stratosphere

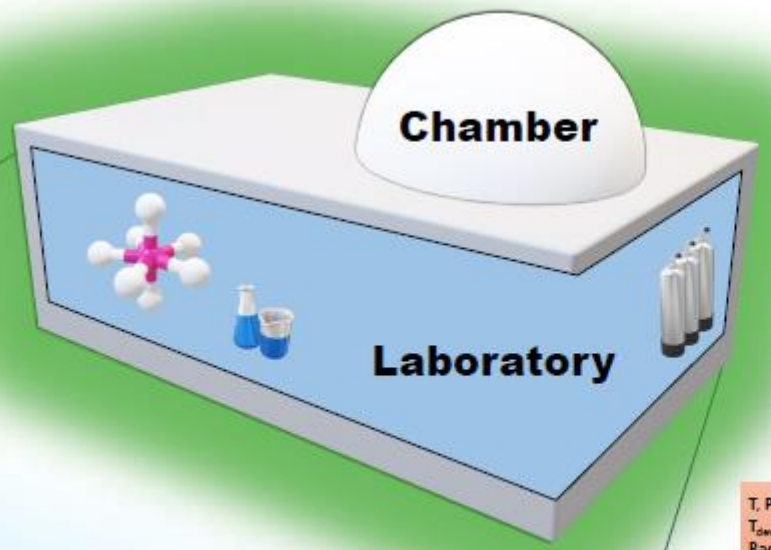
- As you get higher into the atmosphere, shorter UV wavelengths become accessible
- This allows for the photolytic production of O_3, and the destruction of very stable compounds such as CFCs
- This provides a source of chlorine into the stratosphere which has a catalytic effect on ozone depletion
- Society's rapid response to ozone depletion is often cited as a success story in atmospheric chemistry
- But there are other ways of looking at this…
- How will society respond to other future environmental threats?

Approaches to studying the atmosphere

- Studying the atmosphere is a big job
- This requires many different activities
- This can be viewed metaphorically as a 3-legged stool
- In the field, we can observe what the atmosphere is composed of
- In the lab, we can understand the individual processes to create and destroy species
- In models, we can couple our fundamental understanding from the lab with our field observations

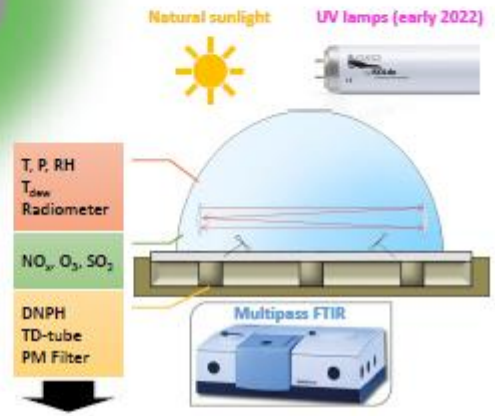
HELIOS platform

A view of the HELIOS platform at sunrise



Scenes inside the HELIOS laboratory

HELIOS instrumentation



Off-line methods

HR mass spec and particle sampling

Guest instruments (LPC2E)

High-precision single-species

ACTRIS
Exploring the Atmosphere