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# Atmospheric chemistry
# Summary

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# Chapman mechanism (1930)

The Chapman mechanism for stratospheric ozone

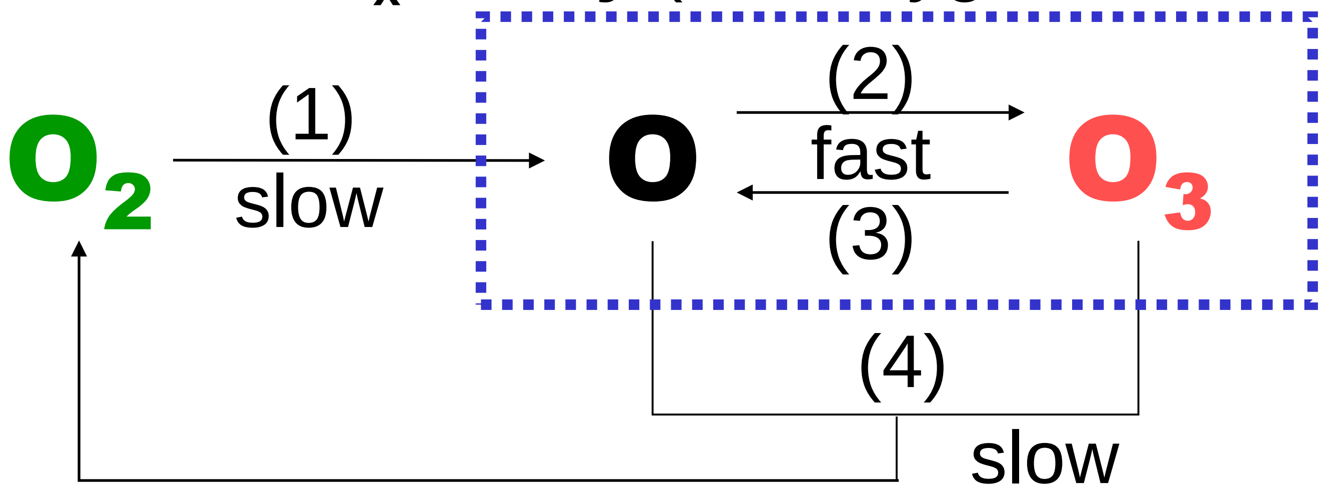
(1) $O_2 + h\nu \rightarrow O + O$ ($\lambda$< 240 nm)

(2) $O + O_2 + M \rightarrow O_3 + M$ (2x) (fast)

(3) $O_3 + h\nu \rightarrow O_2 + O$ (fast, $\lambda$< 320 nm)

(4) $O_3 + O \rightarrow 2O_2$

**$O_x$ family** (odd oxygen molecules)

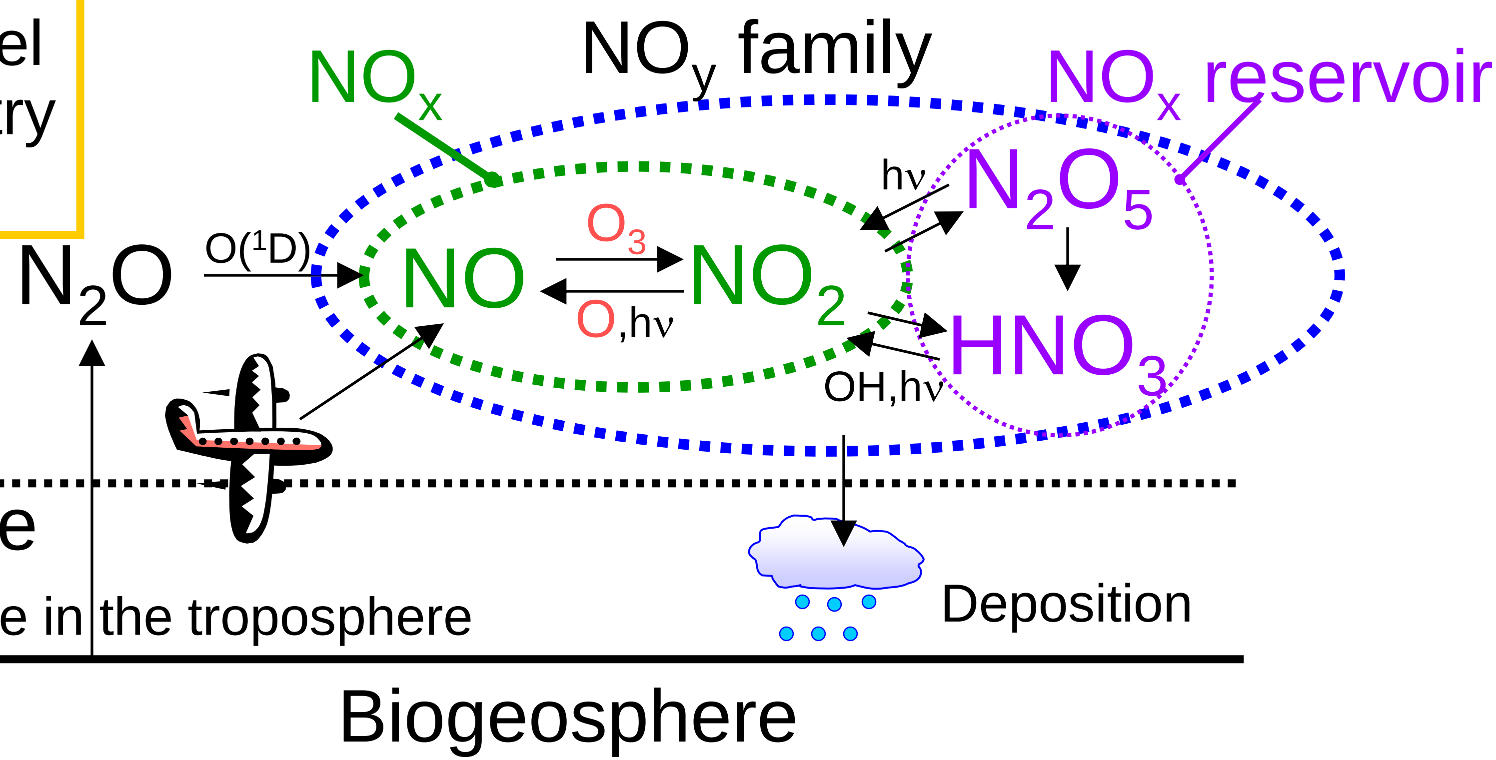


# Catalytic ozone loss – $NO_x$

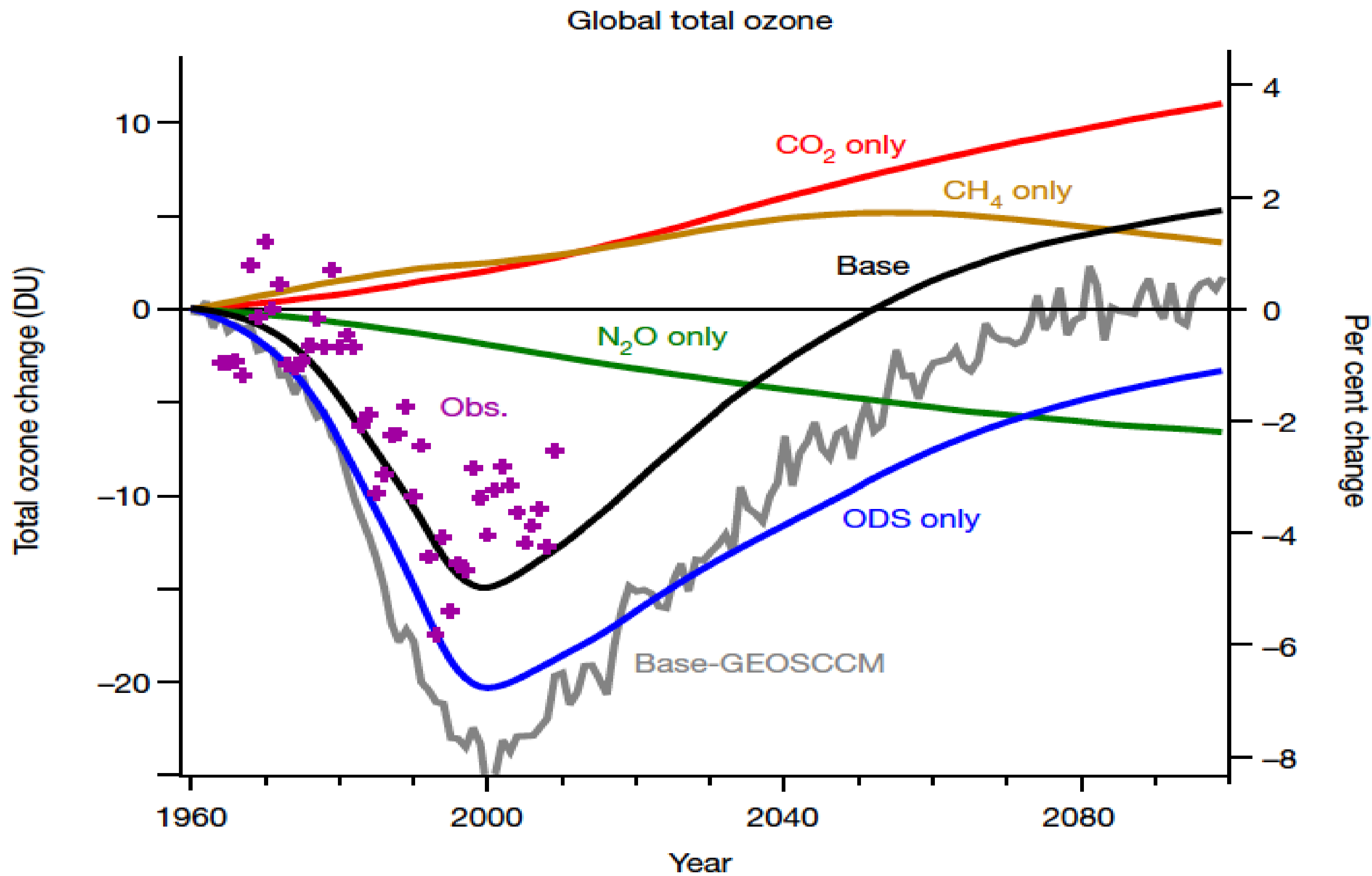
The $O_3$ sinks attributable to $NO_x$ and $HO_x$ are sufficient as complement to the Chapman mechanism to account for the observed natural ozone levels (1970-ies).

Before the discovery of the ozone hole!

Paul Crutzen shared the Nobel prize in Chemistry 1995



# Stratospheric ozone - Recovery



# Filtering of UV by stratospheric ozone

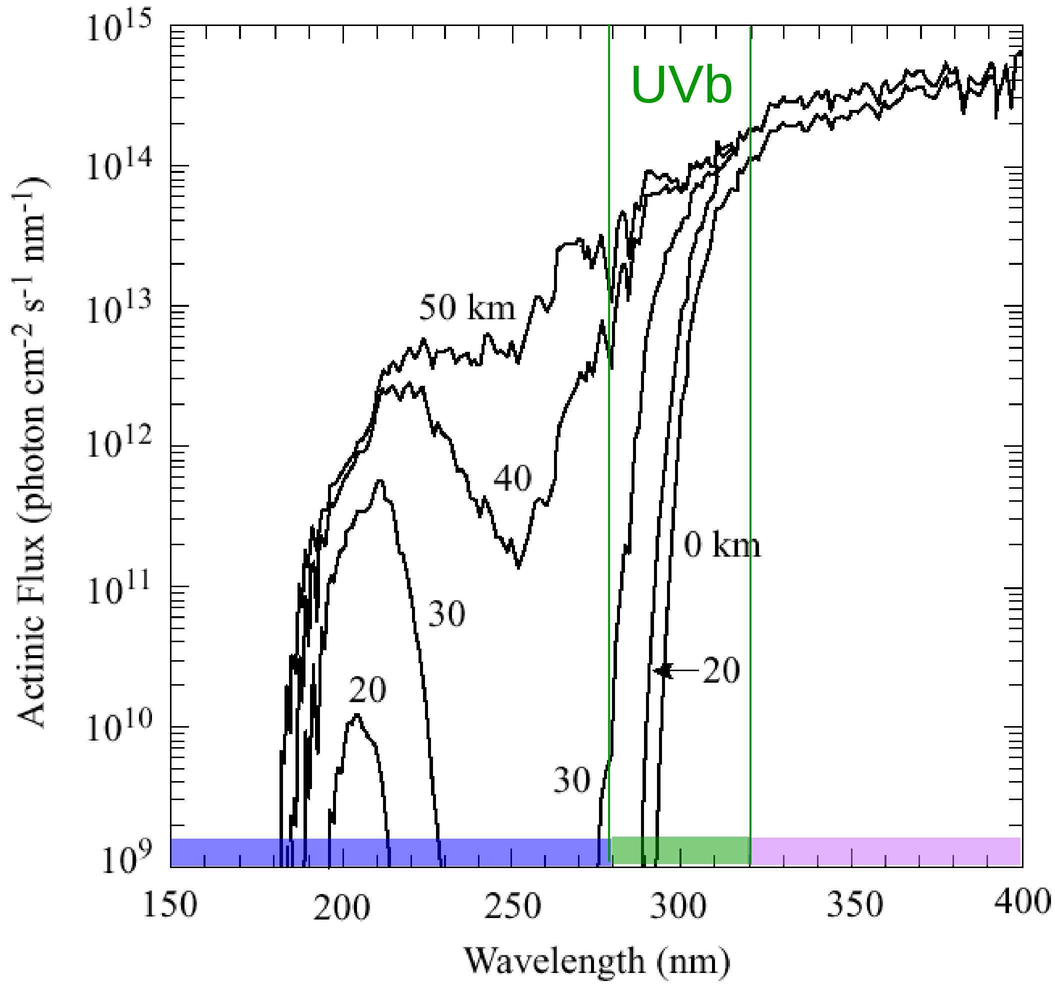
UVc (200 < λ < 280 nm)

$O_2$ photolysis: λ < 240 nm

UVb (280 < λ < 320 nm)

$O_3$ photolysis: λ < 320 nm

UVa (320 < λ < 400 nm)



# Production of the hydroxyl radical OH

Production of $O(^1D)$ occurs in a narrow wavelength band between 300-320 nm.

**Tropospheric ozone is both good and bad.**

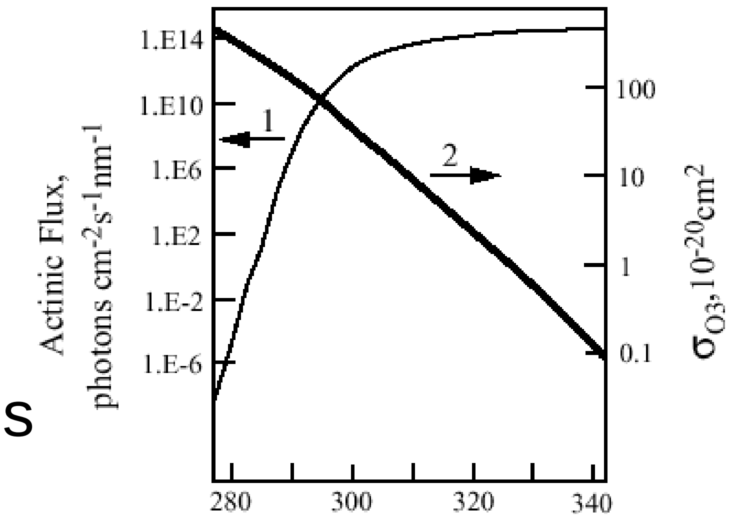
**Ozone is needed** to produce OH radicals via

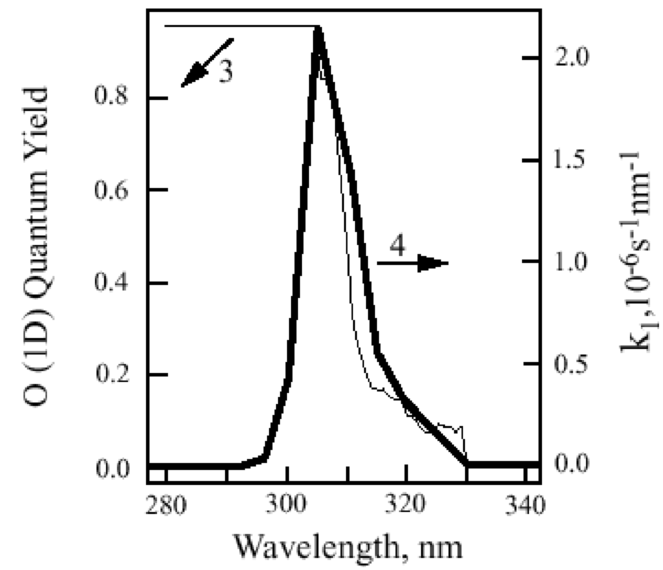
$O_3 + h\nu \rightarrow O_2 + O(^1D)$ and $O(^1D) + H_2O \rightarrow 2OH$

OH is essential for the **oxidizing capacity of the troposphere** and the **lifetime of trace gases**.

**High levels of ozone are dangerous to humans, plants and and materials.**

**Tropospheric ozone is a GHG**



# Photostationary equlibrium for ozone

In a **sunlit atmosphere with** $NO$ **and** $NO_2$ **but without hydrocarbons:**

*(11.11)* $NO_2 + h\nu \rightarrow NO + O$ $(\lambda < 420\ nm)$

*(10.2)* $O + O_2 + M \rightarrow O_3 + M$ (*only way to produce* $O_3$)

*(11.14)* $NO + O_3 \rightarrow NO_2 + O_2$

Net reaction:

$$NO_2 + O_2 \overset{h\nu}{\Leftrightarrow} NO + O_3$$

A **photostationary equilibrium** exists.

More sun light ($\lambda < 420$ nm) gives more ozone $O_3$.

$NO$ consumes ozone. In the vicinity of strong sources of $NO$, then $O_3$ is titrated out and can be entirely depleted (e.g. close to a smoke stack or the tail pipe of a car.)

# Shifting the equilibrium towards more ozone

**Hydrocarbons are needed to shift the equilibrium** to the right, that is towards a **higher ozone production**.

**Hydrocarbons consume** NO (by producing peroxyl radicals $HO_2$ and $RO_2$ , which in turn react with NO).

**More sun light** ($\lambda$< 420 nm) **gives more ozone** $O_3$.

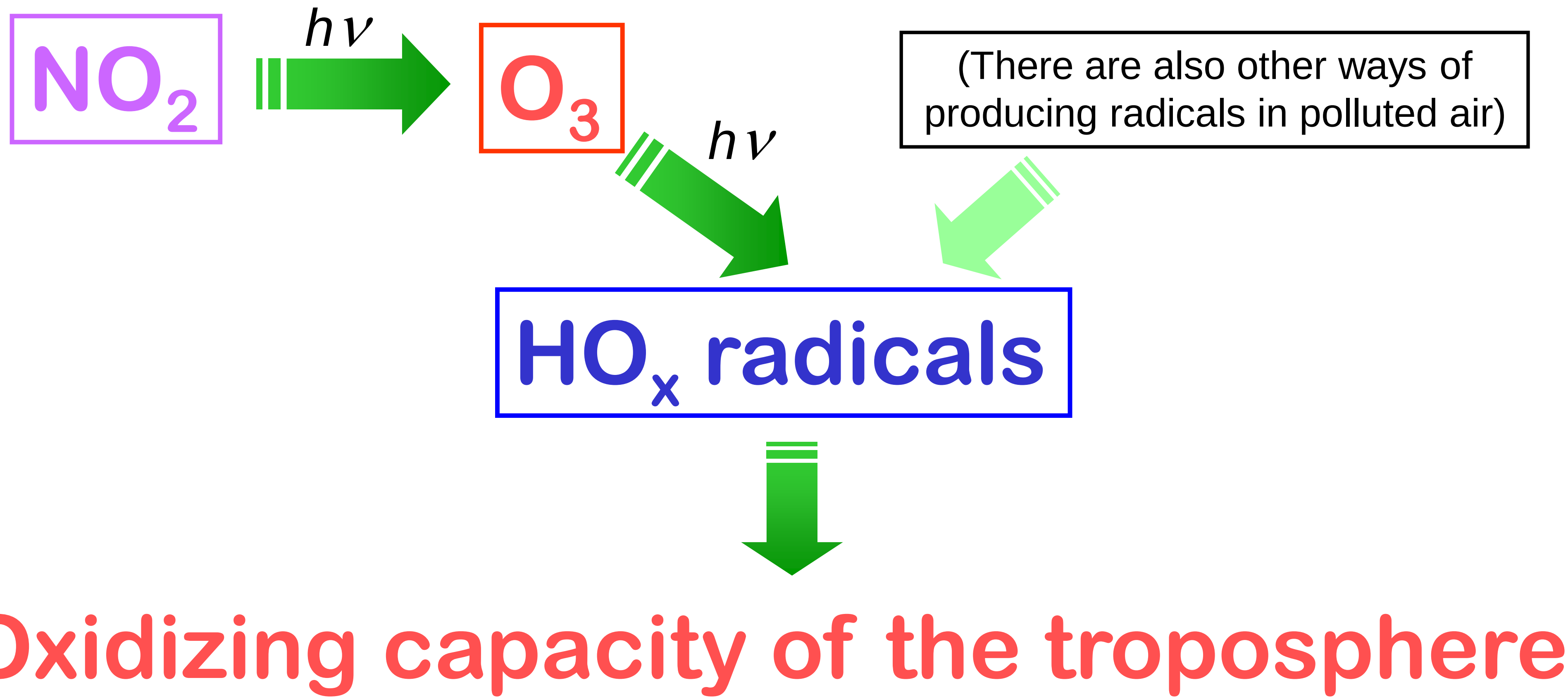
$$NO_2 + O_2 \overset{h\nu}{\Leftrightarrow} NO + O_3$$

**Prerequisites for high ozone levels:**

- **Sun light** ($\lambda$< 420 nm)
- **Hydrocarbons**
- **Nitrogen oxides** ($NO_X$)

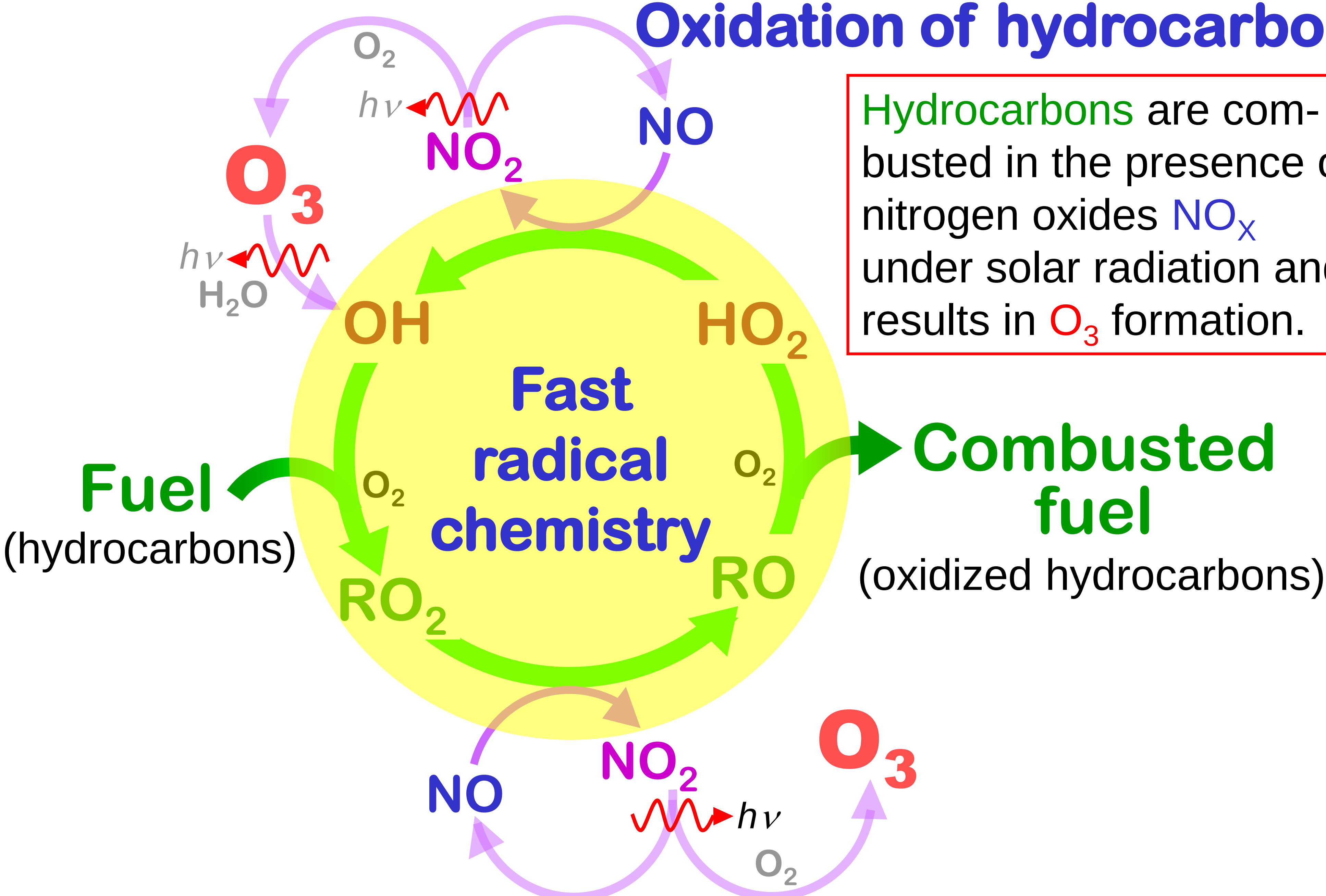
# The troposphere is an oxidizing medium

$NO_2$ and solar radiation controls the production of $O_3$ , which in turn controls the production of $HO_x$ radicals, which in turn controls the oxidizing capacity of the troposphere and the lifetime of trace gases.



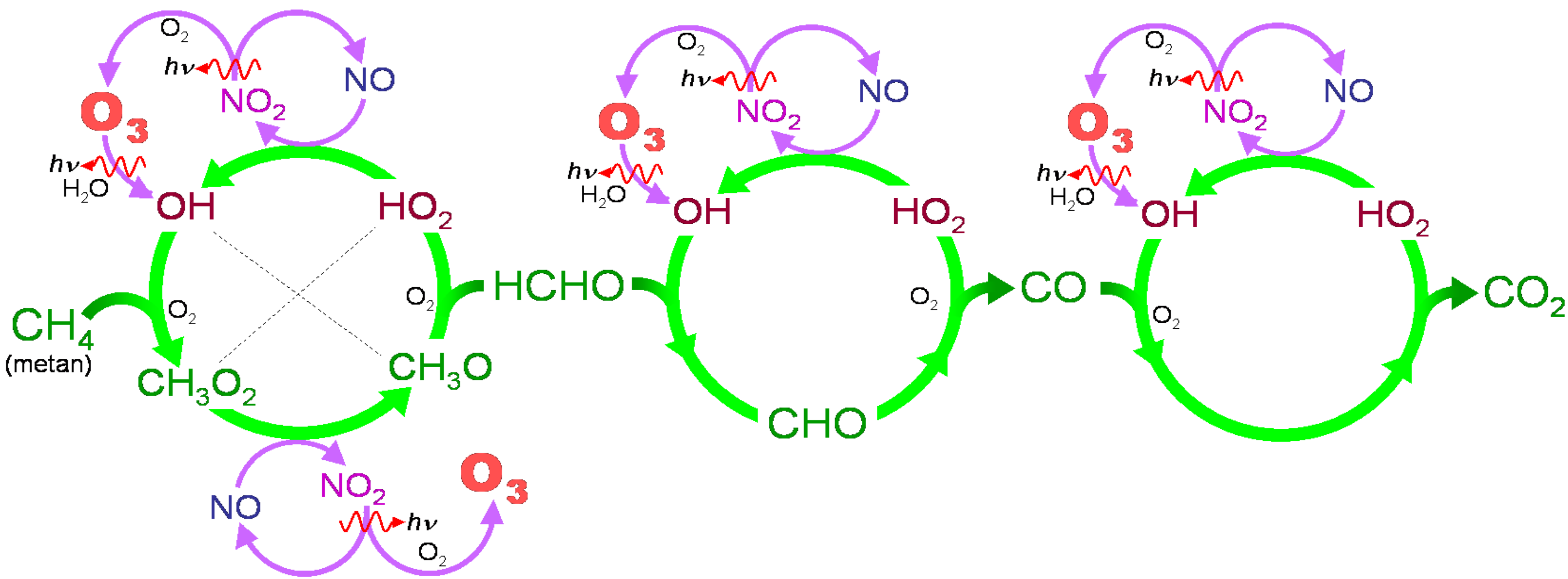
# Oxidation of hydrocarbons

Hydrocarbons are combusted in the presence of nitrogen oxides $NO_X$ under solar radiation and results in $O_3$ formation.

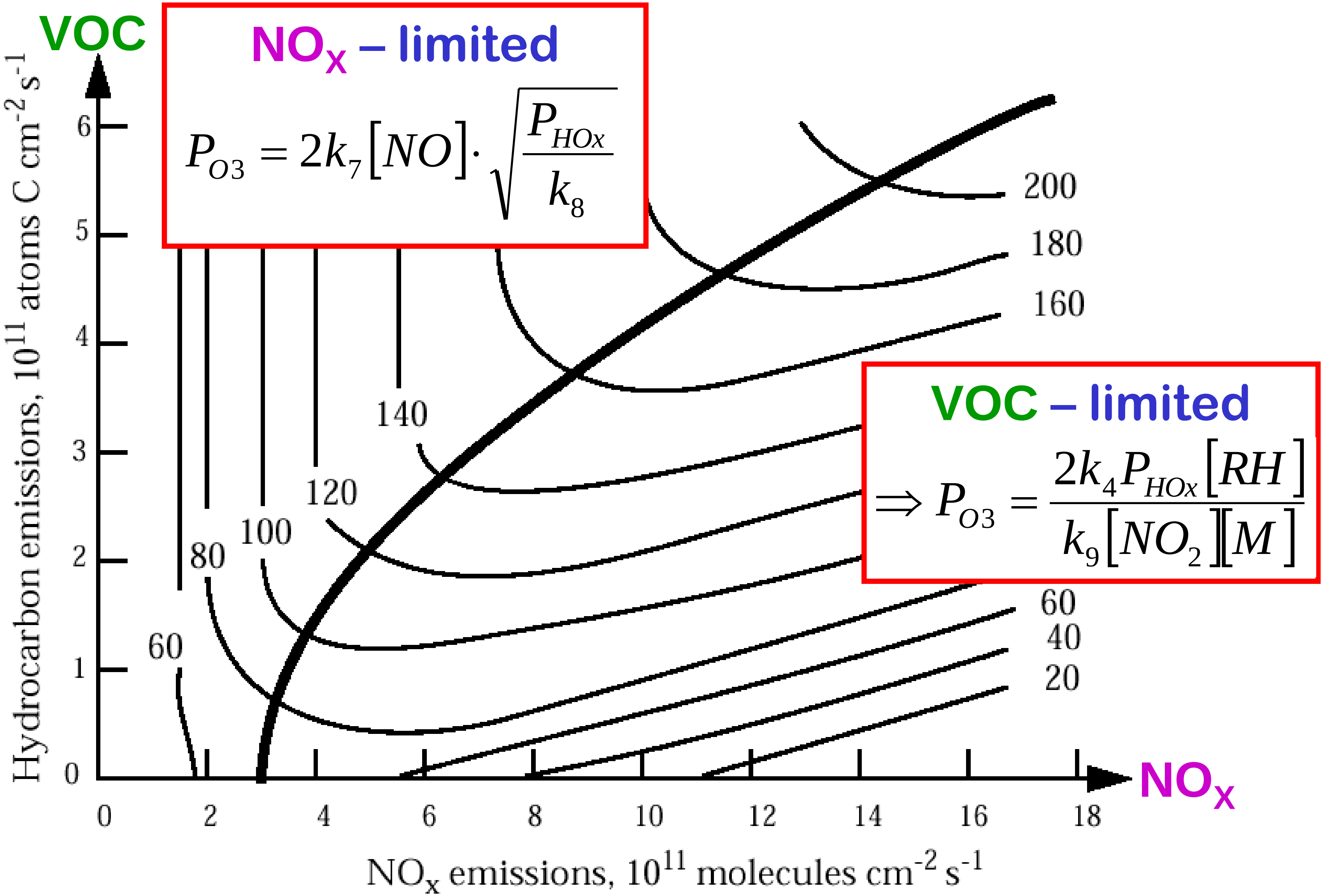


# $CH_4 \rightarrow HCHO \rightarrow CO \rightarrow CO_2$

methane C(-IV) → formaldehyde C(0) → carbon monoxide C(II) → $CO_2$ C(IV)



# Regimes for ozone production




**NO$_x$ – limited**

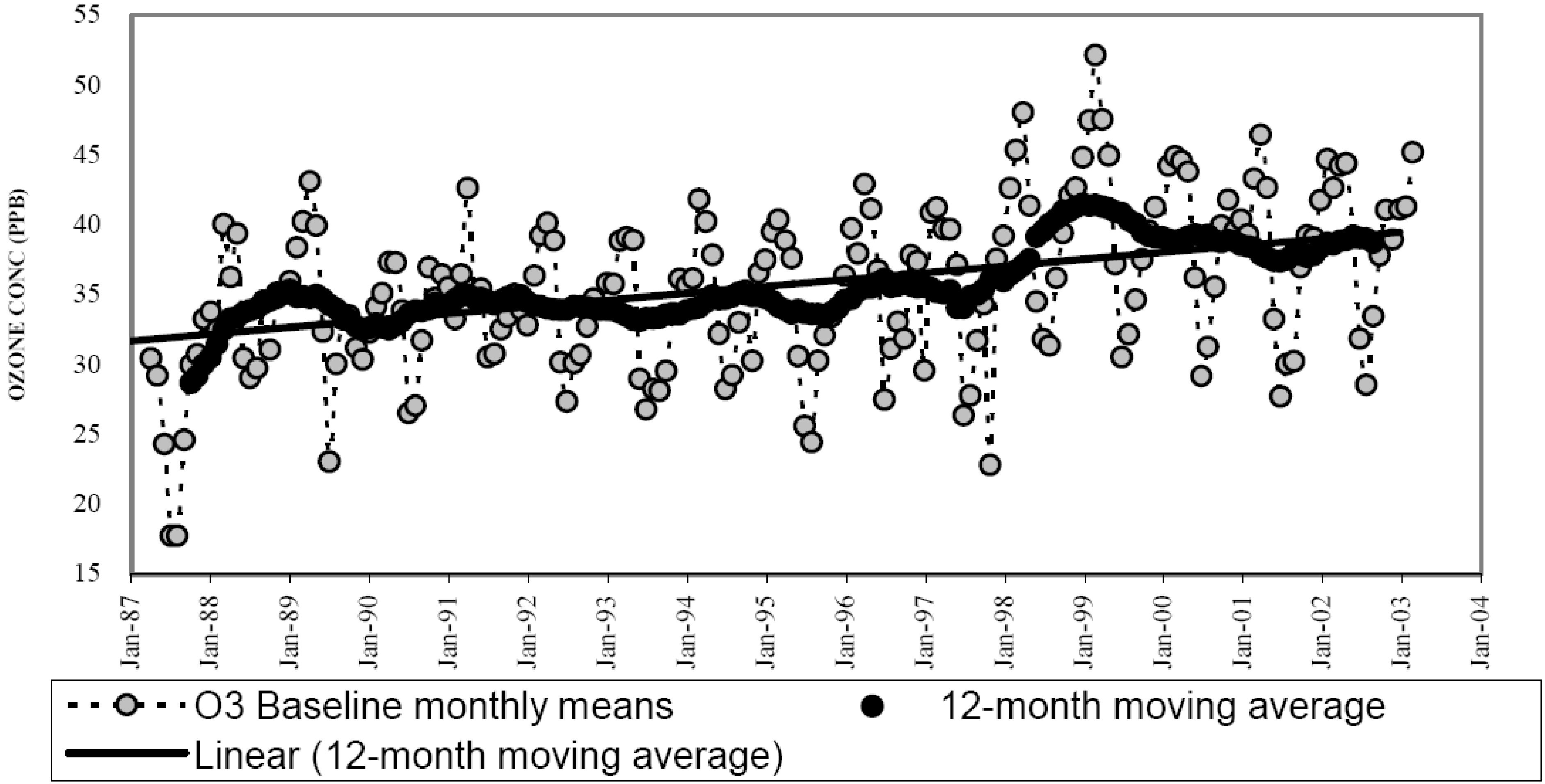
$$P_{O3} = 2k_7[NO]\cdot\sqrt{\frac{P_{HOx}}{k_8}}$$

**VOC – limited**

$$\Rightarrow P_{O3} = \frac{2k_4 P_{HOx}[RH]}{k_9[NO_2][M]}$$

# Hemispheric background levels of ground-level ozone have increased by ~5 ppb per decade the last 20-30 years.

Data from the station Mace Head on the west coast of Ireland.



# Health Effects of Air Pollution in Europe (EU-28)

Source: EEA, ”Air Quality in Europe - 2014 Report”

The EEA recently estimated (EEA, 2014) that

the health impacts attributable to exposure to fine particulate matter (**PM2.5**) in the EU-28 were responsible for around

**430’000 premature deaths annually**.

The health impact of exposure to $O_3$ concentrations on the EU-population was estimated to be about

**16’160 premature deaths per year**.

European Environment Agency

http://www.eea.europa.eu/publications/air-quality-in-europe-2014

# Damage cost of air pollution in Europe (2010) and policy response

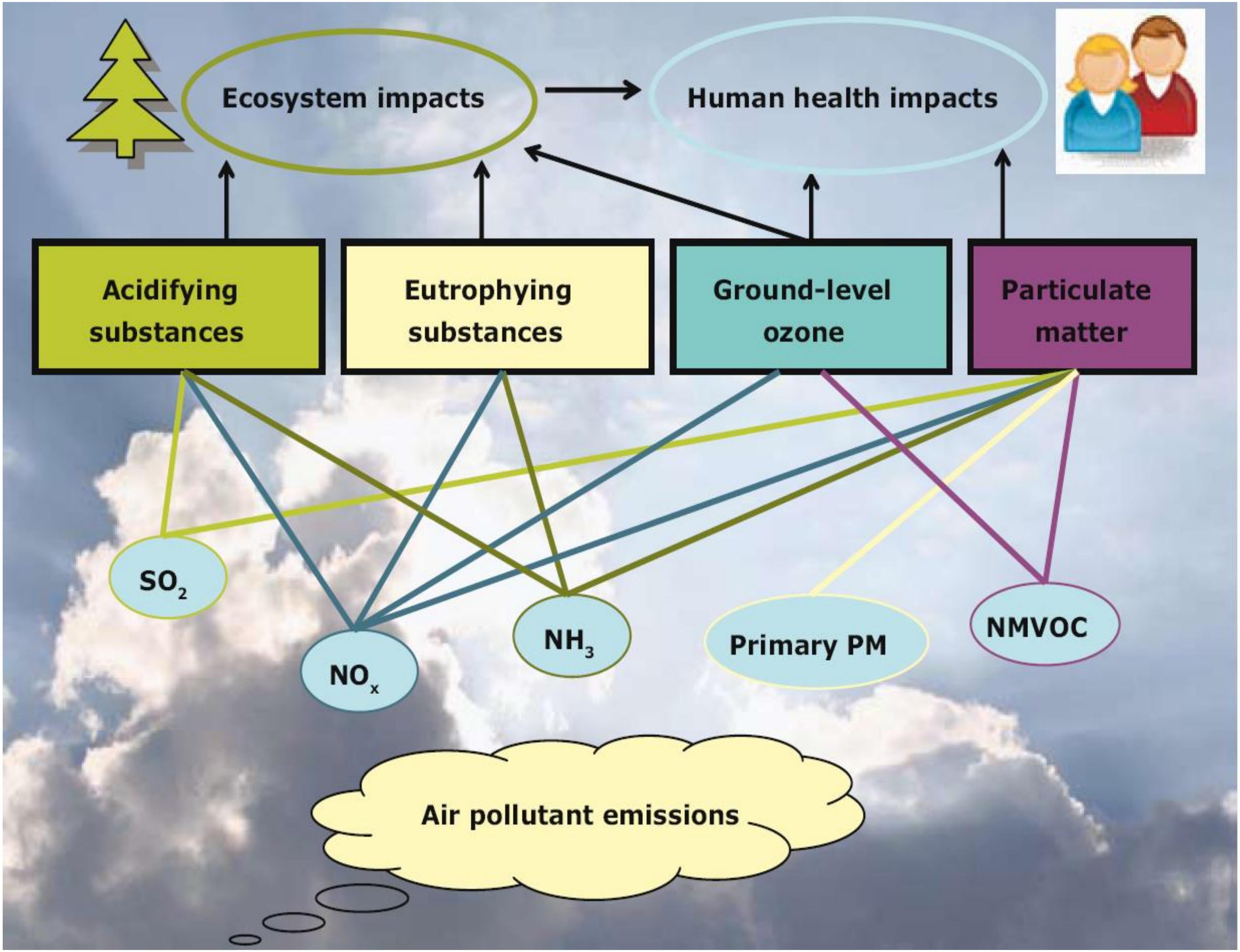
Source: ” EC, 2013: Impact assessment for new policy package to clean up Europe's air”

- Damage cost of mortality – at least EUR 330 billion

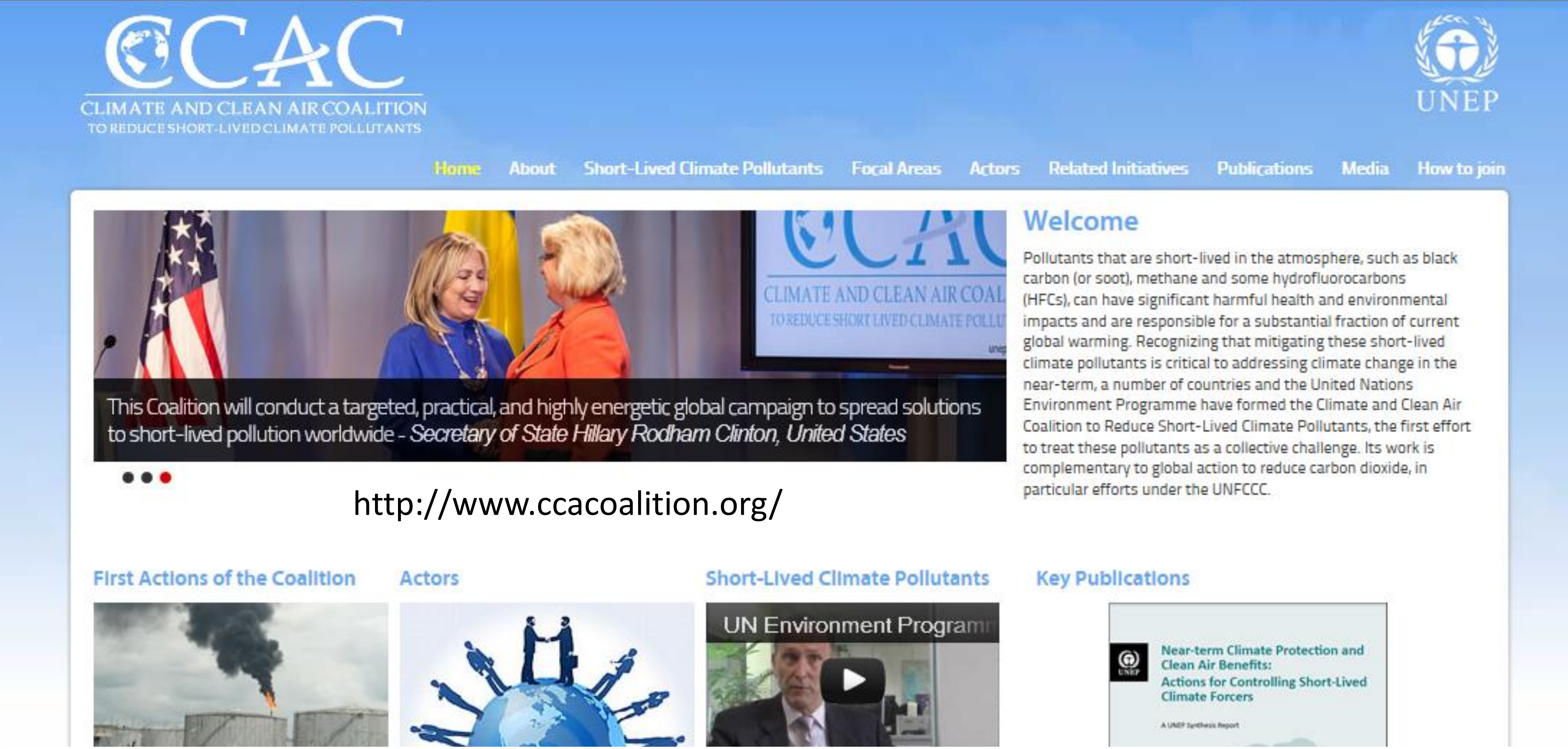
- Direct economic damage - EUR 15 billion from workdays lost

- Direct economic damage - EUR 4 billion in healthcare cost

- Direct economic damage - EUR 3 billion crop yield loss



Ecosystem impacts
Human health impacts
Acidifying substances
Eutrophying substances
Ground-level ozone
Particulate matter
$SO_2$
$NO_x$
$NH_3$
Primary PM
NMVOC
Air pollutant emissions




**CCAC – Climate and Clean Air Coalition**

Short-lived Climate Pollutants (SLCP)

http://www.smhi.se/slcp

# The Convention on Long-Range Transboundary Air Pollution CLRTAP

http://www.unece.org/env/lrtap/welcome.html

Now 51 Parties (countries)

Under UN-ECE (United Nations Economic Commission for Europe)

Since 1979 the CLRTAP has addressed some of the major environmental problems of the UNECE region through scientific collaboration and policy negotiation.

The Convention has been extended by **eight protocols** that identify specific measures to be taken by Parties to cut their emissions of air pollutants.

**8th protocol (Gothenburg):**
The **1999** Protocol to Abate Acidification, Eutrophication and Ground-level Ozone; 25 Parties.
Entered into force on 17 May 2005.

The aim of the Convention is that Parties shall endeavour to **limit** and, as far as possible, gradually reduce and **prevent air pollution including long-range transboundary air pollution**.

Currently, the Convention's priority activities include review and possible **revision of its most recent protocols**, **implementation** of the Convention and its protocols across the entire UNECE region.

# Will the environmental quality objectives be achieved?

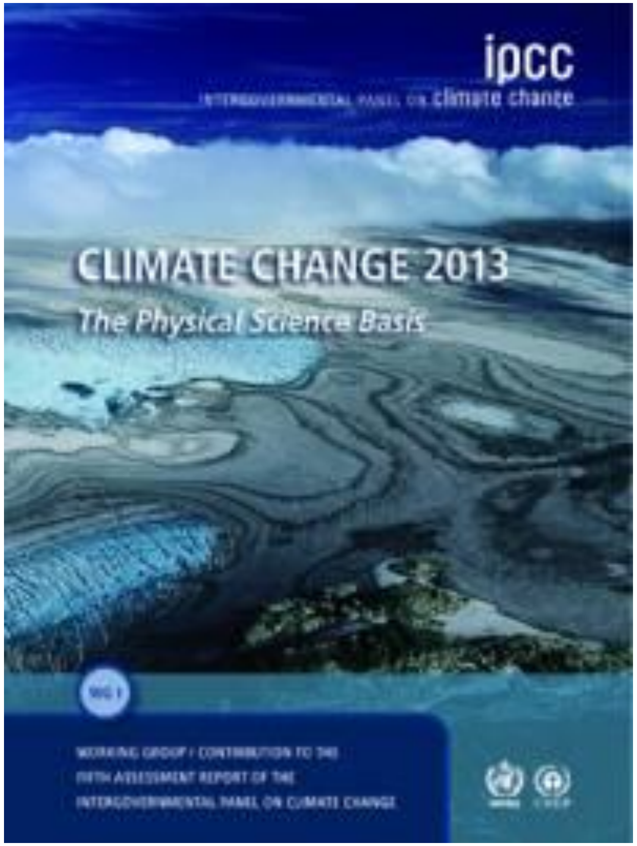
http://miljomal.nu/

| OBJECTIVE | Forecast for 2020 | Trend |
|---|---|---|
| 1. Reduced Climate Impact* | | |
| 2. Clean Air | | |
| 3. Natural Acidification Only | | |
| 4. A Non-Toxic Environment | | |
| 5. A Protective Ozone Layer | | |
| 6. A Safe Radiation Environment | | |
| 7. Zero Eutrophication | | |
| 8. Flourishing Lakes and Streams | | |
| 9. Good-Quality Groundwater | | |
| 10. A Balanced Marine Environment, Flourishing Coastal Areas and Archipelagos | | |
| 11. Thriving Wetlands | | |
| 12. Sustainable Forests | | |
| 13. A Varied Agricultural Landscape | | |
| 14. A Magnificent Mountain Landscape | | |
| 15. A Good Built Environment | | |
| 16. A Rich Diversity of Plant and Animal Life | | |

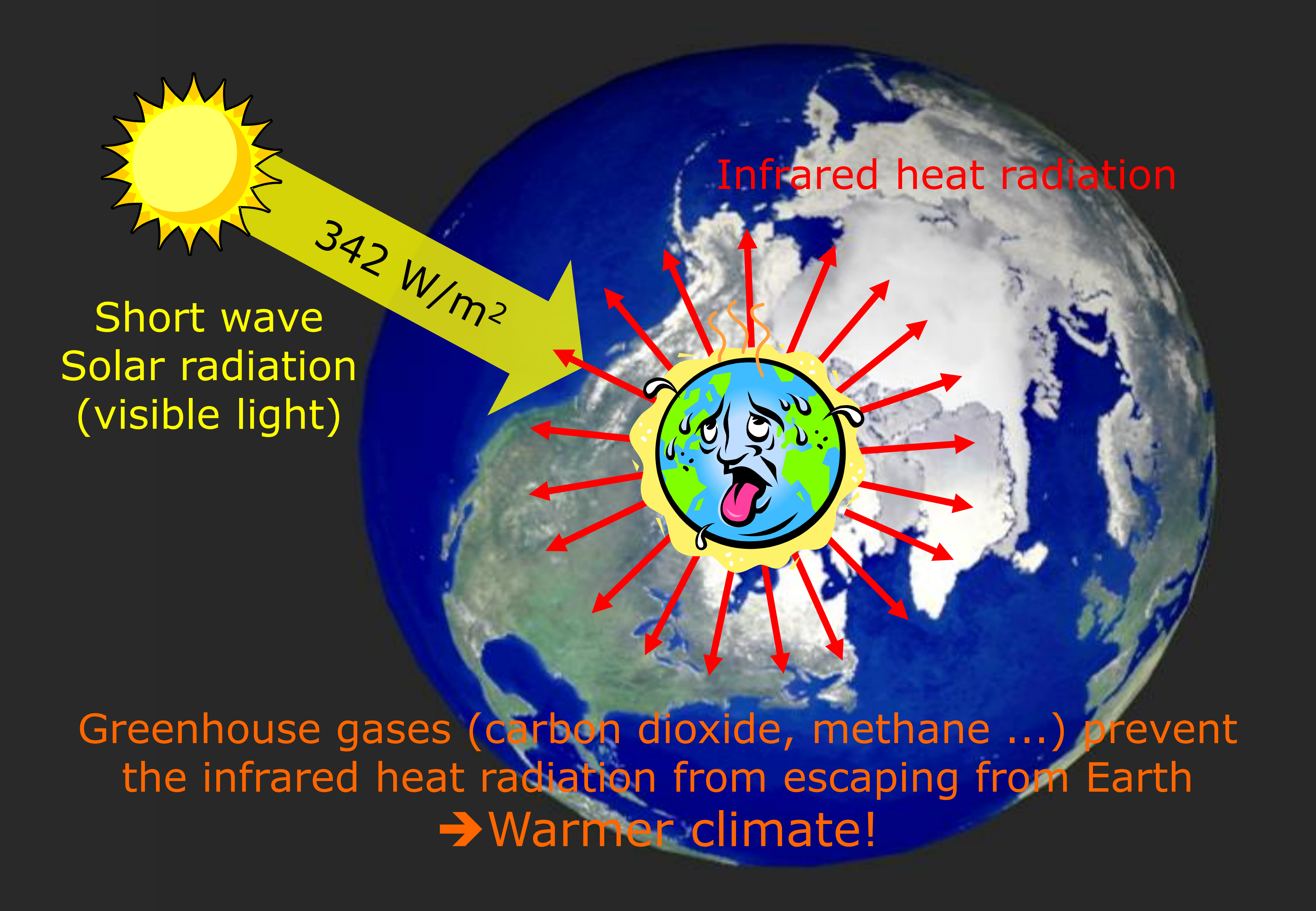
* Target year 2050, as a first step

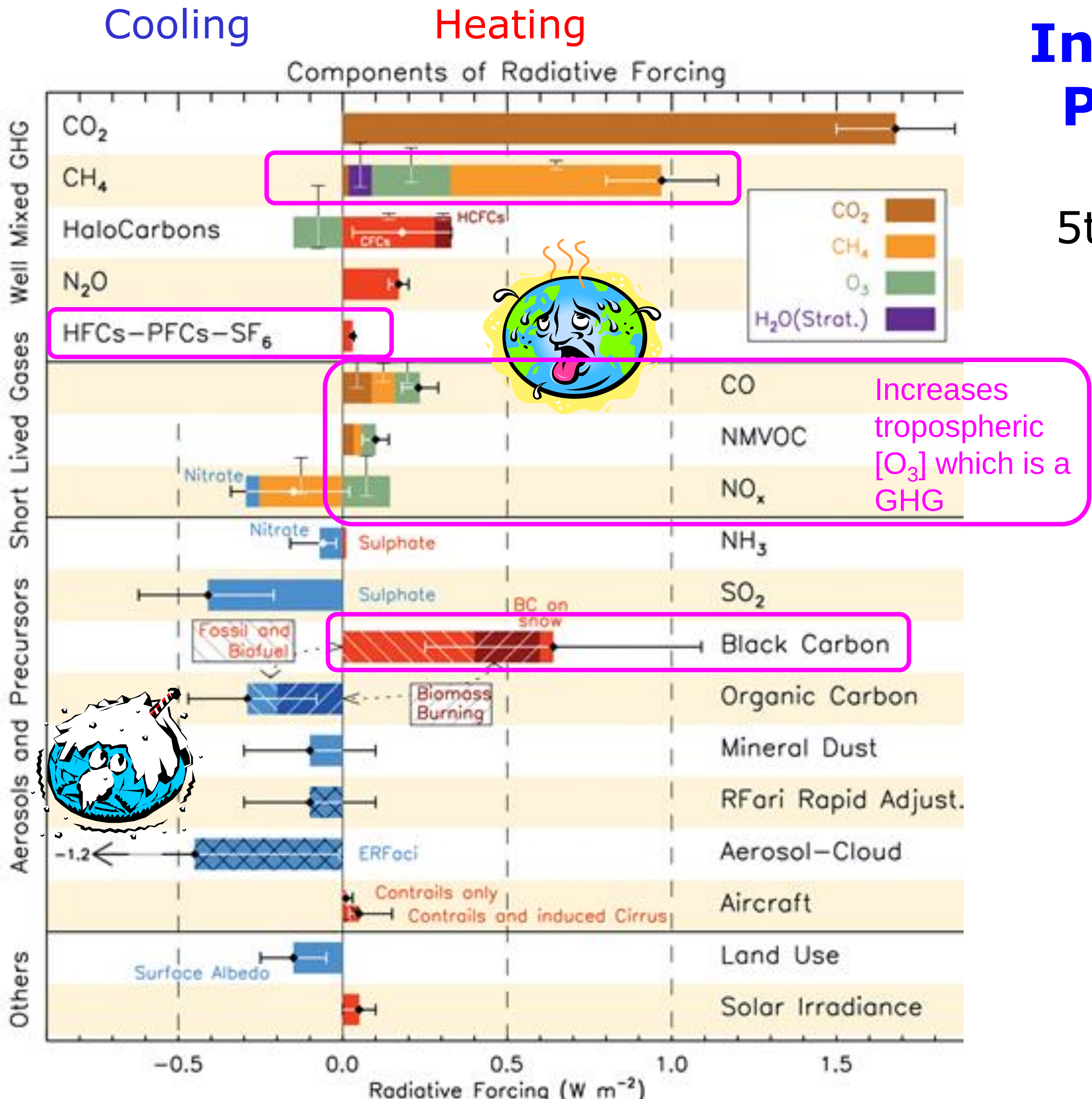
# Main messages
# IPCC AR5 WG1 - 27 Sept 2013

- Climate (continues) to change
- It is our fault
- To mitigate climate change, we need forceful actions – and fast!




http://www.naturvardsverket.se/Om-Naturvardsverket/Publikationer/ISBN/6500/978-91-620-6592-8/


342 W/m²
Short wave
Solar radiation
(visible light)
Infrared heat radiation
Greenhouse gases (carbon dioxide, methane ...) prevent
the infrared heat radiation from escaping from Earth
➔Warmer climate!




Radiative Forcing relative to 1750 ($W/m^2$)

# Intergovernmental Panel on Climate Change

5th Assessment Report 2013

**Air Pollution and Climate issues are linked**

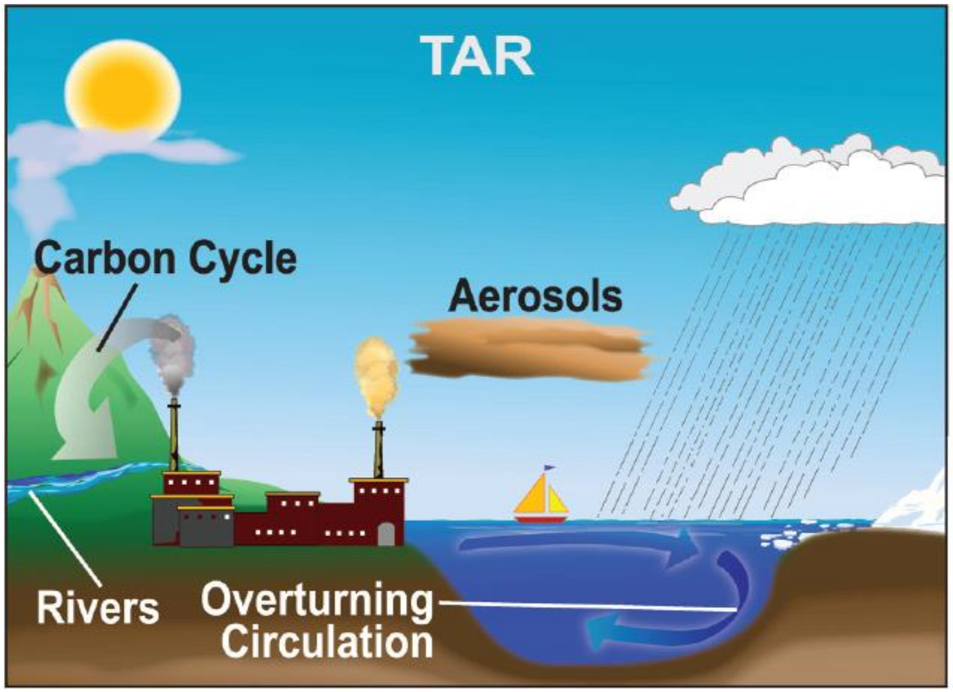
Photochemical smog – ground-level ozone – particles (PM) – health effects – radiative forcing – global warming – more smog etc….

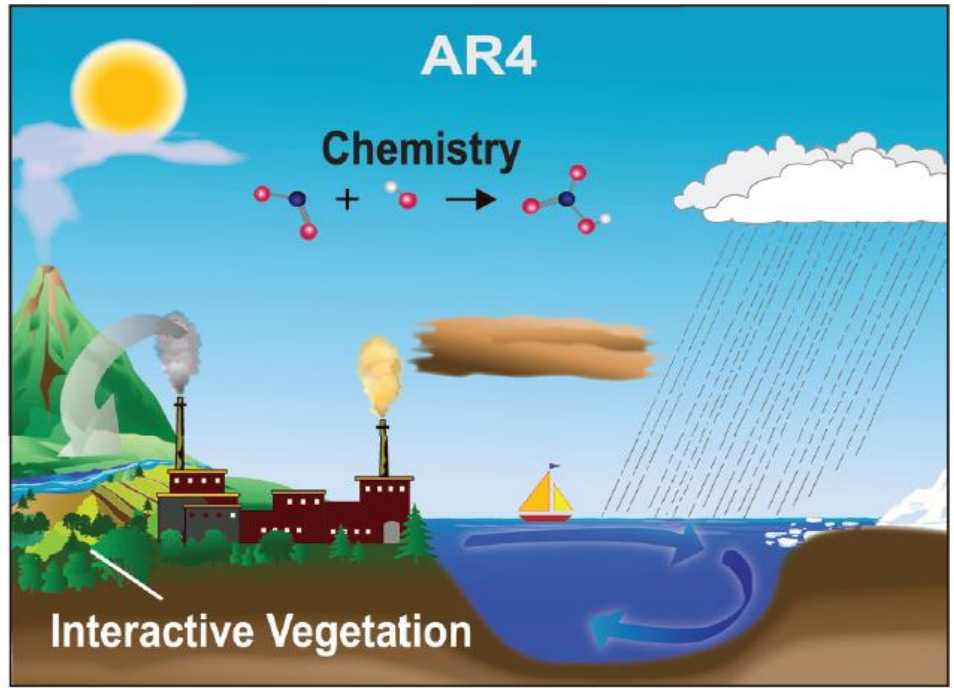
**SLCP: Short lived climate pollutants**

# History of Climate Modelling

Aerosols and atmospheric chemistry has only recently been introduced in global climate models.

Still very crude representations.



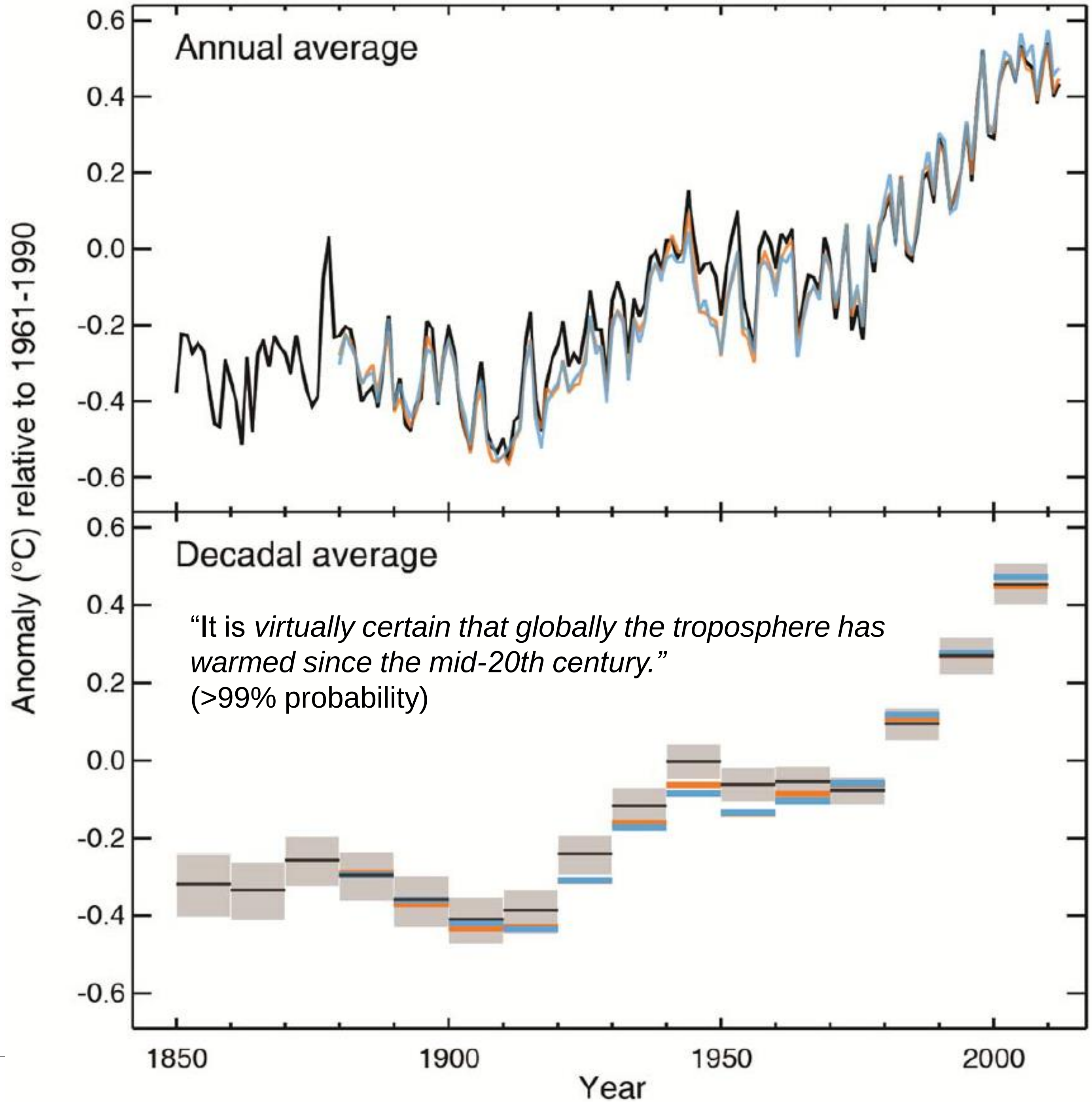
# Planet Earth is warming

Global average

Surface temperature land and sea

Period: 1880–2012

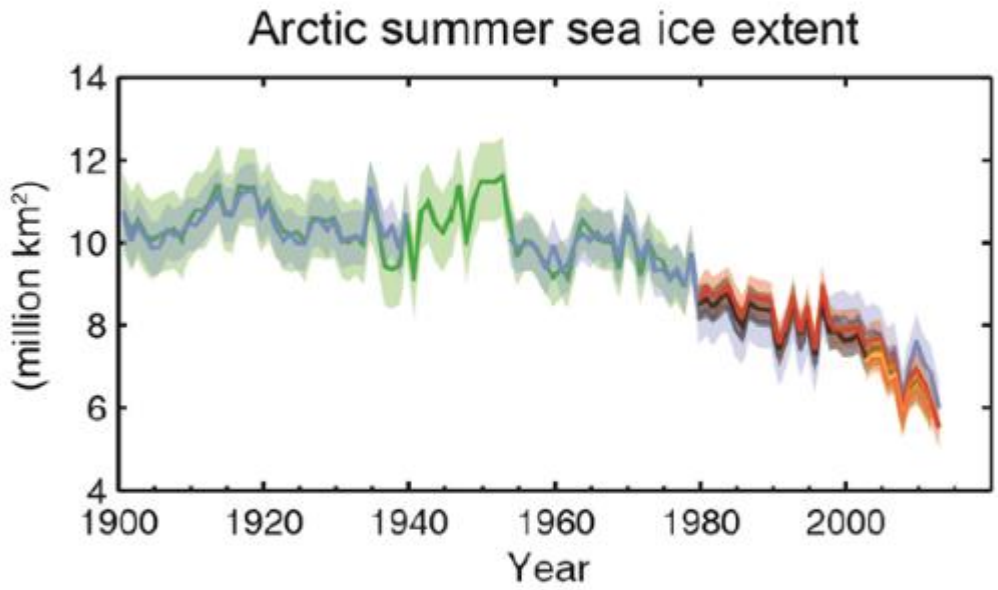
**+0.85 ºC**

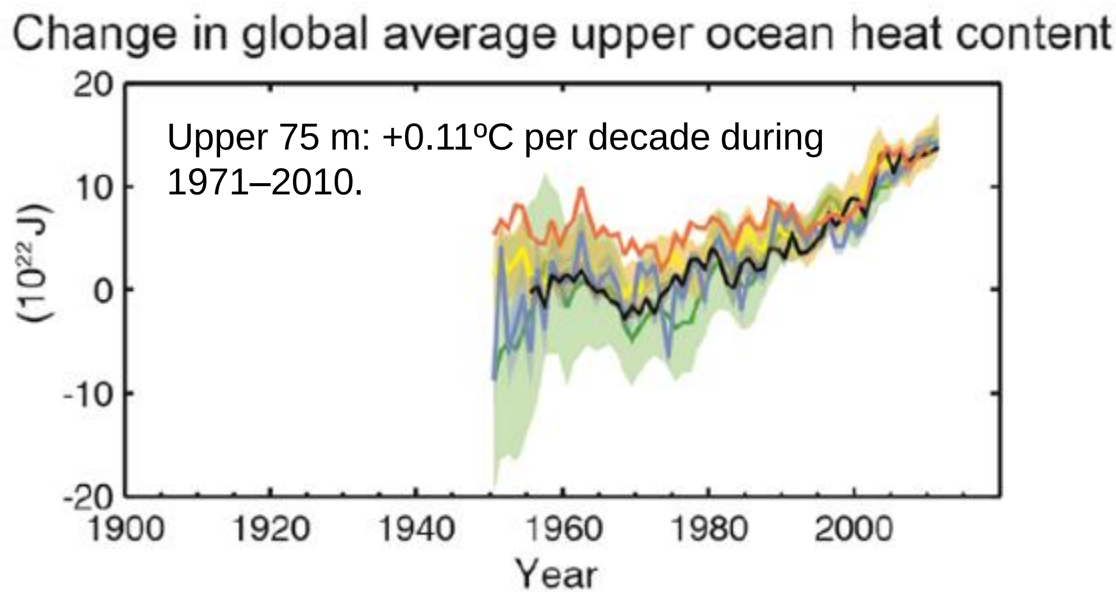



"It is *virtually certain that globally the troposphere has warmed since the mid-20th century.*"
(>99% probability)

IPCC 2013, SPM

- …
- Decreasing Arctic sea ice
- Increasing ocean heat content
- Rising sea level
- Oceans acidify
- Shrinking land ices
- More weather extremes
- …

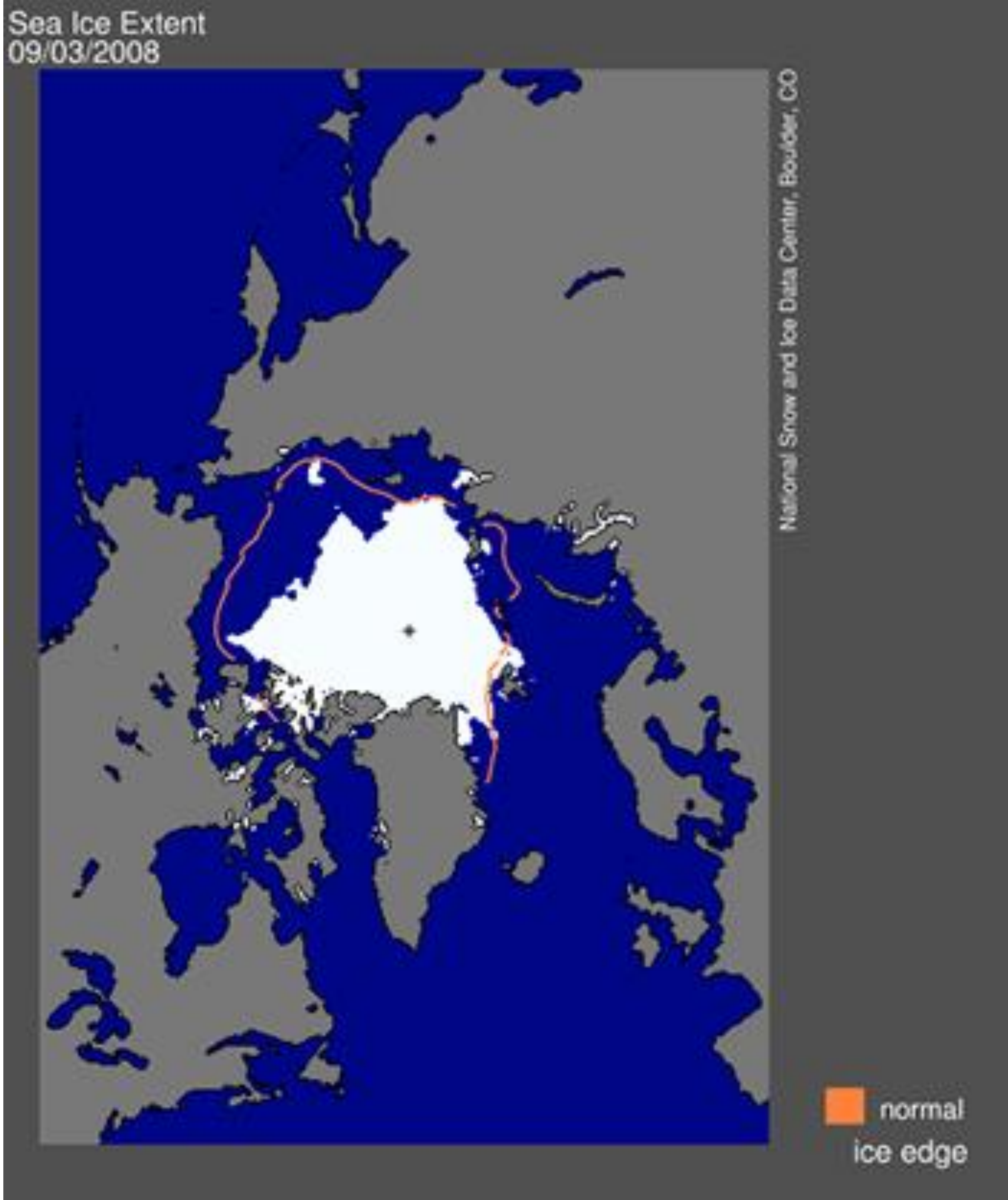



A constant supply of heat through the ocean surface at the rate of 1 W $m^{-2}$ for 1 year would increase the ocean heat content by 1.1 x $10^{22}$ J.

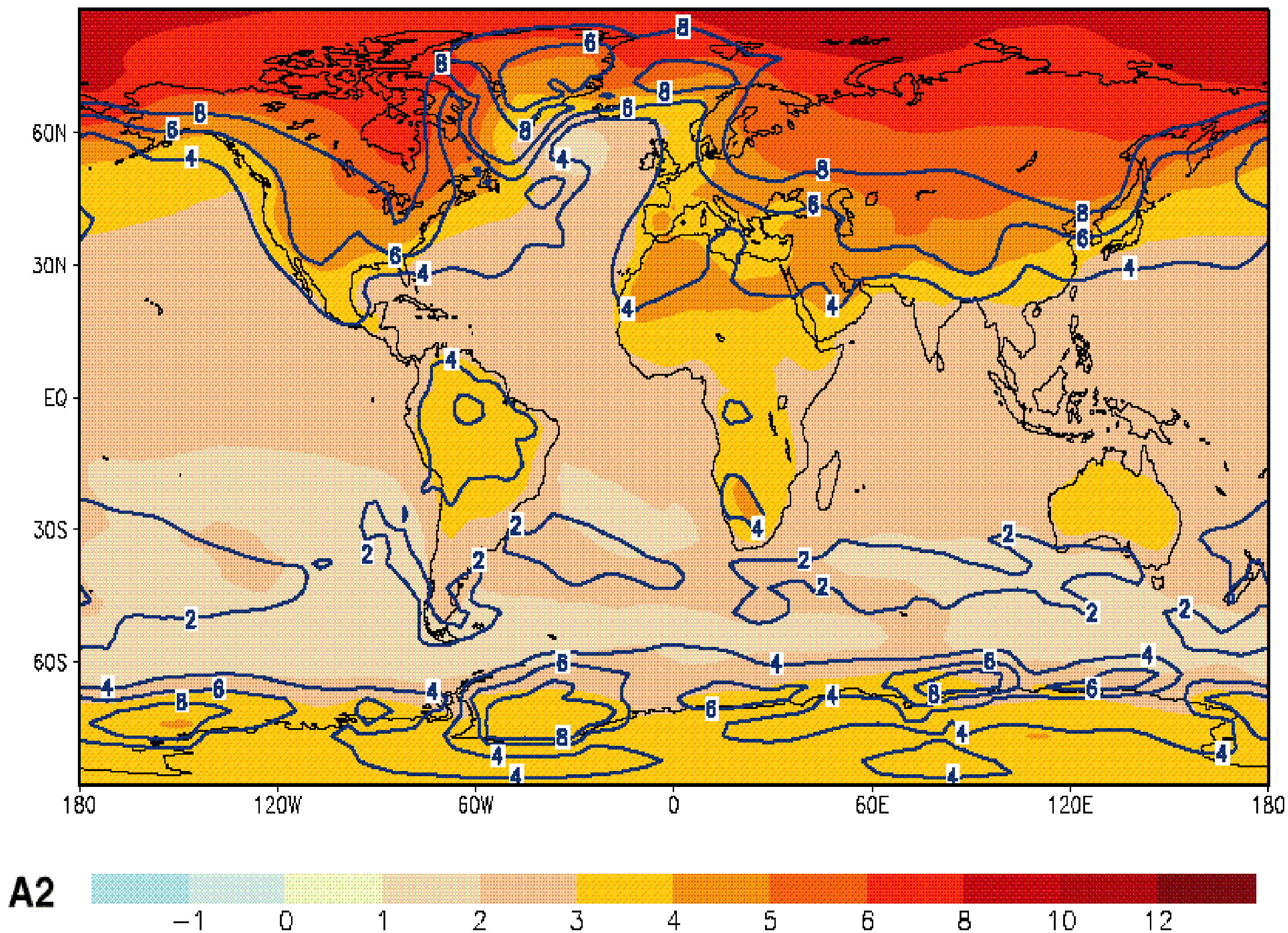
# Arctic Sea Ice Extent

http://nsidc.org



Most climate models predict

rapidly increasing temperatures in the Arctic during the next century.




Temperature increase in °C from 1961-1990 to 2071-2100.

- …
- Decreasing Arctic sea ice
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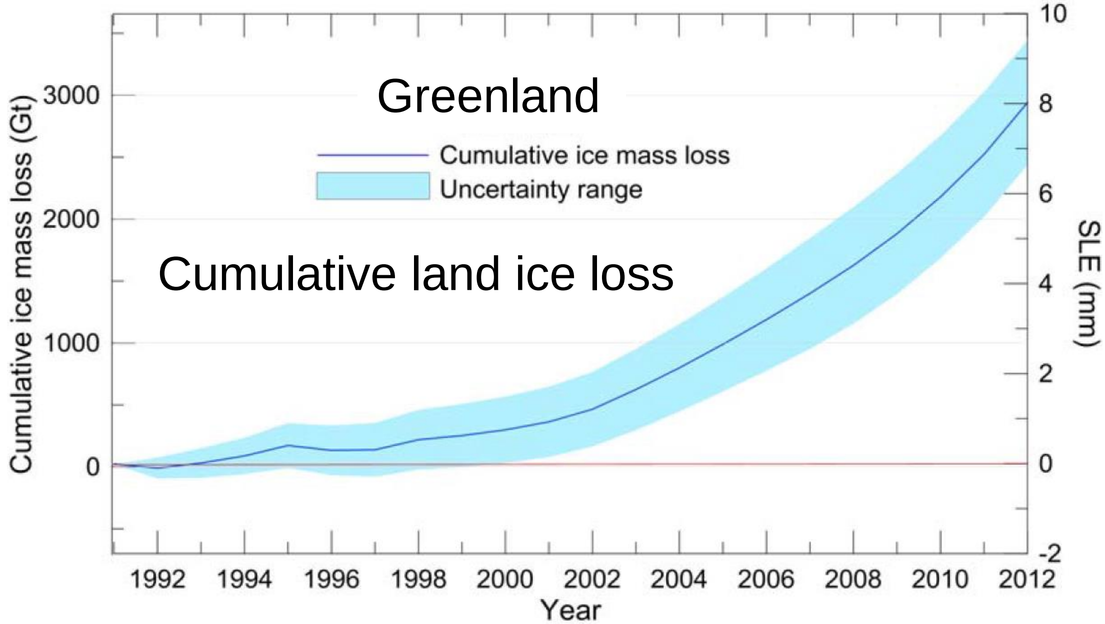
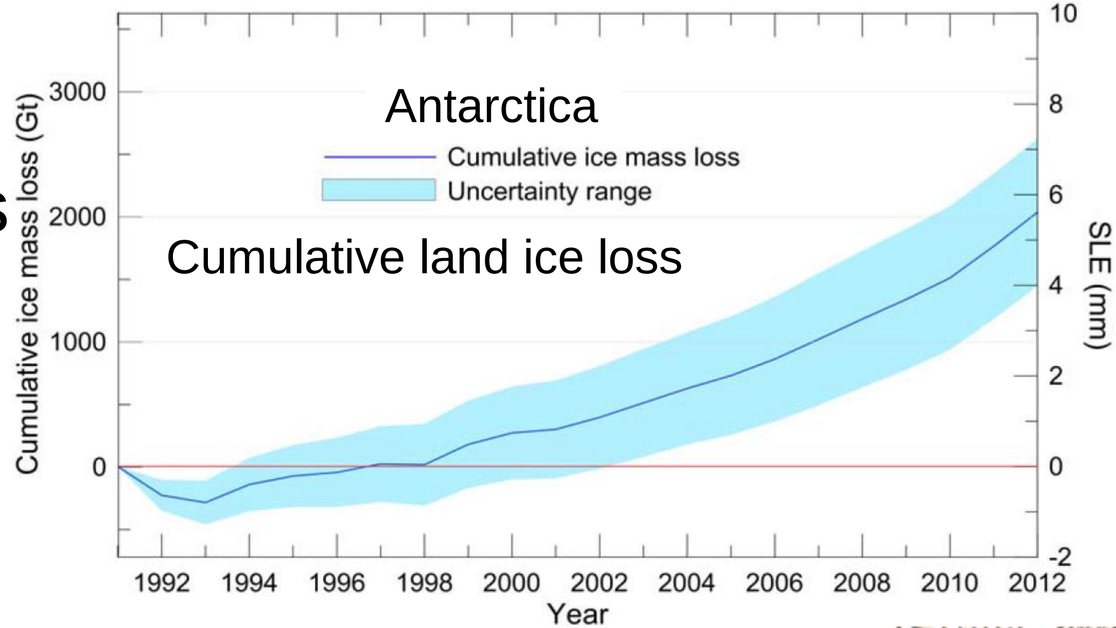
- …






IPCC 2013, SPM

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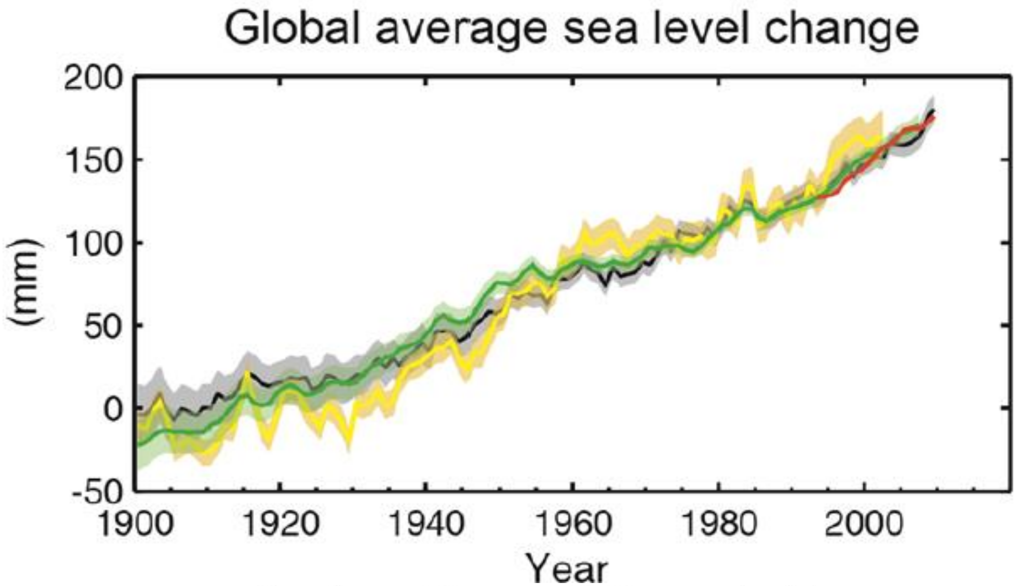
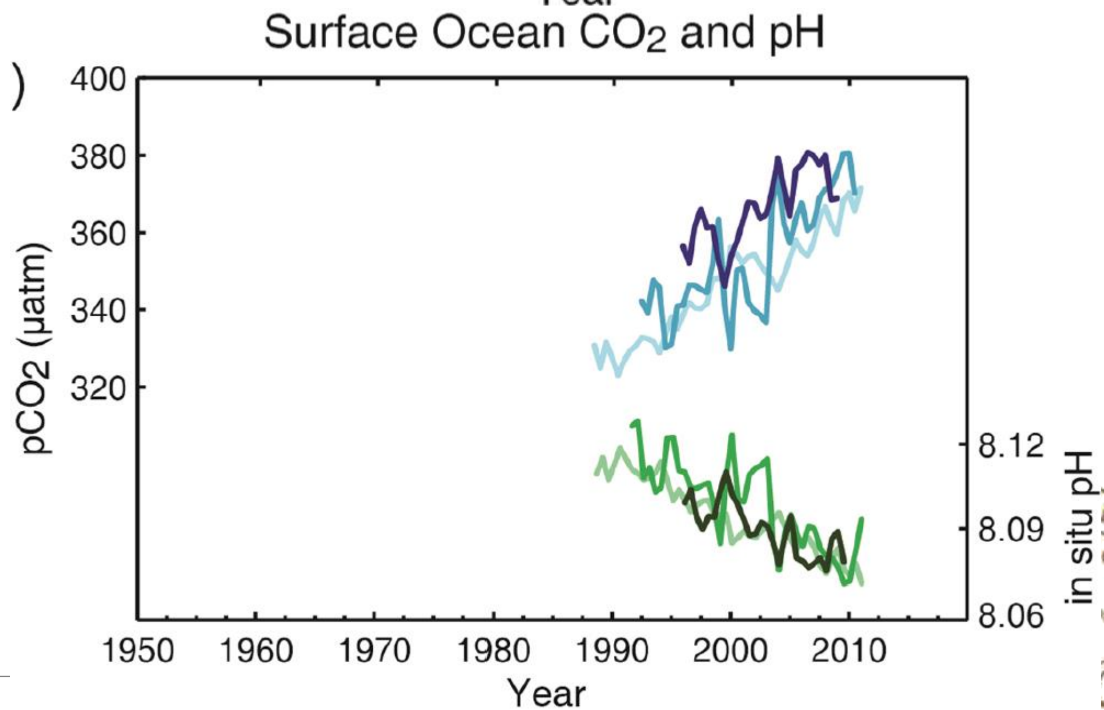
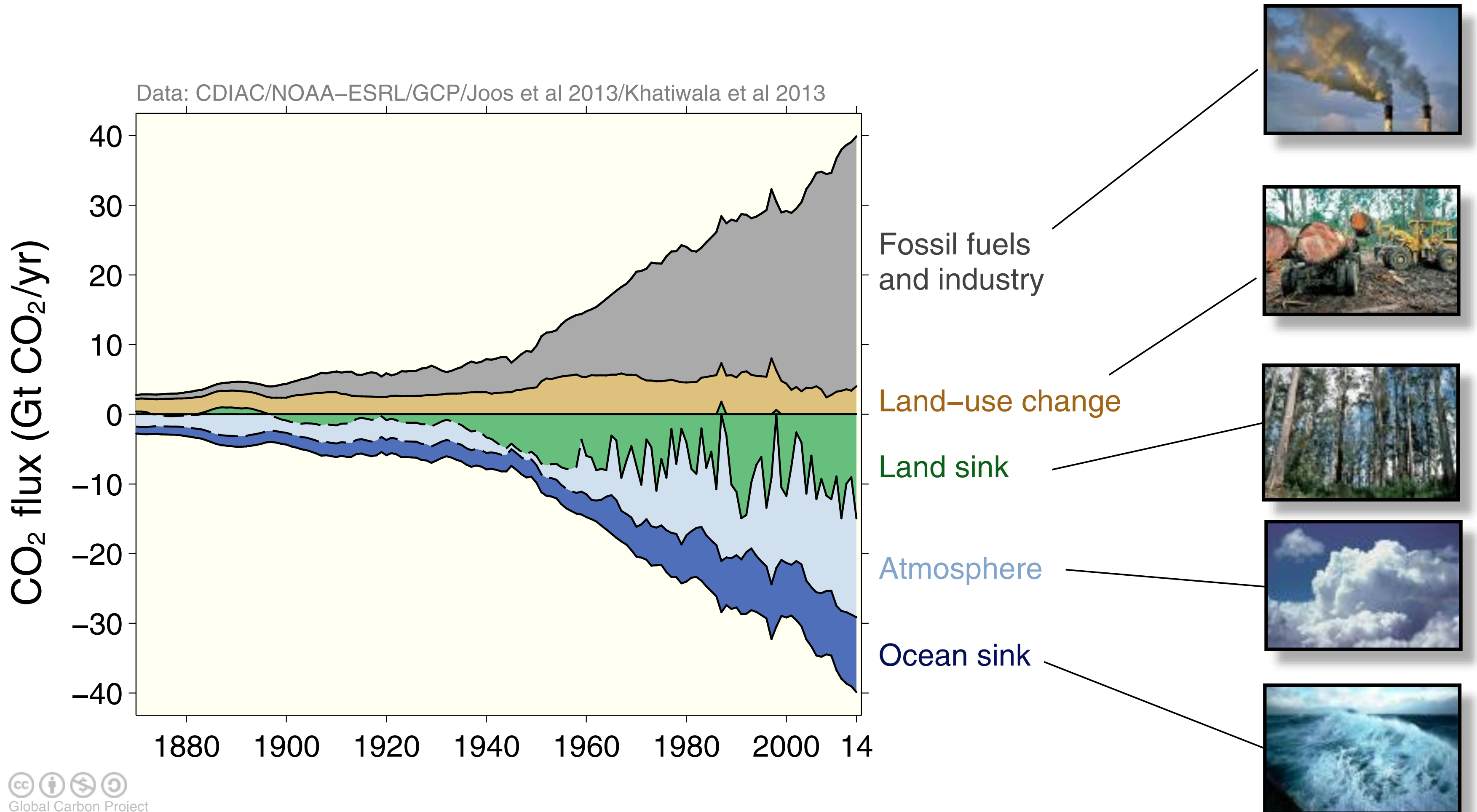


# Global Carbon Budget

## Emissions to the atmosphere are balanced by the sinks

## Averaged sinks since 1959: 44% atmosphere, 28% land, 28% ocean

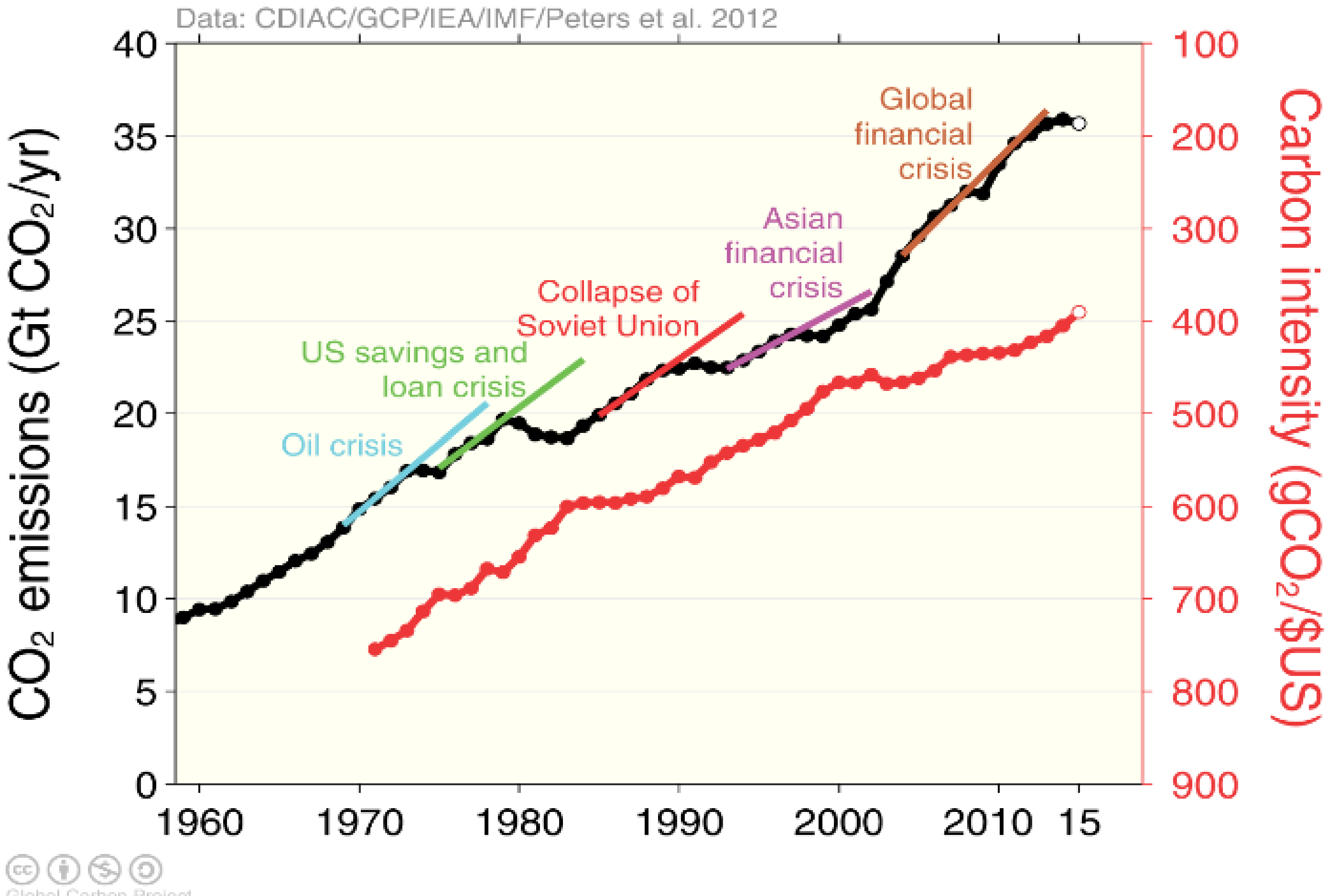



- Source: CDIAC; NOAA-ESRL; Houghton et al 2012; Giglio et al 2013; Joos et al 2013; Khatiwala et al 2013; Le Quéré et al 2015; Global Carbon Budget 2015

# Carbon intensity of economic activity - global

Financial crises have had little lasting effect on emissions growth

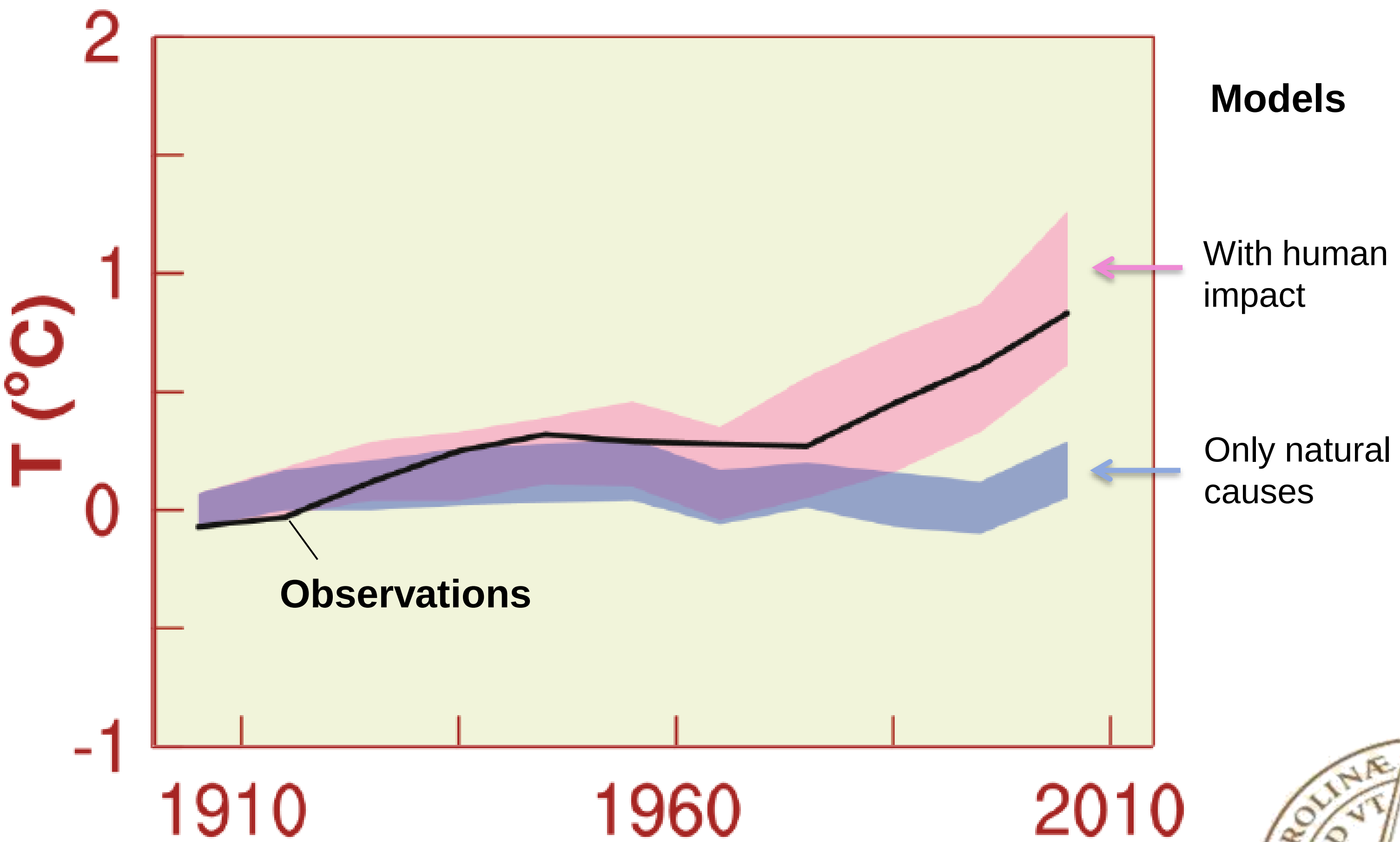
Global carbon intensity has returned to a phase of improvement after stalling for some years




Economic activity is measured in Purchasing Power Parity

Source: CDIAC; Le Quéré et al 2015; Global Carbon Budget 2015

# Humans are the cause of climate change




After IPCC 2013, SPM. Approved 27 Sep 2013.

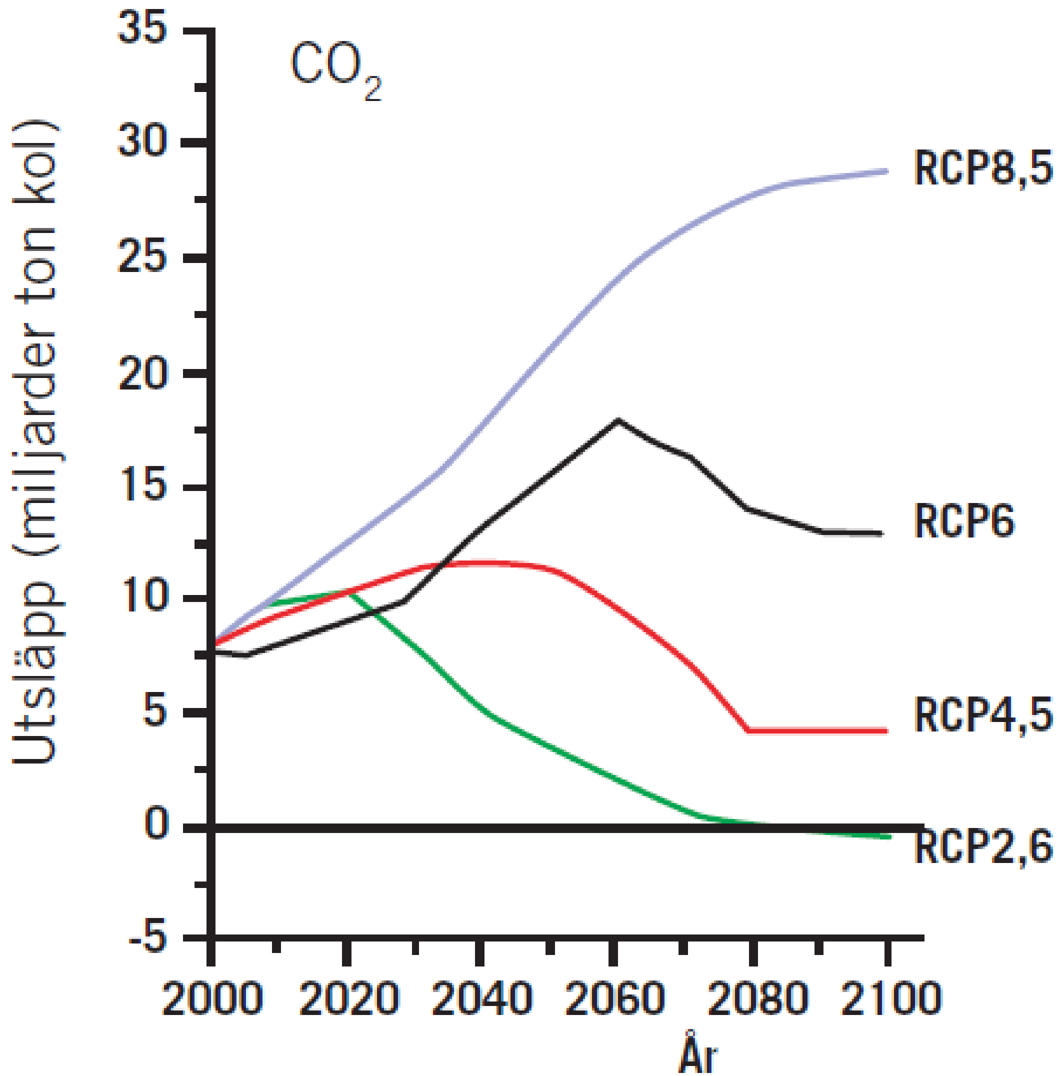
# What matters are near the future $CO_2$ emissions

RCP2,6

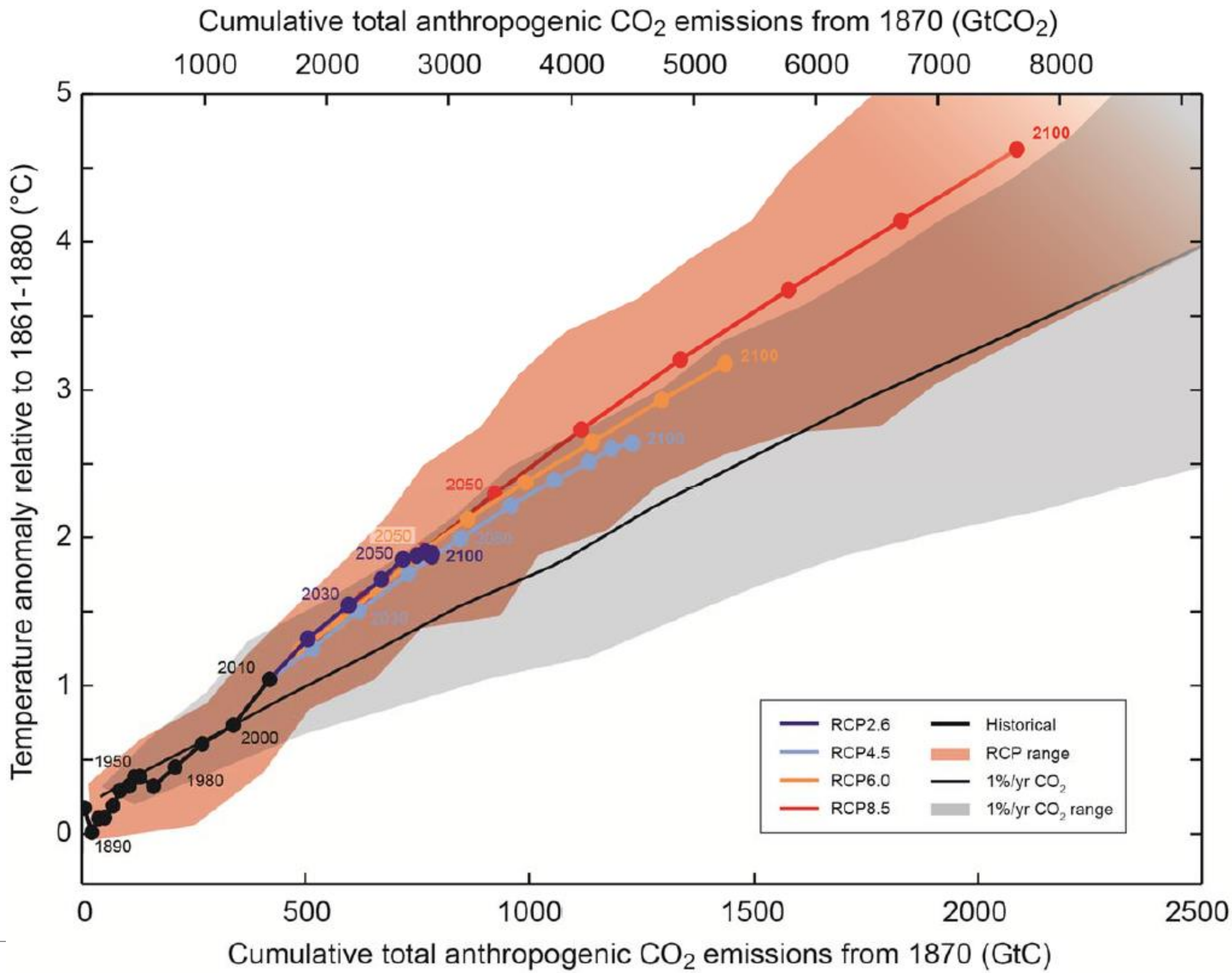
RCP4,5

RCP6,0

RCP8,5



# Cumulative $CO_2$ emissions determine global temperature change



# Methods for environmental monitoring, 7.5 p FKF100

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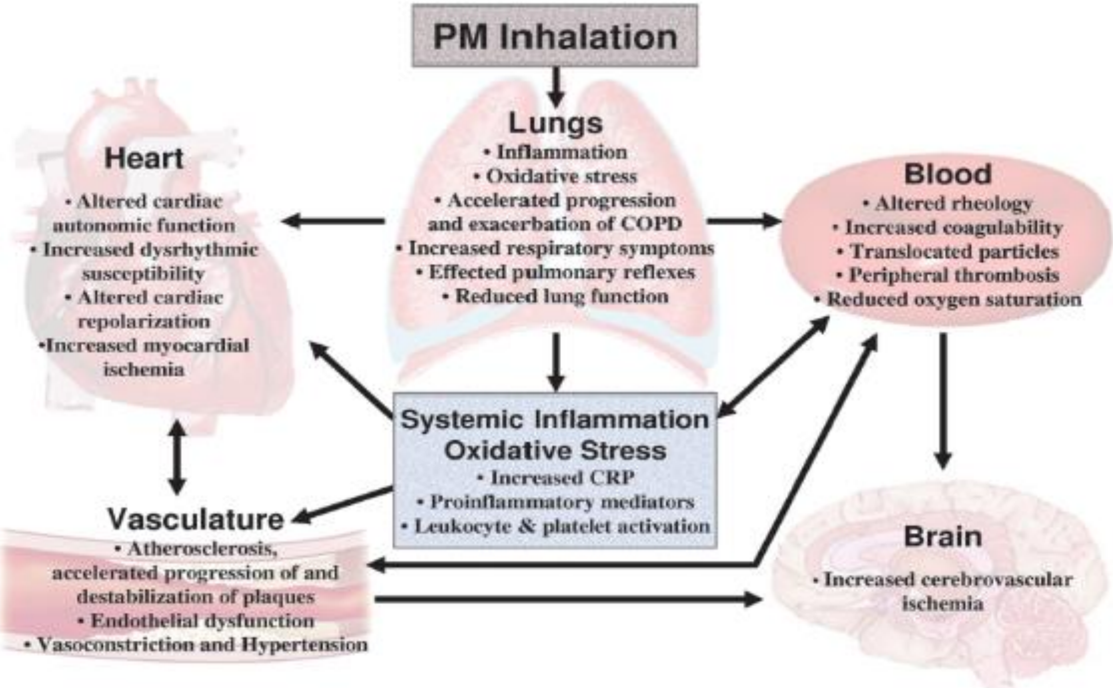
**About different environmental problems, particles, gases, working environment problems, and so on.**
**In the course you gain an understanding for the current environmental issue, and how to construct a measurement strategy to investigate it.**
**A project work is made, that includes the analasys of environmental data and the investigation of how the environment is affected. Real cases!**

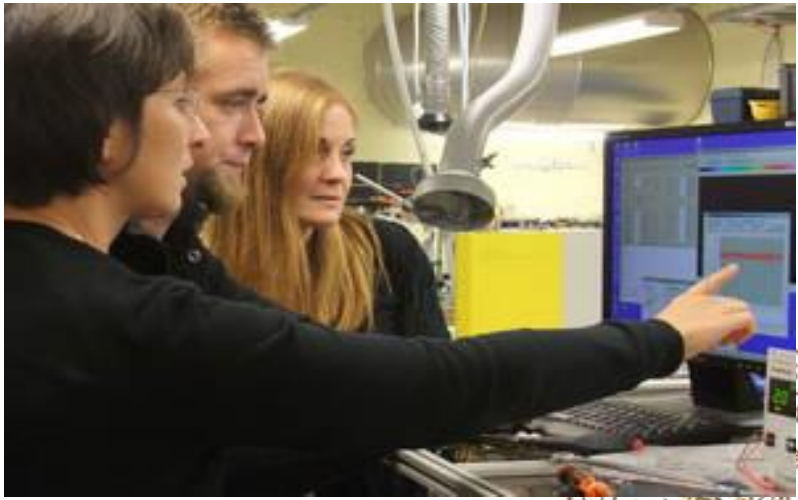
Visit at the Örtofta combined biomass heat and power plant.


**Lab work with preparing the measurement strategy and doing the measurements**

Basic understanding of different measurement techniques

What kind of particles are there in the air, and how can we measure them? What happens when we inhale them? You can get an answer to these questions in the course ***Aerosol technology MAM242,*** *7.5 p.* You will also find out how particles affect our climate and their fate in the atmosphere. Aerosol Technology is widely used in the medical branch and the nano industry.

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