

# ***Gasphase chemistry of the atmosphere and climate change***

Prepared by J. Staehelin  
(Fall Semester 2011)

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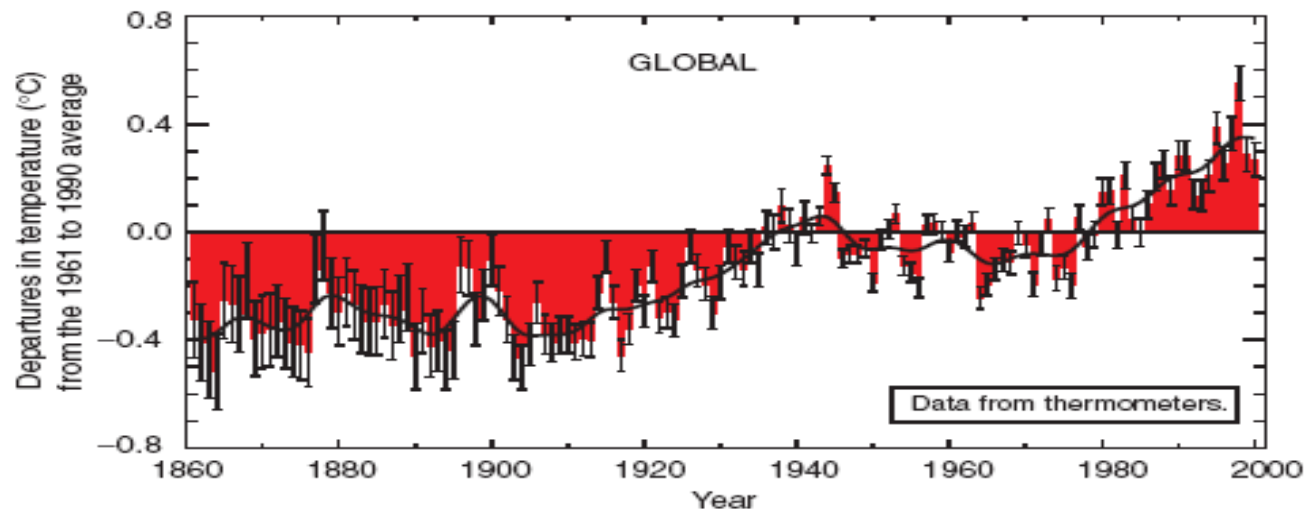
# 1. Introduction

Climate change caused by anthropogenic activities includes many different aspects. Here we focus on aspects of climate change that are closely linked to the gas phase chemistry the troposphere. The lecture includes:

- short introduction
- the concept of radiative forcing
- short overview of global cycles of greenhouse gases
- the Global Warming Potentials (GWP)
- Kyoto Protocol
- Effects of the Montreal Protocol on climate
- tropospheric ozone and climate

# Variations of the Earth's surface temperature for:

## (a) the past 140 years



## (b) the past 1,000 years

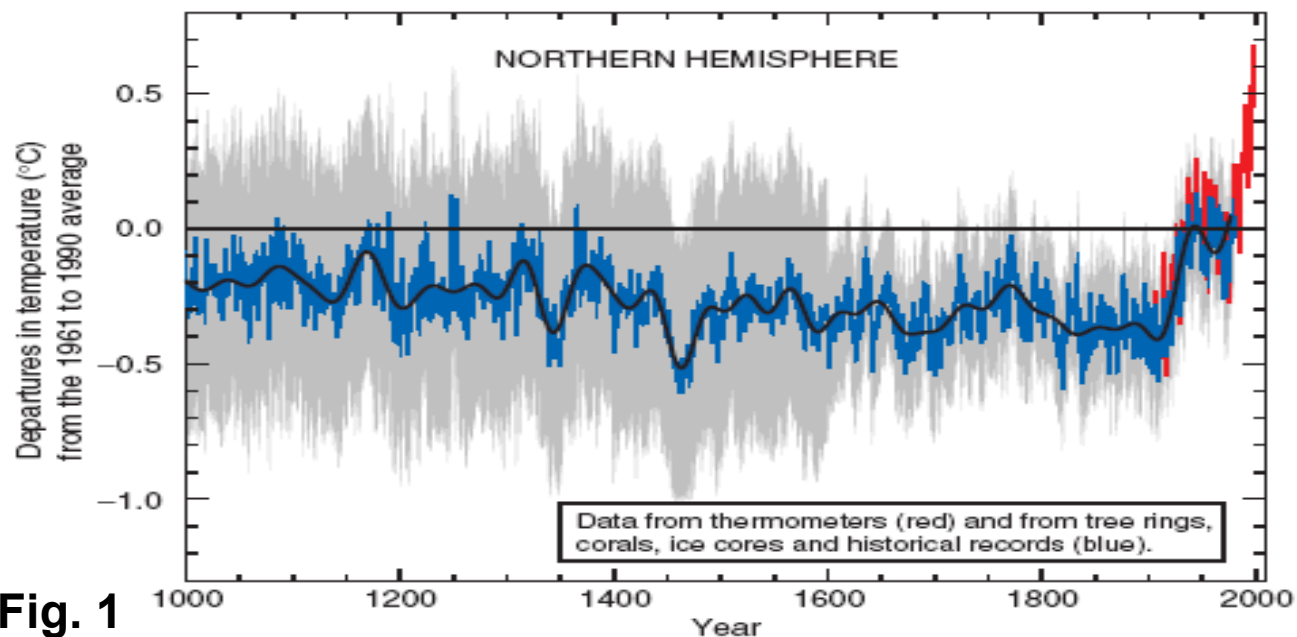


Figure 1: Variations of the Earth's surface temperature over the last 140 years and the last millennium.

(a) The Earth's surface temperature is shown year by year (red bars) and approximately decade by decade (black line, a filtered annual curve suppressing fluctuations below near decadal time-scales). There are uncertainties in the annual data (thin black whisker bars represent the 95% confidence range) due to data gaps, random instrumental errors and uncertainties, uncertainties in bias corrections in the ocean surface temperature data and also in adjustments for urbanisation over the land. Over both the last 140 years and 100 years, the best estimate is that the global average surface temperature has increased by  $0.6 \pm 0.2^\circ\text{C}$ .

(b) Additionally, the year by year (blue curve) and 50 year average (black curve) variations of the average surface temperature of the Northern Hemisphere for the past 1000 years have been reconstructed from "proxy" data calibrated against thermometer data (see list of the main proxy data in the diagram). The 95% confidence range in the annual data is represented by the grey region. These uncertainties increase in more distant times and are always much larger than in the instrumental record due to the use of relatively sparse proxy data. Nevertheless the rate and duration of warming of the 20th century has been much greater than in any of the previous nine centuries. Similarly, it is likely<sup>7</sup> that the 1990s have been the warmest decade and 1998 the warmest year of the millennium.

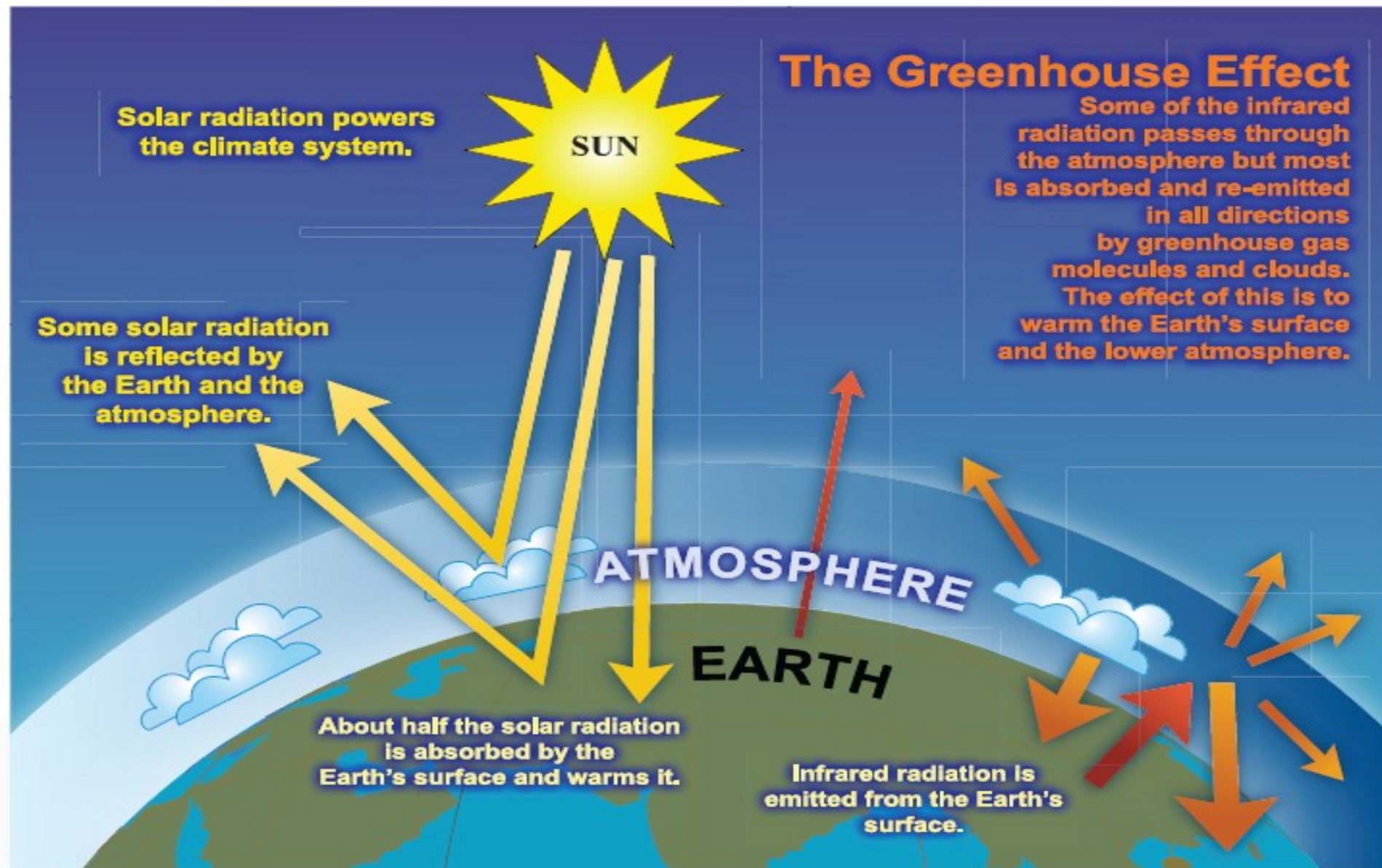
[Based upon (a) Chapter 2, Figure 2.7c and (b) Chapter 2, Figure 2.20]

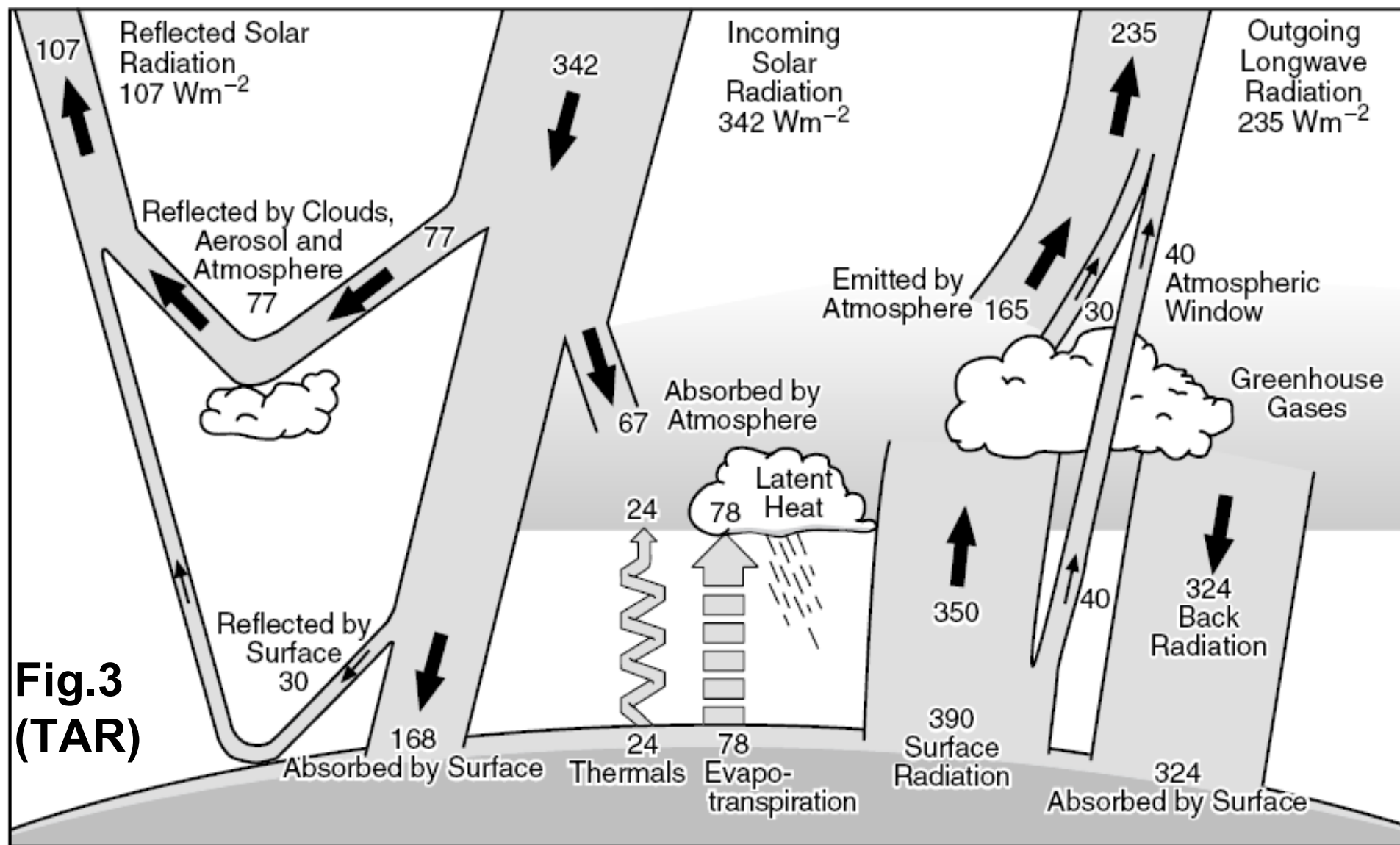
Fig. 1  
(TAR)

# Notes to Fig.1

- Global surface temperatures have remarkably increased in particular since 1980.
- Temperature in the northern hemisphere shows a decreasing tendency from 1000 until around the middle of the 19th century, when the strong increase started.
- The temperature increase in the last century is not uniform, showing the complex interactions between natural and anthropogenic forcing factors.
- According to AR4 it is very likely, that changes in climate (such as global mean temperature) can not be solely explained by natural variability.

Fig. 2: The greenhouse effect (AR4)





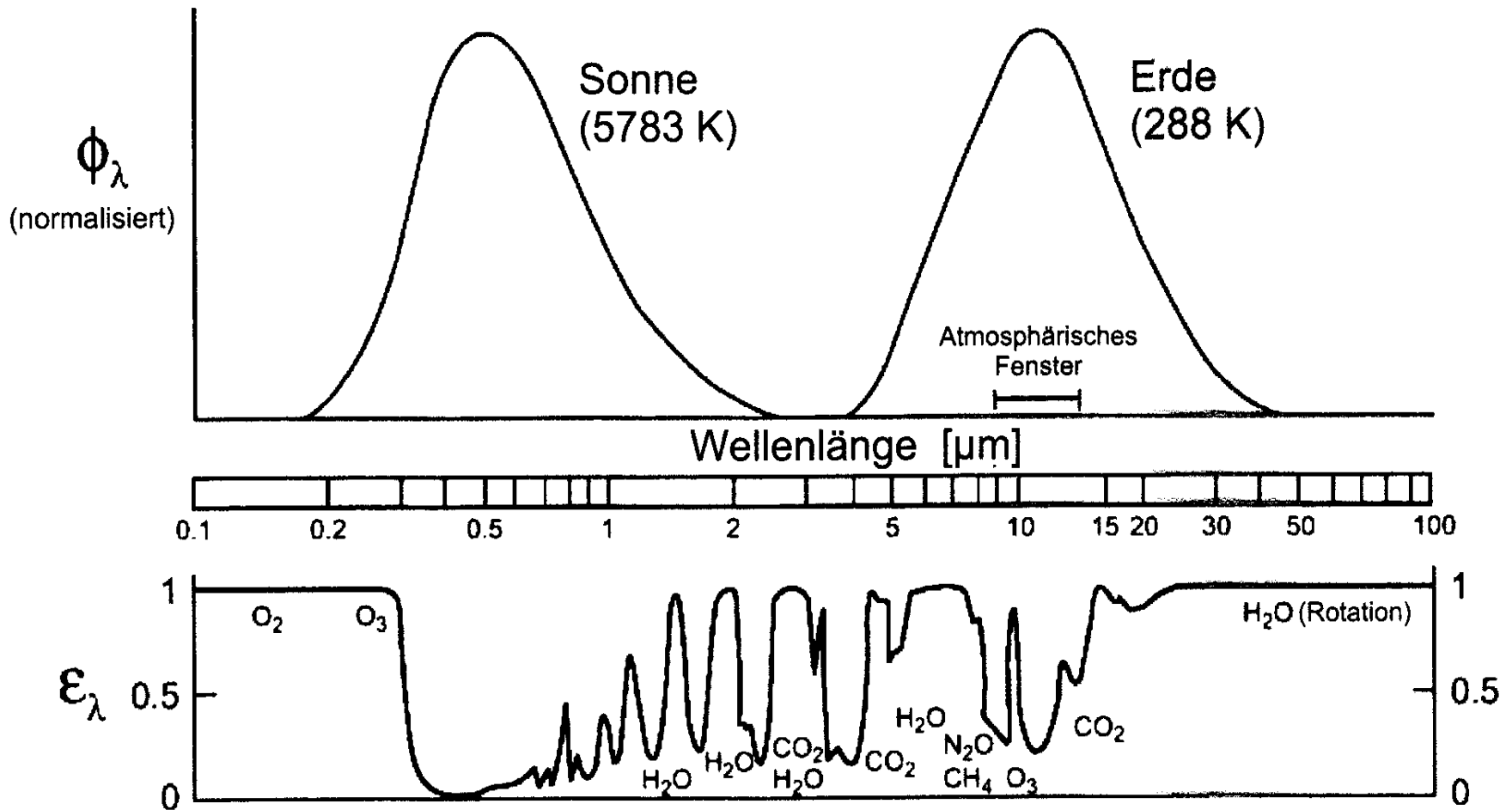
**Fig.3  
(TAR)**

**Figure 1.2:** The Earth's annual and global mean energy balance. Of the incoming solar radiation, 49% ( $168 \text{ Wm}^{-2}$ ) is absorbed by the surface. That heat is returned to the atmosphere as sensible heat, as evapotranspiration (latent heat) and as thermal infrared radiation. Most of this radiation is absorbed by the atmosphere, which in turn emits radiation both up and down. The radiation lost to space comes from cloud tops and atmospheric regions much colder than the surface. This causes a greenhouse effect. Source: Kiehl and Trenberth, 1997: Earth's Annual Global Mean Energy Budget, *Bull. Am. Met. Soc.* 78, 197-208.

## Notes to Fig. 2 and 3

- The Earth's radiation budget is important for weather and climate.
- Greenhouse gas concentrations (Fig. 2) influence the radiative balance and therefore changes in greenhouse gas concentrations affect climate.
- The Earth's radiation balance is rather complex (Fig. 3), including many terms.
- Not only greenhouse gases but also anthropogenic aerosols and its emission changes can cause changes in the global radiation balance and therefore affect climate in different ways.

Fig. 4: Transparency of the atmosphere:  
 Atmospheric windows and black body radiation of the sun and the Earth

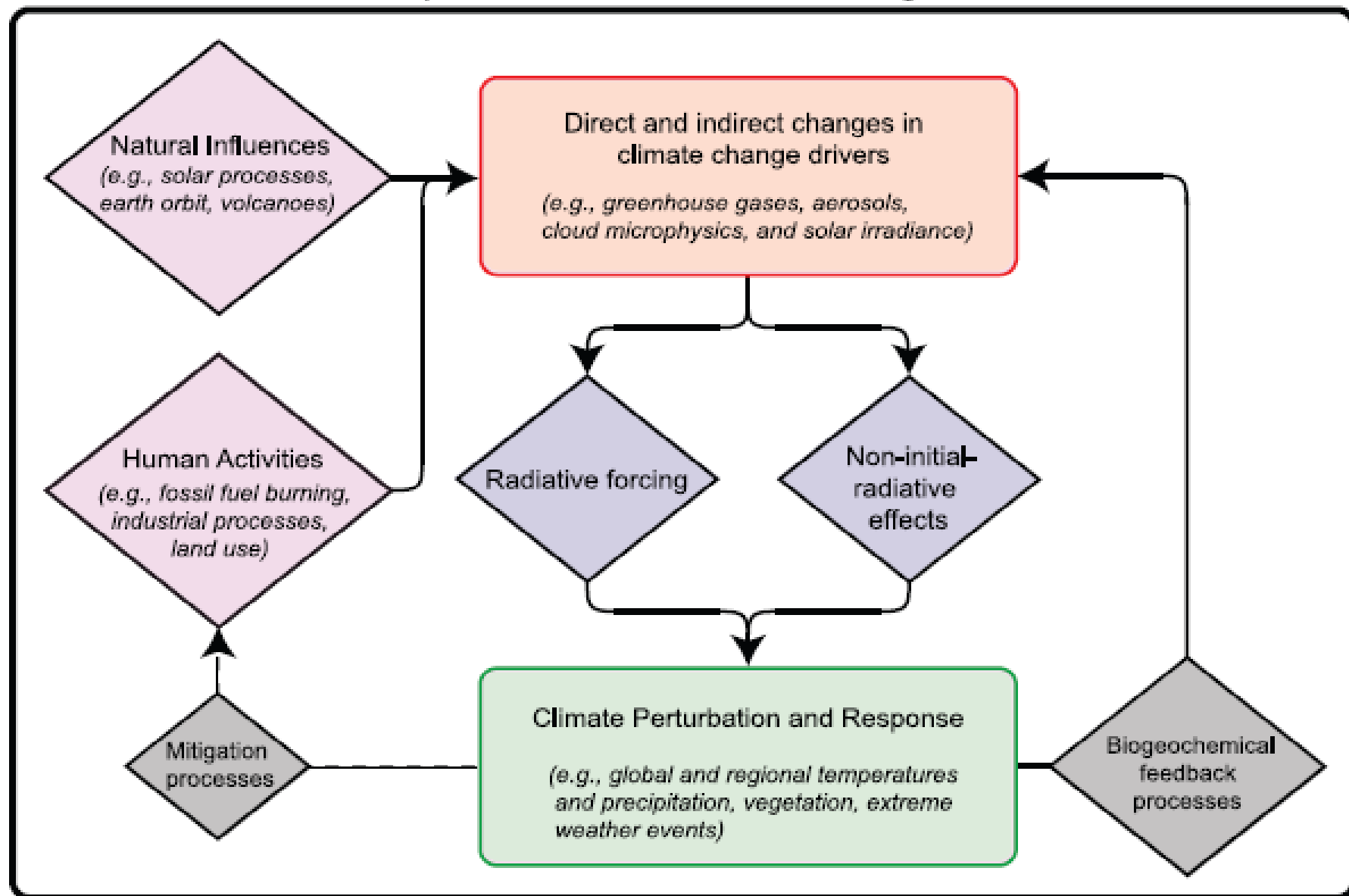


# Notes to Fig. 4

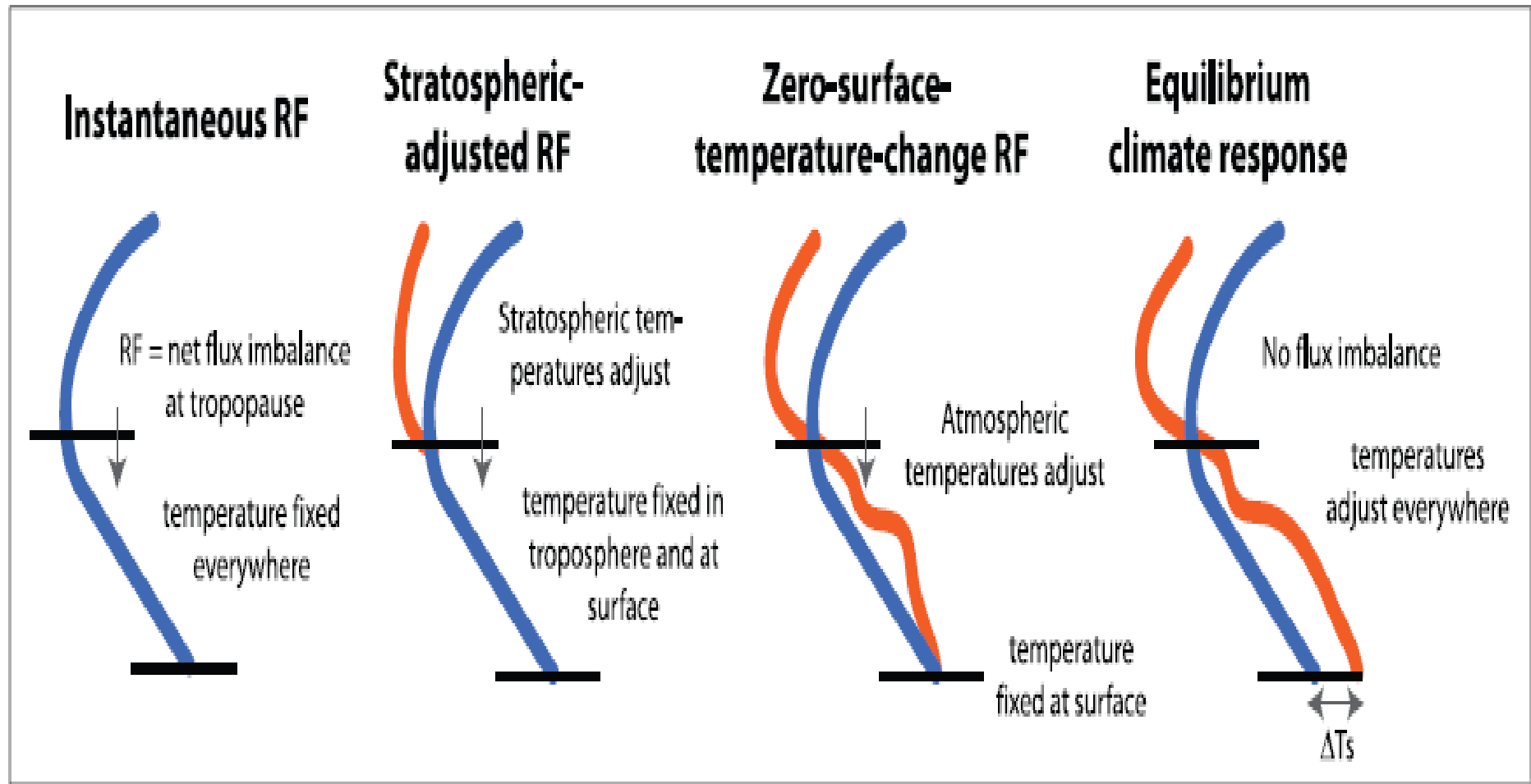
- The black body radiative emissions of the sun peak around  $0.5 \mu\text{m}$  while largest emissions of a black body with the temperature of the Earth are around  $10 \mu\text{m}$ .
- The atmospheric transparency of the atmospheric window (shown in the top figure) shows strong changes with wavelength. At longer wavelengths atmospheric water vapour and carbon dioxide strongly restrict the transparency while at shorter wavelengths the light is absorbed by  $\text{O}_3$  and  $\text{O}_2$ .
- The transparency of the atmospheric window is limited by  $\text{H}_2\text{O}$  (a natural greenhouse gas) and  $\text{CO}_2$  (also a natural greenhouse gas).
- The natural greenhouse effect by  $\text{H}_2\text{O}$  and  $\text{CO}_2$  increases the mean Earth's temperature from  $-18^\circ\text{C}$  to approximately  $+15^\circ\text{C}$ .
- The near IR absorption of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  shows strong dependencies on wavelength. Note that  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{O}_3$  have strong absorption bands at wavelengths where the absorptions of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are weak.

Fig. 5. (AR4)

## Components of the Climate Change Process



# Fig. 6: RF calculation methods (AR4)



## Notes to Fig. 5. and 6: ***Radiative Forcing (in $Wm^{-2}$ ):***

Radiative forcing (RF) is a quantity aiming to describe the effect of the perturbations of past anthropogenic activities on the energy balance of the Earth-Atmosphere; RF is therefore a measure for the physical driving force of anthropogenic climate change (see Fig. 5). RF can be defined as: „Change in net (down minus up) irradiance (solar plus longwave, in  $Wm^{-2}$ ) at the tropopause allowing to readjust to radiative equilibrium, but with surface and tropospheric temperature held fixed at the unperturbed values“. RF has a positive sign if increased concentrations lead to a warming of the Earth's surface temperature (as for greenhouse gases). Increase in many aerosol compounds leads to a cooling of the Earth's surface temperature, which is described by a negative sign of radiative forcing.

The described definition is suitable to assess the effects LLGHGs (long-lived greenhouse gases) on climate. In these cases, RF can be related through a linear relationship to the global mean temperature:

$$\Delta T_s = \lambda RF$$

where:  $T_s$ : surface temperature, and  $\lambda$ : climate sensitivity parameter

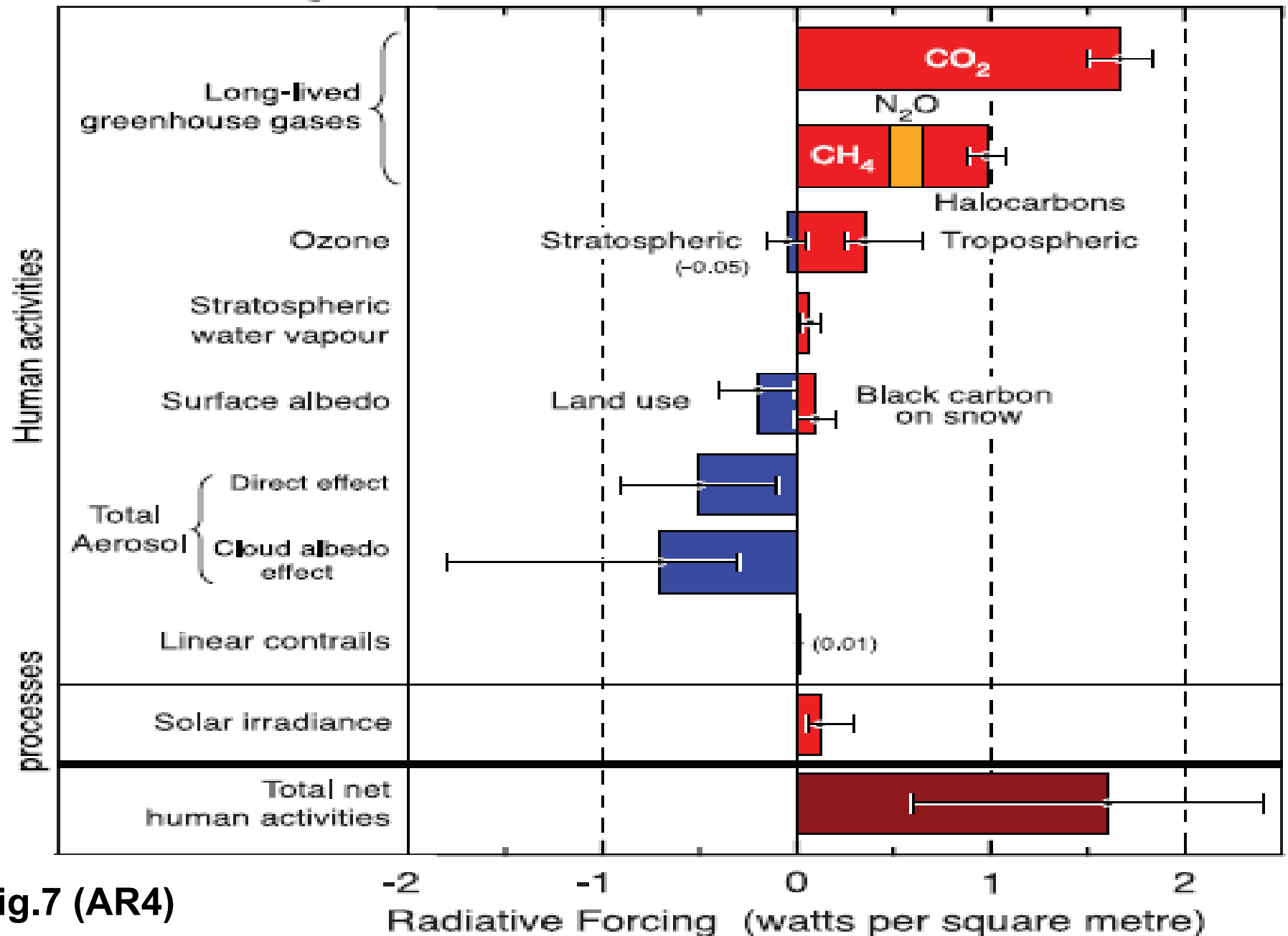
However, for anthropogenic changes other than LLGHGs different calculation methods might be more appropriate for determination of RF, which are summarized in Fig. 6.

Radiative forcings of greenhouse gases depend on:

- change in concentration
- molecular properties: strength of absorption band in IR
- wavelength of absorption
- life time of the compound.

# Radiative forcing of climate between 1750 and 2005

## Radiative Forcing Terms



Concentrations of Greenhouse Gases from 0 to 2005

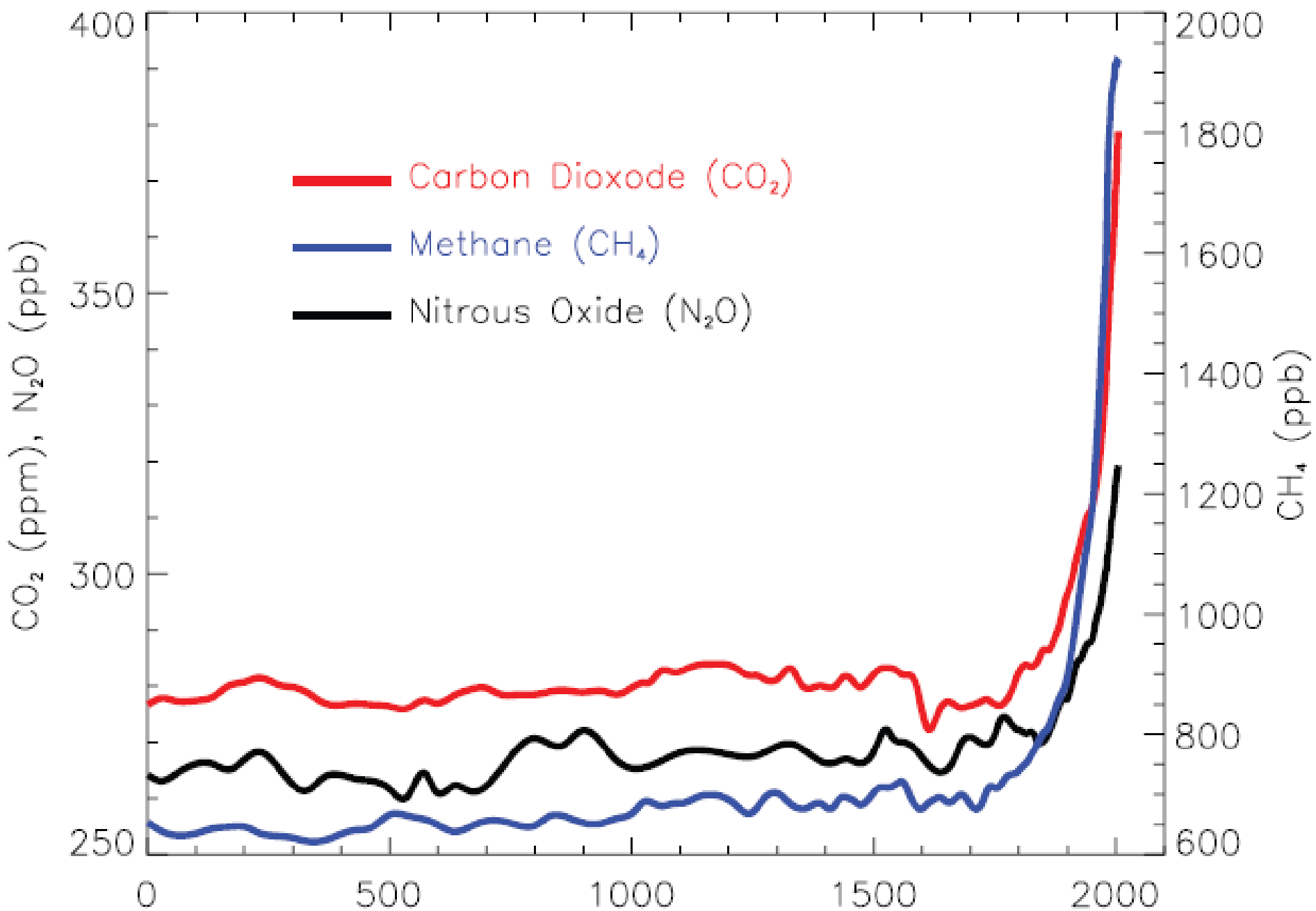


Fig. 8 (AR4)

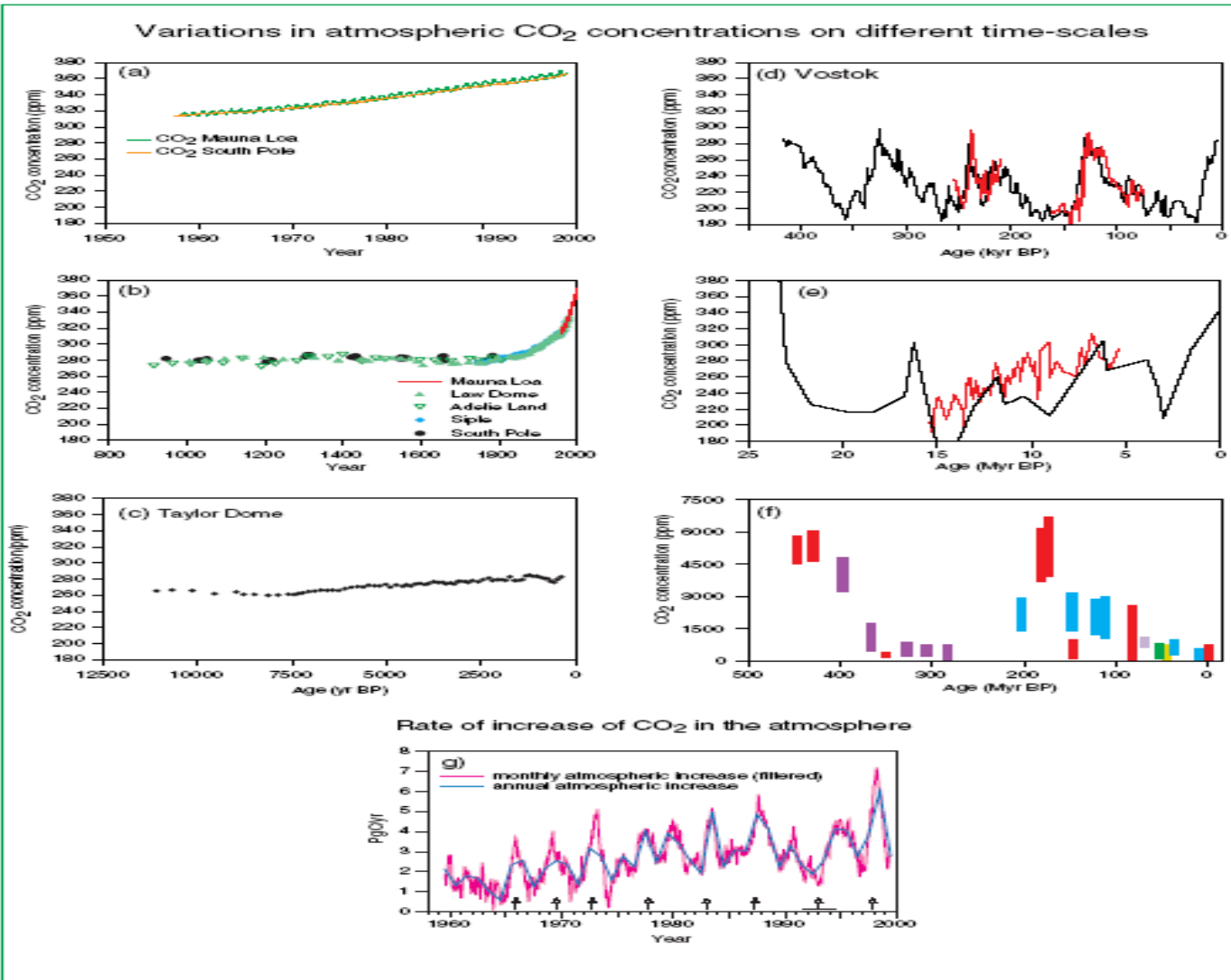
# Notes to Fig. 7 and 8

- The estimated radiative forcings of anthropogenic emissions since pre-industrial time (defined by the reference year 1750) show strong warming contributions by greenhouse gas increases.
- The long-lived greenhouse gases contributed most to the positive radiative forcing. The largest contribution stems from carbon dioxide (CO<sub>2</sub>), followed by methane (CH<sub>4</sub>), the class of halocarbons and nitrous oxide (N<sub>2</sub>O).
- CO<sub>2</sub> and the other most important greenhouse gases have long life times in the troposphere. This implies very similar concentrations in background air in the troposphere.
- Most of the important long-lived greenhouse gases show large and continuous concentration increases since preindustrial time (the time evolution of halocarbons is discussed 2.4).
- Tropospheric ozone change led to a large positive radiative forcing.
- Land use changes caused negative radiative forcing.
- The contributions from anthropogenic emissions of aerosols are mostly negative and the respective uncertainties are much larger than those of greenhouse gases.
- The total of anthropogenic activities caused a significant increase in global radiative forcing. The large uncertainty in its magnitude is mainly caused by the uncertainties related to atmospheric aerosols (not discussed in this lecture).

# 2. Well mixed greenhouse gases

## 2.1. Carbon dioxide (CO<sub>2</sub>) (Fig. 9, from TAR)

Life time: not well defined

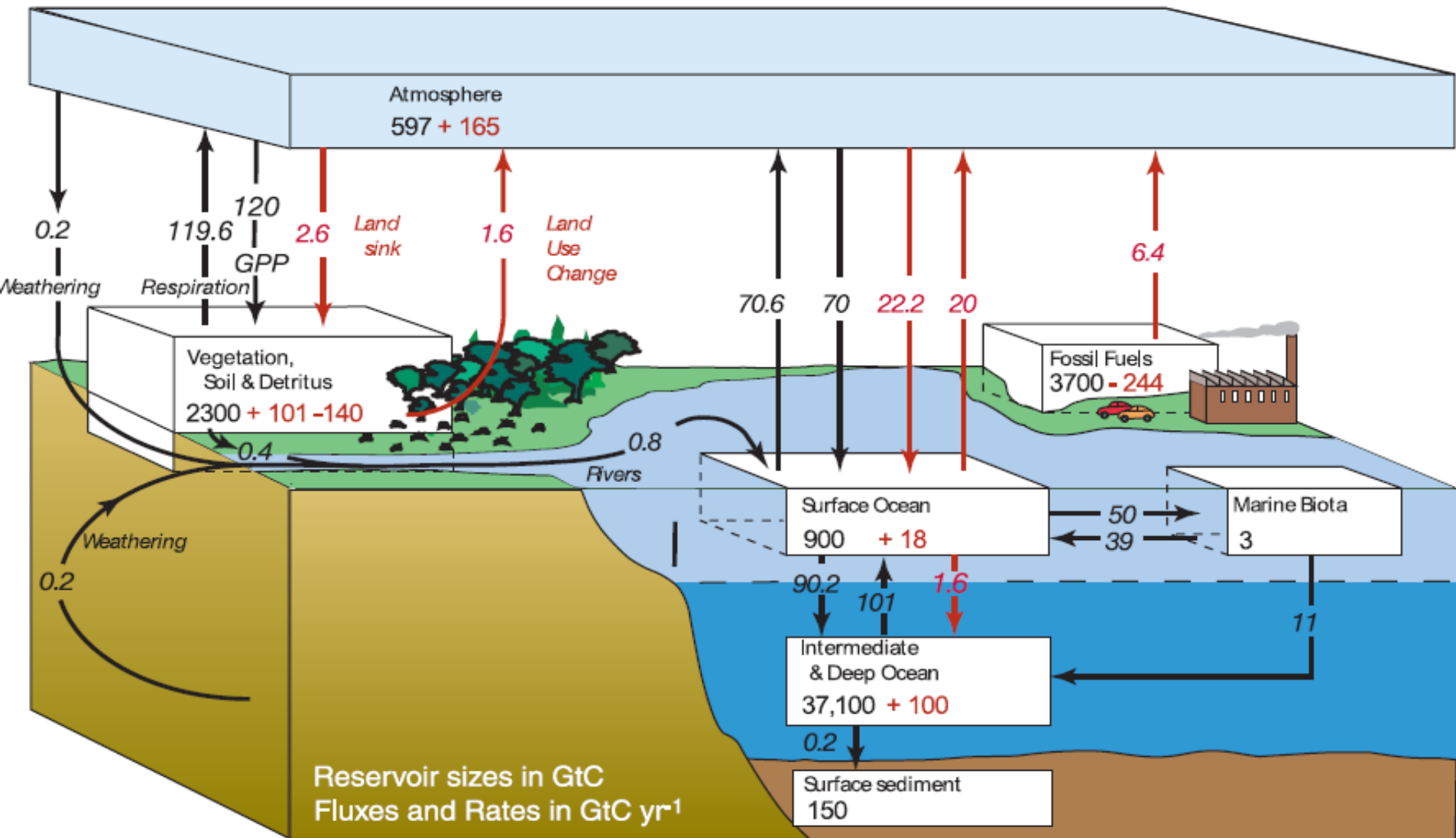


**Figure 10:** Variations in atmospheric CO<sub>2</sub> concentration on different time-scales. (a) Direct measurements of atmospheric CO<sub>2</sub>. (b) CO<sub>2</sub> concentration in Antarctic ice cores for the past millennium. Recent atmospheric measurements (Mauna Loa) are shown for comparison. (c) CO<sub>2</sub> concentration in the Taylor Dome Antarctic ice core. (d) CO<sub>2</sub> concentration in the Vostok Antarctic ice core. (Different colours represent results from different studies.) (e to f) Geochemically inferred CO<sub>2</sub> concentrations. (Coloured bars and lines represent different published studies) (g) Annual atmospheric increases in CO<sub>2</sub>. Monthly atmospheric increases have been filtered to remove the seasonal cycle. Vertical arrows denote El Niño events. A horizontal line defines the extended El Niño of 1991 to 1994. [Based on Figures 3.2 and 3.3]

# Notes to 9

- The historical concentrations of non reactive (long-lived) greenhouse gases in tropospheric air can be derived from the analysis of air bubbles in ice cores allowing to determine their concentrations back to the ice ages.
- CO<sub>2</sub> concentrations show large variabilities connected with the changes between warm and cold periods (e.g. much colder during ice ages).
- Continuous measurements of CO<sub>2</sub> available from Mauna Loa Observatory at Hawaii since 1958 show a continuous increase, in parallel with the increasing emissions of CO<sub>2</sub> from anthropogenic emissions.

Fig. 10: The global carbon cycle for the 1990s (AR4), including reservoirs and fluxes. Main annual fluxes in GtCyr<sup>-1</sup>: black: pre-industrial (natural) and red: anthropogenic.



# Notes to Fig. 10: Carbon cycle

- The global cycles are important in order to understand changes in greenhouse gas concentrations. (They are described in Chapt. 7 in AR4).
- The carbon cycle is particularly complex. The main compartments are ocean, land and atmosphere.
- The ultimate sink of  $\text{CO}_2$  is the deposition as  $\text{CaCO}_3$  in the deep ocean, which is a very slow process.
- The lifetime of  $\text{CO}_2$  is not well defined because of the cycling within the different reservoirs, e.g. in trees.
- The largest part of greenhouse warming is caused by  $\text{CO}_2$  (see Fig. 7).

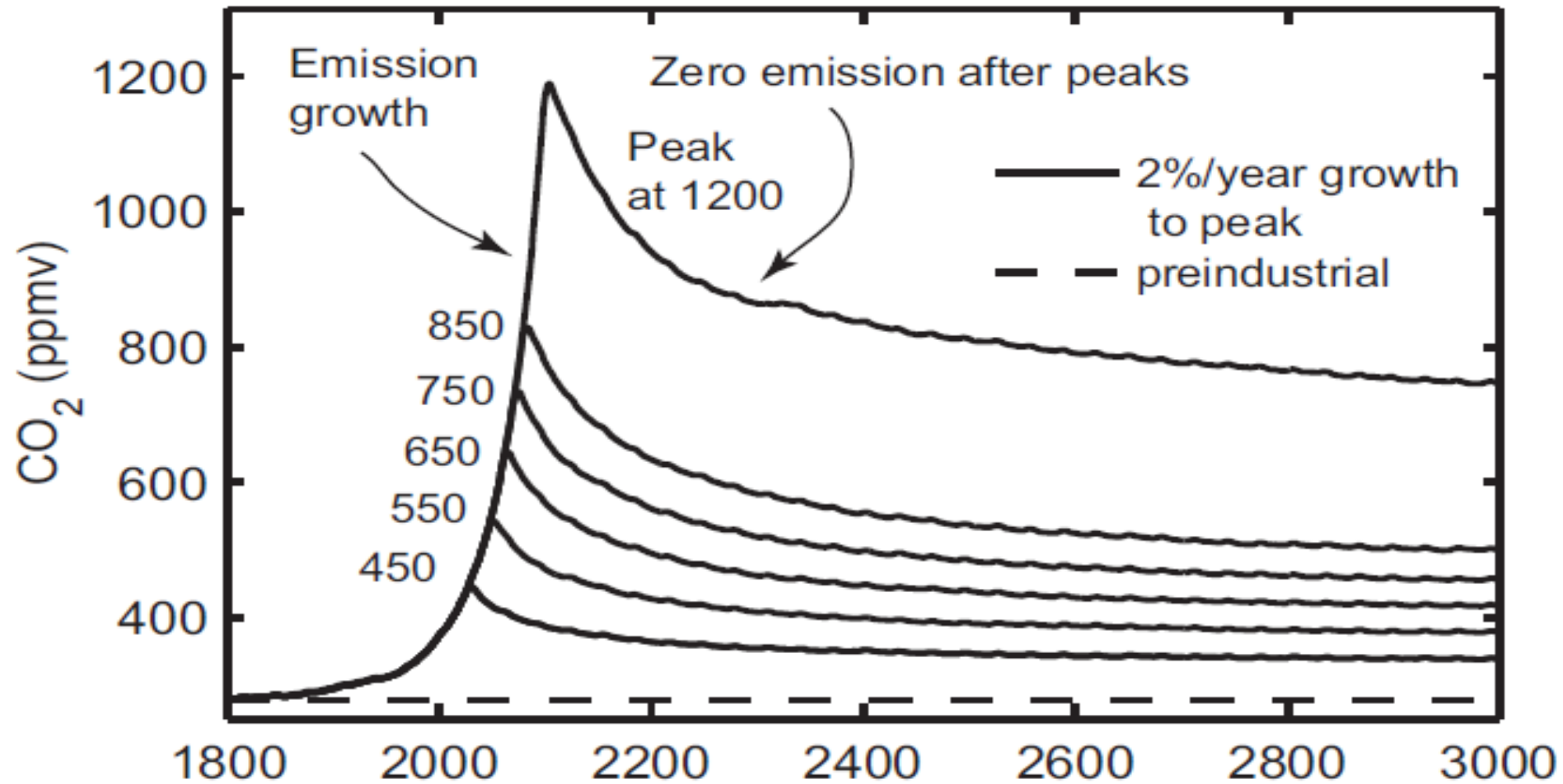
Fig.11: Global carbon budget in GtCyr<sup>-1</sup>(AR4); errors describe standard deviation. Atmospheric increase results from fluxes to and from the atmosphere.

|   | 1980s                  |                          | 1990s      |                        | 2000–2005c |
|---|------------------------|--------------------------|------------|------------------------|------------|
|   | TAR                    | TAR revised <sup>a</sup> | TAR        | AR4                    | AR4        |
| Atmospheric Increase <sup>b</sup>         | 3.3 ± 0.1              | 3.3 ± 0.1                | 3.2 ± 0.1  | 3.2 ± 0.1              | 4.1 ± 0.1  |
| Emissions (fossil + cement) <sup>c</sup>  | 5.4 ± 0.3              | 5.4 ± 0.3                | 6.4 ± 0.4  | 6.4 ± 0.4              | 7.2 ± 0.3  |
| Net ocean-to-atmosphere flux <sup>d</sup> | -1.9 ± 0.6             | -1.8 ± 0.8               | -1.7 ± 0.5 | -2.2 ± 0.4             | -2.2 ± 0.5 |
| Net land-to-atmosphere flux <sup>e</sup>  | -0.2 ± 0.7             | -0.3 ± 0.9               | -1.4 ± 0.7 | -1.0 ± 0.6             | -0.9 ± 0.6 |
| <i>Partitioned as follows</i>             |                        |                          |            |                        |            |
| Land use change flux                      | 1.7<br>(0.6 to 2.5)    | 1.4<br>(0.4 to 2.3)      | n.a.       | 1.6<br>(0.5 to 2.7)    | n.a.       |
| Residual terrestrial sink                 | -1.9<br>(-3.8 to -0.3) | -1.7<br>(-3.4 to 0.2)    | n.a.       | -2.6<br>(-4.3 to -0.9) | n.a.       |

# Notes to Fig. 11: The carbon balance

- The global cycles of the greenhouse gases are derived from the (known) sources and sinks and their imbalances together with their distributions into different reservoirs (should) explain the observed trends in atmospheric concentrations.
- The (anthropogenic) emissions of CO<sub>2</sub> lead partially to an increase in atmospheric concentrations, partially to a flux from the atmosphere to the ocean.
- The largest anthropogenic emission is the combustion of fossil fuels; also significant is (anthropogenic) biomass burning, mainly in the tropics, which makes the main contribution to the term „land use change“. This term also includes some accumulation of carbon by regrowing vegetation (comp. TAR).
- The numbers given in the last IPCC reports are very similar (when related to the same period).

Fig.12: Future development of atmospheric CO<sub>2</sub> concentrations after stop of anthropogenic emission (Solomon et al., 2009)



# Notes to Fig. 12

- Fig. 12 shows time series of predicted atmospheric background concentrations of CO<sub>2</sub> as response to anthropogenic emissions (based on the results of the EMIC-(Earth System Model of Intermediate Complexity)-model of Bern; such models also describe the response of the ocean)
- For anthropogenic emission a growth rate of 2%/year is assumed followed by a complete stop of anthropogenic emissions. Depending on the time of the stop of anthropogenic emissions a certain level of CO<sub>2</sub> concentrations will be reached
- After maximal concentrations and an initial decrease of CO<sub>2</sub> (time constant in the order of 100 years) the decrease becomes extremely slow and within a millennium the decrease is almost nonexistent and concentrations stay much higher than preindustrial
- This extremely small decrease is attributable to the response of the ocean. The first phase is characterized by the relatively short exchange between the land biosphere and the surface layer of the ocean, whereas the removal of CO<sub>2</sub> requires the transport through the deep ocean to the ultimate sink (deposition as carbonate in the deep ocean) which is extremely slow
- This means that a large fraction of all anthropogenically emitted CO<sub>2</sub> stays in the atmosphere for scales of millennia (no regeneration); this implies that a “budget” exists and the sum of anthropogenic determines the effect of CO<sub>2</sub> (on millennium scale)

## 2.2. Methane ( $\text{CH}_4$ , life time: 8.4 y)

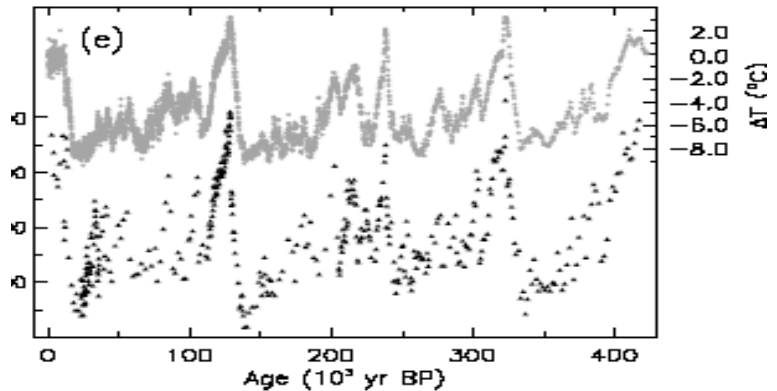
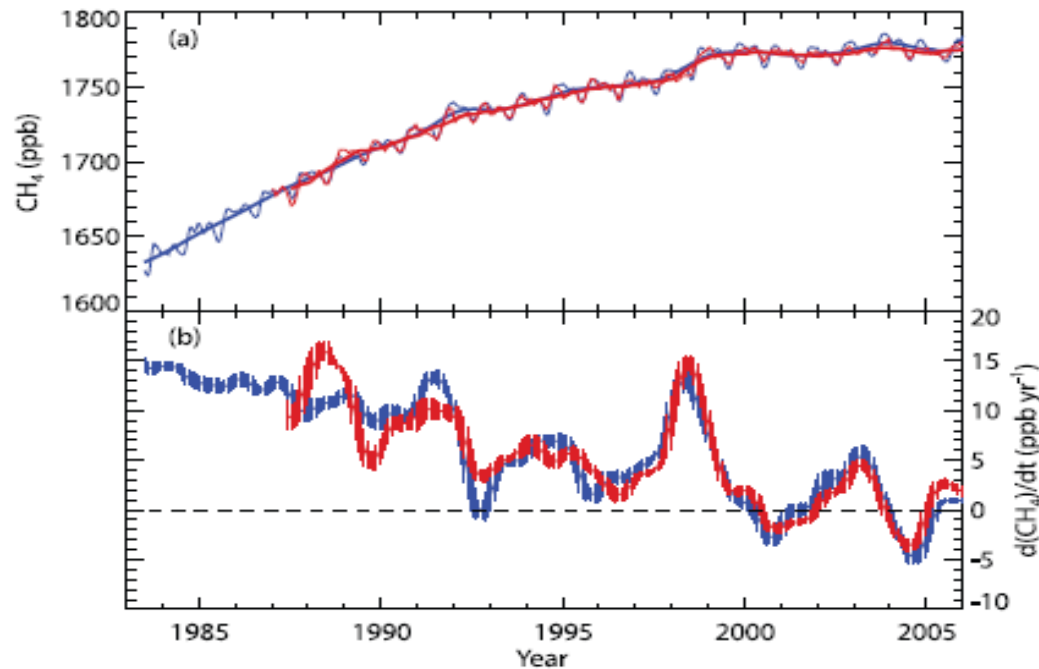
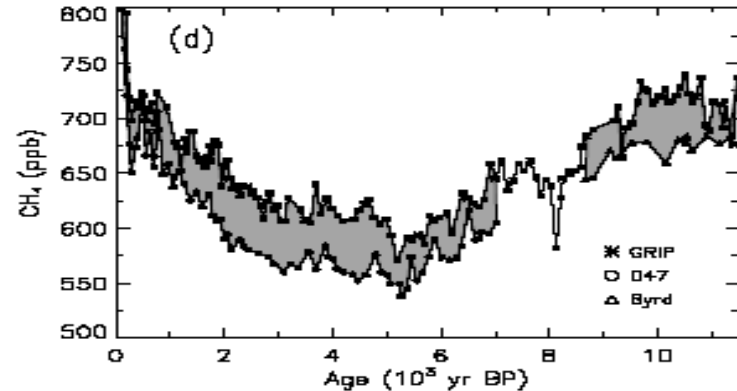
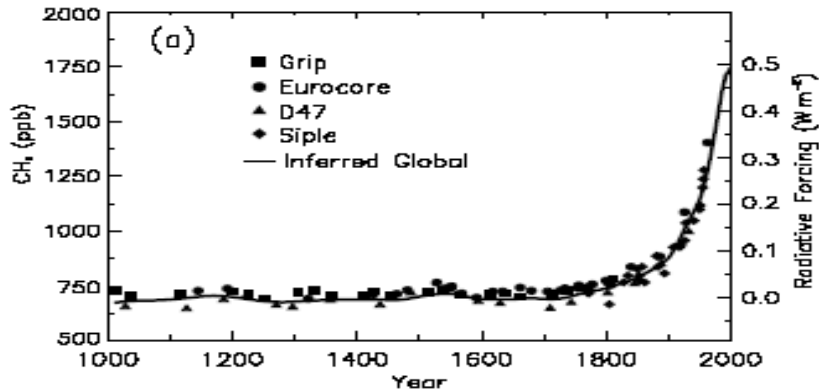


Fig. 13 (TAR and AR4 (most recent changes))

# Notes to Fig. 13: Methane concentration

- CH<sub>4</sub> concentrations strongly increased (by more than a factor of two) since the 19th century.
- Large fluctuations in atmospheric CH<sub>4</sub> concentrations occurred during the changes of ice ages and warm periods.
- CH<sub>4</sub> increasing rates decreased since the early 1990s and were not stable in the last decade. This behaviour is still not completely understood.
- CH<sub>4</sub> is the second largest anthropogenic greenhouse gas.

# Fig. 14: Sources, sinks and atmospheric budget methane (Tg(CH<sub>4</sub>)yr<sup>-1</sup>), AR4

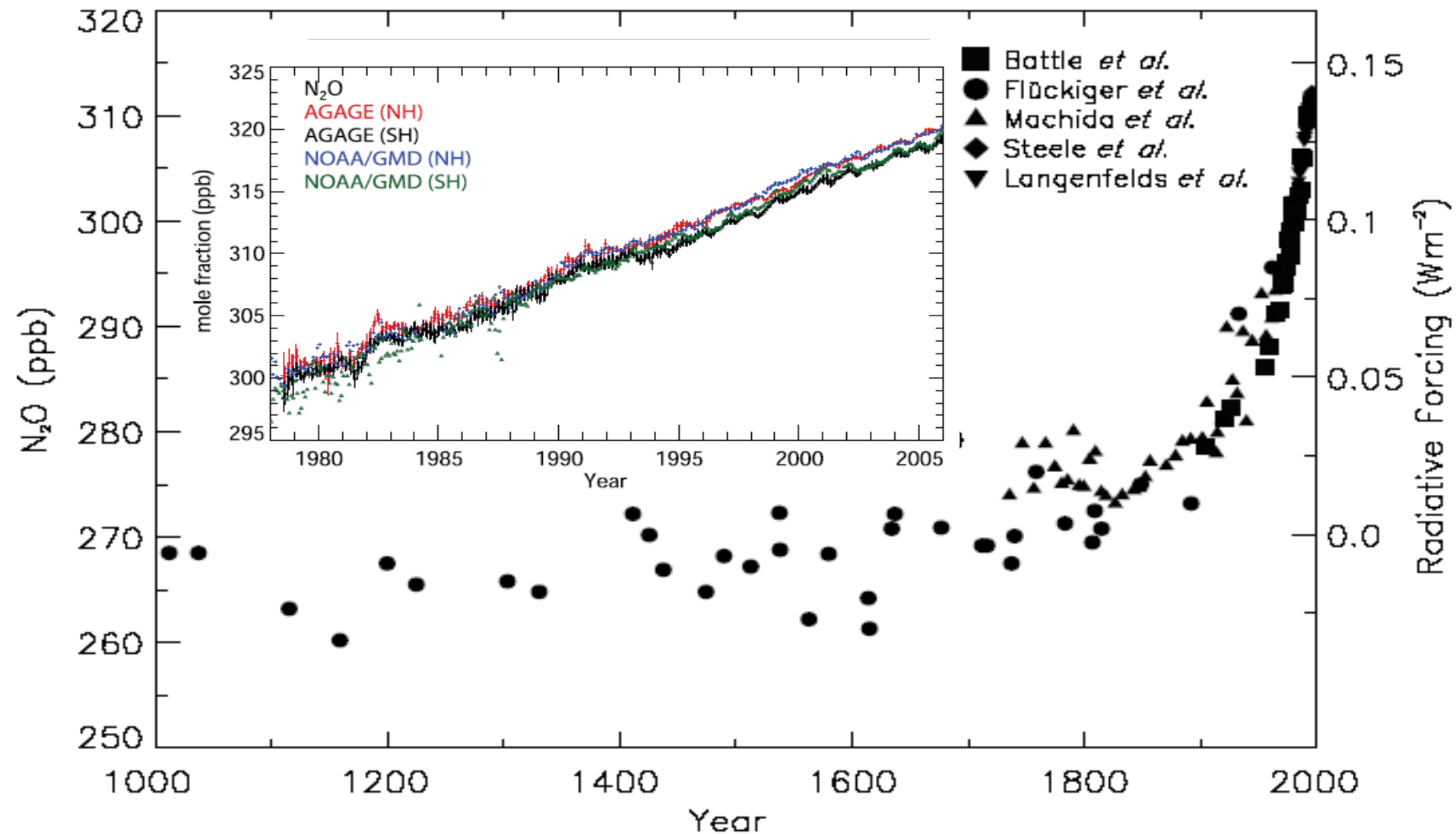
| References                   | Indbatha et al., 1997 <sup>a</sup> | Helmer et al., 1997 <sup>b</sup> | Houwing et al., 2000 <sup>c</sup> | Oehler et al., 2005 | Wubbs and Hayhoe, 2002 | Schneiders et al., 2002 | J. Wang et al., 2004 <sup>e</sup> | Mikaloff Rather et al., 2004 <sup>g</sup> | Chen and Prinn, 2006 <sup>h</sup> | TAR  | AR4               |
|------------------------------|------------------------------------|----------------------------------|-----------------------------------|---------------------|------------------------|-------------------------|-----------------------------------|---|-----------------------------------|------|-------------------|
| Base year                    | 1983–1989                          |                                  |                                   | 2000                |                        | 1990                    | 1994                              | 1999                                      | 1996–2001                         | 1998 | 2000–2004         |
| <b>Natural sources</b>       |                                    |                                  | 222                               |                     | 145                    |                         | 200                               | 280                                       | 188                               |      |                   |
| Wetlands                     | -88                                | 23.1                             | 163                               |                     | 100                    |                         | 176                               | 23.1                                      | 145                               |      |                   |
| Termites                     | -70                                |                                  | 20                                |                     | 20                     |                         | 20                                | 20  | 23                                |      |                   |
| Ocean                        | -60                                |                                  | 15                                |                     | 4                      |                         |                                   |   |                                   |      |                   |
| Hydrates                     | -60                                |                                  |                                   |                     | 5                      |                         | 4                                 |   |                                   |      |                   |
| Geological sources           | -40                                |                                  | 4                                 |                     | 14                     |                         |                                   |   |                                   |      |                   |
| Wild animals                 | -60                                |                                  | 15                                |                     |                        |                         |                                   |   |                                   |      |                   |
| Wildfires                    | -25                                |                                  | 5                                 |                     | 2                      |                         |                                   |   |                                   |      |                   |
| <b>Anthropogenic sources</b> |                                    | 38.1                             |                                   | 32.0                | 35.8                   | 28.4                    | 30.7                              | 35.0                                      | 42.8                              |      |                   |
| <b>Energy</b>                |                                    |                                  |                                   |                     |                        | 7.4                     | 7.7                               |   |                                   |      |                   |
| Coal mining                  | -37                                | 3.2                              |                                   | 3.4                 | 4.6                    |                         |                                   | 3.0                                       | 4.3 <sup>d</sup>                  |      |                   |
| Gas, oil, industry           | -4.4                               | 6.8                              |                                   | 6.4                 | 6.0                    |                         |                                   | 5.2                                       | 3.6 <sup>f</sup>                  |      |                   |
| Landfills & waste            | -55                                | 4.3                              |                                   | 6.6                 | 6.1                    | 6.9                     | 4.0                               | 3.5                                       |                                   |      |                   |
| Ruminants                    | -60                                | 9.2                              |                                   | 9.0                 | 9.1                    | 7.6                     | 9.3                               | 9.1                                       | 19.9 <sup>g</sup>                 |      |                   |
| Rice agriculture             | -63                                | 8.3                              |                                   | 3.9                 | 6.0                    | 3.1                     | 5.7                               | 5.4                                       | 1.12                              |      |                   |
| Biomass burning              | -25                                | 4.3                              |                                   |                     | 5.0                    | 1.4                     | 4.1                               | 8.8                                       | 4.3 <sup>h</sup>                  |      |                   |
| C3 vegetation                | -25                                |                                  |                                   | 2.7                 |                        |                         |                                   |   |                                   |      |                   |
| C4 vegetation                | -12                                |                                  |                                   | 0                   |                        |                         |                                   |   |                                   |      |                   |
| <b>Total sources</b>         |                                    | 89.2                             |                                   |                     | 503                    |                         | 507                               | 610                                       | 508                               | 508  | 582               |
| <b>Imbalance</b>             |                                    | -3.3                             |                                   |                     |                        |                         |                                   |   |                                   | +2.2 | +1                |
| <b>Sinks</b>                 |                                    |                                  |                                   |                     |                        |                         |                                   |   |                                   |      |                   |
| Soils                        | -18                                | 2.6                              |                                   |                     | 30                     |                         | 34                                | 30  |                                   | 30   | 30.9              |
| Tropospheric OH              | -3.9                               | 4.88                             |                                   |                     | 44.5                   |                         | 42.8                              | 50.7                                      |                                   | 50.6 | 51.1 <sup>h</sup> |
| Stratospheric loss           |                                    | 4.5                              |                                   |                     | 4.0                    |                         | 3.0                               | 4.0                                       |                                   | 4.0  | 4.0 <sup>h</sup>  |
| <b>Total sink</b>            |                                    | 55.0                             |                                   |                     | 515                    |                         | 492                               | 577                                       |                                   | 578  | 581 <sup>h</sup>  |

# Notes to Fig. 14: Budget of CH<sub>4</sub>

- The emissions of CH<sub>4</sub> include many sources, and present emissions are believed to be dominated by anthropogenic emissions.
- The most important sink of CH<sub>4</sub> is tropospheric oxidation by OH, whereas transport into the stratosphere (followed by oxidation in the stratosphere) and absorption in soils are minor sinks.
- The oxidation by OH leads to a life time which is much shorter than for CO<sub>2</sub>.

## 2.3. Nitrous oxide ( $N_2O$ , life time: 114 y)

Fig.15 (from TAR and AR4)



**Table 4.4:** Estimates of the global nitrous oxide budget (in TgN/yr) from different sources compared with the values adopted for this report (TAR).

| Reference:                             | <i>Mosier et al. (1998b)</i> |                   | <i>Olivier et al. (1998)</i> |                   | SAR                     | TAR              |
|--|------------------------------|-------------------|------------------------------|-------------------|-------------------------|------------------|
| Base year:                             | 1994                         | range             | 1990                         | range             | 1980s                   | 1990s            |
| <b>Sources</b>                         |                              |                   |                              |                   |                         |                  |
| Ocean                                  | 3.0                          | 1 – 5             | 3.6                          | 2.8 – 5.7         | 3                       |                  |
| Atmosphere (NH <sub>3</sub> oxidation) | 0.6                          | 0.3 – 1.2         | 0.6                          | 0.3 – 1.2         |                         |                  |
| <b>Tropical soils</b>                  |                              |                   |                              |                   |                         |                  |
| Wet forest                             | 3.0                          | 2.2 – 3.7         |                              |                   | 3                       |                  |
| Dry savannas                           | 1.0                          | 0.5 – 2.0         |                              |                   | 1                       |                  |
| <b>Temperate soils</b>                 |                              |                   |                              |                   |                         |                  |
| Forests                                | 1.0                          | 0.1 – 2.0         |                              |                   | 1                       |                  |
| Grasslands                             | 1.0                          | 0.5 – 2.0         |                              |                   | 1                       |                  |
| All soils                              |                              |                   | 6.6                          | 3.3 – 9.9         |                         |                  |
| Natural sub-total                      | 9.6                          | 4.6 – 15.9        | 10.8                         | 6.4 – 16.8        | 9                       |                  |
| <b>Anthropogenic sources</b>           |                              |                   |                              |                   |                         |                  |
| Agricultural soils                     | 4.2                          | 0.6 – 14.8        | 1.9                          | 0.7 – 4.3         | 3.5                     |                  |
| Biomass burning                        | 0.5                          | 0.2 – 1.0         | 0.5                          | 0.2 – 0.8         | 0.5                     |                  |
| Industrial sources                     | 1.3                          | 0.7 – 1.8         | 0.7                          | 0.2 – 1.1         | 1.3                     |                  |
| Cattle and feedlots                    | 2.1                          | 0.6 – 3.1         | 1.0                          | 0.2 – 2.0         | 0.4                     |                  |
| Anthropogenic Sub-total                | 8.1                          | 2.1 – 20.7        | 4.1                          | 1.3 – 7.7         | 5.7                     | 6.9 <sup>a</sup> |
| <b>Total sources</b>                   | <b>17.7</b>                  | <b>6.7 – 36.6</b> | <b>14.9</b>                  | <b>7.7 – 24.5</b> | <b>14.7<sup>b</sup></b> |                  |
| Imbalance (trend)                      | 3.9                          | 3.1 – 4.7         |                              |                   | 3.9                     | 3.8              |
| <b>Total sinks (stratospheric)</b>     | <b>12.3</b>                  | <b>9 – 16</b>     |                              |                   | <b>12.3</b>             | <b>12.6</b>      |
| Implied total source                   | 16.2                         |                   |                              |                   | 16.2                    | 16.4             |

**Fig. 16  
(TAR)**

# Notes to Fig.15 and 16: N<sub>2</sub>O.

- (Also) N<sub>2</sub>O concentrations show a steady increase since the start of the 19th century.
- The sources of N<sub>2</sub>O are not well known, about half are believed to be anthropogenic.
- N<sub>2</sub>O has no sink in the troposphere and is therefore degraded in the stratosphere, leading to a long life time.
- The contribution of N<sub>2</sub>O to the change in global radiative forcing is comparatively small (comp.7).

## 2.4. Halocarbons

CFCs regulated by the Montreal Protocol

Fig. 17 (TAR)

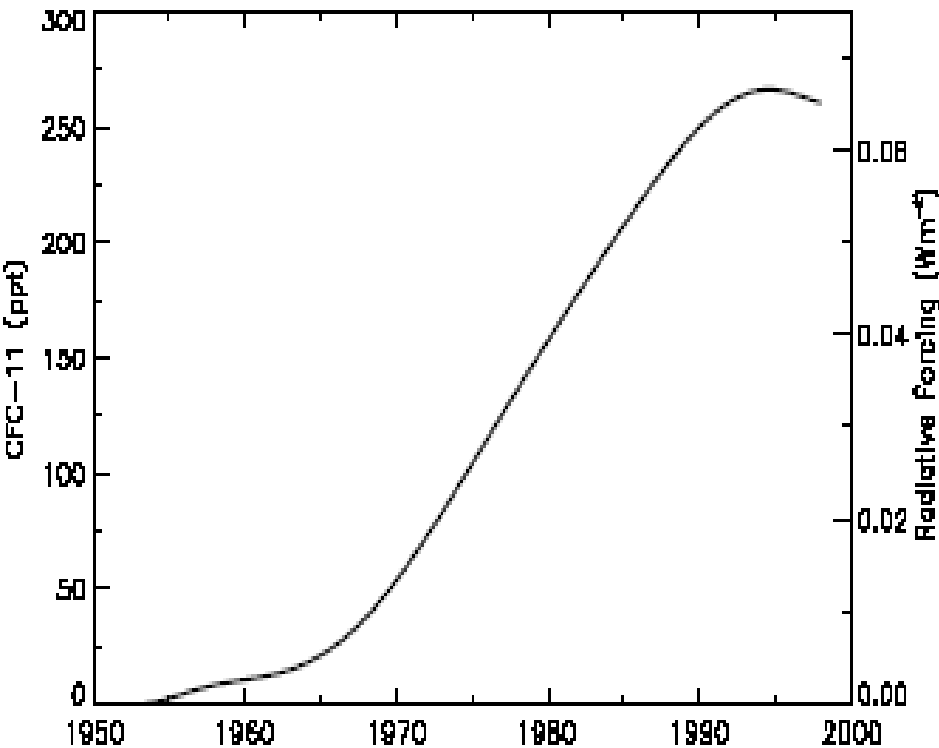


Figure 4.6: Global mean CFC-11 ( $\text{CFCl}_3$ ) tropospheric abundance (ppt) from 1950 to 1998 based on smoothed measurements and emission models (Prinn *et al.*, 2000). CFC-11's radiative forcing is shown on the right axis.

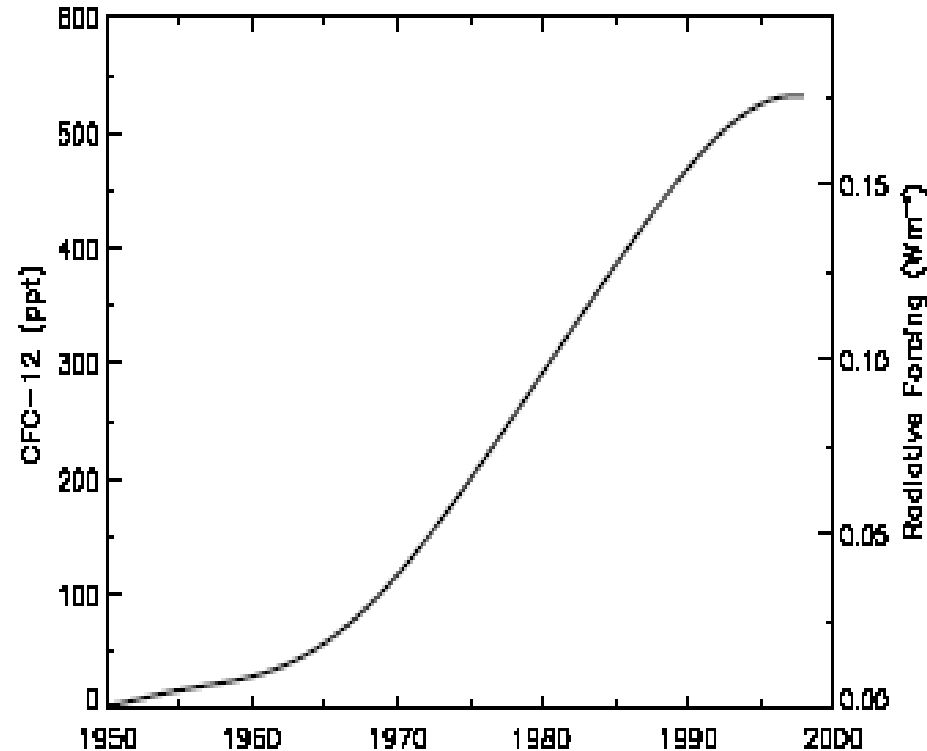


Figure 4.7: Global mean CFC-12 ( $\text{CF}_2\text{Cl}_2$ ) tropospheric abundance (ppt) from 1950 to 1998 based on smoothed measurements and emission models (Prinn *et al.*, 2000). CFC-12's radiative forcing is shown on the right axis.

# Notes to Fig. 17:

## Chlorofluorocarbons (CFCs)

- CFCs belong to a family of organic compounds that contain Cl and F.
- They are efficient greenhouse gases, many CFCs have long atmospheric life times.
- CFCs were banned by the Montreal Protocol 1987 (and its enforcements) because they destroy stratospheric ozone.
- The concentrations of CFCs in tropospheric air have stabilized and (most) are decreasing.
- The budgets of CFCs are rather well known, because they are (almost exclusively) of anthropogenic origin and their sinks are rather well characterized.

Fig. 18: Hydrochlorofluorocarbons (HCFCs) and Hydrofluorocarbons (HFCs) (TAR)

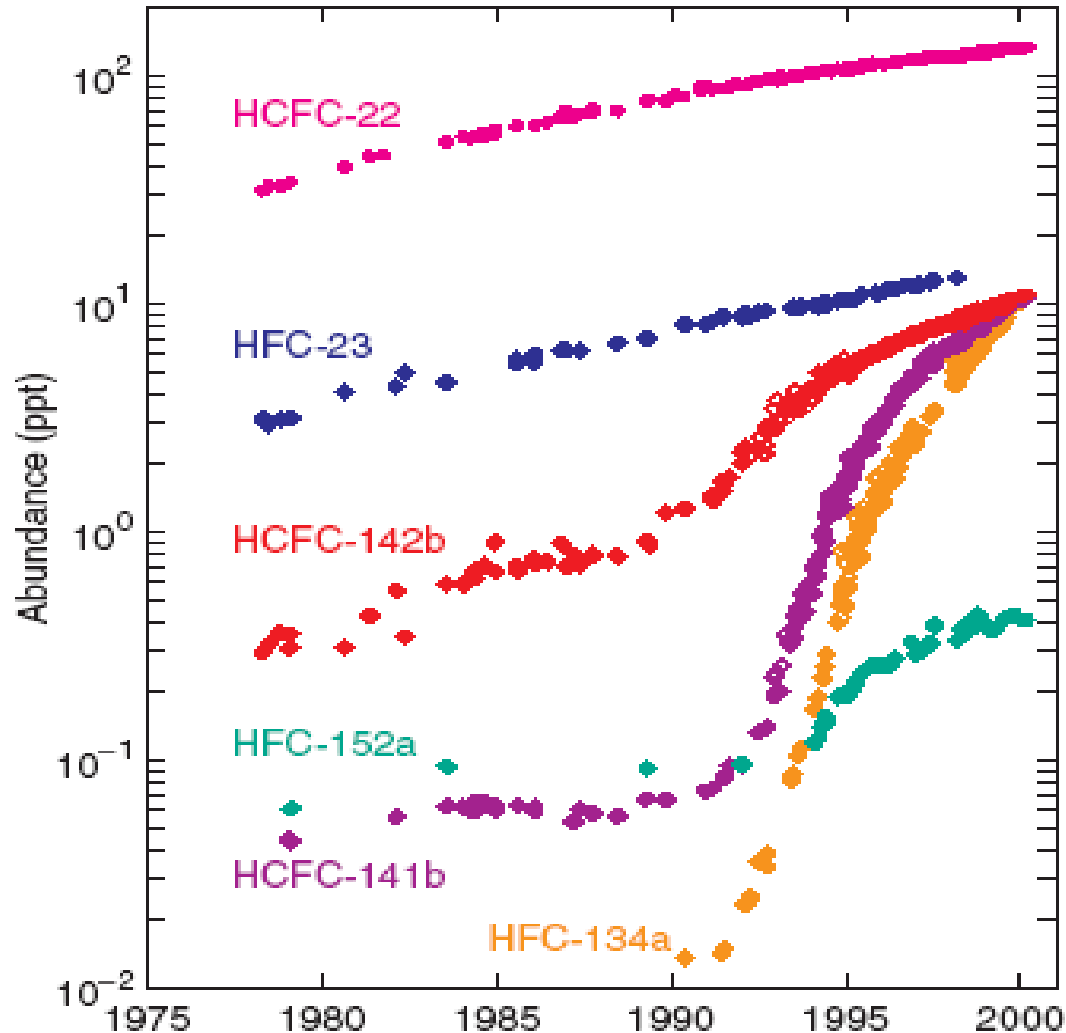
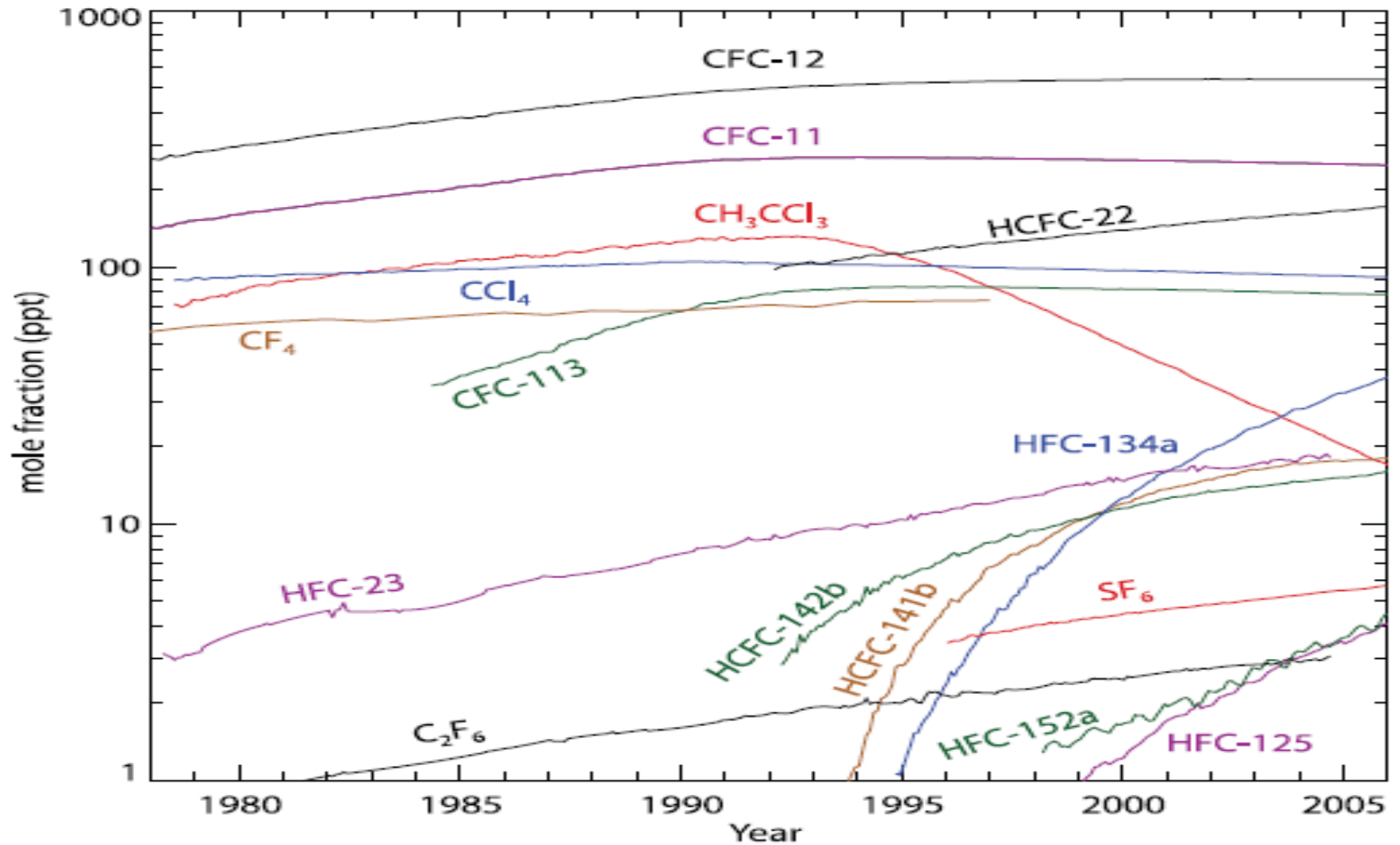


Fig. 19: Halocarbon concentration changes (AR4).



# Notes to Fig. 18 and 19 (HCFCs, HFCs)

- HCFCs (organic gaseous compounds containing H, Cl and F) are used as substitutes of CFCs. Their concentrations strongly increased over the past years.
- (Some) HCFCs are strong greenhouse gases and some HFCs have long atmospheric life times. The increase in their concentration depends on their atmospheric life times and emissions.

**see: HCFC-22 ( $\text{CHF}_2\text{Cl}$ , life time: 11.0 y);**

**HCFC-142.b ( $\text{CH}_3\text{CF}_2\text{Cl}$ , life time: 19 y); HCFC-141b  
( $\text{CH}_3\text{CFCl}_2$ ; life time: 9.3 y)**

- HFCs is another class of organic compounds which contain F and H. They don't destroy stratospheric ozone but some of them are strong greenhouse gases

**see: HFC-23 ( $\text{CHF}_3$ , life time: 260 y); HFC-152a  
( $\text{CH}_3\text{CHF}_2$ ; life time: 1.4 y); HFC-134a ( $\text{CF}_3\text{CH}_2\text{F}$ : 13.8 y)**

Fig. 20: Fully fluorinated compounds with very long life times:  $\text{CF}_4$  50000 y;  $\text{SF}_6$ : 3200 y (TAR)

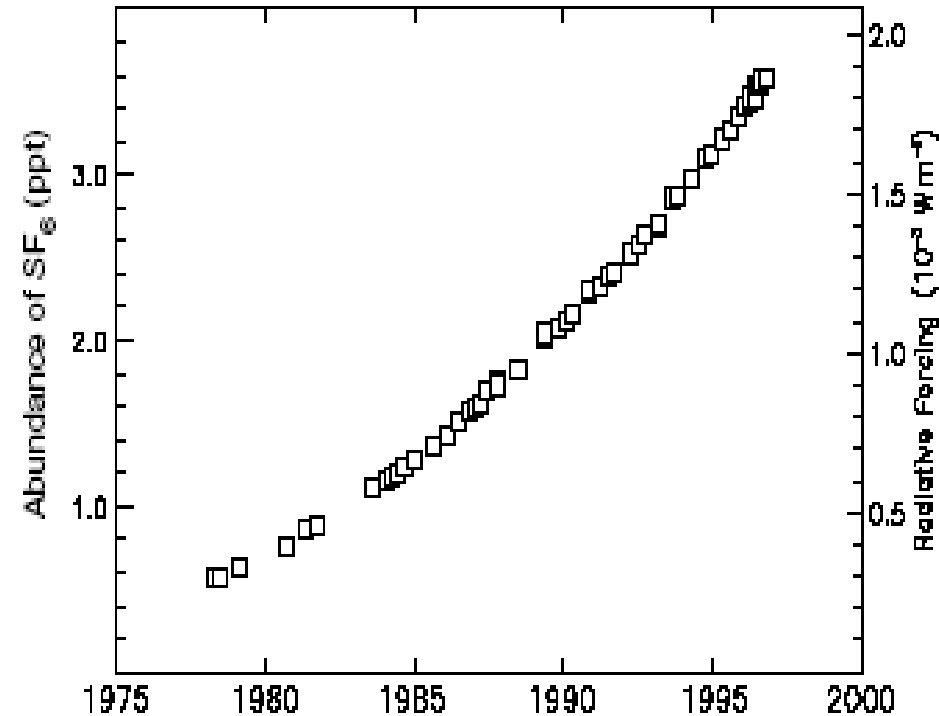
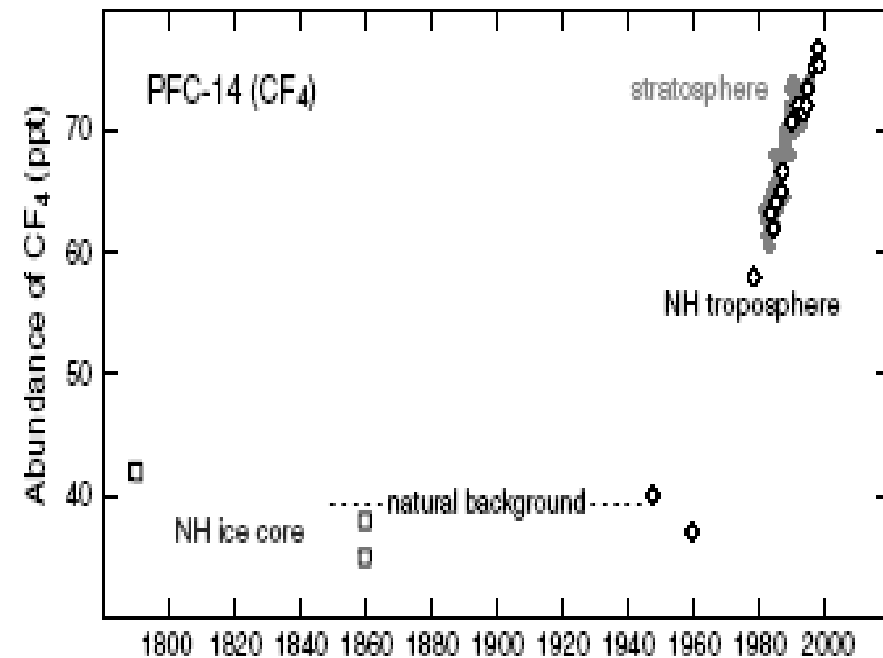


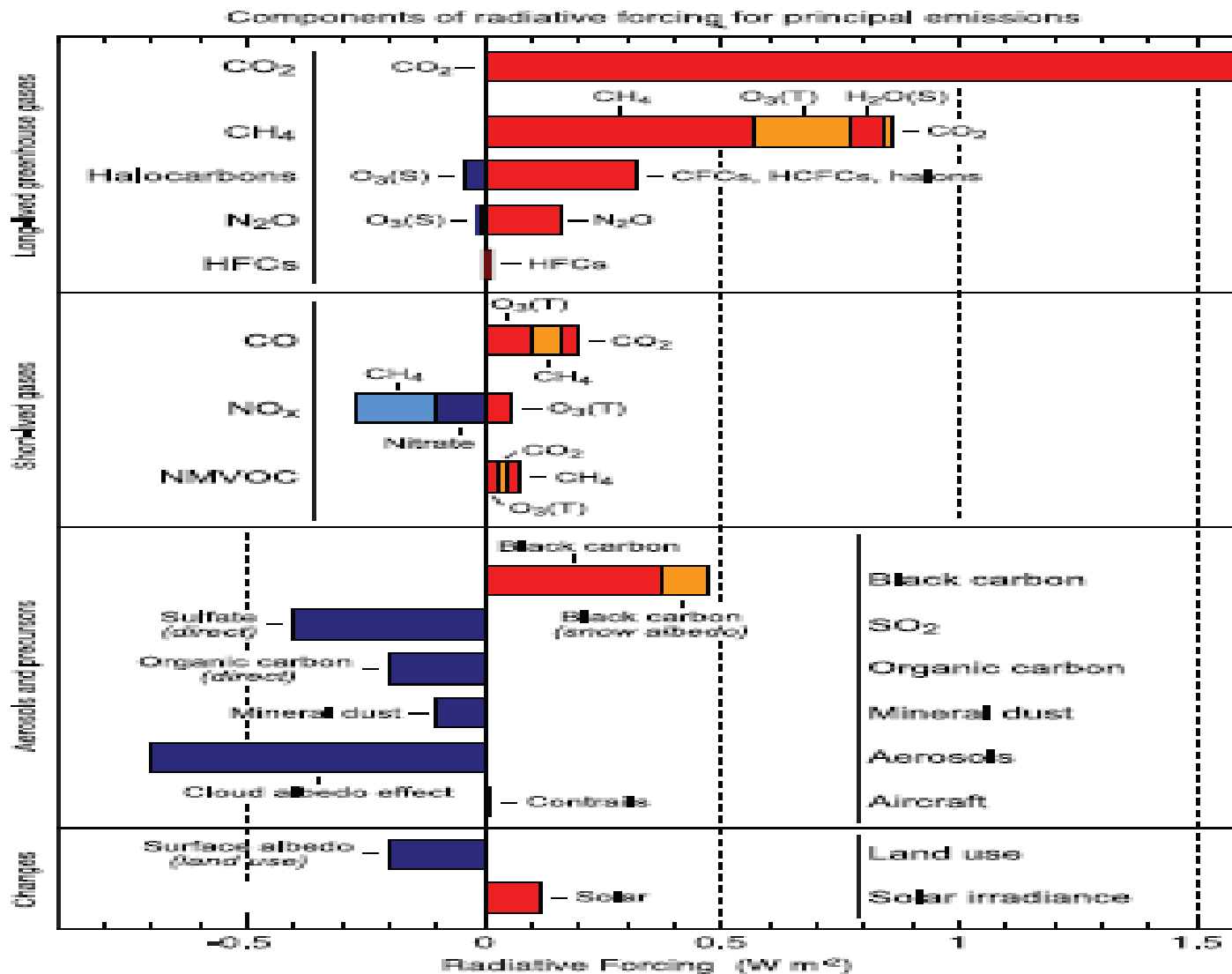
Figure 4.4: Abundance of  $\text{CF}_4$  (ppt) over the last 200 years as measured in tropospheric air (open diamonds), stratospheric air (small filled diamonds), and ice cores (open squares) (Harnisch *et al.*, 1996; 1999).

Figure 4.5: Abundance of  $\text{SF}_6$  (ppt) measured at Cape Grim, Tasmania since 1978 (Maiss *et al.*, 1996; Maiss and Brenninkmeijer, 1998). Cape Grim values are about 3% lower than global averages.

# Notes to Fig. 20: PFCs and SF<sub>6</sub>

- Totally fluorinated organic gases (i.e. solely composed of C and F, Perfluorocarbons, PFCs) and SF<sub>6</sub> have extremely long life times. They are not degraded by OH radicals and their UV-absorptions are very weak.
- They have strong absorptions in the IR and are very strong greenhouse gases.
- Their anthropogenic emissions are particularly harmful because their atmospheric concentrations decrease extremely slowly.

Fig. 21: Radiative forcing since 1750 (AR4): summary (comp. 7) based on information on primary emissions



### ***3. Global Warming Potentials (GWP), see Fig. 22 and 23***

In order to allow setting priorities to reduce greenhouse gas emissions the following scale for policy makers was introduced:

The Global Warming Potential (GWP) of a compound  $i$  is defined as:

Time-integrated global mean Radiative Forcing of a pulse emission of 1kg of compound  $i$  relative to the emission of 1 kg of the reference gas  $\text{CO}_2$ .

Therefore the time horizons of GWPs needs to be specified (GWPs of 20, 100 and 500 years are tabulated in IPCC).

(Radiative forcing describes the integrated effect of past anthropogenic emissions (since 1750), while GWPs describe the future effect of present emissions.)

For example (see Fig. 22 and 23):

One kg emission of  $\text{CH}_4$  leads to 62x larger radiative forcing than the release of one kg  $\text{CO}_2$  for the first 20 years after release, but because of the shorter atmospheric life time the effect of radiative forcing of 1 kg  $\text{CH}_4$  is only 7 times larger than of  $\text{CO}_2$  when intergrated over 500 years.

Totally fluorinated species are very efficient greenhouse gases because of their molecular properties. Their integrated greenhouse gas effect is strongly increasing from 20 to 500 years because of their extremely long atmospheric life times (being much longer than for the reference  $\text{CO}_2$ ).

**Fig. 22 (AR4)**

| Industrial Designation or Common Name (years)         | Chemical Formula  | Lifetime (years)       | Radiative Efficiency ( $W\ m^{-2}\ ppb^{-1}$ ) | Global Warming Potential for Given Time Horizon |        |        |        |
|---|---|------------------------|--|---|--------|--------|--------|
|   |   |                        |  | SARF (100-yr)                                   | 20-yr  | 100-yr | 500-yr |
| Carbon dioxide  | CO <sub>2</sub>   | See below <sup>a</sup> | 1.4x10 <sup>-6</sup>                           | 1   | 1      | 1      | 1      |
| Methane <sup>a</sup>                                  | CH <sub>4</sub>   | 12 <sup>a</sup>        | 3.7x10 <sup>-4</sup>                           | 21  | 72     | 25     | 7.6    |
| Nitrous oxide   | N <sub>2</sub> O  | 114                    | 3.03x10 <sup>-3</sup>                          | 310   | 289    | 298    | 153    |
| <i>Substances controlled by the Montreal Protocol</i> |   |                        |  |   |        |        |        |
| CFC-11  | CCl <sub>3</sub> F  | 45                     | 0.25   | 3,800   | 6,730  | 4,750  | 1,620  |
| CFC-12  | CCl <sub>2</sub> F <sub>2</sub>                                     | 100                    | 0.32   | 8,100   | 11,000 | 10,900 | 5,200  |
| CFC-13  | CClF <sub>3</sub>   | 640                    | 0.25   |   | 10,800 | 14,400 | 16,400 |
| CFC-113   | CCl <sub>2</sub> FCClF <sub>2</sub>                                 | 85                     | 0.3  | 4,800   | 6,540  | 6,130  | 2,700  |
| CFC-114   | CClF <sub>2</sub> CClF <sub>2</sub>                                 | 300                    | 0.31   |   | 8,040  | 10,000 | 8,730  |
| CFC-115   | CClF <sub>2</sub> CF <sub>3</sub>                                   | 1,700                  | 0.18   |   | 5,310  | 7,370  | 9,990  |
| Halon-1301  | CB <sub>2</sub> F <sub>3</sub>                                      | 65                     | 0.32   | 5,400   | 8,480  | 7,140  | 2,760  |
| Halon-1211  | CB <sub>2</sub> ClF <sub>2</sub>                                    | 16                     | 0.3  |   | 4,750  | 1,890  | 575    |
| Halon-2402  | CB <sub>2</sub> F <sub>2</sub> CB <sub>2</sub> BrF <sub>2</sub>     | 20                     | 0.33   |   | 3,680  | 1,640  | 503    |
| Carbon tetrachloride                                  | CCl <sub>4</sub>  | 26                     | 0.13   | 1,400   | 2,700  | 1,400  | 435    |
| Methyl bromide  | CH <sub>3</sub> Br  | 0.7                    | 0.01   |   | 17     | 5      | 1      |
| Methyl chloroform                                     | CH <sub>3</sub> CCl <sub>3</sub>                                    | 5                      | 0.06   |   | 506    | 146    | 45     |
| HCFC-22   | CHClF <sub>2</sub>  | 12                     | 0.2  | 1,500   | 5,160  | 1,810  | 549    |
| HCFC-123  | CHCl <sub>2</sub> CF <sub>3</sub>                                   | 1.3                    | 0.14   | 90  | 273    | 77     | 24     |
| HCFC-124  | CHClFCF <sub>3</sub>  | 5.8                    | 0.22   | 470   | 2,070  | 609    | 185    |
| HCFC-141b   | CH <sub>2</sub> CCl <sub>2</sub> F                                  | 9.3                    | 0.14   |   | 2,250  | 725    | 220    |
| HCFC-142b   | CH <sub>2</sub> CClF <sub>2</sub>                                   | 17.9                   | 0.2  | 1,800   | 5,490  | 2,310  | 705    |
| HCFC-225ca  | CHCl <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>                   | 1.9                    | 0.2  |   | 429    | 122    | 37     |
| HCFC-225cb  | CHClFCF <sub>2</sub> CClF <sub>2</sub>                              | 5.8                    | 0.32   |   | 2,030  | 595    | 181    |
| <i>Hydrofluorocarbons</i>                             |   |                        |  |   |        |        |        |
| HFC-23  | CHF <sub>3</sub>  | 270                    | 0.19   | 11,700  | 12,000 | 14,800 | 12,200 |
| HFC-32  | CH <sub>2</sub> F <sub>2</sub>                                      | 4.9                    | 0.11   | 650   | 2,330  | 675    | 206    |
| HFC-125   | CHF <sub>2</sub> CF <sub>3</sub>                                    | 29                     | 0.23   | 2,800   | 6,350  | 3,500  | 1,100  |
| HFC-134a  | CH <sub>2</sub> FCF <sub>3</sub>                                    | 14                     | 0.16   | 1,300   | 3,830  | 1,430  | 435    |
| HFC-143a  | CH <sub>3</sub> CF <sub>3</sub>                                     | 52                     | 0.13   | 3,800   | 5,890  | 4,470  | 1,590  |
| HFC-152a  | CH <sub>2</sub> CHF <sub>2</sub>                                    | 1.4                    | 0.09   | 140   | 437    | 124    | 38     |
| HFC-227ea   | CF <sub>3</sub> CHFCF <sub>3</sub>                                  | 34.2                   | 0.26   | 2,900   | 5,310  | 3,220  | 1,040  |
| HFC-236fa   | CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>                     | 240                    | 0.28   | 6,300   | 8,100  | 9,810  | 7,660  |
| HFC-245fa   | CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>                    | 7.6                    | 0.28   |   | 3,380  | 1030   | 314    |
| HFC-365mfc  | CH <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>     | 8.6                    | 0.21   |   | 2,520  | 794    | 241    |
| HFC-43-10mee  | CF <sub>3</sub> CHFC <sub>2</sub> HFCF <sub>2</sub> CF <sub>3</sub> | 15.9                   | 0.4  | 1,300   | 4,140  | 1,640  | 500    |
| <i>Perfluorinated compounds</i>                       |   |                        |  |   |        |        |        |
| Sulphur hexafluoride                                  | SF <sub>6</sub>   | 3,200                  | 0.52   | 23,900  | 16,300 | 22,800 | 32,600 |
| Nitrogen trifluoride                                  | NF <sub>3</sub>   | 740                    | 0.21   |   | 12,300 | 17,200 | 20,700 |
| PFC-14  | CF <sub>4</sub>   | 50,000                 | 0.10   | 6,500   | 5,210  | 7,390  | 11,200 |
| PFC-116   | C <sub>2</sub> F <sub>6</sub>                                       | 10,000                 | 0.26   | 9,200   | 8,630  | 12,200 | 18,200 |

**Fig. 23 (IPCC, 2007)**

| Industrial Designation<br>or Common Name<br>(years)      | Chemical Formula                  | Lifetime<br>(years) | Radiative<br>Efficiency<br>( $W\ m^{-2}\ ppb^{-1}$ ) | Global Warming Potential for<br>Given Time Horizon |        |        |        |
|--|-----------------------------------|---------------------|--|--|--------|--------|--------|
|  |                                   |                     |  | GWP <sup>a</sup><br>(100-yr)                       | 20-yr  | 100-yr | 500-yr |
| <i>Perfluorinated compounds (continued)</i>              |                                   |                     |  |  |        |        |        |
| PFC-218  | $C_2F_8$                          | 2,600               | 0.26   | 7,000  | 6,310  | 8,830  | 12,500 |
| PFC-318  | <i>o</i> - $C_3F_8$               | 3,200               | 0.32   | 8,700  | 7,310  | 10,300 | 14,700 |
| PFC-3-1-10   | $C_4F_{10}$                       | 2,600               | 0.33   | 7,000  | 6,330  | 8,860  | 12,500 |
| PFC-4-1-12   | $C_5F_{12}$                       | 4,100               | 0.41   |  | 6,510  | 9,160  | 13,300 |
| PFC-5-1-14   | $C_6F_{14}$                       | 3,200               | 0.49   | 7,400  | 6,600  | 9,300  | 13,300 |
| PFC-9-1-18   | $C_{10}F_{18}$                    | >1,000 <sup>a</sup> | 0.56   |  | >5,500 | >7,500 | >9,500 |
| trifluoromethyl<br>sulphur pentafluoride                 | $SF_5CF_3$                        | 800                 | 0.57   |  | 13,200 | 17,700 | 21,200 |
| <i>Fluorinated ethers</i>                                |                                   |                     |  |  |        |        |        |
| HFE-125  | $CHF_2OCF_3$                      | 136                 | 0.44   |  | 13,800 | 14,900 | 8,490  |
| HFE-134  | $CHF_2OCHF_2$                     | 26                  | 0.45   |  | 12,200 | 6,320  | 1,960  |
| HFE-143a   | $CH_3OCF_3$                       | 4.3                 | 0.27   |  | 2,630  | 756    | 230    |
| HCFE-235da2  | $CHF_2OCHClCF_3$                  | 2.6                 | 0.38   |  | 1,230  | 360    | 106    |
| HFE-245cb2   | $CH_3OCF_2CHF_2$                  | 5.1                 | 0.32   |  | 2,440  | 708    | 215    |
| HFE-245ba2   | $CHF_2OCH_2CF_3$                  | 4.9                 | 0.31   |  | 2,280  | 659    | 200    |
| HFE-254cb2   | $CH_3OCF_2CHF_2$                  | 2.6                 | 0.28   |  | 1,260  | 369    | 109    |
| HFE-347mcc3  | $CH_3OCF_2CF_2CF_3$               | 5.2                 | 0.34   |  | 1,980  | 575    | 175    |
| HFE-347pc12  | $CHF_2CF_2OCH_2CF_3$              | 7.1                 | 0.25   |  | 1,900  | 580    | 175    |
| HFE-356pcc3  | $CH_3OCF_2CF_2CHF_2$              | 0.33                | 0.93   |  | 385    | 110    | 33     |
| HFE-449sl<br>(HFE-7100)                                  | $C_2F_5OCH_3$                     | 3.8                 | 0.31   |  | 1,040  | 297    | 90     |
| HFE-569sl2<br>(HFE-7200)                                 | $C_2F_5OC_2H_5$                   | 0.77                | 0.3  |  | 207    | 59     | 18     |
| HFE-43-10pccc124<br>(H-Galden 1040x)                     | $CHF_2OCF_2OC_2F_4OCHF_2$         | 6.3                 | 1.37   |  | 6,320  | 1,870  | 569    |
| HFE-236ca12<br>(HG-10)                                   | $CHF_2OCF_2OCHF_2$                | 12.1                | 0.66   |  | 8,000  | 2,800  | 860    |
| HFE-338pcc13<br>(HG-01)                                  | $CHF_2OCF_2CF_2OCHF_2$            | 6.2                 | 0.87   |  | 5,100  | 1,500  | 460    |
| <i>Perfluoropolyethers</i>                               |                                   |                     |  |  |        |        |        |
| PFPME  | $CF_3OCF_2(CF_2)_nCF_2OCF_2OCF_3$ | 800                 | 0.65   |  | 7,620  | 10,300 | 12,400 |
| <i>Hydrocarbons and other compounds – Direct Effects</i> |                                   |                     |  |  |        |        |        |
| Dimethylether  | $CH_3OCH_3$                       | 0.015               | 0.02   |  | 1      | 1      | <<1    |
| Methylene chloride                                       | $CH_2Cl_2$                        | 0.38                | 0.03   |  | 31     | 8.7    | 2.7    |
| Methyl chloride  | $CH_3Cl$                          | 1.0                 | 0.01   |  | 45     | 13     | 4      |

# 4. Kyoto Protocol

## Fig. 24

Reductions of greenhouse gases according to Kyoto Protocol 1997 (United Nations 1): for all 15 EU member states. Reductions to be achieved between 2008-2012 relative to 1990 include CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, HCFs (hydrogen containing fluorinated organic gases), PFCs (polyfluorinated organic gases), and SF<sub>6</sub> as equivalents of CO<sub>2</sub>

| Country                    | Target (%) | Country       | Target (%) | Country            | Target (%) |
|----------------------------|------------|---------------|------------|--------------------|------------|
| Australia                  | +8         | Iceland       | +10        | Poland             | -6         |
| Bulgaria                   | -8         | Japan         | -6         | Romania            | -8         |
| Canada                     | -6         | Latvia        | -8         | Russian Federation | 0          |
| Croatia                    | -5         | Liechtenstein | -8         | Slovakia           | -8         |
| Czech Republic             | -8         | Lithuania     | -8         | Slovenia           | -8         |
| Estonia                    | -8         | Monaco        | -8         | Switzerland        | -8         |
| Europ. Comm. <sup>1)</sup> | -8         | New Zealand   | 0          | Ukraine            | 0          |
| Hungary                    | -6         | Norway        | +1         | United States      | -7         |

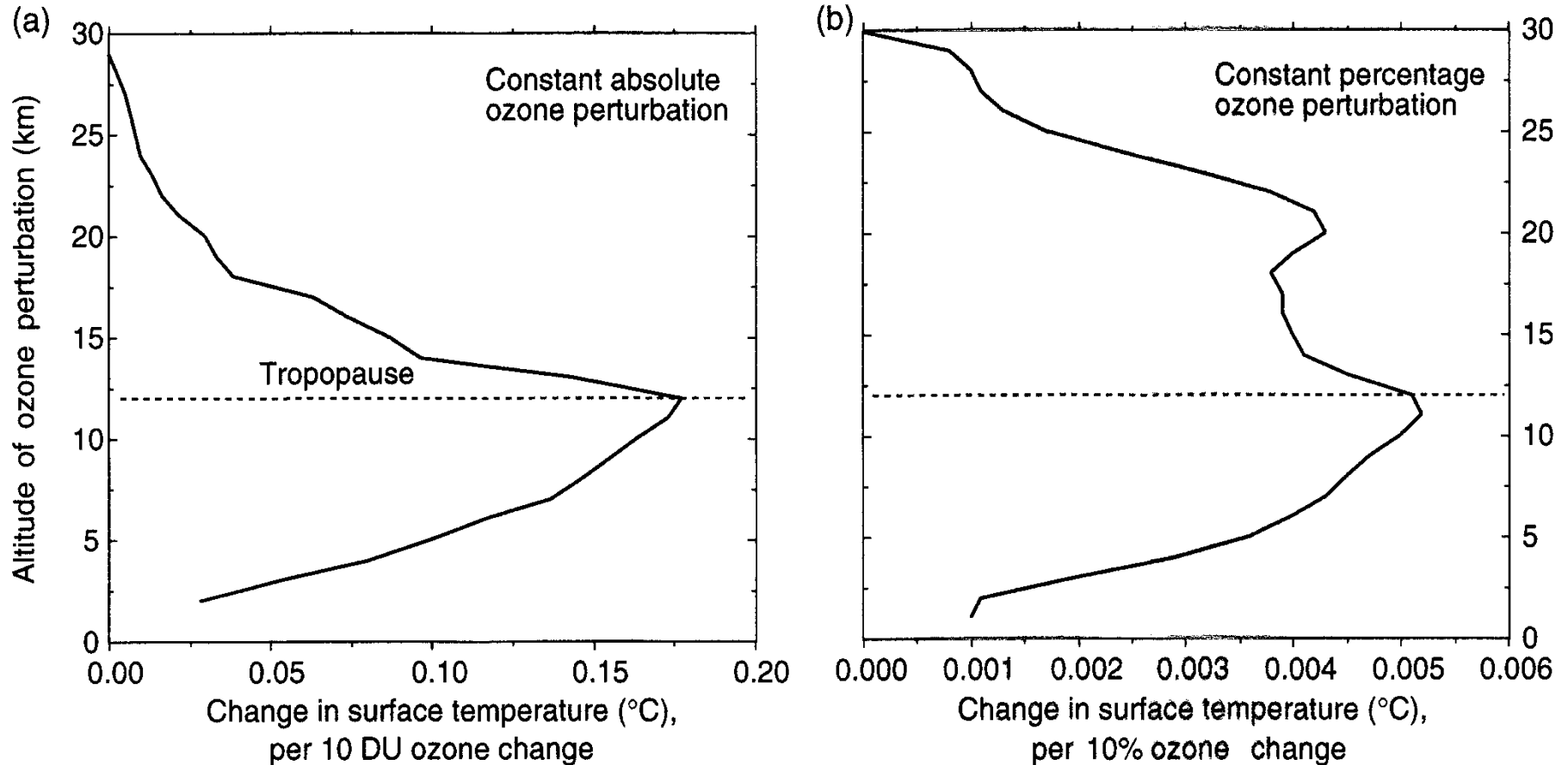
# Notes to Fig. 24

- The UN framework Convention on Climate Change (UNFCCC) was signed in 1992. Its objective is „stabilization of greenhouse gases in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system“
- Based on UNFCCC the Kyoto protocol (1997) sets goals for industrialized countries in order to decrease the emissions of 4 greenhouse gases and two classes of greenhouse gases. The relative contributions are fixed using GWPs for a time horizon of 100 years.
- Important industrialized nations did not sign the Kyoto Protocol.
- It seems rather unlikely that the goals of the Kyoto protocol will be reached by 2012.
- Emissions of air and ship traffic over the oceans (outside national territories) are not included in the Kyoto protocol.
- The countries that have signed the Kyoto protocol have decided to continue their efforts after 2012, when the Kyoto protocol expires.

# 5. Ozone and climate

## 5.1. Ozone profile forcing

Fig.  
25



**Figure 6.1:** Dependence of the surface temperature response on the height and type of O<sub>3</sub> perturbation; (a) shows the sensitivity to a constant absolute change (10 DU), while (b) shows the sensitivity to a constant percentage change (10%). The model tropopause is at 12 km. From Forster and Shine (1997).

# Notes to Fig. 25 (*from Forster and Shine, 1997*)

- Atmospheric ozone is an important greenhouse gas. Changes in ozone concentrations have significantly contributed to the change in radiative forcing since pre-industrial time (see Fig. 7).
- The effectiveness of ozone as greenhouse strongly depends on altitude, maximizing around the tropopause where temperature is lowest.
- Radiative changes caused by stratospheric ozone depletion are negative. However, the effect of stratospheric ozone in 2007 is small (see 7); as consequence of stratospheric ozone recovery a (rather small) positive contribution to radiative forcing is expected for the next decades.
- A significant contribution in radiative forcing since pre industrial time is caused by the increase in tropospheric ozone due to increasing anthropogenic emissions of ozone precursors.
- The determination of the radiative forcing of tropospheric ozone is more difficult than for other (long-lived) greenhouse gases because no measurements exist to document the ozone concentrations in pre industrial time. (Measurements of the 19th century based on the Schönbein paper method are unreliable and should be ignored for trend analysis.)
- The increase in radiative forcing by tropospheric ozone can be only determined by global numerical simulations. However, these models are complex because of the complex chemistry (see Chapter «Tropospheric Chemistry of Gas Phase») and the many ozone precursors of tropospheric ozone and transport. The budget of tropospheric ozone is complex (see next section) and tropospheric ozone has a relatively short and variable life time in the troposphere leading to significant spatial concentration gradients. This makes the assessment of tropospheric ozone model results by measurements a difficult task.

## 5.2. Tropospheric ozone

### Global NO<sub>x</sub> emissions (Fig. 26, TAR)

Table 4.8: Estimates of the global tropospheric NO<sub>x</sub> budget (in TgN/yr) from different sources compared with the values adopted for this report.

| Reference:                | TAR         | Ehhalt<br>(1999) | Holland <i>et al.</i><br>(1999) | Penner <i>et al.</i><br>(1999) | Lee <i>et al.</i><br>(1997) |
|---------------------------|-------------|------------------|---------------------------------|--------------------------------|-----------------------------|
| Base year                 | 2000        | ~1985            | ~1985                           | 1992                           |                             |
| Fossil fuel               | 33.0        | 21.0             | 20 – 24                         | 21.0                           | 22.0                        |
| Aircraft                  | 0.7         | 0.45             | 0.23 – 0.6                      | 0.5                            | 0.85                        |
| Biomass burning           | 7.1         | 7.5              | 3 – 13                          | 5 – 12                         | 7.9                         |
| Soils                     | 5.6         | 5.5              | 4 – 21                          | 4 – 6                          | 7.0                         |
| NH <sub>3</sub> oxidation | –           | 3.0              | 0.5 – 3                         | –                              | 0.9                         |
| Lightning                 | 5.0         | 7.0              | 3 – 13                          | 3 – 5                          | 5.0                         |
| Stratosphere              | <0.5        | 0.15             | 0.1 – 0.6                       | –                              | 0.6                         |
| <b>Total</b>              | <b>51.9</b> | <b>44.6</b>      |                                 |                                | <b>44.3</b>                 |

# Notes to Fig. 26: Global NO<sub>x</sub> emissions of the year 2000

- NO<sub>x</sub> emissions are important for global tropospheric ozone production.
- The global NO<sub>x</sub> budget includes many terms, some are still not well quantified.
- The dominant terms of present NO<sub>x</sub> emissions are anthropogenic fossil fuel combustion and biomass burning.
- Non anthropogenic emission (lightning NO<sub>x</sub> production, soil emissions and transport from the stratosphere) contribute only by 20% to the present emissions. These emissions determined ozone production in the pre industrial troposphere.
- Part of the differences in the emission budgets presented in Fig. 26 are attributable to the different reference years.

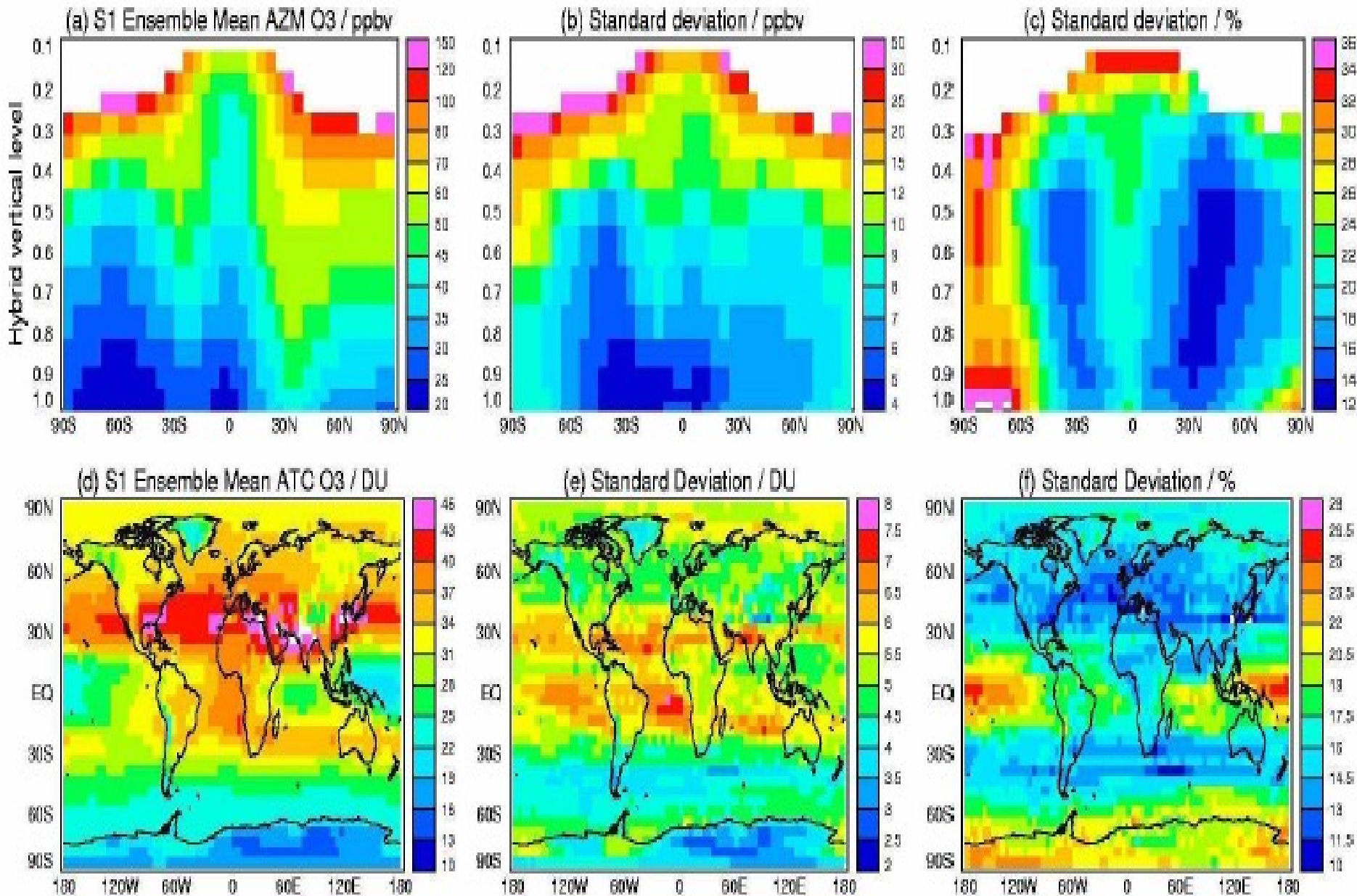
## Tropospheric ozone budget and changes in tropospheric ozone concentrations until 2030, based on Stevenson et al., 2006

- In Stevenson et al., 2006 simulations of tropospheric ozone of 26 models of present day (2000) and 2030 are used. The model ensemble includes chemical transport models (CTMs), fully coupled chemistry climate models (CCMs) and general circulation models (GCMs).
- Fig. 27 shows the used emissions for the ozone precursors, S1 are the emissions used for 2000. The other simulations are related to the year 2030, including the scenario of emissions predicted for current legislation (S2), maximum feasible reduction (S3) implying that best technologies will be used all over the world, IPCC SRES A2 emission scenario, predicting high emissions (S4). The simulations S5 attempt to describe the influence of climate change using the emissions of scenario S2. (Note that the predicted NO<sub>x</sub> emissions for 2030 differ by as much as a factor of 4.)

Fig. 27: Emissions: S1: 2000; S2-S4: 2030;  
 S2: Current legislation; S3: maximum  
 feasible reduction; S4: IPCC SRES A2

|                                   | S1   | S2   | S3   | S4   | S5   | TAR  |
|-----------------------------------|------|------|------|------|------|------|
| <b>NO<sub>x</sub> (Tg N)</b>      | 27.8 | 32.8 | 13.1 | 54.6 | 32.8 | 33   |
| <b>CO (Tg)</b>                    | 470  | 397  | 222  | 761  | 397  | 650  |
| <b>NMVOC (Tg)</b>                 | 116  | 114  | 73   | 176  | 114  | 161  |
| <b>SO<sub>2</sub> (Tg S)</b>      | 54   | 57   | 17   | 100  | 57   | 76   |
| <b>NH<sub>3</sub> (Tg N)</b>      | 49   | 65   | 65   | 69   | 65   | 36   |
| <b>CH<sub>4</sub> conc (ppbv)</b> | 1760 | 2088 | 1760 | 2163 | 2012 | 1745 |

# Present day: overview over all simulations (Fig. 28)

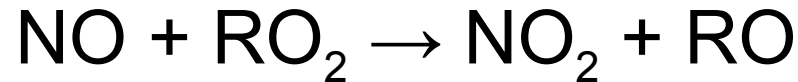


# Notes to Fig. 28: Ozone simulations for the year 2000.

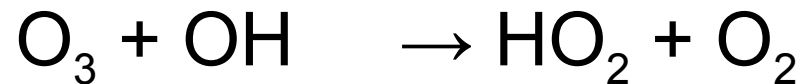
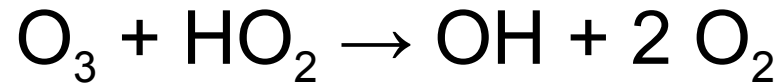
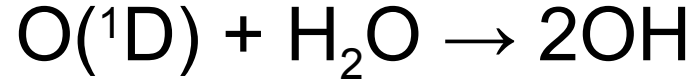
- Ozone concentrations of the ensemble of the model runs are largest downwind of large agglomerations in Northern midlatitudes.
- In Southern midlatitudes biomass burning plumes cause enhanced ozone concentrations.
- Ozone concentrations in Southern midlatitudes are much lower than in Northern midlatitudes.
- The differences between the individual numerical simulations are large in the tropics, in South polar regions and near to the tropopause.

# Tropospheric ozone budget: Terms and Determination (Fig. 29)

***P***: Chemical production:  $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$



***L***: Chemical loss (major terms)



***D***: Surface deposition flux

***S<sub>inf</sub>***: Stratospheric input:  $S_{\text{inf}} = L + D - P$

## *Summary of 2000 budget (Fig. 30)*

|                             | <b>P</b>     | <b>L</b>     | <b>D</b>     | <b>S<sub>inf</sub></b> | <b>B<sub>O3</sub></b> | <b>τ<sub>O3</sub></b> | <b>τ<sub>CH4</sub></b> |
|-----------------------------|--------------|--------------|--------------|------------------------|-----------------------|-----------------------|------------------------|
| <b>A. CHASER CTM</b>        | 5042         | 4594         | 948          | 501                    | 331                   | 21.8                  | 8.42                   |
| <b>B. CHASER GCM</b>        | 5032         | 4620         | 948          | 536                    | 333                   | 21.8                  | 8.37                   |
| <b>C. FRSGC/UCI</b>         | 5135         | 4733         | 907          | 505                    | 331                   | 21.4                  | 7.61                   |
| <b>D. GEOS-CHEM</b>         | 4490         | 3770         | 1016         | 296                    | 294                   | 22.4                  | 10.17                  |
| <b>E. GISS</b>              | --           | --           | --           | --                     | 341                   | --                    | 8.48                   |
| <b>F. GMI/CCM3</b>          | 5331         | 5059         | 862          | 590                    | 388                   | 23.9                  | 7.50                   |
| <b>G. GMI/DAO</b>           | 5124         | 4940         | 763          | 579                    | 386                   | 24.7                  | 7.64                   |
| <b>H. GMI/GISS</b>          | 4722         | 4396         | 856          | 530                    | 372                   | 25.9                  | 8.54                   |
| <b>I. IASB</b>              | --           | --           | --           | --                     | 377                   | --                    | 8.12                   |
| <b>J. LLNL-IMPACT</b>       | 5432         | 5160         | 1014         | 742                    | 406                   | 24.0                  | 7.18                   |
| <b>K. LMDz/INCA-CTM</b>     | 4912         | 4182         | 1232         | 502                    | 330                   | 22.3                  | 8.57                   |
| <b>L. LMDz/INCA-GCM</b>     | 4931         | 4027         | 1227         | 324                    | 316                   | 22.0                  | 8.78                   |
| <b>M. MATCH-MPIC/ECMWF</b>  | --           | --           | --           | --                     | 377                   | --                    | --                     |
| <b>N. MATCH-MPIC/NCEP</b>   | --           | --           | --           | --                     | 399                   | --                    | 9.48                   |
| <b>O. MOZ2-GFDL</b>         | 5263         | 5087         | 963          | 787                    | 349                   | 21.0                  | 8.42                   |
| <b>P. MOZECH</b>            | 6920         | 6617         | 963          | 660                    | 407                   | 19.6                  | 6.31                   |
| <b>R. MOZART4</b>           | 4964         | 4670         | 906          | 612                    | 375                   | 24.5                  | 9.07                   |
| <b>S. p-TOMCAT</b>          | --           | --           | --           | --                     | 248                   | --                    | 12.46                  |
| <b>T. STOCHEM-HadAM3</b>    | 5331         | 4821         | 945          | 435                    | 274                   | 17.3                  | 8.44                   |
| <b>U. STOCHEM-HadGEM</b>    | 5114         | 3757         | 1507         | 151                    | 293                   | 20.3                  | 10.36                  |
| <b>V. TM4</b>               | 4806         | 4594         | 720          | 508                    | 344                   | 23.6                  | 8.80                   |
| <b>W. TM5</b>               | 4580         | 4623         | 827          | 871                    | 339                   | 22.7                  | 7.93                   |
| <b>X. UIO CTM2</b>          | --           | --           | --           | --                     | --                    | --                    | 10.33                  |
| <b>Y. ULAQ</b>              | 5009         | 4469         | 1356         | 623                    | 328                   | 21.3                  | 8.06                   |
| <b>Z. UM CAM</b>            | 3922         | 3363         | 1172         | 614                    | 303                   | 24.4                  | 10.57                  |
| <b>Mean</b>                 | <b>5056</b>  | <b>4561</b>  | <b>1014</b>  | <b>519</b>             | <b>343</b>            | <b>22.4</b>           | <b>8.72</b>            |
| <b>± Standard Deviation</b> | <b>± 571</b> | <b>± 722</b> | <b>± 219</b> | <b>± 195</b>           | <b>± 42</b>           | <b>± 2.0</b>          | <b>± 1.30</b>          |
| <b>IPCC TAR</b>             | <b>3420</b>  | <b>3470</b>  | <b>770</b>   | <b>770</b>             | <b>300</b>            | <b>24</b>             | <b>8.4</b>             |

# Notes to Fig. 30

- The budget terms of the individual models show large differences, including roughly a factor 2 for Chemical ozone production (P) and Chemical losses (L). The differences for dry deposition and transport from the stratosphere are even larger.
- Chemical net ozone production results from  $P-L$ , thus from the difference of 2 large numbers implying large uncertainty.
- Dry deposition and transport from the stratosphere are not well known. On a relative basis the transport from the stratosphere shows the largest differences between the individual models.
- The differences of the terms of the individual models are correlated which is probably caused by the fact that the modelers attempt to provide realistic tropospheric ozone concentrations, which implies some tuning of the model parameterizations. Note that many of the involved processes need to be parametrized, because an explicit calculation is not feasible.

## Changes in ozone budgets (Fig. 31, comp. Fig. 27):

S1: 2000; S2-S4: 2030; S2: Current legislation; S3: maximum feasible reduction; S4: IPCC SRES A2; S5: S2 and climate change (H<sub>2</sub>O, more S<sub>inf</sub>)

|              | $\Delta P$<br>T <sub>g</sub> (O <sub>3</sub> )yr <sup>-1</sup> | $\Delta L$<br>T <sub>g</sub> (O <sub>3</sub> )yr <sup>-1</sup> | $\Delta D$<br>T <sub>g</sub> (O <sub>3</sub> )yr <sup>-1</sup> | $\Delta S_{inf}$<br>T <sub>g</sub> (O <sub>3</sub> )yr <sup>-1</sup> | $\Delta B_{O_3}$<br>T <sub>g</sub> (O <sub>3</sub> ) | $\Delta \tau_{O_3}$<br>days | $\Delta \tau_{CH_4}$<br>years |
|--------------|--|--|--|--|--|-----------------------------|-------------------------------|
| <b>S2-S1</b> | 389±59<br>(7.7%)   | 318±53<br>(7.0%)   | 59±15<br>(5.8%)  | -12±20<br>(-2.3%)  | 20±4<br>(5.8%)                                       | -0.20±0.09<br>(-0.9%)       | 0.23±0.20<br>(2.6%)           |
| <b>S3-S1</b> | -444±70<br>(-8.8%)   | -335±51<br>(-7.3%)   | -92±25<br>(-9.1%)  | 17±33<br>(3.3%)  | -16±4<br>(-4.7%)                                     | 0.75±0.15<br>(3.3%)         | 0.06±0.30<br>(0.7%)           |
| <b>S4-S1</b> | 1203±148<br>(24%)  | 961±123<br>(21%)   | 204±52<br>(20%)  | -37±75<br>(-7.1%)  | 53±11<br>(15%)                                       | -1.1±0.2<br>(-4.9%)         | 0.01±0.33<br>(0.1%)           |
| <b>S5-S2</b> | 41±59<br>(0.8%)  | 98±70<br>(2.0%)  | -13±11<br>(-1.2%)  | 43±32<br>(8.1%)  | -1.3±4.5<br>(-0.4%)                                  | -0.38±0.41<br>(-1.7%)       | -0.40±0.18<br>(-4.6%)         |

## Notes to Fig. 31

- (Mean) tropospheric ozone change predictions (burden) for the time horizon 2000 to 2030 show strong differences, depending on the scenarios as expected from the large range in emission predictions (see Fig. 27).
- Current legislation predictions (S2) lead to an increase of mean tropospheric ozone concentration of 5.8%, while, when maximal feasible technology is assumed (S3), a decrease of 4.7% is predicted and an increase by 15% is expected if emission changes are following IPCC SRES A2 (S4). Climate change leads e.g. to higher humidity enhancing OH production (S5).

# Methane lifetimes: Positive Feedback: more O<sub>3</sub> more OH (Fig. 32)

**Table 8** *Radiative forcings between 2000 and the three 2030 scenarios, and the impact of climate change on the CLE scenario in 2030 (S5-S2). Methane forcings are calculated from the prescribed global concentrations given in Table 3, using the formula of Ramaswamy et al. [2001; Table 6.2] – they do not therefore reflect the model responses. Carbon dioxide forcings from IPCC [2001; Table II.3] are given for comparison, for the appropriate SRES scenario. Given the standard deviations of the ozone forcings, combined forcings are only quoted to the appropriate number of significant figures.*

|       | O <sub>3</sub><br>mW m <sup>-2</sup> | CH <sub>4</sub><br>mW m <sup>-2</sup> | CH <sub>4</sub> +O <sub>3</sub><br>mW m <sup>-2</sup> | CO <sub>2</sub><br>mW m <sup>-2</sup> |
|-------|--------------------------------------|---------------------------------------|---|---------------------------------------|
| S2-S1 | 63 ± 16                              | 116                                   | 180   | 780-810 (B2)                          |
| S3-S1 | -43 ± 15                             | 0                                     | -40   | 780-810 (B2)                          |
| S4-S1 | 155 ± 38                             | 141                                   | 300   | 1010-1080 (A2)                        |
| S5-S2 | -4.4 ± 13                            | -26                                   | -30   | --                                    |

# Notes to Fig. 32

- The life time of the greenhouse gas  $\text{CH}_4$  depends on tropospheric ozone concentration since photolysis of  $\text{O}_3$  in the wavelength range of approximately 300 to 320 nm leads to OH production (see Fig. 8 in Tropospheric Chemistry of Gas Phase) which limits the life time of  $\text{CH}_4$  (see Section 2.2).
- Tropospheric ozone changes lead to OH concentration changes and therefore radiative forcing changes of  $\text{CH}_4$  depends also on  $\text{O}_3$  changes.

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