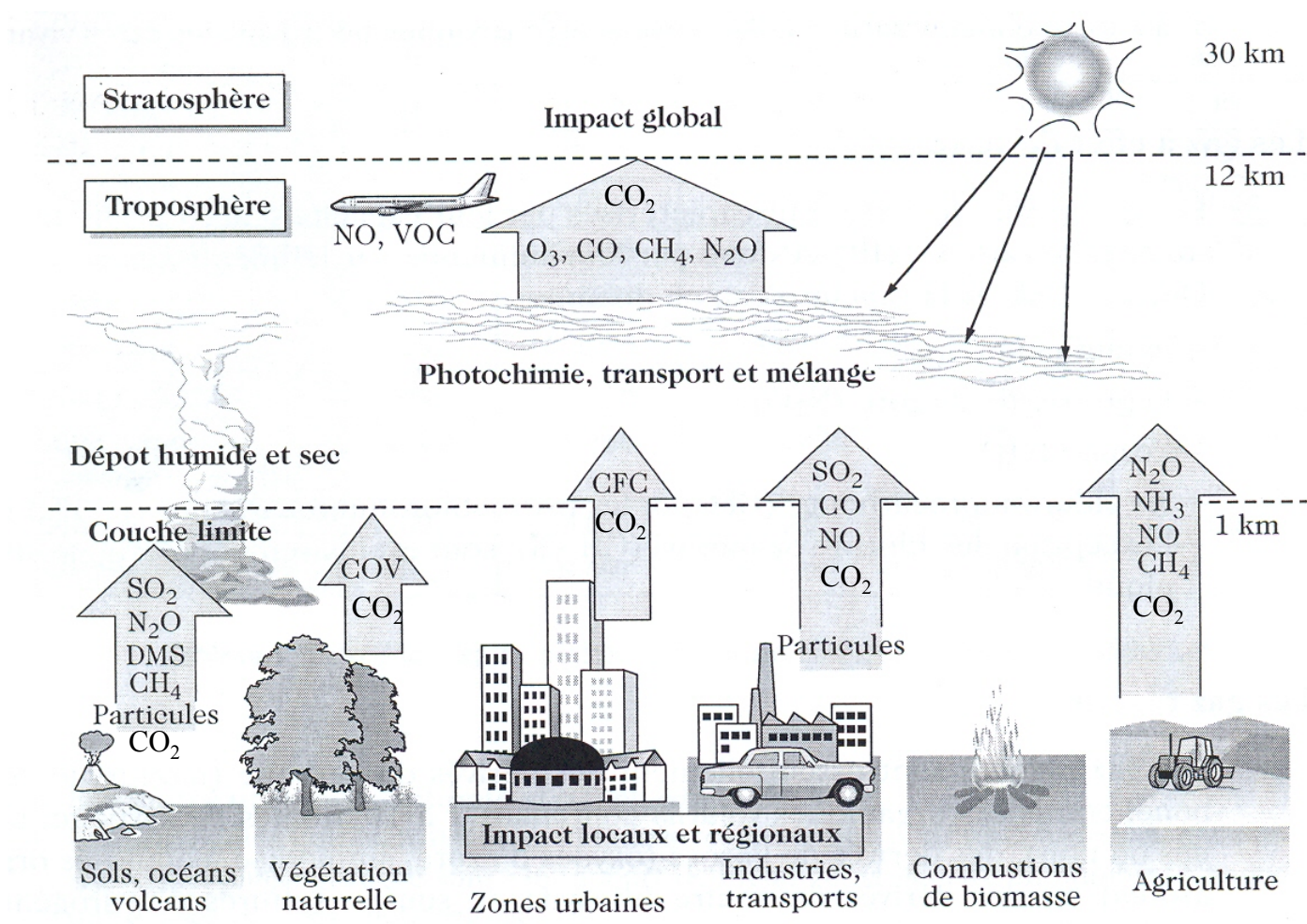# The budget of tropospheric ozone and its evolution
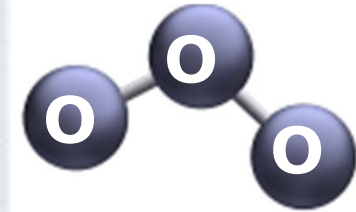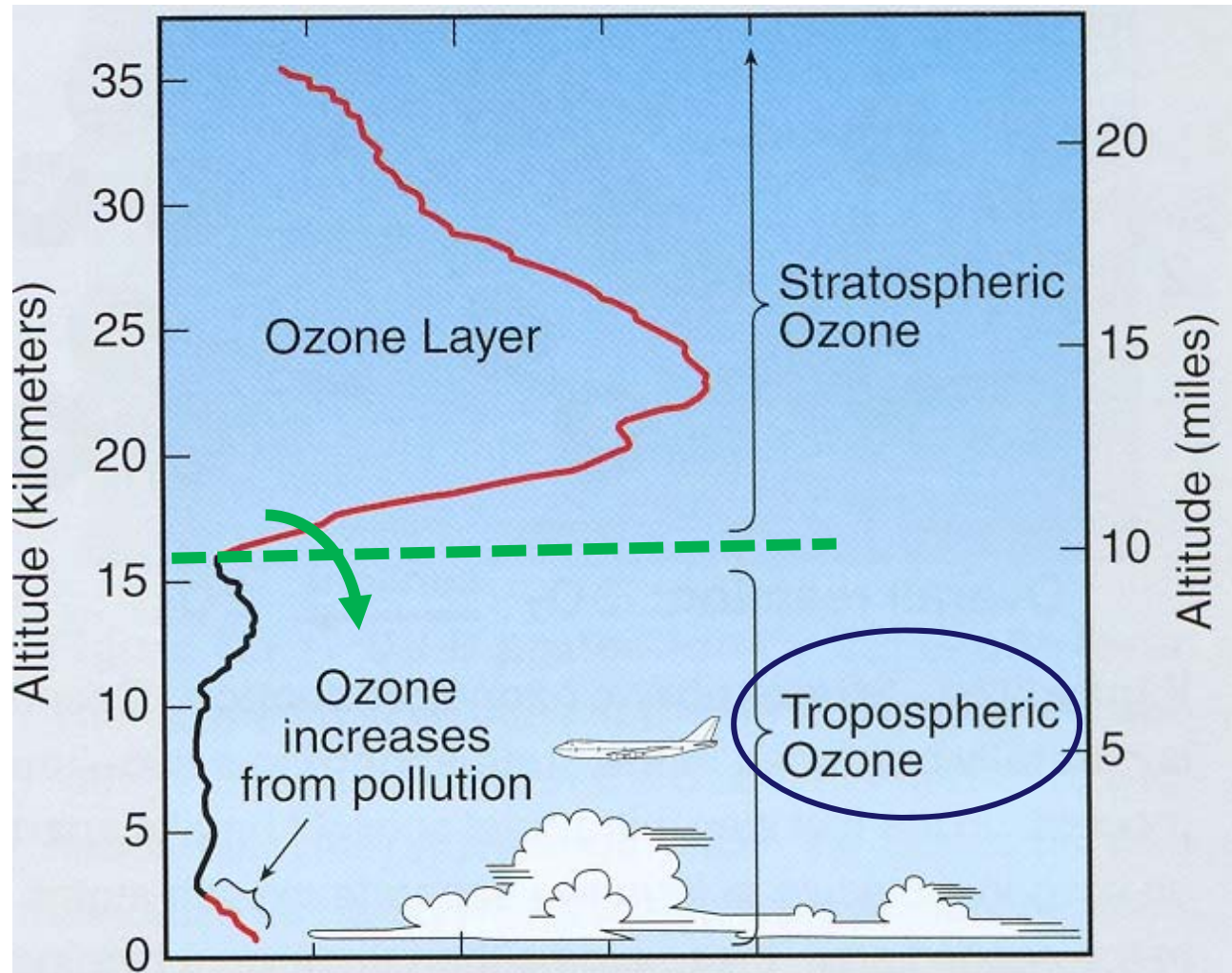
Didier Hauglustaine

**Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-sur-Yvette
Laboratoire Image Ville Environnement (LIVE), Strasbourg**

Major processes controlling the atmospheric composition.

About 90% of the ozone molecules contained in the atmosphere are located in the stratosphere
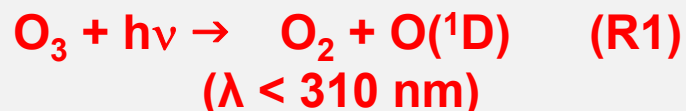

Ozone vertical profile (10^{12} molec. cm^{-3}).

1. Atmospheric oxidation

Formation and destruction of the hydroxyl radical OH·

Photochemical source of OH

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (R1)$$
$$(\lambda < 310 \text{ nm})$$

$$O(^1D) + M \rightarrow O(^3P) + M \quad (R2)$$
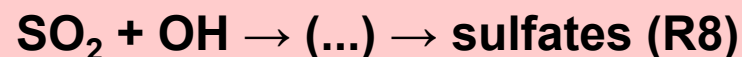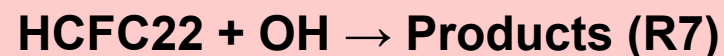
$$O(^1D) + H_2O \rightarrow 2\ OH \quad (R3)$$

The OH concentration is controlled by the ozone distribution (O_3), water vapour (H_2O) and solar radiation (ultraviolet).

Global average:
[OH] = 1.0×10^6 molecules cm^{-3}
(10^{-14} in volume mixing ratio)

OH is the major tropospheric oxidant and hence controls the residence time of most pollutants in the atmosphere.

$$CO + OH\ (+O_2) \rightarrow CO_2 + HO_2 \quad (R4)$$

$$CH_4 + OH\ (+O_2) \rightarrow CH_3O_2 + H_2O \quad (R5)$$

$$RH + OH \rightarrow R + H_2O \quad (R6)$$

$$HCFC22 + OH \rightarrow Products \quad (R7)$$

$$SO_2 + OH \rightarrow (...) \rightarrow sulfates \quad (R8)$$

1. Atmospheric oxidation

Residence time of constituents in the atmosphere:

T (sec) = Burden (kg) / Loss (kg/sec)

dB/dt = Emission − Loss = E − B/T

Solution when emissions go to zero :

$B(t) = B_0 \ exp \ (-t/T)$

1. Atmospheric oxidation
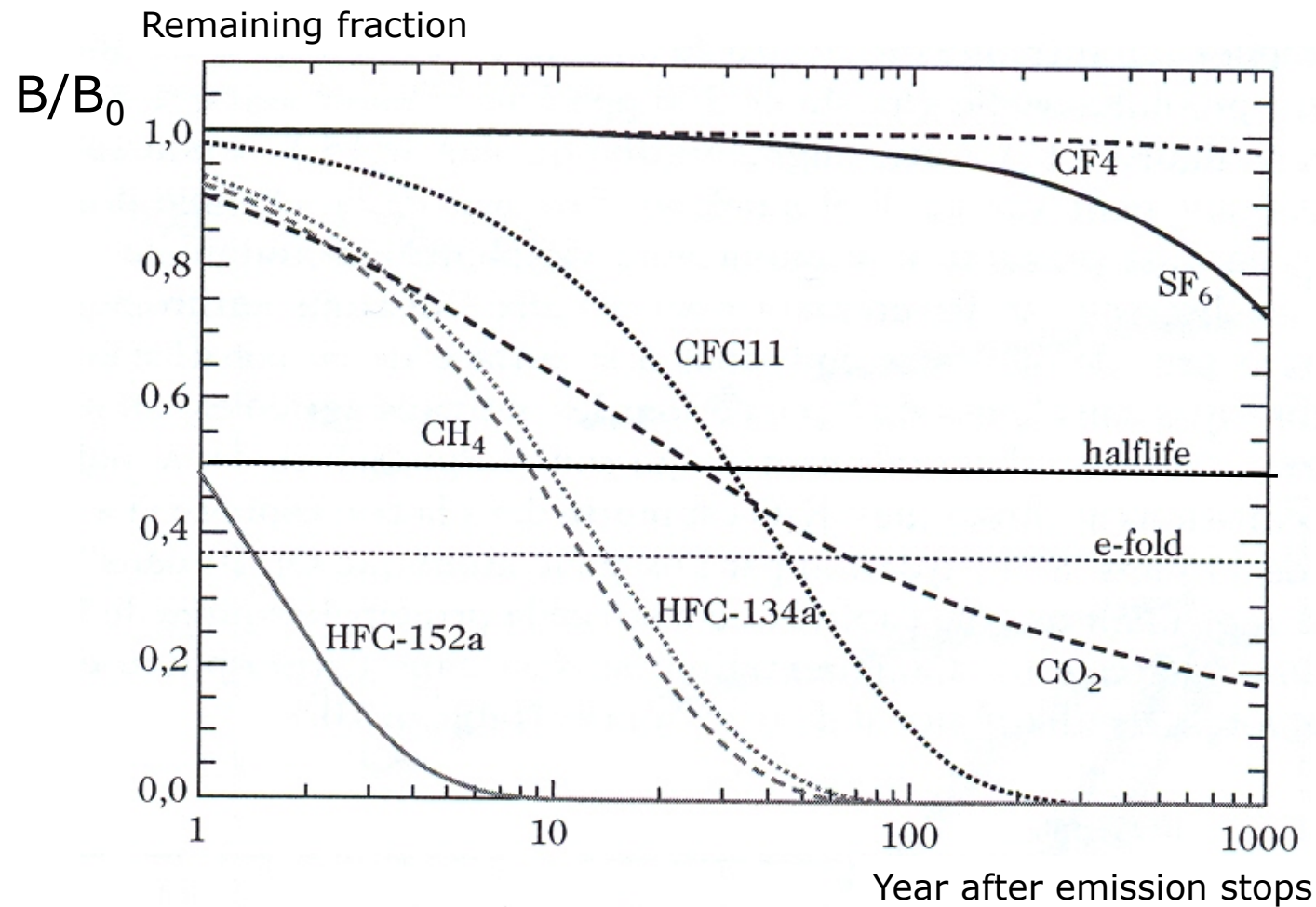
Evolution of the remaining mass of constituents in the atmosphere when their emission stops.

1. Atmospheric oxidation

$$CH_4 + OH \rightarrow CH_3 + H_2O \ (k5)$$

$$k5 = \text{kinetic rate constant } (cm^3/molec./sec)$$

$$T = B / L$$

$$T_{CH4} = [CH4] / L_{CH4}$$

$$T_{CH4} = [CH4] / (k5 [CH4] [OH])$$

$$T_{CH4} = 1 / (k5 [OH]) \text{ about 10 years}$$

$$T_{CO} = 1 / (k4 [OH]) \text{ about 2 months}$$
$$T_{RH} = 1 / (k6 [OH]) \text{ (ethane: 2 months, pentane: 5d)}$$
$$T_{HCFC22} = 1 / (k7 [OH]) \text{ (about 12 years)}$$

$$T_{OH} = 1 / (k4 [CH_4] + k5 [CO] + k6 [RH] + k7 [HCFC22] + ...)$$

1. Atmospheric oxidation
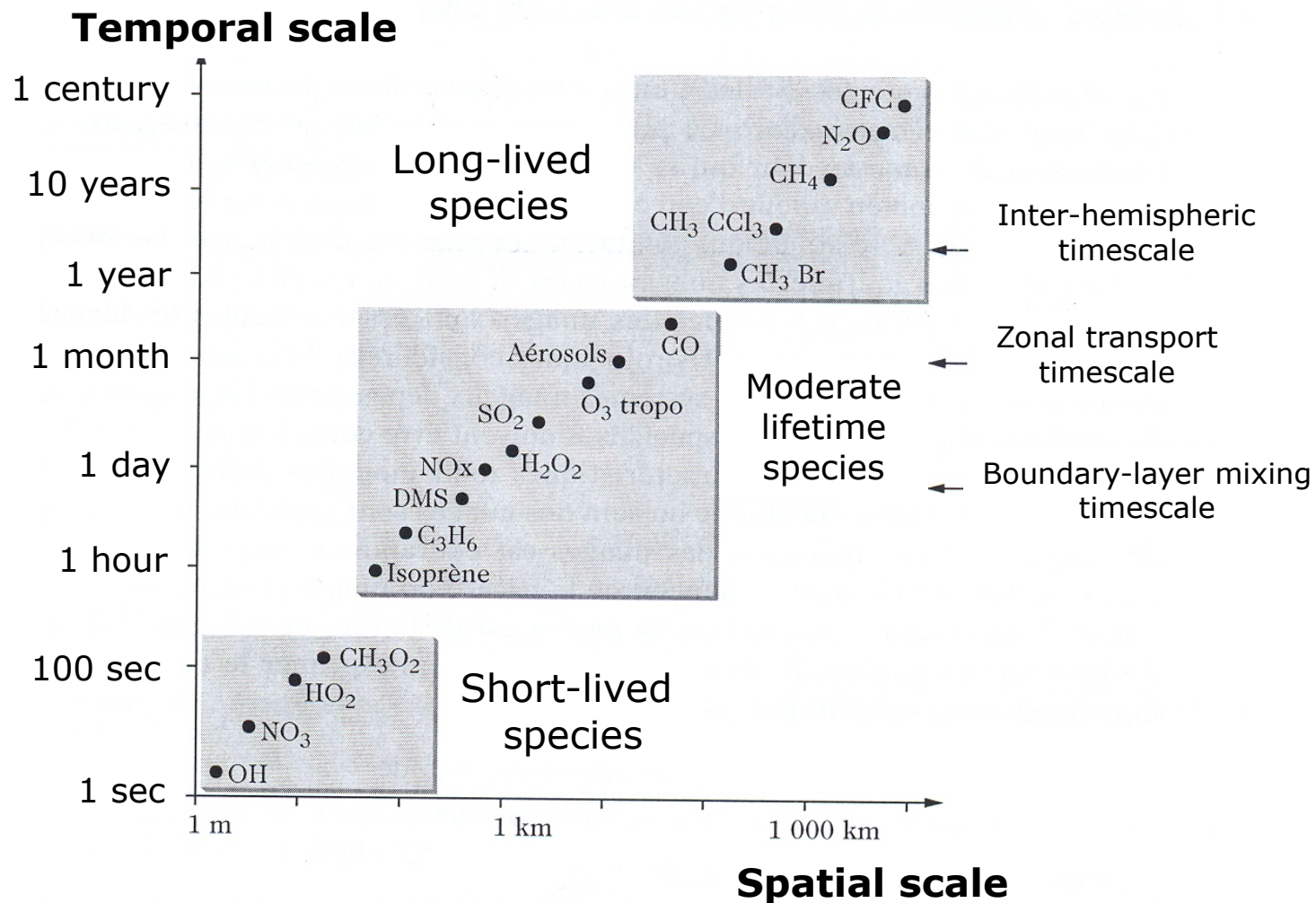
Correlation between the residence time of constituants and the spatial scale of their distribution.

2. Methane and other hydrocarbons

Global Distribution of Atmospheric Methane
NOAA ESRL Carbon Cycle

Seasonal evolution of measured methane mixing ratio (ppb) over the 1999-2008 period.

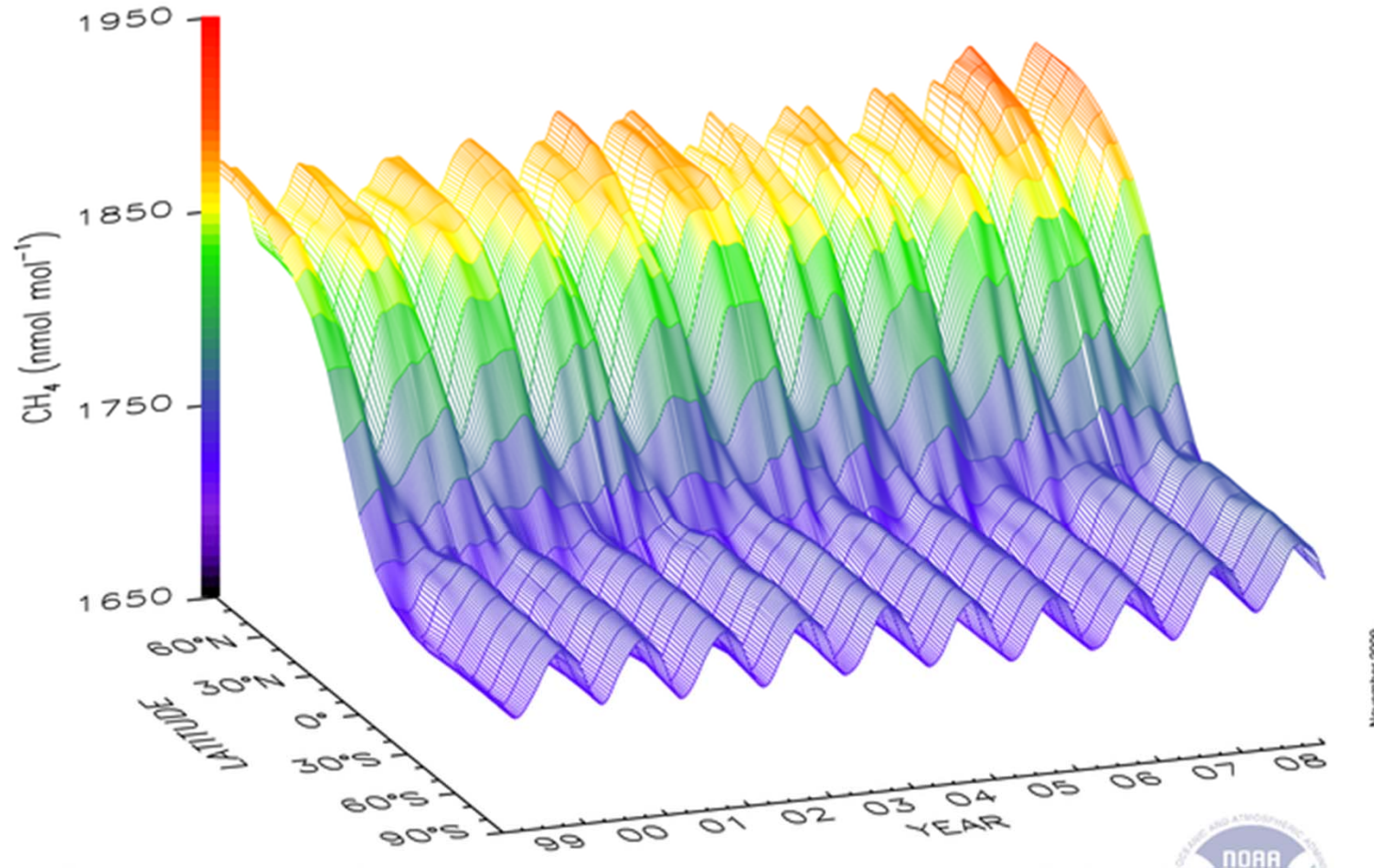# 2. Methane and other hydrocarbons

While domestic emission controls on NO$_x$, NMHC and CO combined are clearly most effective for lowering domestic O$_3$, the O$_3$ response to anthropogenic emissions of CH$_4$ from distant source regions is nearly as large as that to emissions of the traditional O$_3$ precursors in these regions.
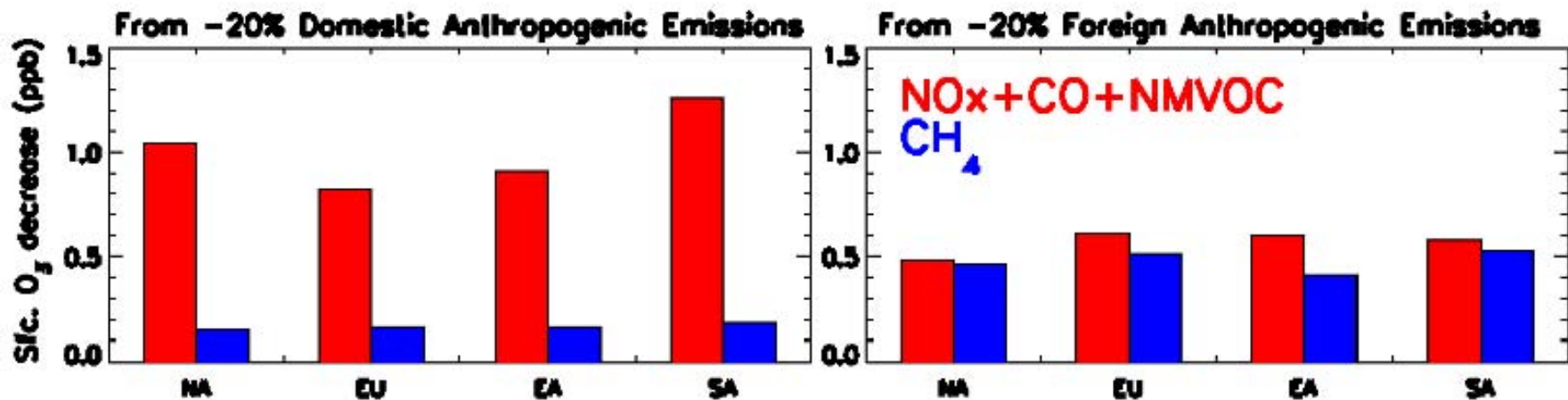
Figure 4.9. Model ensemble surface O$_3$ decrease (ppbv), annually and spatially averaged over the HTAP regions from 20% decreases in anthropogenic emissions of NO$_x$, CO and NMVOC (red) versus 20% decreases in anthropogenic CH$_4$ (blue). Influence of each source region on surface O$_3$ within the same region (termed "domestic", left panel), and the sum of the O$_3$ responses to emission changes within the three other source regions (termed "foreign", right panel). Adapted from Fiore et al. [2010].

2. Methane and other hydrocarbons

A/

- Biomass burning 11%
- Fossil fuel 6%
- Ocean 2%
- Vegetation 81%

B/

- Acetone 6%
- Other VOCs 1%
- Methanol 15%
- Terpenes 17%
- Isoprene 61%

VOCs : 1300 TgC
CH$_4$: 368 TgC
CO : 771 TgC
Total : 2439 TgC (2.4 PgC)
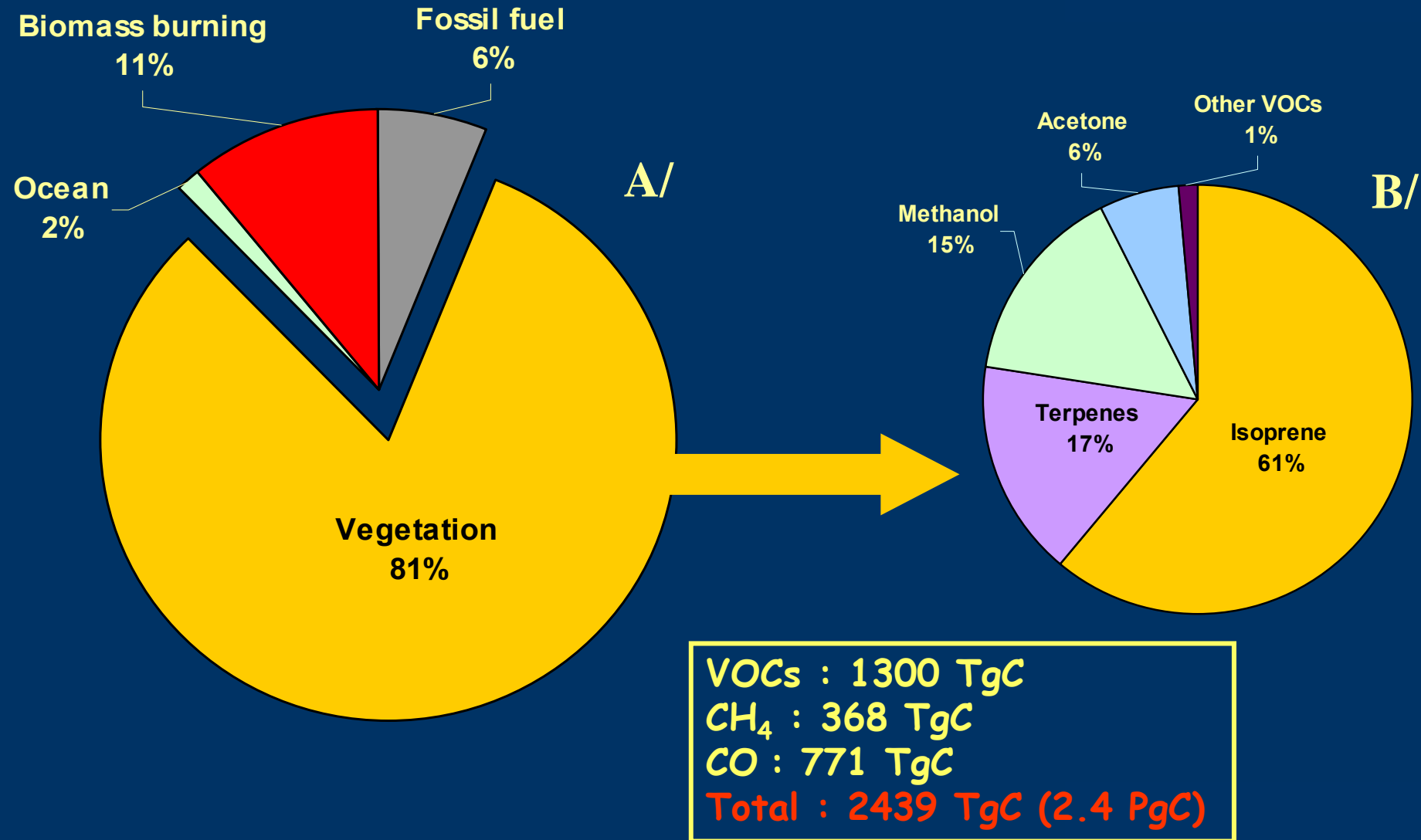
Total (A) and biospheric (B) emissions of non-methane hydrocarbons (%).

2. Methane and other hydrocarbons

$$F \text{ (gC/m²/h)} = LAI \times S \times E_f \text{(PFT,COV)} \times C_T \text{(T,COV)} \times C_L \text{(PAR)}$$

LAI = Leaf Area Index (m2/m2)
S = Vegetation density (g/m2)
Ef = Emission factor (gC/h/g)
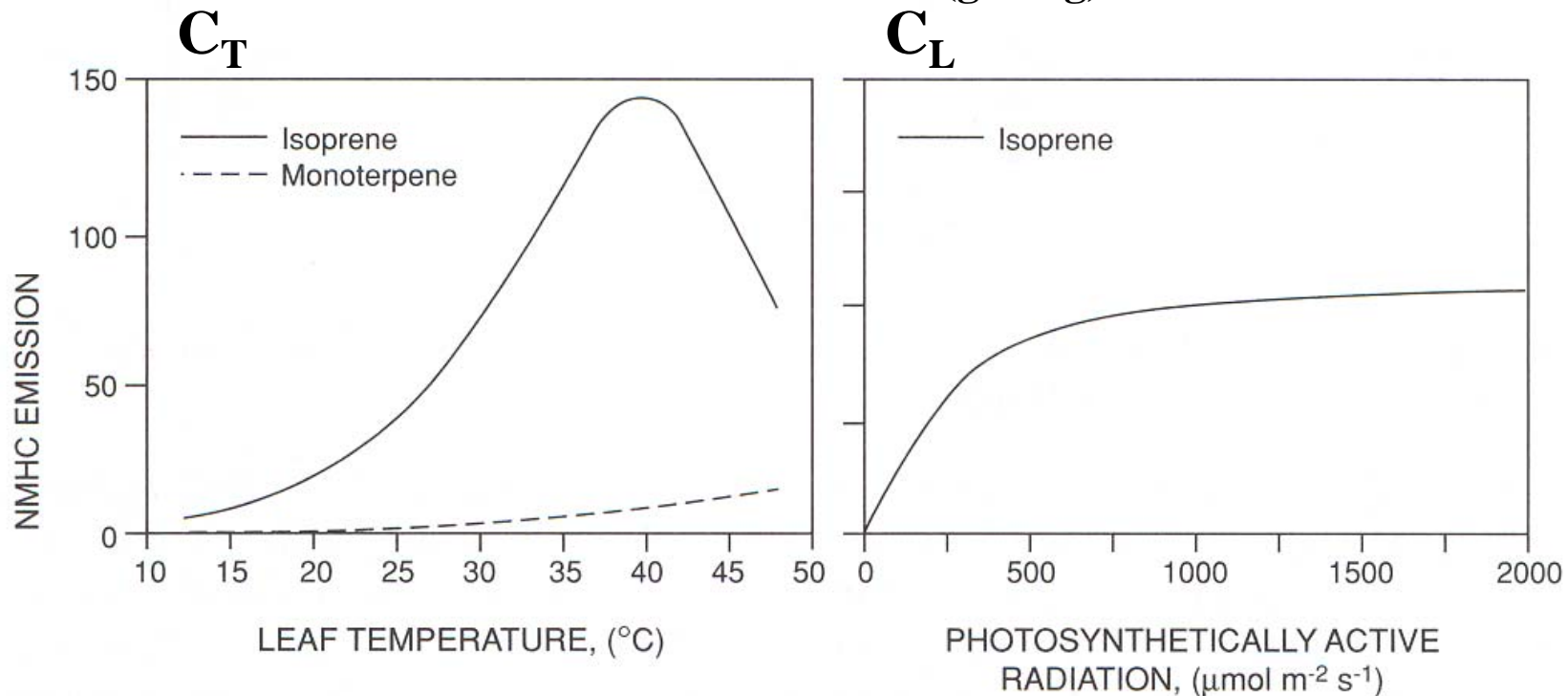
Temperature (C_T) and radiation (C_L) dependence of isoprene and monoterpenes emissions.

2. Methane and other hydrocarbons
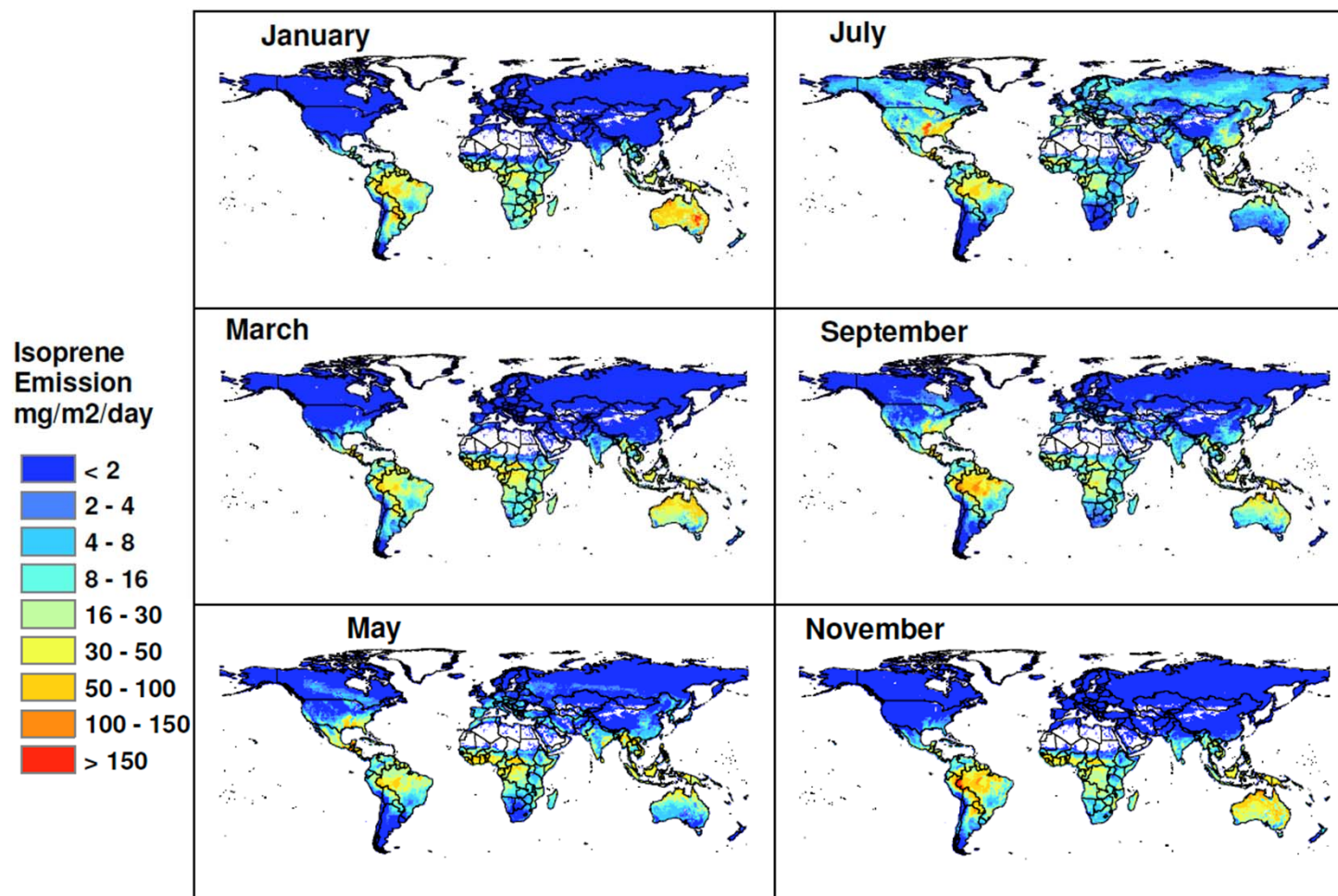
Isoprene emissions for various months simulated by the MEGAN model.

2. Methane and other hydrocarbons

Surface ozone in 2100

Surface ozone change in 2100 (AIB)

Surface ozone change in 2100 (Biogenics)

30% of O₃ increase

Surface ozone change in 2100 (Climate)
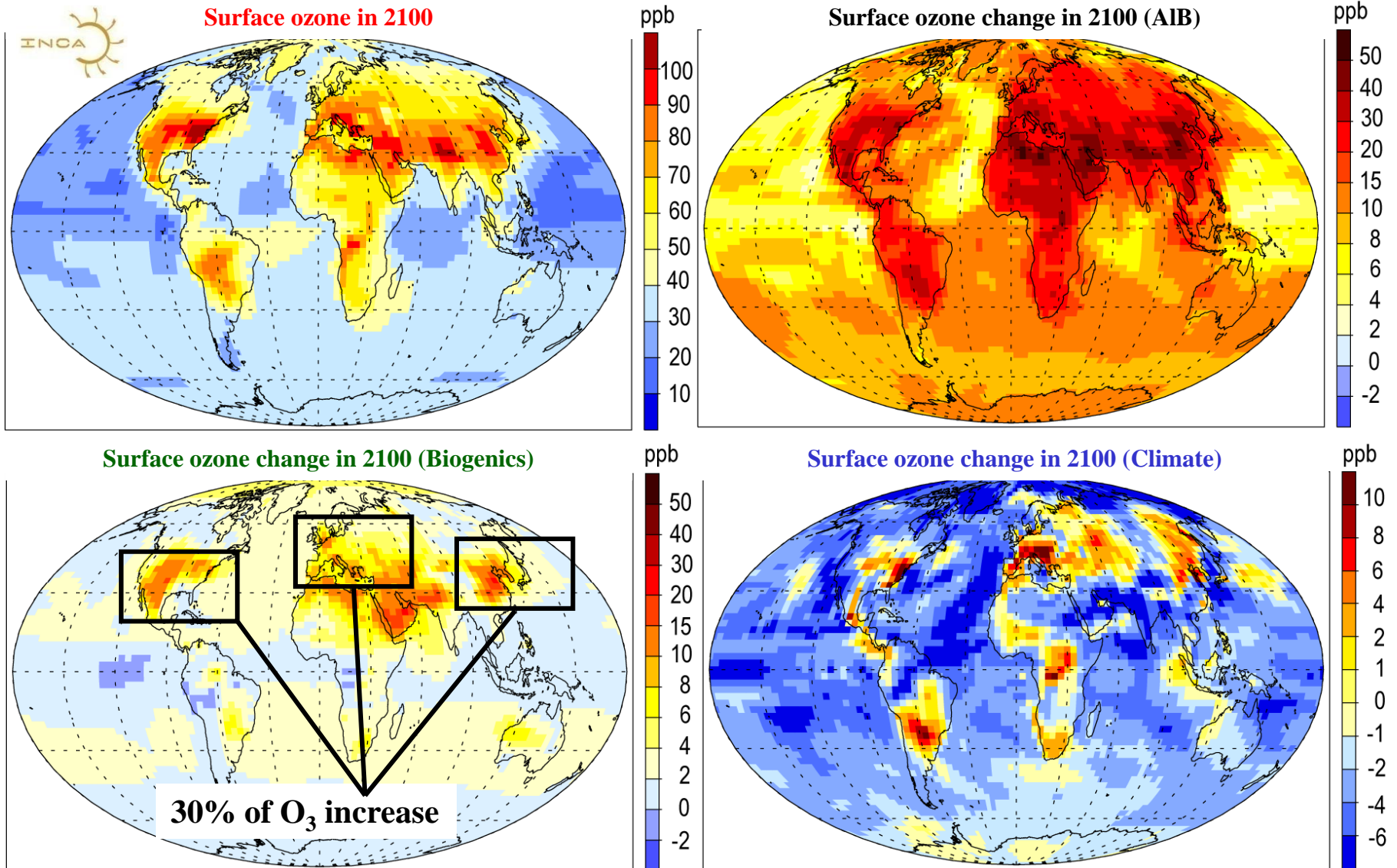
Hauglustaine et al., 2005

3. Carbon monoxide

Global Distribution of Atmospheric Carbon Monoxide
NOAA ESRL Carbon Cycle
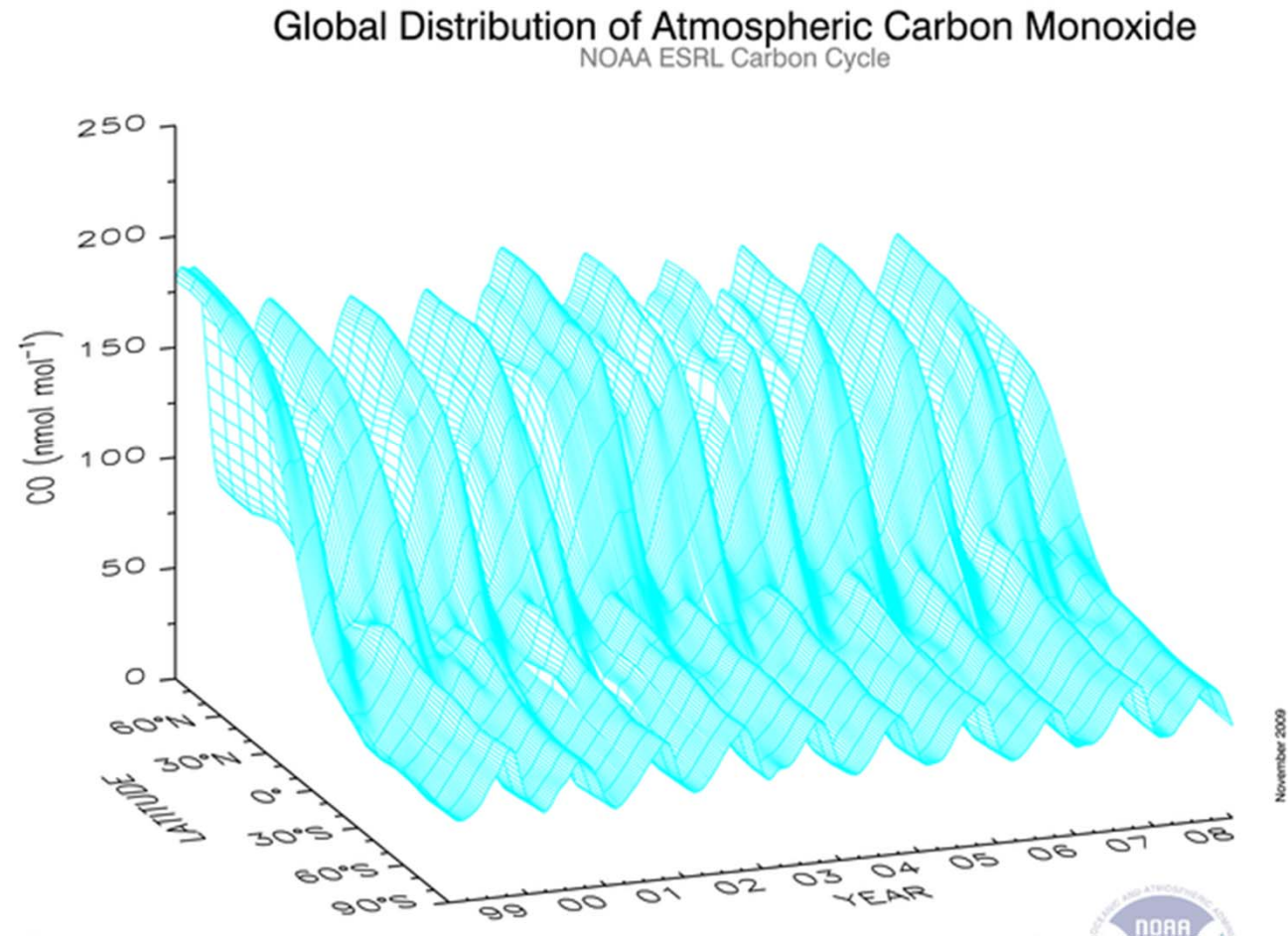
Seasonal evolution of measured CO mixing ratio (ppbv) over the 1999-2008 period.

3. Carbon monoxide

Carbon monoxide measured by IASI on board (METOP)

2008 - 2009

NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT

Total Column CO x10^{18} molecules/cm^2

4. Nitrogen compounds

In the stratosphere:
$$N_2O + O(^1D) \rightarrow NO + NO$$
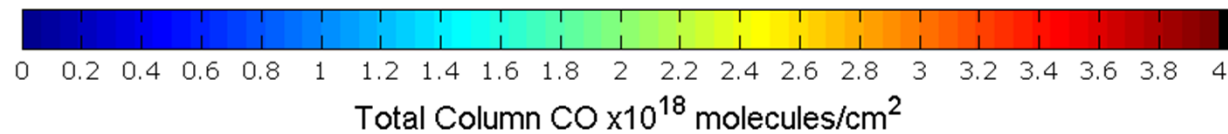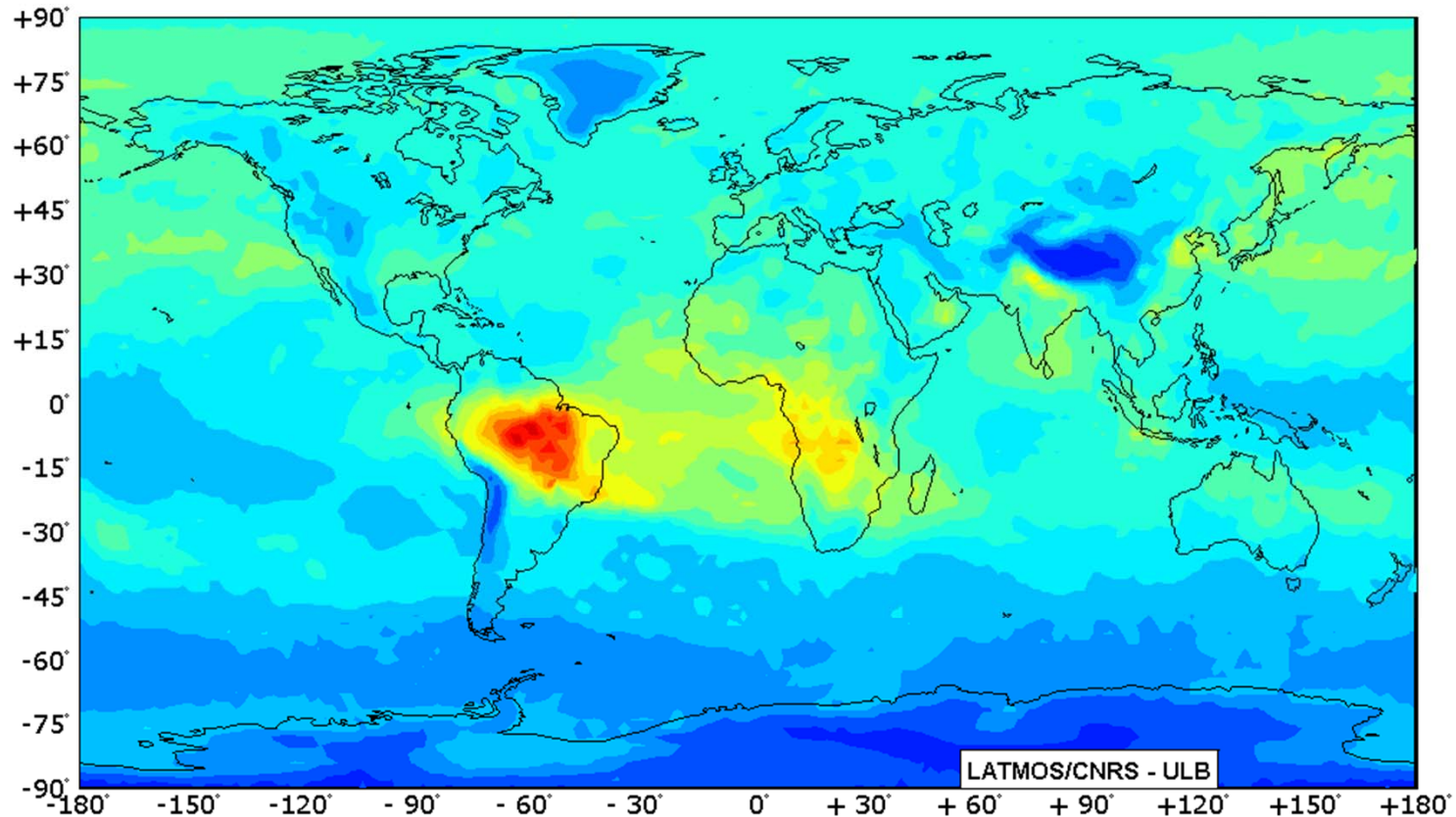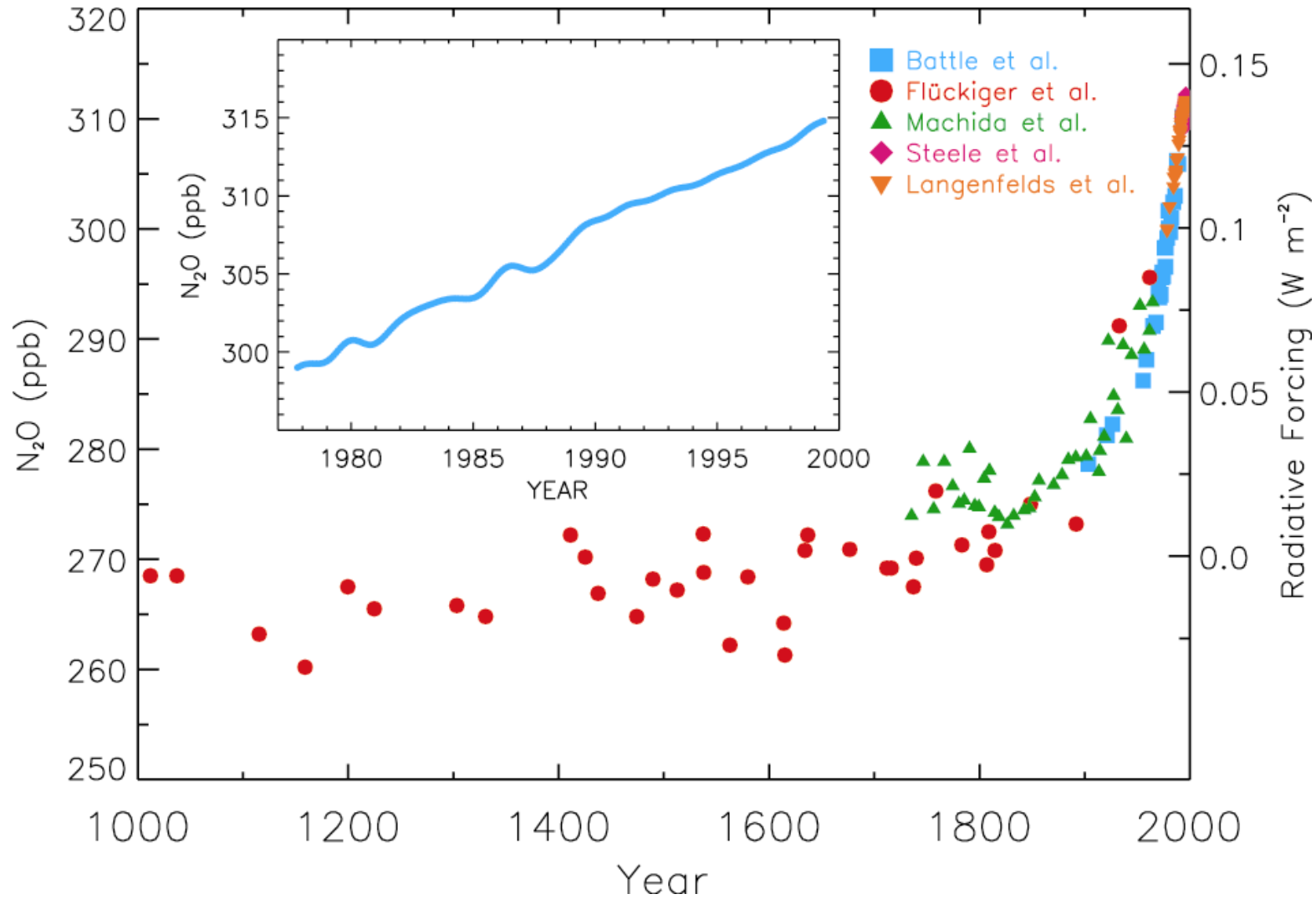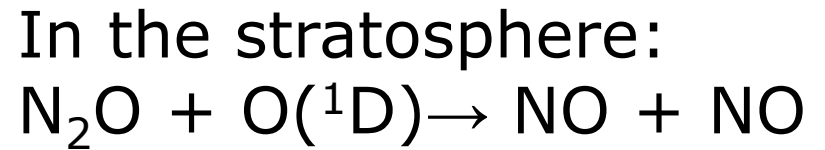
Evolution of N$_2$O mixing ratio over the last millenium (ppb).

4. Nitrogen compounds

Tropospheric NO$_2$ column (10^{15} molec cm^{-2})
August 1997

KNMI / IUP / ESA

0.0 0.2 0.5 1.0 1.5 2.0 3.0 4.0 6.0 8.0 10.0 20.0
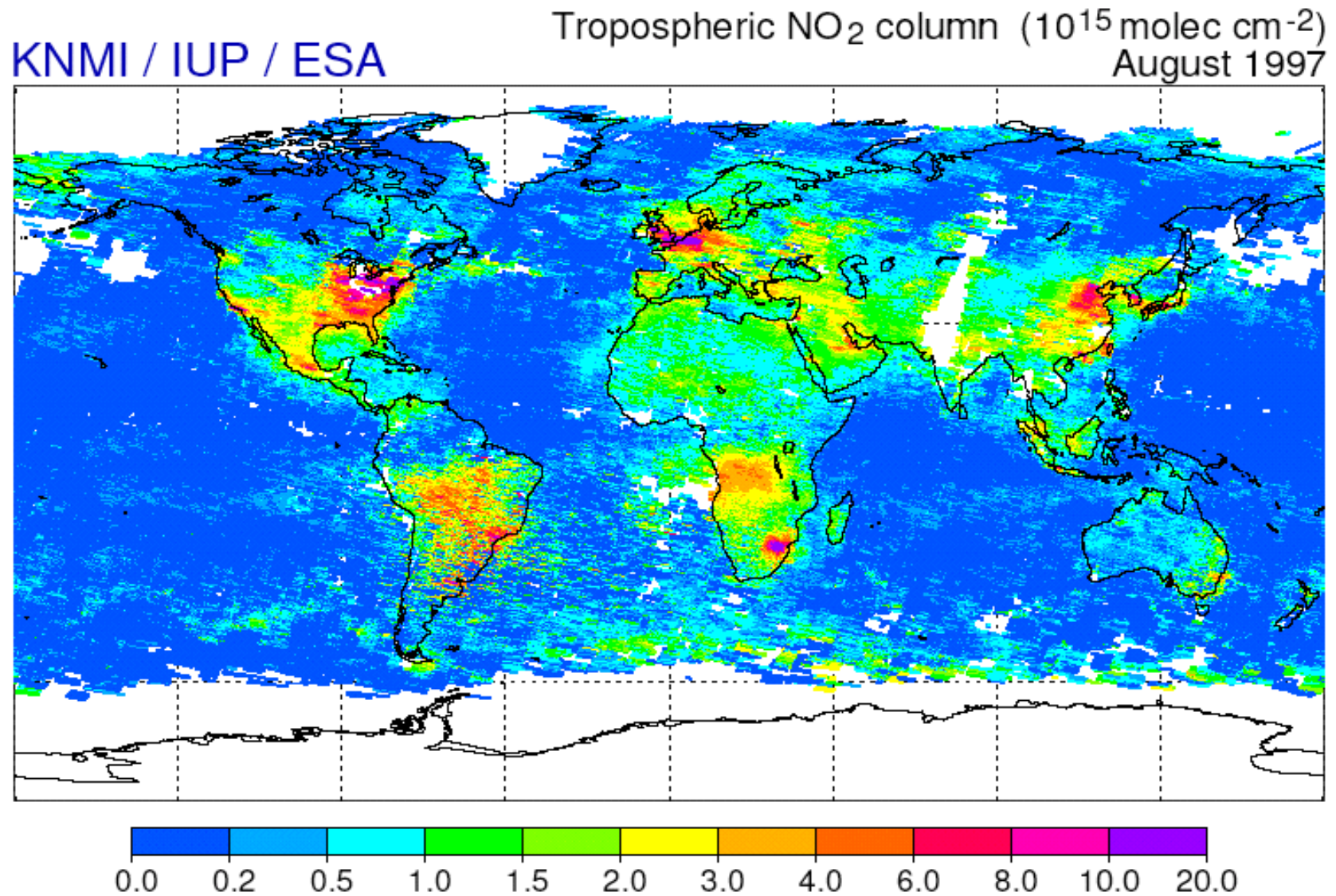
5. Tropospheric ozone

Tropospheric ozone photochemical production

Photostationnary state O_3-NO-NO_2 (T≈1min)

During daytime

$$NO + O_3 \rightarrow NO_2 + O_2 \ (k_{10})$$
$$NO_2 + hv \rightarrow NO + O \ (j_{NO2})$$
$$O + O_2 \rightarrow O_3$$

$$NO_2/NO = k_{10} \ O_3 \ / \ j_{NO2}$$

Ozone production

2.   **1.**

$$NO + HO_2 \rightarrow NO_2 + OH \ (k_{11})$$
$$NO + CH_3O_2 \rightarrow NO_2 + CH_3OH \ (k_{12})$$
$$NO + RO_2 \rightarrow NO_2 + RO \ (k_{13})$$

$$NO_2 + hv \rightarrow NO + O \ (j_{NO2})$$
3. $$O + O_2 \rightarrow \mathbf{O_3}$$
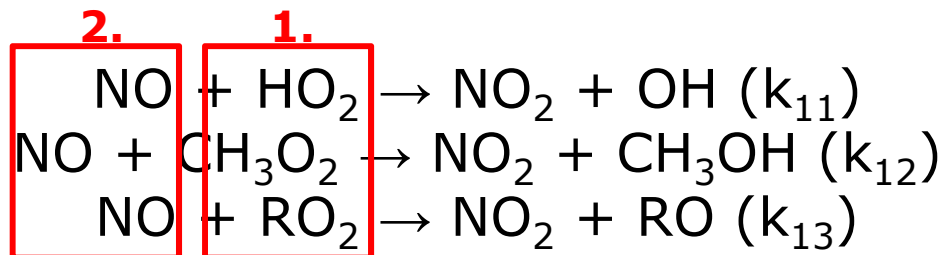
5. Tropospheric ozone

Ozone photochemical destruction

1. $O_3 + h\nu \rightarrow O_2 + O(^1D)$ ($\lambda < 310$ nm)
   $O(^1D) + H_2O \rightarrow 2\ OH$

2. $O_3 + HO_2 \rightarrow OH + 2\ O_2$

3. $O_3 + OH \rightarrow HO_2 + O_2$
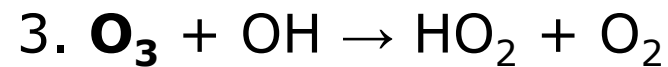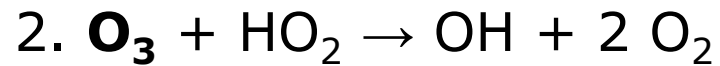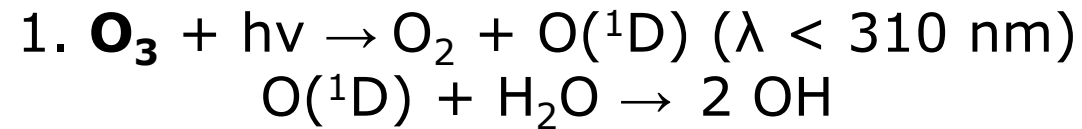
5. Tropospheric ozone
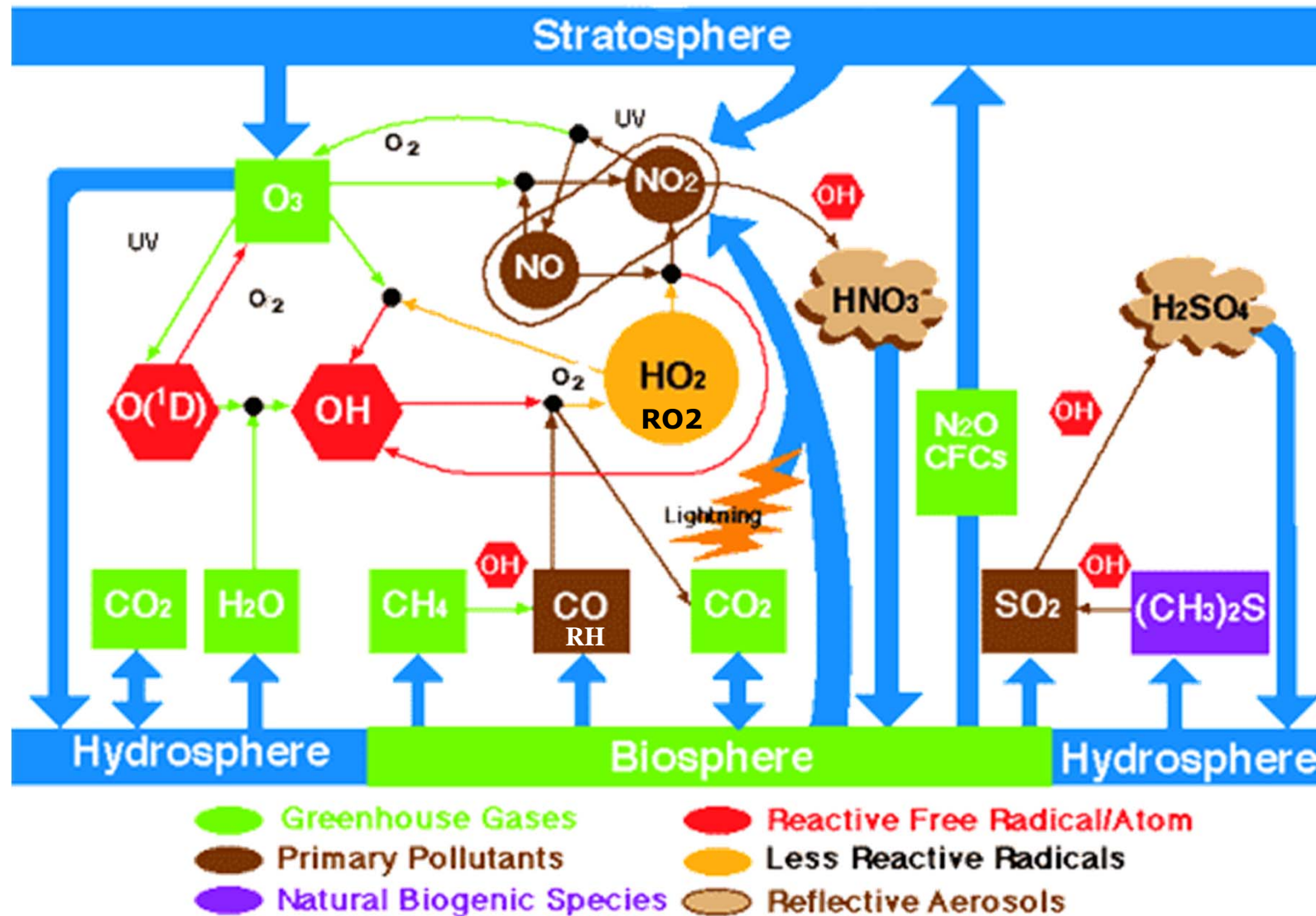
Summary of major processes controlling the tropospheric ozone budget and the hydroxyl radical OH.

5. Tropospheric ozone
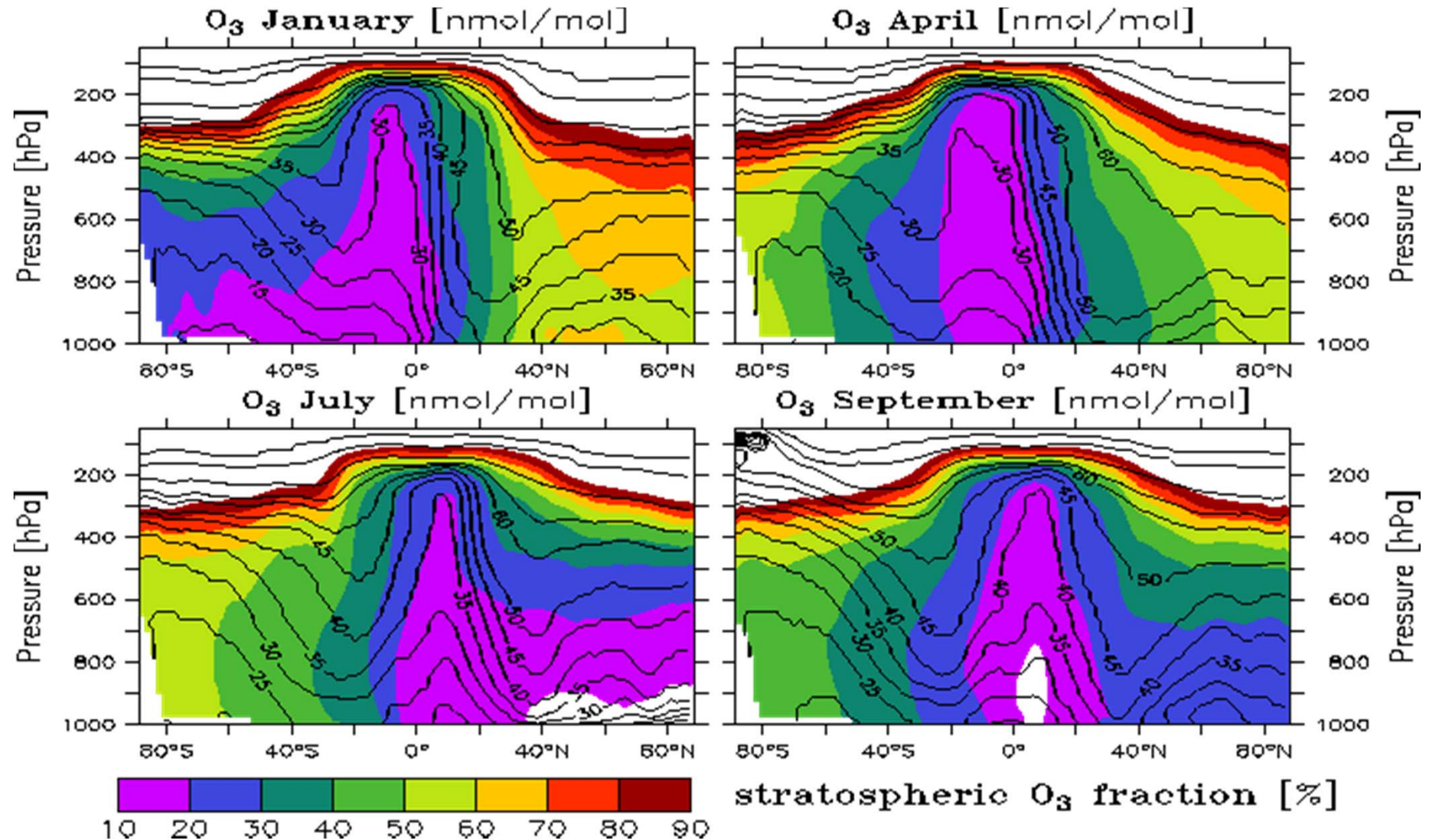
Zonal mean ozone distribution (isolines in ppbv) and stratospheric ozone fraction (%) calculated in January, April, July and September.

5. Tropospheric ozone

Tropospheric ozone budget simulated by global tropospheric models (ensemble mean).

Ozone budget terms	Tg(O_3)/yr
Sources	
Photochemical production (P)	3948 ± 761
Stratospheric Influx	636 ± 273
Sinks	
Photochemical destruction (L)	3745 ± 554
Surface deposition	902 ± 255
Net photochemistry (P-L)	245 ± 346
Burden	307 ± 38

T = B / L
T = 307 / (3745+902) = 24 days

Wild et al., 2012

5. Tropospheric ozone
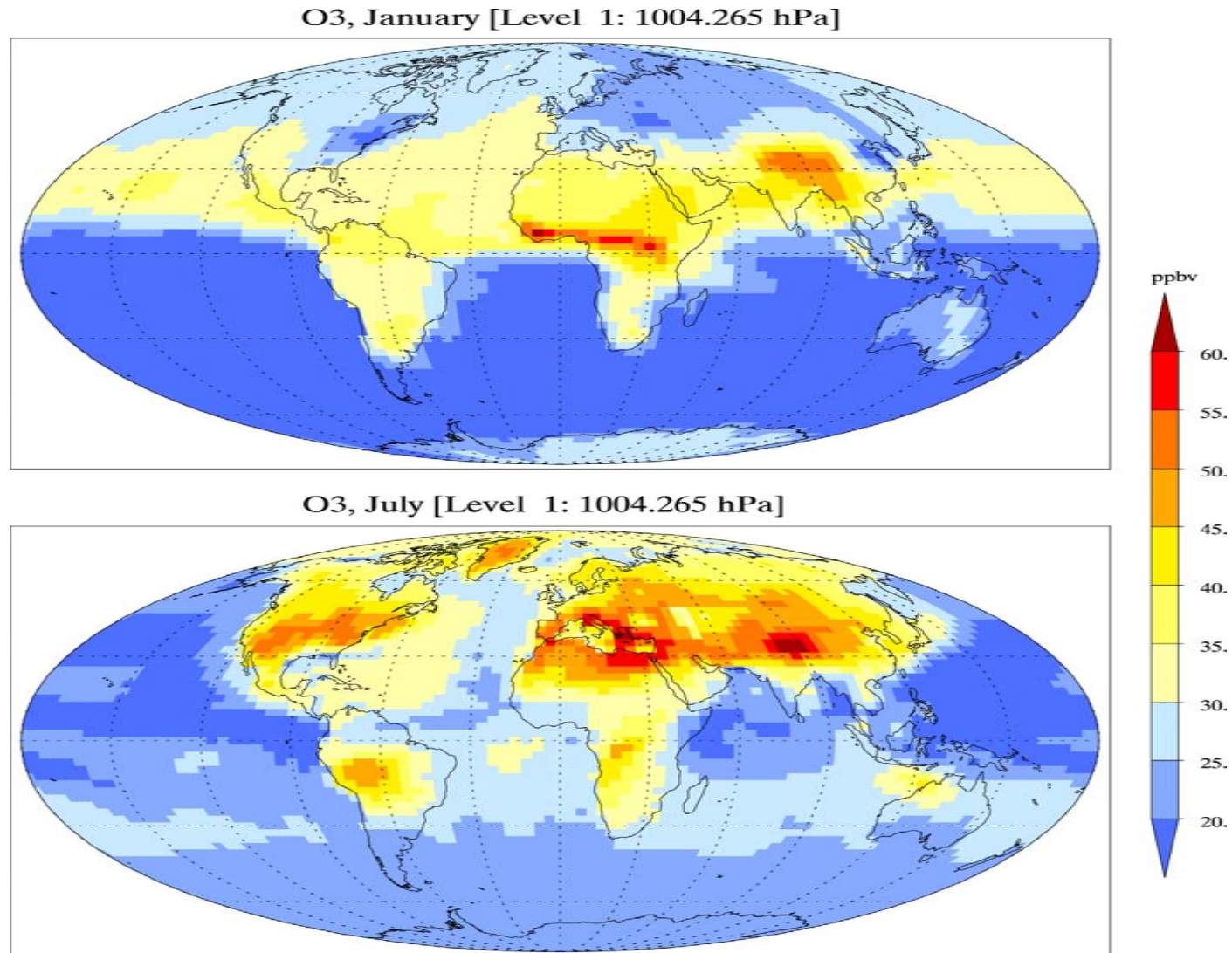
Surface ozone distribution (ppbv) calculated by LMDz-INCA for January and July present-day conditions.

6. Evolution of tropospheric ozone and environmental impacts

Evolution of background tropospheric ozone since the pre-industrial.
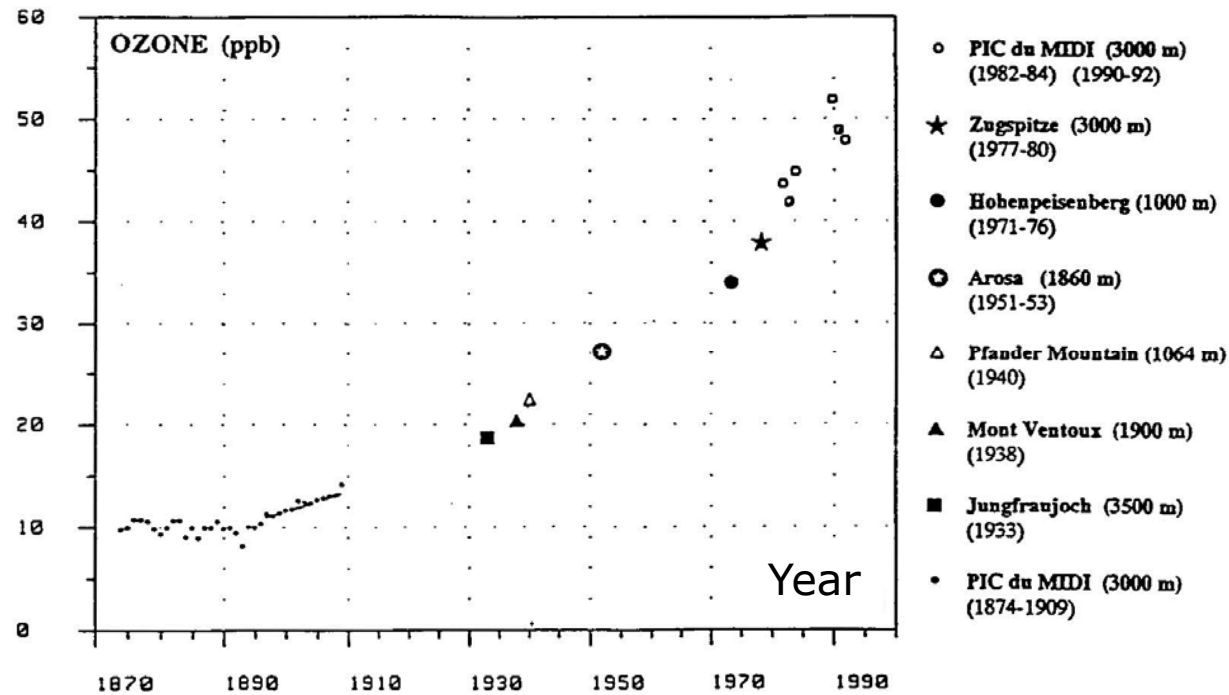
6. Evolution of tropospheric ozone and environmental impacts

Evolution of tropospheric ozone in the free-troposphere
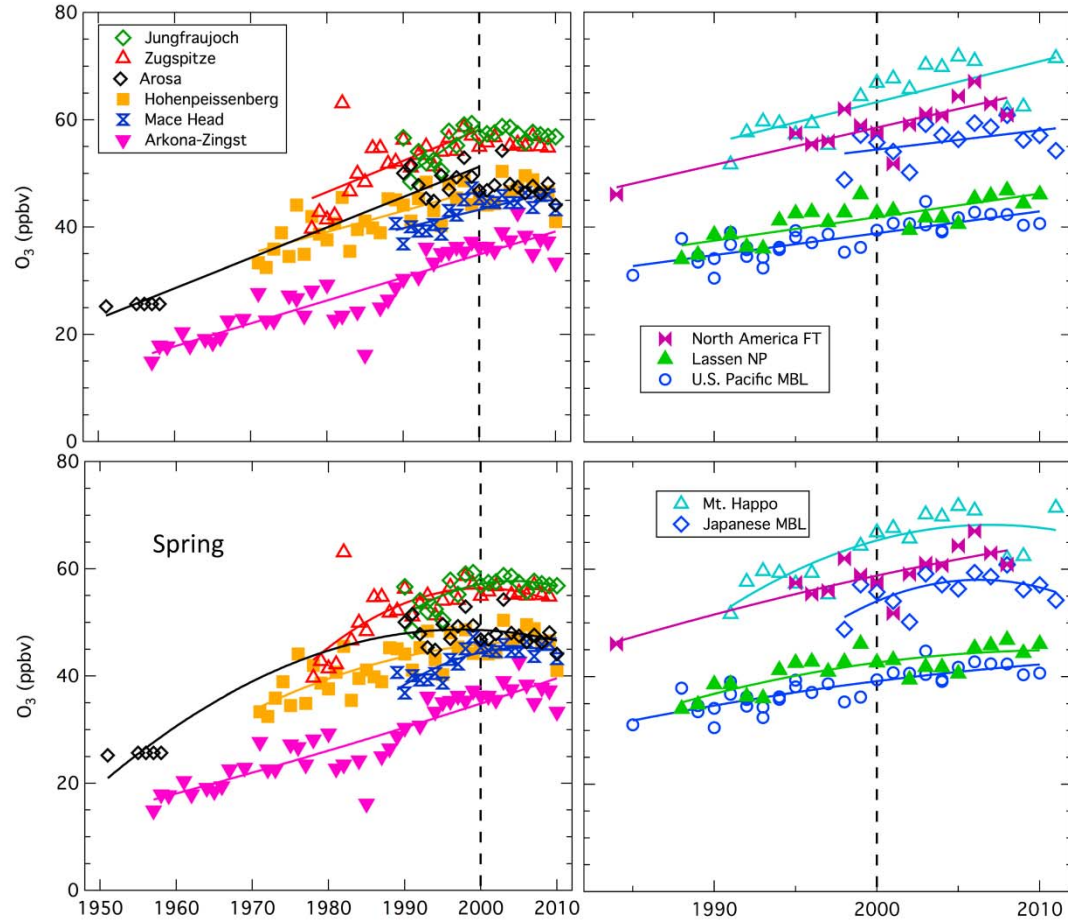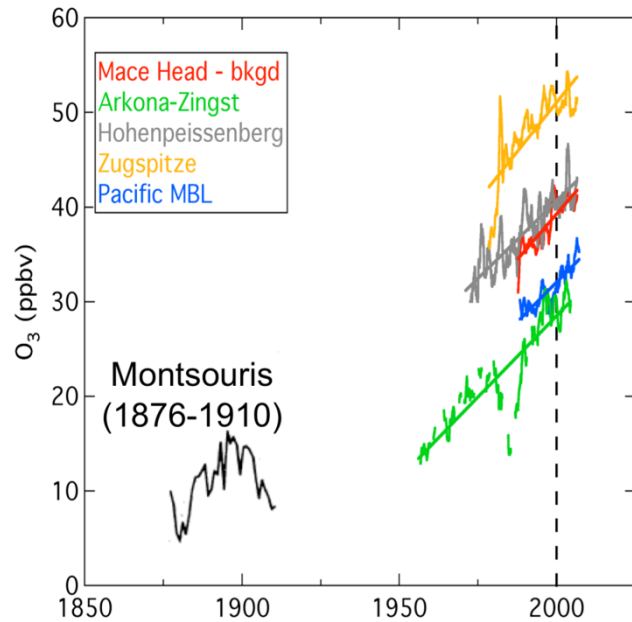
6. Evolution of tropospheric ozone and environmental impacts
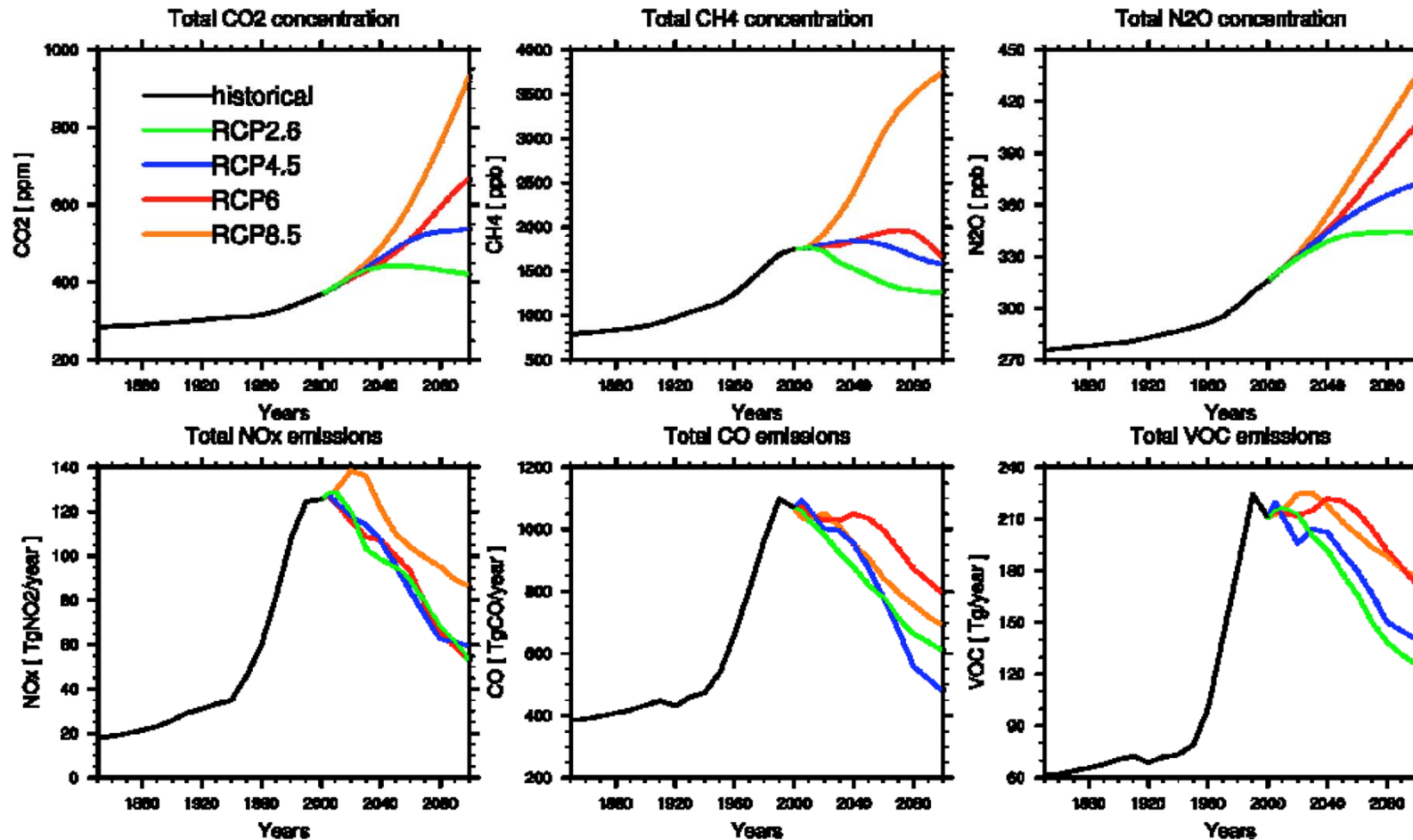
Evolution of future emissions of greenhouse gases and ozone precursors under the four *Representative Concentration Pathway* **(RCP) scenarios from GIEC/AR5.**

6. Evolution of tropospheric ozone and environmental impacts
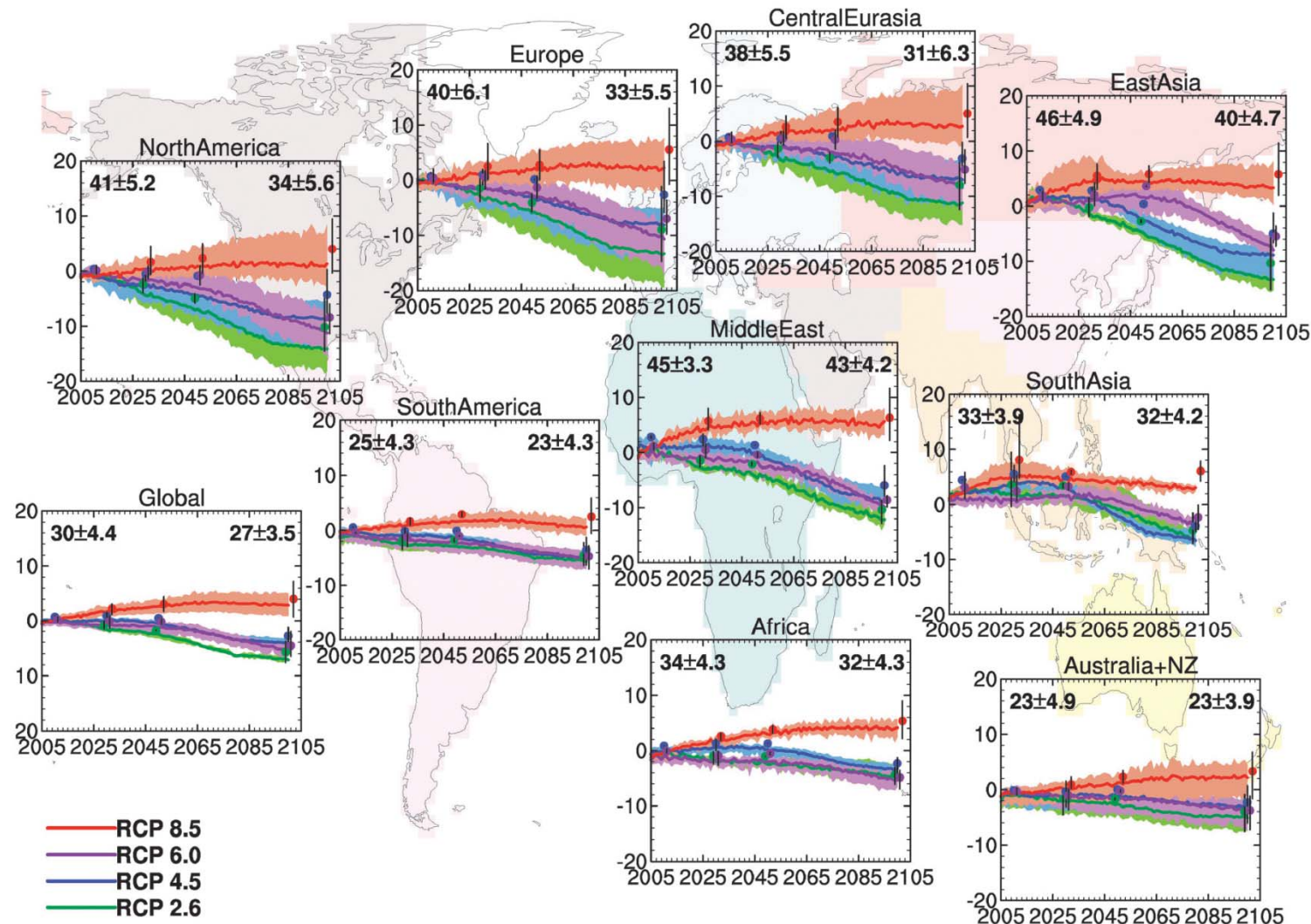
Global and regional future surface ozone levels (ppbv) simulated by the ACCMIP models for the four RCP scenarios.

Fiore et al., 2012

6. Evolution of tropospheric ozone and environmental impacts

A 100-yr time horizon emphasizes the importance of long-lived greenhouse gases (CO_2, N_2O, CH_4) emission reduction as far as long-term climate change is concerned.

In the meantime, a shorter time horizon (20 years) shows the importance of reactive species (ozone precursors) and aerosol emission control for a rapid benefic for climate.

Integrated Radiative Forcing for Year 2000 Global Emissions
(Weighted by 100-yr and 20-yr time horizons)

6. Evolution of tropospheric ozone and environmental impacts

- More than 400 measures for reactive species (ozone precursors) and aerosol emission control have been considered.

- 14 key measures were selected as they improve both air quality and climate change. They involve CH_4 (and hence O_3) and BC.

- Measures acting only on CO_2 emissions cannot prevent the global warming to reach more than 2 degrees during the XXIst century because of the long residence time of carbon dioxide in the atmosphere.

- Action on both CO_2 and on short term climate agents such as CH_4 (and hence O_3) and BC, help to achieve this objective.
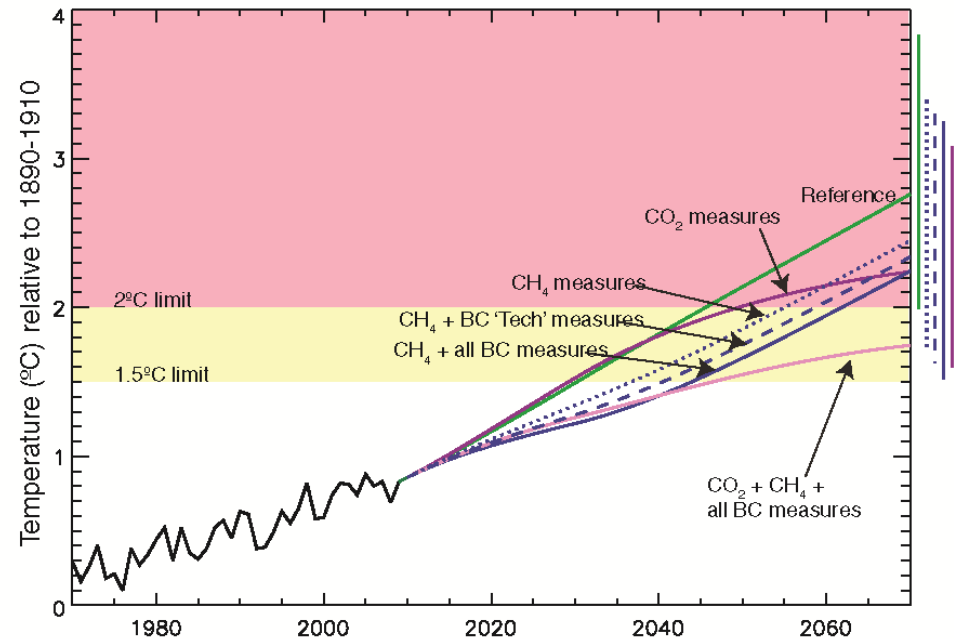
Fig. 1. Observed temperatures (42) through 2009 and projected temperatures thereafter under various scenarios, all relative to the 1890–1910 mean. Results for future scenarios are the central values from analytic equations estimating the response to forcings calculated from composition-climate modeling and literature assessments (7). The rightmost bars give 2070 ranges, including uncertainty in radiative forcing and climate sensitivity. A portion of the uncertainty is systematic, so that overlapping ranges do not mean there is no significant difference (for example, if climate sensitivity is large, it is large regardless of the scenario, so all temperatures would be toward the high end of their ranges; see www.giss.nasa.gov/staff/dshindell/Sci2012).

Shindell et al., 2012

IPCC, 2007

6. Evolution of tropospheric ozone and environmental impacts

Number of prematured deaths per year and per 10^6 people due to ozone and PM pollution.

Ozone, respiratory mortalities

Total: 700.000

PM, cardiopulmonary mortalities

Total: 3.5M

PM, lung cancer mortalities

Total: 220.000

Anenberg et al., 2010

International Agency for Research on Cancer

World Health Organization

PRESS RELEASE N° 213

12 June 2012

IARC: DIESEL ENGINE EXHAUST CARCINOGENIC

Lyon, France, June 12, 2012 – After a week-long meeting of international experts, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), today classified diesel engine exhaust as *carcinogenic to humans (Group 1)*, based on sufficient evidence that exposure is associated with an increased risk for lung cancer.

Background
In 1988, IARC classified diesel exhaust as *probably carcinogenic to humans (Group 2A)*. An Advisory Group which reviews and recommends future priorities for the IARC Monographs Program had recommended diesel exhaust as a high priority for re-evaluation since 1998.

There has been mounting concern about the cancer-causing potential of diesel exhaust, particularly based on findings in epidemiological studies of workers exposed in various settings. This was re-emphasized by the publication in March 2012 of the results of a large US National Cancer Institute/National Institute for Occupational Safety and Health study of occupational exposure to such emissions in underground miners, which showed an increased risk of death from lung cancer in exposed workers (1).

Evaluation
The scientific evidence was reviewed thoroughly by the Working Group and overall it was concluded that there was *sufficient evidence* in humans for the carcinogenicity of diesel exhaust. The Working Group found that diesel exhaust is a cause of lung cancer (*sufficient evidence*) and also noted a positive association (*limited evidence*) with an increased risk of bladder cancer (Group 1).
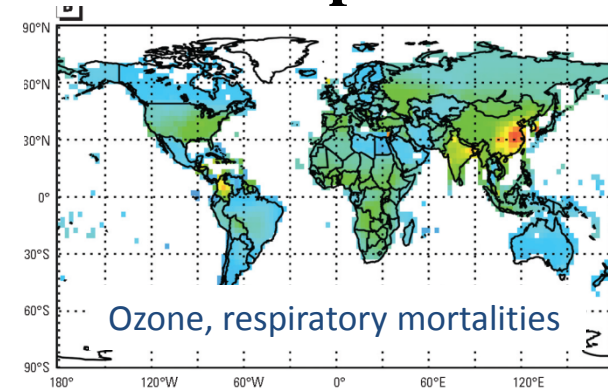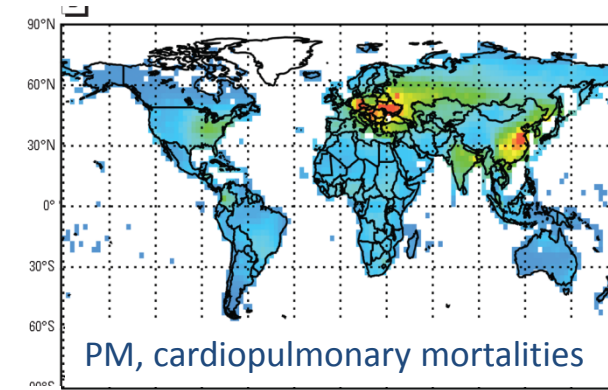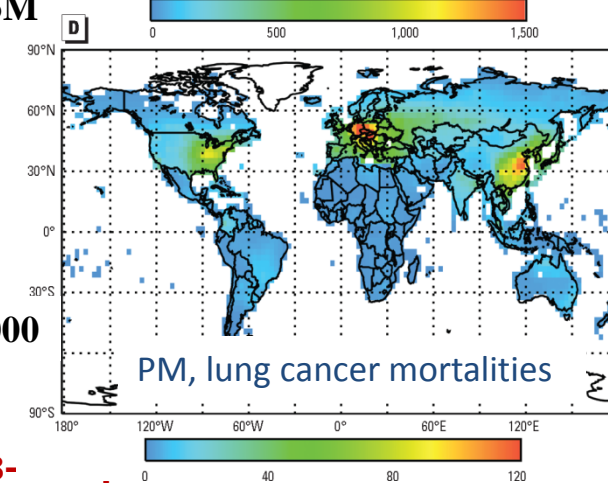
The Working Group concluded that gasoline exhaust was possibly carcinogenic to humans (Group 2B), a finding unchanged from the previous evaluation in 1989.

Public health
Large populations are exposed to diesel exhaust in everyday life, whether through their occupation or through the ambient air. People are exposed not only to motor vehicle exhausts but also to exhausts from other diesel engines, including from other modes of transport (e.g. diesel trains and ships) and from power generators.

Given the Working Group's rigorous, independent assessment of the science, governments and other decision-makers have a valuable evidence-base on which to consider environmental standards for diesel exhaust emissions and to continue to work with the engine and fuel manufacturers towards those goals.

Increasing environmental concerns over the past two decades have resulted in regulatory action in North America, Europe and elsewhere with successively tighter emission standards for both diesel and gasoline engines. There is a strong interplay between standards and technology – standards drive technology and new technology enables more stringent standards. For diesel engines, this required changes in the fuel such as marked decreases in sulfur content, changes in engine design to burn diesel fuel more efficiently and reductions in emissions through exhaust control technology.

However, while the amount of particulates and chemicals are reduced with these changes, it is not yet clear how the quantitative and qualitative changes may translate into altered health effects; research into

# 6. Evolution of tropospheric ozone and environmental impacts

- Annual avoided O_3 cardiopulmonary mortalities per million people resulting from 20% NO_x, NMVOC, and CO emission reductions in the region shown and a 20% global CH_4 mixing ratio reduction.

- Avoided mortalities in northern hemisphere when 20% reduction is applied in the different regions (hundreds). NH: 218; NA: 36; EU: 38; SA: 85; EA: 59.

- Domestic versus NH mortalities (hundreds). NA: 9 vs 36. EU: 17 vs 38; SA: 76 vs 85; EA: 43 vs 59.

- Methane reduction. More uniform reduction in mortality. NH: 160; NA: 11; EU: 39; SA: 48; EA: 38.
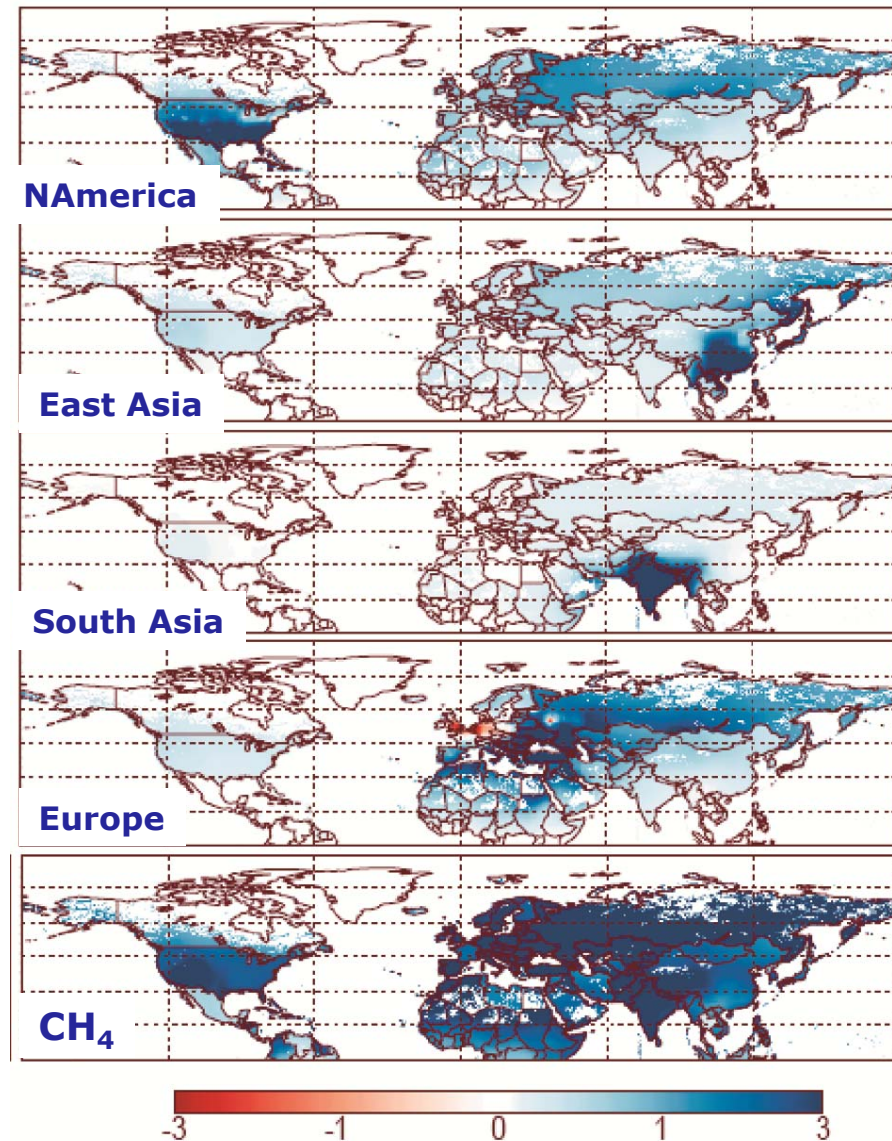
Anenberg et al., 2012

6. Evolution of tropospheric ozone and environmental impacts

Present day ozone impact on four types of crops. Wheat: loss of 45 to 82 Mtons per year (7-12% of production). Rice: 17-23 Mtons (3-4%). Maize: 14-25 Mtons (3-5%). Soybean: 9-30 Mtonss (6-16%). Economic loss estimated globally 14-26 billion $ per year. 40% of the damage in China and India.

Van Dingenen et al., 2009
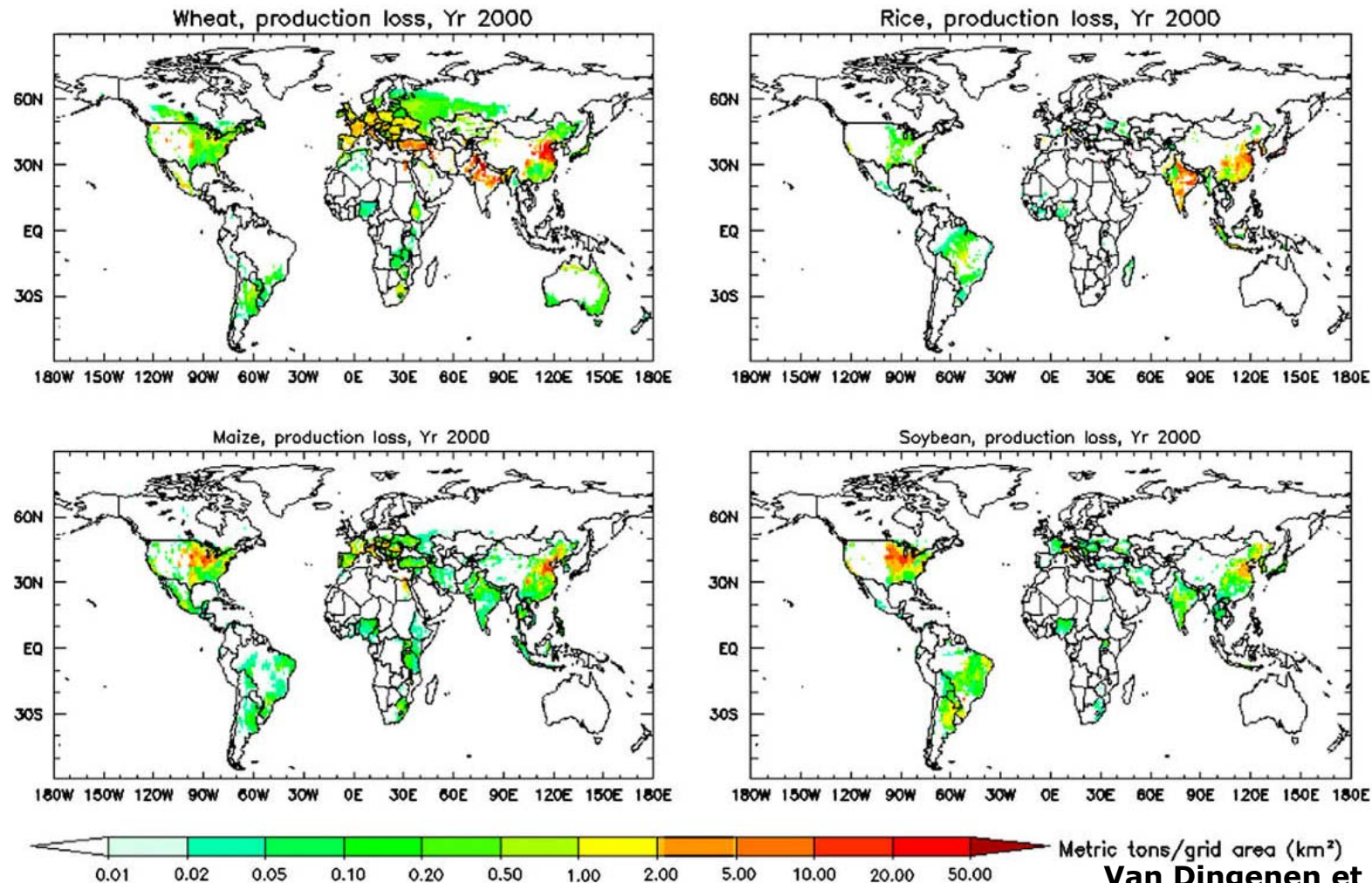
Summary. **Tropospheric ozone O$_3$:**

1. Is photochemically produced in the troposphere by the oxidation of methane CH$_4$, non-methane hydrocarbons NMHC, and carbon monoxide CO in the presence of nitrogen oxides NO$_x$.

2. Is a greenhouse gas contributing for about 0.35 W/m^2 to the present-day anthropogenic radiative forcing of climate.

3. Controls the oxidizing capacity of the atmosphere (OH) and hence affects the radiative forcing of other long-lived greenhouse gases such as CH$_4$ or aerosols such as sulfates.

4. Causes deleterious impacts to human health, including cardiovascular and respiratory mortality.

5. Can damage crops, leading yield reduction and deteriorating crop quality.

6. Can damage other land ecosystems and hence affect the capacity of plants to take up carbon dioxide from the atmosphere.