The hydrogen economy and adverse environmental effects

Frank Markert
Systems Analysis Department
Risø National Laboratory
Technical University of Denmark

2nd European Summer School on Hydrogen Safety
Belfast, 30.7 – 8.8.2007

Introduction

The lecture is dealing with the environmental aspects associated with global emissions of hydrogen:

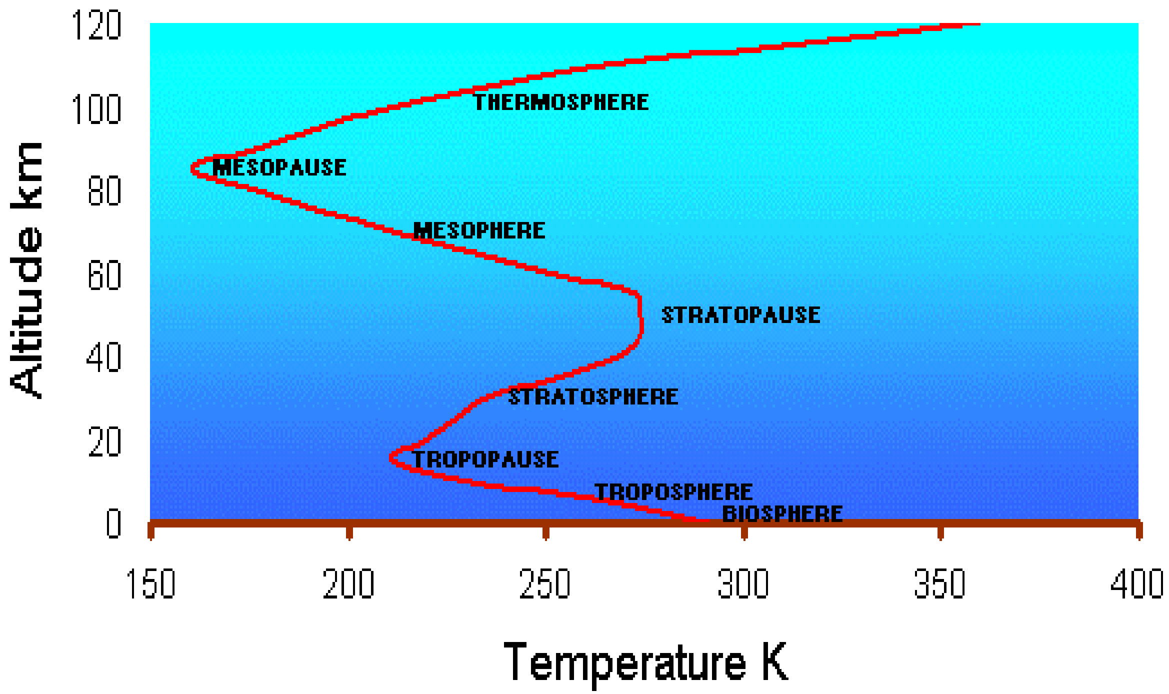
Natural and technical emission sources
Fate of atmospheric hydrogen - degradation mechanisms
Scenarios for future usage of hydrogen.
Presently knowledge on the potential adverse environmental effects

Outline of lecture

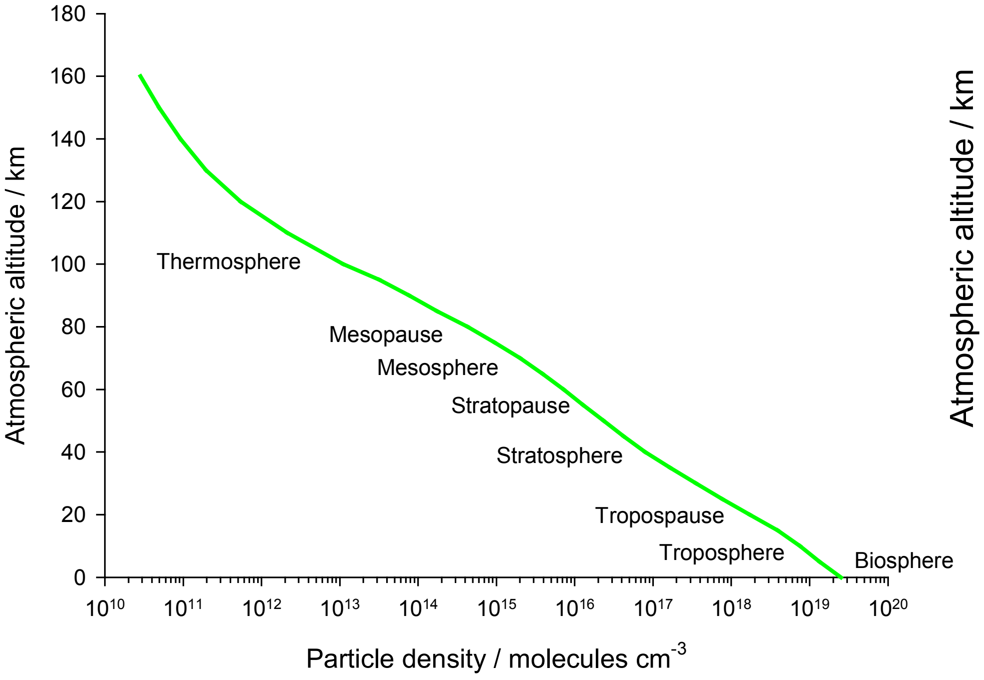
- Introduction
- Hydrogen in the environment
  - Measurements and concentrations
  - Sources for hydrogen emissions
  - Fate of hydrogen: deposition ; atmospheric chemistry
  - Literature review on the present findings on possible adverse effects
- Production of Hydrogen
- Application of hydrogen technologies

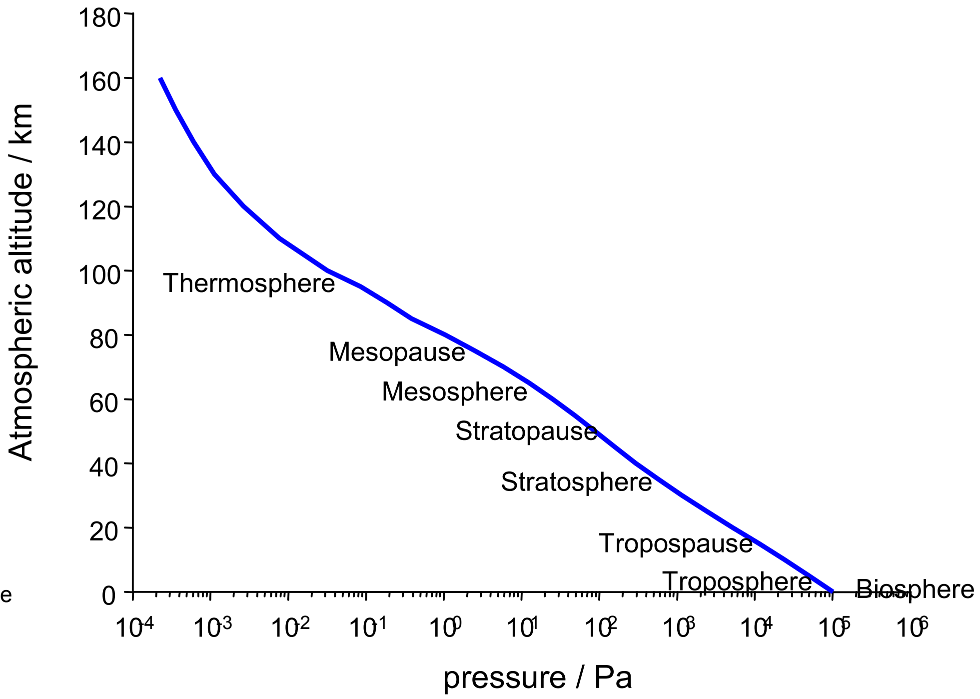
Structure of the atmosphere given by the typical temperature profile

- Troposphere - unstable temperature profile.
- Tropospause is a sink for water vapour.
- Stratosphere - region of ozone shield
- Mesosphere.
- Thermosphere
- Exosphere (not indicated) is the boundary to space.



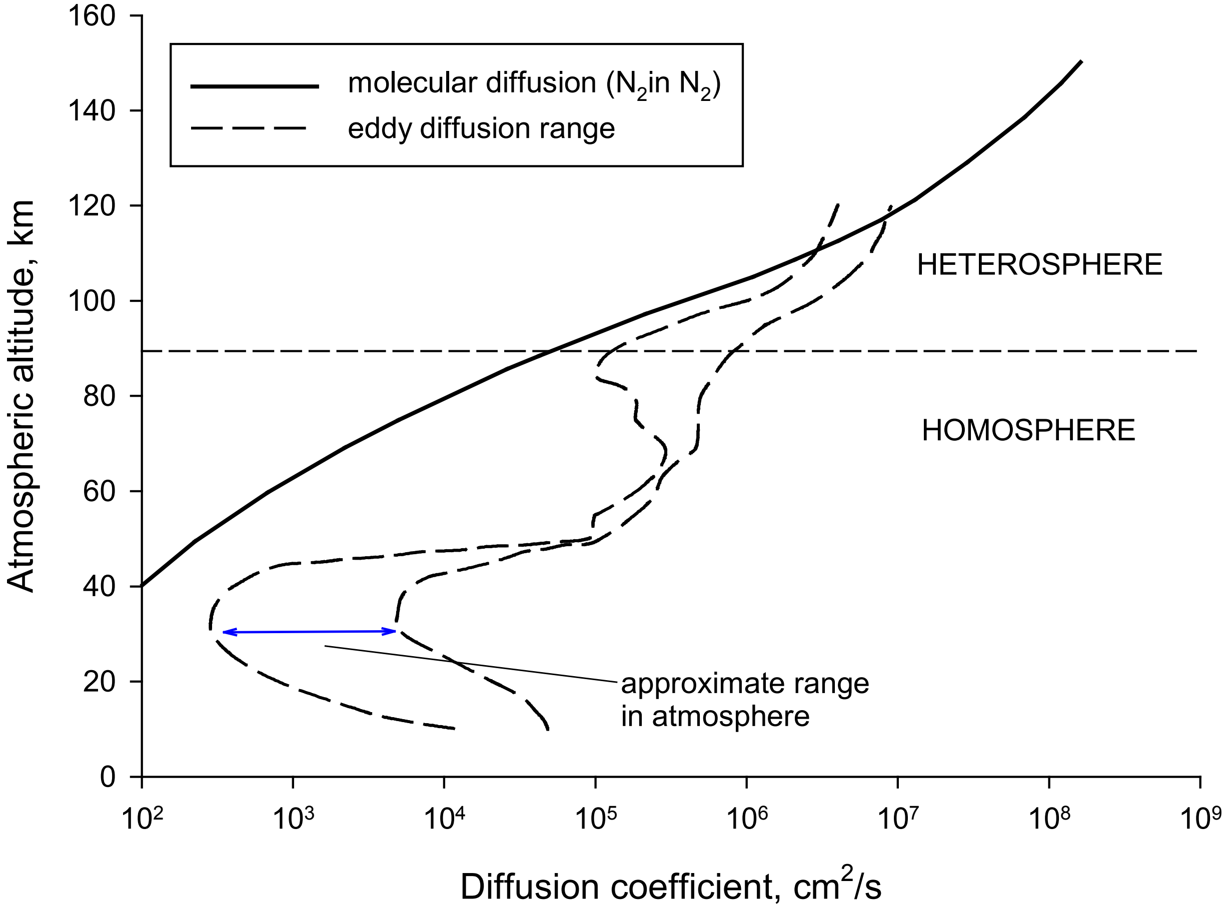
PRESSURE AND DENSITY PROFILES





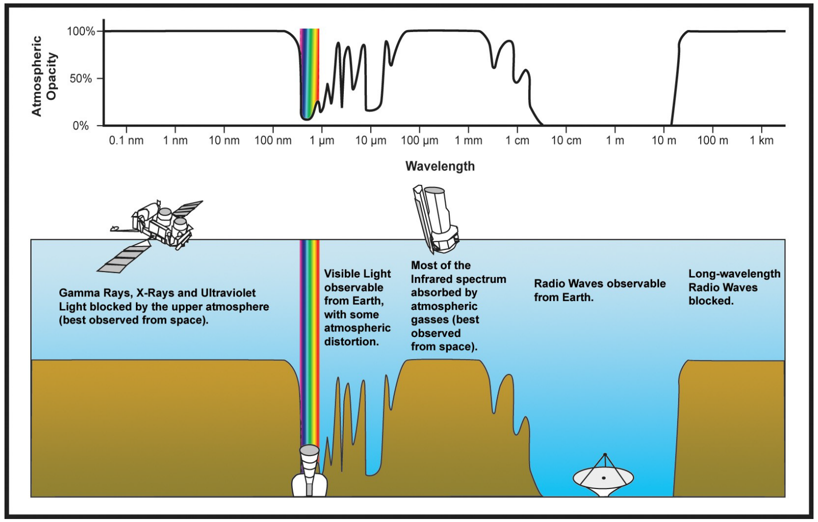
ATMOSPHERIC DIFFUSION

Calculated molecular and turbulent diffusion coefficients
the eddy diffusion in the dominating process in troposphere

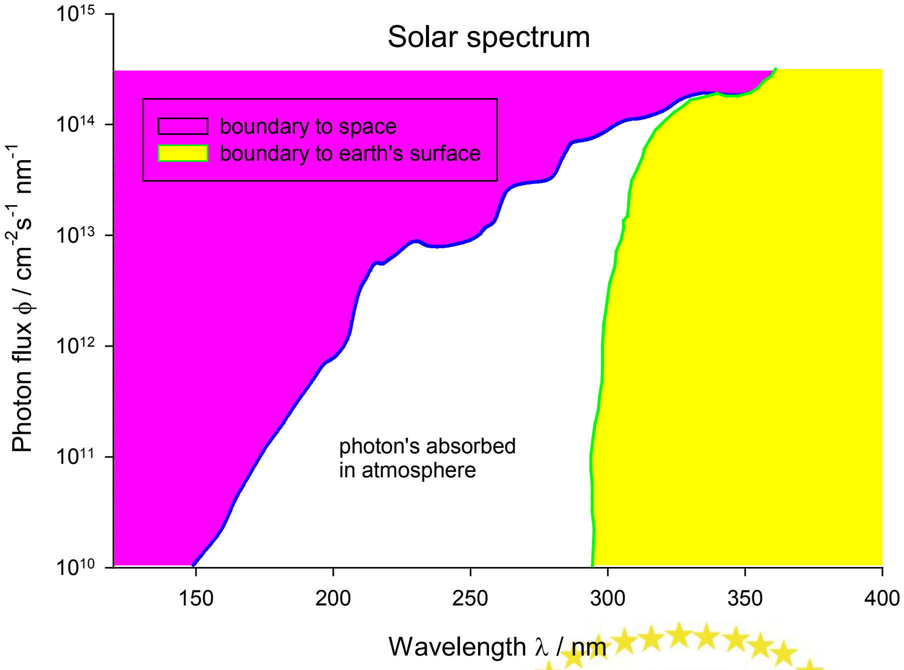


Radiation from the SUN

spectrum of electromagnetic radiation and absorption characteristics

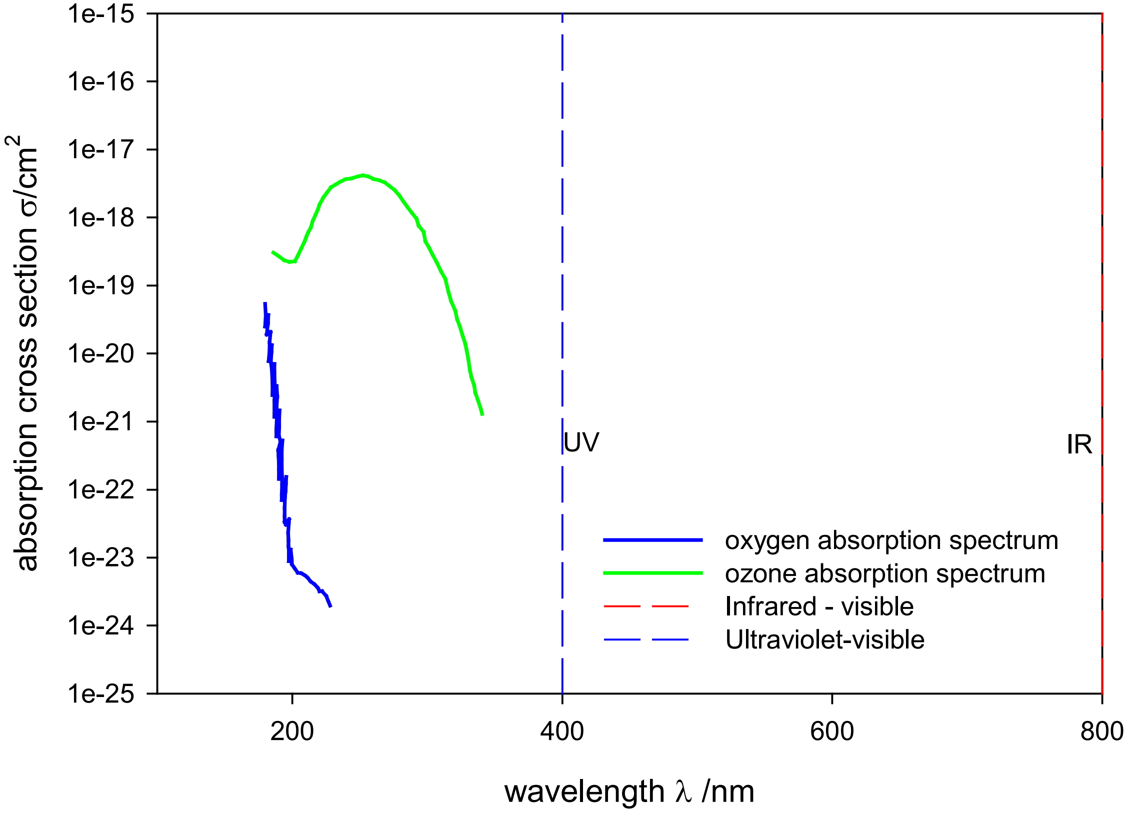


UV absorption in the atmosphere



Absorption of oxygen and ozone

The difference in the sun spectrum shown before is partly due to oxygen and ozone absorption in Meso- and stratosphere



PHOTON ENERGIES

Wavelength /nm	Photon energy /kJ mol^{-1}
1000	119.7
800	149.6
600	199.5
400	299.3
300	399.0
200	598.5
100	1197.1
10	11970.5
1	119705.3
0.1	1197053.2

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

E_{photon} – energy of a photon, J ;

h - Planck’s constant, $6.626 \cdot 10^{-34}$ J·s;
ν - radiations frequency, s^{-1};
c - speed of light, $3 \cdot 10^{8}$ m/s;
λ - wavelength, m

The table shows the relation between a photon’s energy and the wavelength.

The photon energy is absorbed by molecules and initiates photo chemical reactions.

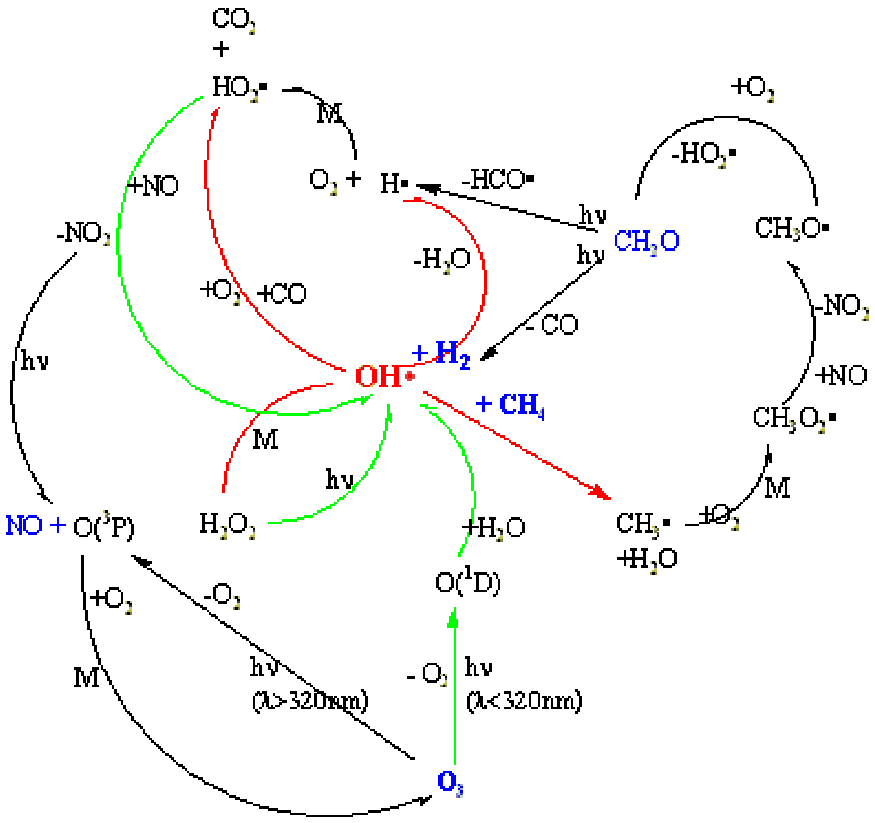
For atmospheric relevant photo chemical reactions UV radiation is needed.

COMPOSITION OF ATMOSPHERE

Gas	Concentration ppm
Nitrogen, N2	780840
Oxygen, O2	209460
Argon, Ar	9340
Carbon dioxide, CO2	325
Sum of nobel gases (He, Ne, Kr, Xe)	24.647
Methane, CH4	1.4
Hydrogen, H2	0.5
Nitrous oxide, N2O	0.25
Carbon monoxide, CO	0.08
Ozone, O3	0.025
Nitroxides, here NO+NO2	0.006

PHOTO CHEMICAL REACTIONS

The reaction schemes show some examples for source and sink mechanisms for the hydroxyl free radical.



1. The basic atmospheric degradation of pollutants is normally initiated by the hydroxyl free radicals (OH·).
2. The mean OH concentration is about 10^6 molecules/cm^3 air.
3. This determines mainly the “oxidizing capacity” of the atmosphere

REACTIONS OF THE OH FREE RADICAL

Initiating reactions for carbon monoxide and methane

$$CO + OH\cdot \xrightarrow{O_2} HO_2\cdot + CO_2$$

$$CH_4 + OH\cdot \longrightarrow CH_3\cdot + H_2O$$

General initiating reaction

$$RH + OH\cdot \longrightarrow R\cdot + H_2O$$

Chain reaction steps with oxygen nitrogen monoxid

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$NO + RO_2\cdot \longrightarrow RO\cdot + NO_2$$

Photochemical reaction steps generating ozone and singlet oxygen atoms

$$NO_2 \xrightarrow{h\nu} NO + O(^3P)$$

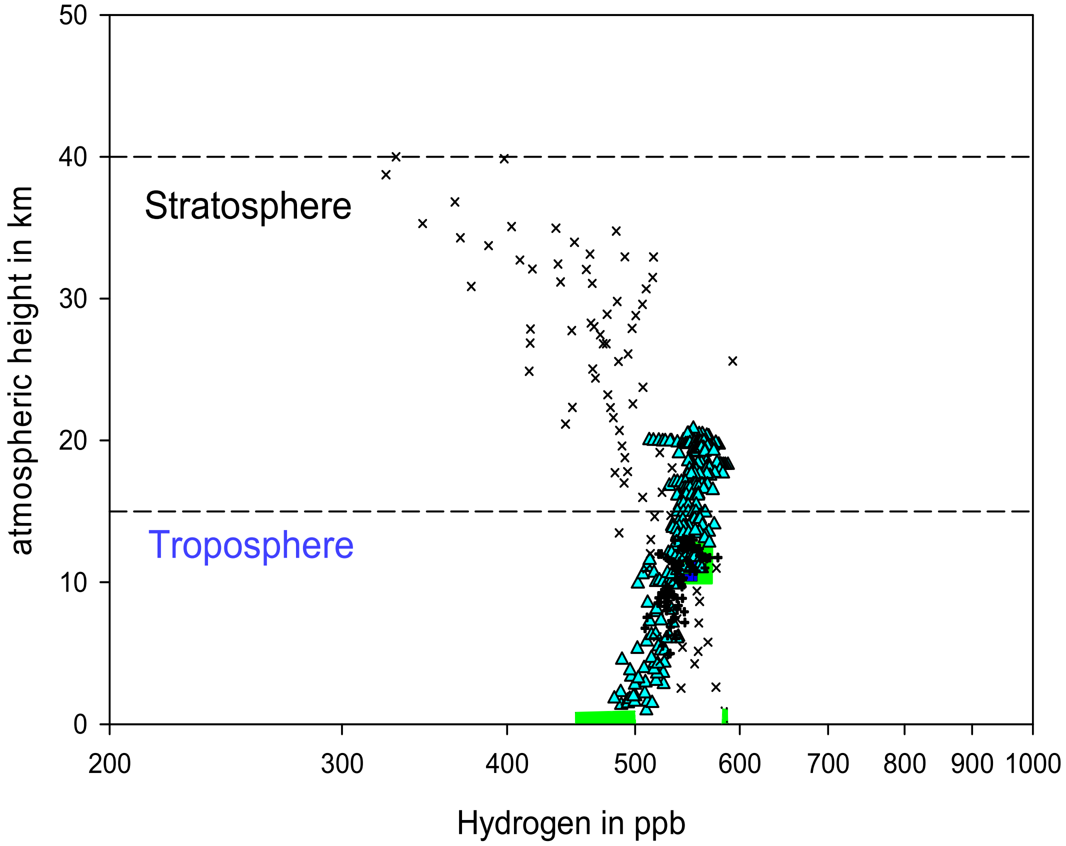
$$O(^3P) + O_2 \xrightarrow{M} O_3$$

$$O_3 \xrightarrow{h\nu} O_2 + O(^1S)$$

Regenerating OH free radicals

$$O(^1S) + H_2O \rightarrow 2OH\cdot$$

HYDROGEN CONCENTRATIONS



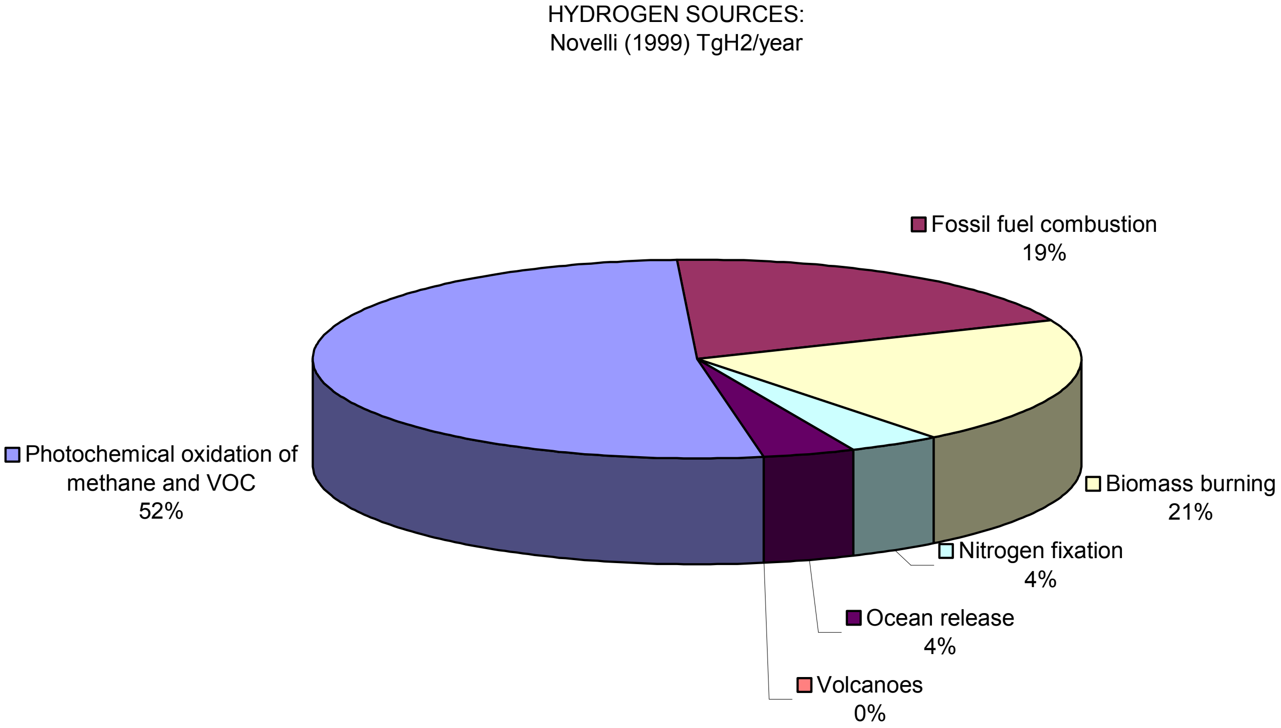
- concentration is about 0.5 ppm
- southern hemisphere has a higher hydrogen mixing ratio than northern hemisphere
- Remote, tropospheric hydrogen range from 0.45 to 0.55 ppm
- variation with the seasonal cycles by about 0.050 ppm.
- moderate polluted rural sites 0.8 ppm may be observed.
- Close to combustion sources higher.
- In a tunnel near Zürich concentrations up to 6 ppm.
- latter measurements correlate carbon monoxide concentration with a slope of 0.54 ppm H2 / ppm CO

SOURCES FOR HYDROGEN

SOURCES:						
TgH2/year	**Sanderson (2003)**	**Hauglustaine (2002)**	**Novelli (1999) ±σ**	**Ehhalt (1999) ±σ**	**Warneck (1988)**	**Seiler (1987) ±σ**
Photochem. oxidation of methane and VOC	30.2	31	40 ±16	35 ±15	50	40 ±15
Fossil fuel combustion	20	16	15 ±10	15 ±10	17	20 ±10
Biomass burning	20	13	16 ±11	16 ±5	15	20 ±10
Nitrogen fixation	4	5	3 ±1	3 ±2	3	3 ±2
Ocean release	4	5	3 ±2	3 ±2	4	4 ±2
Volcanoes	-	-	-	-	0.2	-
Total sources	**78.2**	**70**	**77 ±16**	**72 ±20**	**89.2**	**87**

$Tg = 10^6$ ton (megaton)$=10^{12}g$

SOURCES IN PERCENT

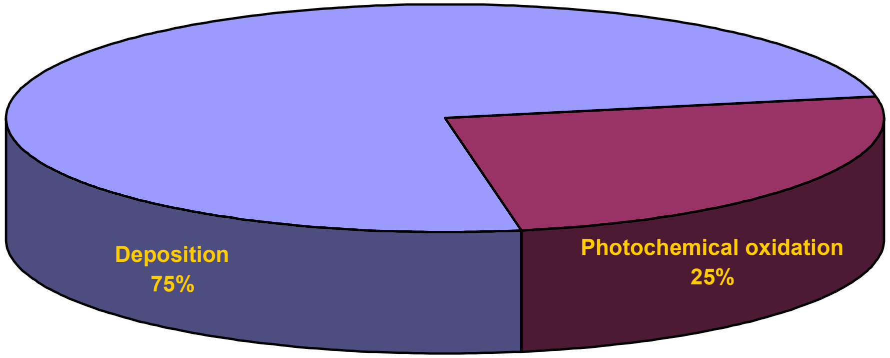


SINKS FOR HYDROGEN

SINKS						
TgH2/year	**Sanderson (2003)**	**Hauglastine (2002)**	**Novelli (1999) ±σ**	**Ehhalt (1999) ±σ**	**Warneck (1988)**	**Seiler (1987) ±σ**
Deposition	58.3	55	56 ±41	40 ±30	78	90 ±20
Photochemical oxidation	17.1	15	19 ±5	25 ±5	11	8 ±3
Total sinks	**75.4**	**70**	**75 ±41**	**65 ±30**	**89**	**98 ±23**

SINKS IN PERCENT

HYDROGEN SINKS
Novelli (1999) TgH2/year



ATMOSPHERIC FATE

The atmospheric photochemical degradation of hydrogen is initiated by the hydroxyl free radical.

The rate determining step for the whole sequence of reactions following.

initiation $H_2 + OH\cdot \rightarrow H\cdot + H_2O$

chain $H\cdot + O_2 \xrightarrow{M} HO_2\cdot \xrightarrow{\text{further reactions}}$

Hydrogen follows the general atmospheric reaction mechanisms as explained in detail before. The final product is water.
The overall reaction steps can be summarized by:

sum reaction: $2H_2 + O_2 \rightarrow 2H_2O$

BIOLOGICAL PROCESSES

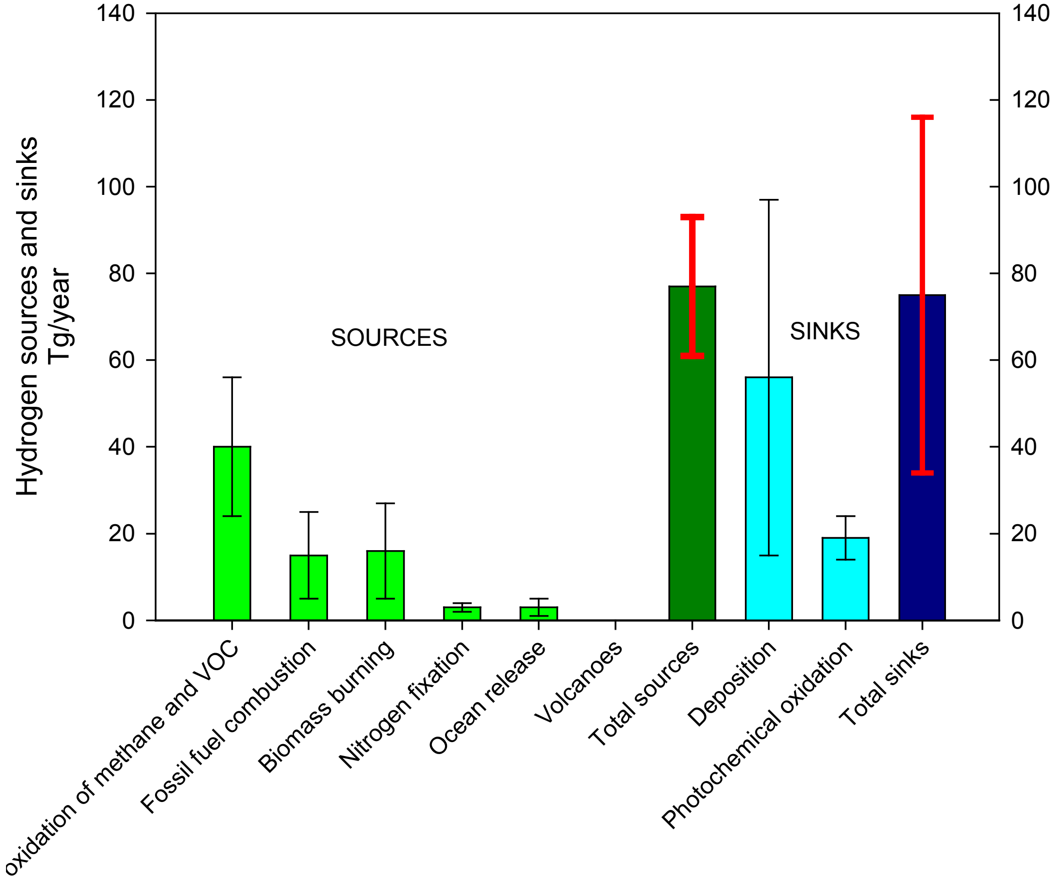
The exact biological mechanisms are still unknown, but the following processes seem to be important:

- methanogeneses
- respiratory processes of anaerobic bacteria
- oxidation by ’Knallgas’ bacteria
- oxidation by free hydrogenase enzymes in soils

It has been hypothesized that the free hydrogenase enzymes are more important than the soil micro-organisms, as e.g. the Knallgas bacteria only oxidize hydrogen at elevated mixing ratios above the normal atmospheric concentrations.

The overall consumption is larger than production

SOURCE AND SINKS UNCERTAINTY



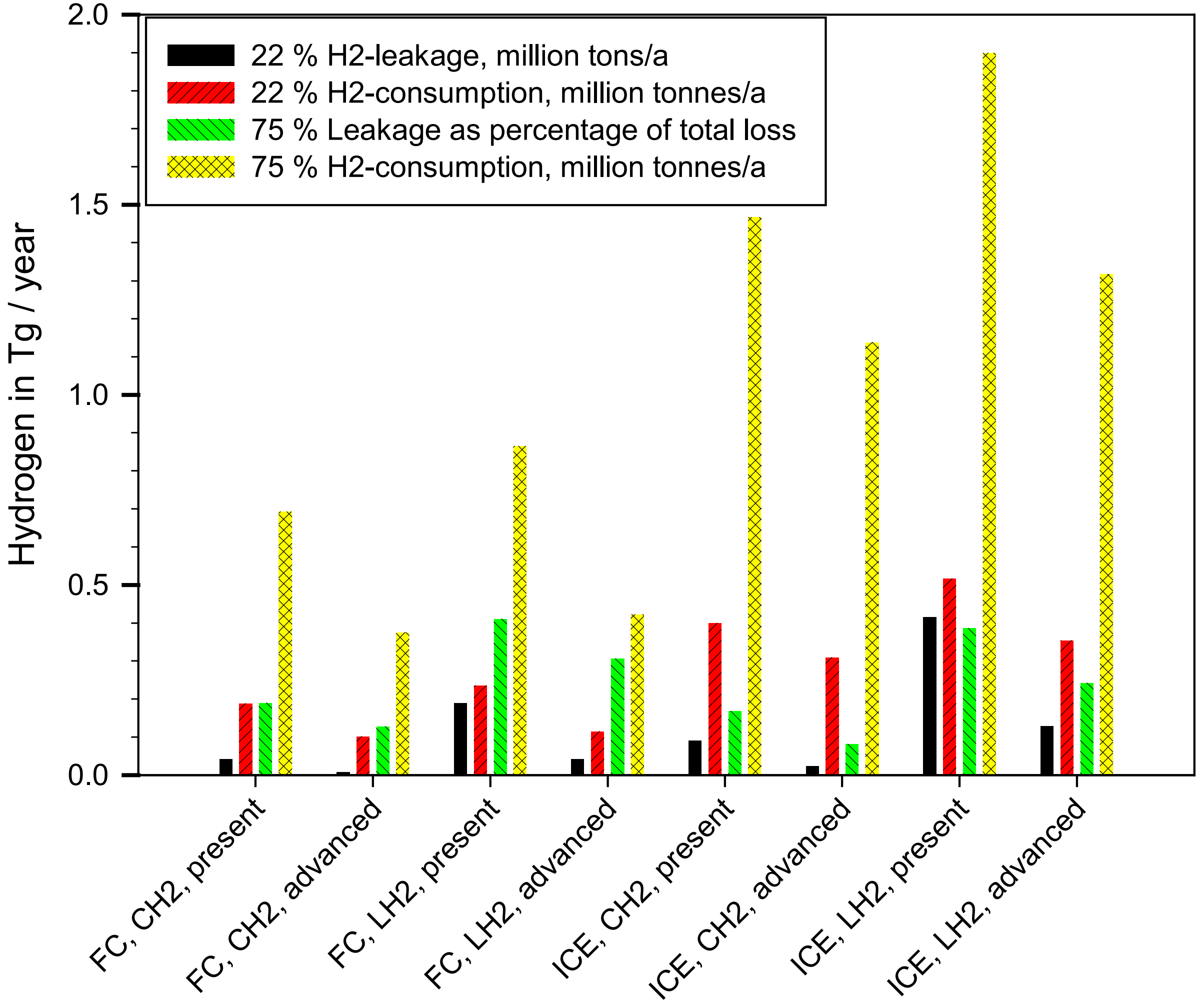
Future emissions of hydrogen

Two scenarios for hydrogen in the transport sector (well to wheal approach).

Assumptions:

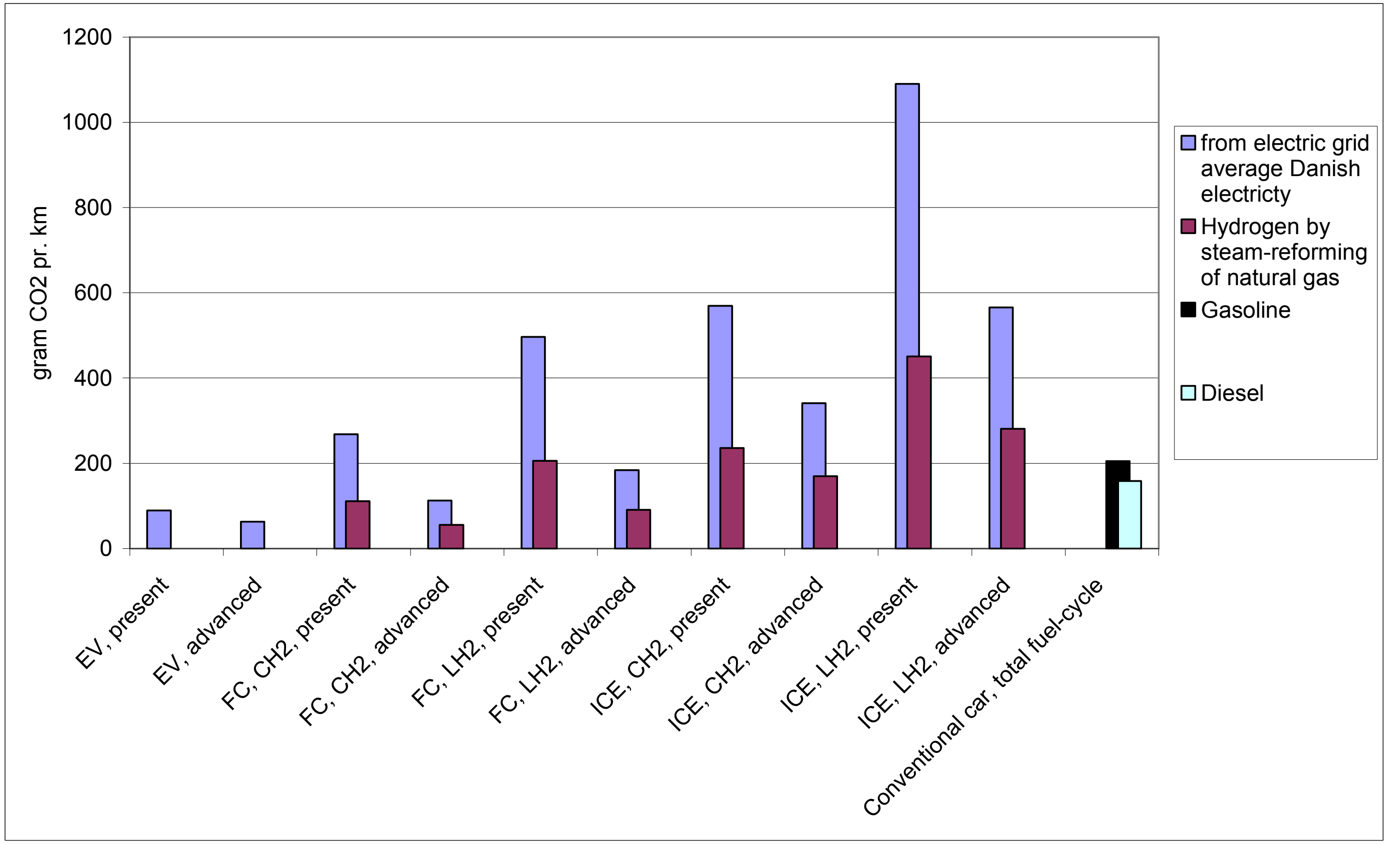
2030 - 22% and in 2050 - 75% of the traffic energy consumption based on hydrogen and 2 technologies:

present / advanced .



FC – fuel cell
ICE – internal combustion engine
CH2- compressed hydrogen
LH2 – liquid hydrogen

CARBON DIOXIDE EMISSIONS IN FUTURE



Scenario 2030 -22% and in
scenario 2050 -75% based on hydrogen

HYPOTHESES on potential impacts from a global hydrogen economy

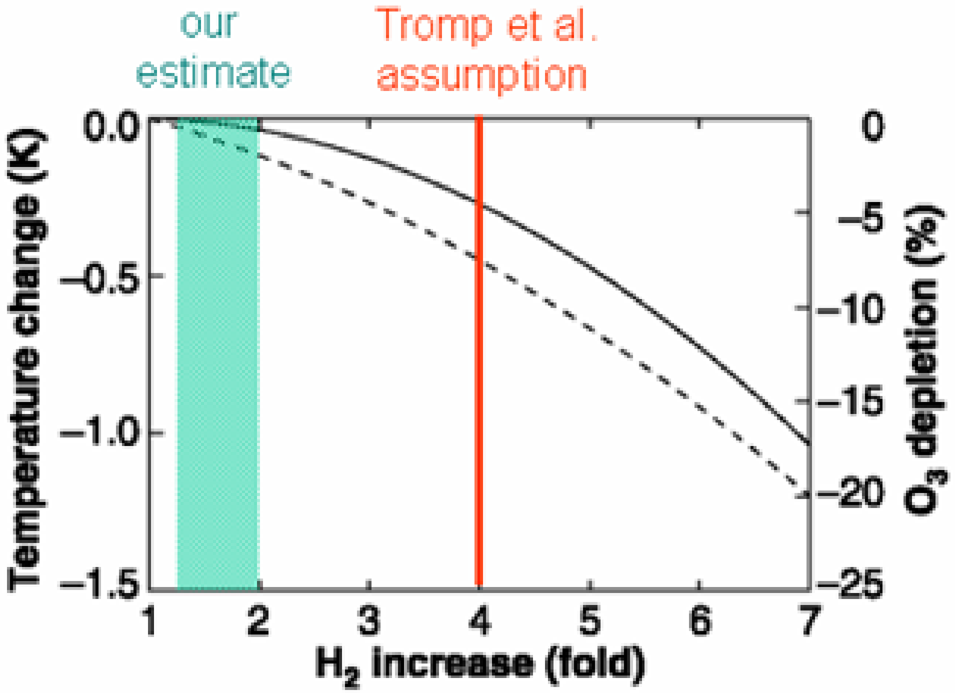
1. Increased hydrogen release would lower the atmosphere oxidizing capacity and so increase the lifetime of air pollutants and greenhouse gases
2. Increased hydrogen release would lead to increased water vapour concentrations in the atmosphere, with potential consequences for cloud formation, stratospheric temperatures and stratospheric ozone loss.
3. Increased hydrogen release could exceed the uptake capacity of hydrogen by micro-organisms in the soil.
4. If hydrogen were to be generated using electricity derived from burning coal, NOx emissions could increase significantly. This would have serious effects on air pollution and the global tropospheric ozone budget.
5. Generating hydrogen from fossil fuels could lead to increased emissions of carbon dioxide, which would accelerate global warming, unless the CO_2 is captured and stored.
6. Generating hydrogen from sustainable sources would reduce emissions of CO, CO_2 and NOx, with a consequent fall in tropospheric ozone levels. This would improve air quality in many regions of the world.

KNOWLEDGE ON POTENTIAL EFFECTS

Although hydrogen acts as an indirect greenhouse gas (by lengthening the lifetime of methane),

- its impact is small compared to other factors perturbing the global oxidizing capacity: H constitutes only about 5% of the average OH sink, and OH reacts much stronger to changes in reactive nitrogen emissions compared to changes in H emissions
- The amount of water vapour produced from increased hydrogen release and hydrogen combustion is negligible compared to the natural evaporation of water vapour. (exception would be cryoplanes), which could lead to additional cirrus formation (and therefore cooling of the upper troposphere).
- Changes in the stratospheric water vapour concentration due to increased hydrogen emissions would be less than the observed changes during past decades.
- The implications of these changes for the cooling of the lower stratosphere and the potential reduction of stratospheric ozone levels are still unclear, but not all like CFC problems.

TEMPERATUR CHANGE AND OZONE DEPLETION



Relative temperature changes in the lower stratosphere at 74°N (solid line) and the resulting maximum ozone depletion in the northern polar vortex (dashed line) as a function of increased atmospheric hydrogen concentrations relative to the today's actual hydrogen concentration of about 0.5 ppmv. The cause of the temperature change is the stratospheric water vapour resulting from the oxidation of hydrogen.

PRECAUTIONARY PRINCIPLE ON HYDROGEN

- Hydrogen should not be produced using electricity generated by burning fossil fuels. Instead, natural gas or coal reformers should be used at first, and replaced by renewable energy sources as soon as possible. CO2 capture from reformers should be seriously considered.
- Hydrogen should be used predominantly on the ground rather than in aircraft, and to achieve full benefits, fuel cells would be preferable against internal combustion engines.
- Leakage in the hydrogen energy chain should be limited to 1% wherever feasible, and global average leakage should not exceed 3%.
- Atmospheric hydrogen concentrations should be carefully monitored. Enough research should be carried out to obtain a better understanding of hydrogen sources and sinks, and to provide an early warning system in case we have overlooked something.

CONCLUSION

- At the moment a precaution may be to reduce the emissions as much as possible, which is of environmental but also of safety concerns, as hydrogen fires and gas phase explosions are very prominent concerns for hydrogen applications. There may also be some economic benefits as production, distribution and storage of hydrogen needs substantial amounts of energy and the hydrogen is rather costly, but more detailed analyses are needed here. Therefore, it would be a win-win situation to minimize leakages.

THANK YOU FOR YOUR ATTENTION