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HYDROGEN – ENVIRONMENTAL AND SAFETY ASPECTS

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Abstract

On the face of it hydrogen seems to have low impact on the environment, but there are a number of uncertainties concerning the consequences of a large-scale shift towards a hydrogen economy.
Likewise hydrogen is probably no more hazardous than conventional fuels, but because of the many properties that make hydrogen distinct from conventional fuels, it is necessary to deal with the risk assessments for all the elements in the use and supply chain of hydrogen.

1. INTRODUCTION

Hydrogen (H_2) is widely regarded as a key component in future energy systems because it is a sustainable, clean, and transportable energy carrier. It can be generated from pure water, and burned to produce nothing but water. Thus if hydrogen generated using clean andsustainable processes replaces fossil fuels as our main energy carrier, we will have significantly lower emissions of greenhouse gases, especially carbon dioxide (CO2), and air pollutants, notably nitrogen oxides and volatile organic compounds.
This view is somewhat idealistic, however, as the technology for the clean and sustainable production of hydrogen is still in the pioneering phase. A great deal of effort will have to be made to build up sufficient hydrogen production capacity from sustainable energy sources such as wind power and solar cells. The production and distribution of hydrogen inevitably involves energy losses. If the energy source is a fossil fuel, the energy losses and pollution involved in producing and distributing hydrogen may turn out to be greater than those from direct use of the fuel via conventional technology. When considering the use of hydrogen in any application, it is therefore important to check the overall environmental balance and to compare this with alternatives such as the direct use of electricity from windmills or solar cells.

The use of hydrogen as such is regarded as sustainable and would improve air quality in urban areas. Nevertheless, it is important to assess the overall impact of hydrogen on the environment. The environment is a complex, highly coupled, non-linear system which may react in unforeseen ways to changes in the status quo. Emissions of man-made compounds including CFCs, which destroy ozone and act as greenhouse gases, other halogenated compounds and of course carbon dioxide have already caused environmental problems. We do not want to repeat the same mistakes with hydrogen.
This chapter gives an overview, based on the scientific literature, of current knowledge of the consequences of hydrogen in the soil and in the atmosphere.

2. Sources, sinks and concentrations of atmospheric hydrogen

The (incomplete) combustion of fossil fuel and biomass in boilers and internal combustion engines generates hydrogen along with carbon monoxide and carbon dioxide. At present, this source accounts for about 40% of all the hydrogen released into the atmosphere. Another important source, accounting for an estimated 50% of atmospheric hydrogen emissions, is the atmospheric photochemical oxidation of methane (CH4) and non-methane hydrocarbons (NMHCs). Emissions from volcanoes, oceans and nitrogen-fixing legumes account for the remaining 10%. These estimates are still very uncertain.

Movement of hydrogen into the upper atmosphere and then to space is negligible in terms of the global hydrogen budget. Instead, hydrogen is removed from the atmosphere largely through dry deposition at the surface and subsequent microbiological uptake in soils. The rate of uptake depends on microbial activity, soil texture and moisture content. This sink is largest in the northern hemisphere because of its larger landmass, and it is thought to account for about 75% of all hydrogen removal.

The remaining 25% of hydrogen is removed through oxidation by hydroxyl free radicals (OH) in the atmosphere:

$$\text{(R1)} \qquad H_2 + OH \rightarrow H + H_2O$$

$$\text{(R2)} \qquad H + O_2 + M \rightarrow HO_2 + M$$

The hydrogen peroxy radical (HO_2) produced in reaction (R2) continues to react with nitrogen oxide (NO), a key step in photochemical ozone formation (see R6 below), or it reacts with itself or other peroxy radicals, thereby terminating the photochemical oxidation chain.

Hydroxyl radicals are also the main initiating reactant in the atmospheric degradation of volatile organic compounds (VOCs), greenhouse gases such as methane (CH_4), and carbon monoxide:

$$\text{(R3)} \qquad CO + OH + O_2 \rightarrow HO_2 + CO_2$$

Hydroxyl radicals are produced mainly through the photolysis of an ozone molecule (O_3) to produce an oxygen molecule (O_2) and an electronically excited "singlet" oxygen atom (O), which then reacts with a molecule of water vapour (H_2O) to produce two hydroxyl radicals:

$$\text{(R4)} \qquad O_3 + hv \rightarrow O_2 + O$$

$$\text{(R5)} \qquad O + H_2O \rightarrow 2\ OH$$

Ozone is produced mainly by the photolysis of nitrogen dioxide to yield low-energy triplet oxygen atoms ($O(^3P)$), which then react with oxygen to produce ozone:

$$\text{(R6)} \qquad NO + HO_2 \rightarrow OH + NO_2$$
$$\text{(R7)} \qquad NO_2 + hv \rightarrow NO + O(^3P)$$

$$\text{(R8)} \qquad O(^3P) + O_2 + M \rightarrow O_3 + M$$

“hv” denotes a photon of ultraviolet light. Ozone in the troposphere is also an important component of summer smog.

These atmospheric reactions, which are closely linked, are important because they determine the capacity of the atmosphere to neutralise pollutants. The concentration of hydroxyl radicals is particularly important, since it is these radicals that begin the whole oxidative degradation process, and the reactions involved (R1 and R3) are the slowest in the whole sequence. More hydrogen in the atmosphere will tend to lower the concentration of hydroxyl radicals and so inhibit the capacity of the atmosphere to oxidise greenhouse gases and other pollutants.

On the other hand, in a hydrogen economy, emissions of other compounds (e.g. CO, NMHC, and NOx), which affect the hydroxyl radical concentration more effectively, will be reduced. The resulting effect is discussed in more detail below (section on oxidizing capacity).

Measurements from ground stations, balloons and research aircrafts typically find about 0.5 ppmv (parts per million by volume) of hydrogen in the troposphere (the part of the atmosphere extending from the earth's surface up to about 10 km), and 0.4-0.5 ppmv in the stratosphere (10-60 km altitude). No significant trend can be deduced from observations made after 1990, although earlier observations did indicate a positive trend.

3. Estimates of future emissions

The future environmental consequences of a large-scale hydrogen economy will depend on how much hydrogen we use, how it is produced, how fast our use increases, the amount of fossil fuel emissions that can be saved, and the steps we take to control hydrogen emissions. The present atmospheric hydrogen concentration of 0.5 ppmv implies a total mass of about 175 million tonnes of hydrogen, of which around 20% is thought to be from the combustion of fossil fuels. There has been considerable recent controversy in the scientific literature over how much hydrogen a globalscale hydrogen economy would release into the atmosphere.

Estimates range from less than 0.1% of hydrogen consumption, for tightly-controlled industrial applications, to 10-20% for evaporation from liquid hydrogen tanks in poorly-designed automobiles. 3% would be a more realistic upper limit, however, simply because higher leakage rates would be neither economic nor safe. Assuming the complete replacement of today's energy system with a hydrogen chain, about 1400-1800 million tons H_2/year would be required. Correcting for the present emissions of 42-54 million tons H_2/year and

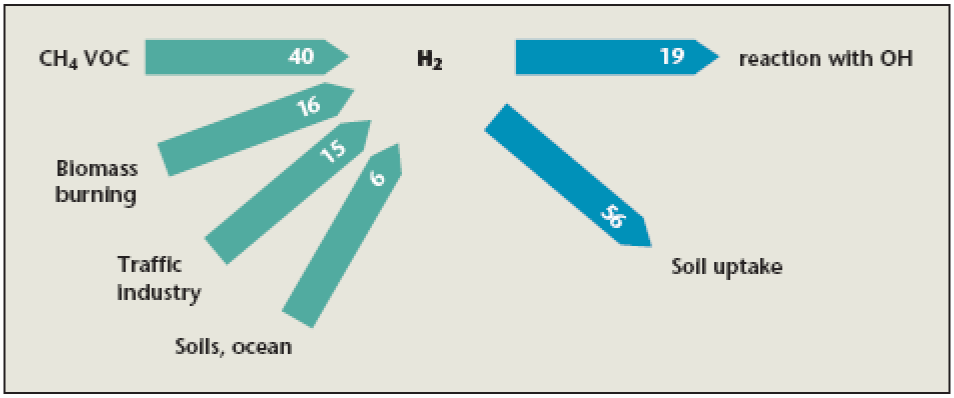

Figure 1.1. Sources and sinks for hydrogen in the atmosphere (million tonnes/year). The numbers are uncertain, especially for traffic and industry emissions (±10 million tonnes/year) and soil deposition (±15 million tonnes/year).

assuming a 3% loss of 42-54 million tons H_2/year the H_2 emissions would increase by 17-49 million tons H_2/year (or 22%-64%), it is worthwhile to note that lower leak rates than 3% could even lead to a net reduction of hydrogen emissions. Of course, a simple 1:1 replacement scenario of the present-day energy demand is overly simplistic, and considerable future efforts are needed to develop more reliable emission scenarios for hydrogen applications.
Our view is that these hydrogen emissions are probably much less important than the overall atmospheric emissions of CO_2, CO, and NO_x from reformers and other hydrogen plants, and emissions of these gases will be reduced as conventional technologies are replaced by their hydrogen equivalents. Of particular interest here are emissions of carbon dioxide and NOx. Carbon dioxide is important because it is the biggest contributor to climate change. NOx levels drive the oxidizing capacity of the atmosphere (essentially the OH concentration), and so regulate the lifetime of the greenhouse gas methane, and they control the amount of photochemical ozone formed in the troposphere. Table 1 lists current estimates of NOx sources.

NO_x source	Estimated budget (million tonnes N/year)
Fossil fuel combustion	30-36
Aircraft	0.5-0.8
Biomass combustion	4-12
Soils	4-7
Ammonia oxidation	0.5-3.0
Lightning	2-12
Transport from the stratosphere	<0.5
Total	51.9

Table 1. Global tropospheric NOx emissions estimates for 2000

As Table 1. shows, the burning of fossil fuels is by far the largest present-day source of NOx. Emissions from fossil fuels are likely to increase in the future, despite successful regulations in Europe, North America and Japan. A largescale shift to hydrogen would eliminate or at least reduce a significant fraction of traffic-related NOx emissions. This would improve air quality, or at least help to slow the decline in air quality, over large regions of the world.

4. Possible impacts: a review of some articles

The potential environmental impacts of a global hydrogen economy are:

- Increased hydrogen release would lower the oxidizing capacity of the atmosphere, and so increase the lifetime of air pollutants and greenhouse gases such as methane, HCFCs and HFCs.
- 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.
- Increased hydrogen release could exceed the uptake capacity of hydrogen by micro-organisms in the soil, currently the main way in which hydrogen is removed from the atmosphere. The result would be that hydrogen concentrations in the atmosphere would increase quicker, which would reinforce the consequences described above.
- 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.
- Generating hydrogen from fossil fuels could lead to increased emissions of carbon dioxide, which would accelerate global warming, unless the CO2 is captured and stored.
- Conversely, generating hydrogen from sustainable sources would reduce emissions of carbon monoxide and NOx, with a consequent fall in tropospheric ozone levels. This would improve air quality in many regions of the world. Furthermore, CO2 emissions would be reduced, thereby slowing the global warming trend.

The following sections address each of these points and attempt to judge the likelihood that they will become topics of concern in the future.

4.1. Changes in oxidising capacity

Hydrogen acts as a significant sink for hydroxyl radicals, and increased atmospheric concentrations of hydrogen could lead to a decrease in OH concentration. This in turn could increase the atmospheric lifetime of greenhouse gases and other pollutants, with undesirable consequences for climate change and air quality.

While this argument is qualitatively correct, the anticipated changes in OH levels due to changes in the atmospheric hydrogen concentration are marginal. At present, hydrogen accounts for the destruction of less than 10% of all OH globally, so if hydrogen concentrations were to double (which seems unlikely, given the emissions estimates above) this would produce a change in OH concentrations of only a few percent.

However, significant changes in the oxidising capacity of the atmosphere could well arise from other emission changes associated with the shift towards hydrogen, most notably emissions of NOx. There is still considerable uncertainty about the global OH budget and its historical trends. Generally, scientists believe that the burning of fossil fuels has produced only small changes in the balance between NOx (which tends to increase OH) and carbon monoxide (which tends to decrease OH) since pre-industrial times, and that the global average

4.2. Changes in atmospheric water vapour

The oxidation of hydrogen produces water vapour, which could have different consequences depending on where in the atmosphere it is released. One recent article suggests that increasing atmospheric hydrogen concentrations by a factor of four would increase the amount of water vapour in the stratosphere by up to 30%. According to these researchers, this could decrease the lower stratospheric temperature at the polar vortex by about 0.2°C, which in turn could trigger additional polar ozone losses of up to 8% (polar ozone depletion is very sensitive to small temperature changes). Another model, however, showed a much weaker effect on stratospheric temperatures and ozone loss.

As discussed above, hydrogen levels are more likely to increase by 20% than by 400% in the coming decades. Even when we use the more pessimistic model, the consequences for stratospheric temperatures and ozone concentrations therefore are expected to be negligible (figure 1.2.)

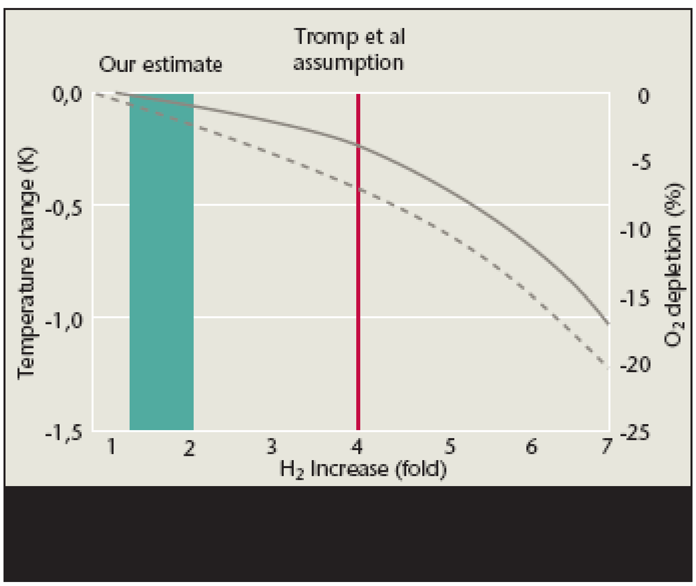

Figure 1.2. Relative temperature changes in the lower stratosphere at 74°N (solid line) and the resulting maximum ozone depletion in the northern polar vortex (dashed line) as a function of increased atmospheric hydrogen concentrations relative to the today's actual hydrogen concentration of about 0.5 ppmv. The cause of the temperature change is the stratospheric water vapour resulting from the oxidation of hydrogen. The graph is taken from Tromp et al., with additions.

If hydrogen combustion engines were used widely in aircrafts, another source of concern could be emissions of NOx. Even under present-day conditions, NOx emissions are believed to significantly perturb the amount of ozone in the upper troposphere. These processes in the upper troposphere and lower stratosphere region are still the subject of much research, and more measurements and better models are needed to assess them reliably.

4.3. Soil uptake

The uptake of atmospheric hydrogen by soil microorganisms or organic remnants is associated with large uncertainties. Studies using isotopically-labelled hydrogen suggest that soil uptake provides about 75% of the total hydrogen sink, but there is a large margin of error. Little is known about the detailed processes by which hydrogen is absorbed in the soil.

4.4. Carbon dioxide emissions

In a recent study, today's surface traffic fuels were assumed to be replaced by hydrogen generated from renewable sources leading to a 20% CO2 emission reduction.
However, as long as hydrogen is generated from fossil fuels, CO2 emissions from reforming can easily rival today's emissions from power plants and traffic. From the standpoint of avoiding CO2 emissions in the short to medium term, centralized facilities appear preferable, because this might allow efficient capturing and storing of the CO2 produced.9 In the long term, it is obvious that hydrogen generation has to be based on renewable sources to avoid the environmentally adverse effects of carbon dioxide.

4.5. Air quality effects

Probably the most immediate implication of a large-scale shift to hydrogen, especially in road transport, would be a significant drop in emissions of air pollutants (NOx, benzene and other VOCs) and an associated decrease in ground-level ozone concentrations.
In most regions of the world, ozone formation is limited by the amount of NOx in the atmosphere. However, many big cities emit such large amounts of NOx that ozone formation is limited instead by the availability of VOCs and carbon monoxide, which are produced by plants and soil bacteria as well as vehicles and industrial processes.

5. Conclusions

While there are still large uncertainties about the current budget of atmospheric hydrogen and the consequences of a large-scale shift towards a hydrogen economy, present knowledge indicates that there are no major environmental risks associated with this energy carrier, and that it bears great potential for reducing air pollution world wide, provided that the following rules are followed:

• 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 aircrafts, 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.

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