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HYDROGEN FOR HEATING: ATMOSPHERIC IMPACTS

A literature review

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HYDROGEN FOR HEATING: ATMOSPHERIC IMPACTS
– A LITERATURE REVIEW

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Summary

Introduction

The Department for Business, Energy and Industrial Strategy (BEIS) is undertaking work to strengthen the evidence base on the potential long-term approaches for decarbonising heating. One approach being explored is whether hydrogen could be used in place of natural gas in the gas grid to provide a source of low-carbon heat in the future. BEIS commissioned rdscientific to carry out a literature review to assess the evidence on the potential atmospheric impacts of increased emissions to the atmosphere of hydrogen.

Headline Findings

This review summarises the present state of our understanding of the potential global atmospheric impacts of any future increased use of hydrogen through release of additional hydrogen into the atmosphere. This review has identified two global atmospheric dis-benefits from a future hydrogen economy: stratospheric ozone depletion through its moistening of the stratosphere, and contribution to climate change through increasing the growth rates of methane and tropospheric ozone.

- The consensus from the limited number of studies using current stratospheric ozone models is that the impacts of hydrogen on the stratospheric ozone layer are small.
- The best estimate of the carbon dioxide (CO₂) equivalence of hydrogen is 4.3 megatonnes of carbon dioxide per 1 megatonne emission of hydrogen over a 100-year time horizon, the plausible range 0 – 9.8 expresses 95% confidence. On this basis, the impact of hydrogen emissions on global climate is very unlikely to be zero and is very likely to be small and warming (positive influence).
- If a 1% leakage for the entire low-carbon hydrogen system for the UK domestic sector was considered a realistic estimate, then the global warming consequences of a low-carbon hydrogen system are very likely to be small. Despite the uncertainties in the CO₂ equivalence of hydrogen, the confidence in the accuracy of the CO₂ equivalence is considered adequate to begin an initial policy analysis of the global atmospheric impacts of hydrogen within BEIS.

Context

Although it is not a pollutant in its own right, hydrogen can take part in atmospheric chemical reactions in the lower and upper atmospheres and these chemical reactions may lead to environmental damage. In the upper atmosphere, hydrogen may moisten and cool the stratosphere, slowing down the recovery of the ozone layer. In the lower atmosphere, hydrogen may hasten the build-up of the greenhouse gases: methane and ozone and hence contribute to climate change. Hydrogen therefore has the potential to cause global environmental impacts both on the stratospheric ozone layer and on climate change.

However, the impacts of hydrogen have not been well studied by the atmospheric science community. This review assembles the available evidence on the two global atmospheric impacts of hydrogen so that a start can be made on assessing the potential atmospheric impacts of a hypothetical scenario where Great Britain has moved from natural gas to hydrogen as a source of energy for heating.

Impact on the Ozone Layer

The current assessment of the stratospheric ozone layer modelling studies performed to date is that the likely impact of increased hydrogen emissions on the stratospheric ozone layer is small. However, although the number of such studies is small, there is no conflict between them, and they all confirm the view that impacts of hydrogen on stratospheric ozone depletion are indeed likely to be small.

Impact on Climate Change

Only one model study has evaluated the global warming potential (GWP) of hydrogen. From this model study, a best estimate can be derived of the GWP or carbon dioxide equivalence of hydrogen as 4.3 megatonnes (1 megatonne = 1 million tonnes = 1 Tg) of carbon dioxide emissions per 1 megatonne emission of hydrogen over a 100-year time horizon, with a plausible range expressing 95% confidence of 0 – 9.8 megatonne per megatonne. The uncertainties in the estimate of the GWP for hydrogen are therefore large and encompass zero. The central estimate is based on only one model and on one study which was published many years ago. This model, like all greenhouse gas models, has its biases and limitations, many of which still remain because of the dearth of observations with which to check how well the model represents the real world. The results from this model, like those from other greenhouse gas models, should be approached critically as there are no agreed acceptance criteria.

Exploring the potential impacts of hydrogen leakage in a low-carbon hydrogen for heat system

To assist with policy development, this review and assessment has employed the GWP concept to evaluate the potential impact of a low-carbon hydrogen energy system on the UK domestic sector. If this future hydrogen system was a perfectly sealed system, with no leakage and no upstream emissions associated with hydrogen production, then it could eliminate the greenhouse gas emissions from the current natural gas-based energy system. That is to say, the low-carbon hydrogen system offers the potential for generating savings in greenhouse gas emissions of the order of 54.0 million tonnes of CO₂ per year from the UK domestic sector. If there were to be significant atmospheric leakage from the production, distribution and end-use of hydrogen in the low-carbon system, then the indirect global warming from hydrogen would reduce or offset some of the savings in greenhouse gas emissions from the energy system it replaced. If a 1% leakage for the entire low-carbon hydrogen system for the UK domestic sector was considered a realistic estimate, then the global warming consequences of a low-carbon hydrogen system are very likely to be small. Despite the uncertainties in the CO₂ equivalence of hydrogen, the confidence in the

accuracy of the CO₂ equivalence is considered adequate to begin an initial policy analysis of the global atmospheric impacts of hydrogen within BEIS.

Recommendations for further work

During the preparation of this review and assessment, a number of recommendations have been considered and are summarised below. The following recommendations set out actions that could be taken to improve data collection on hydrogen emissions and reduce the hydrogen GWP uncertainty range.

Item	Evidence gap	Recommendation	Priority
Baseline monitoring	It is important to establish the atmospheric hydrogen baseline in the period before the hydrogen economy begins	Support long-term baseline hydrogen and ozone monitoring at Mace Head, Ireland	High
Global and regional hydrogen emission inventories	The magnitudes of the hydrogen emissions from motor traffic and other sources are not currently monitored	Encourage and support the emission inventory communities to address hydrogen, so that magnitudes of hydrogen emissions from various sources can be established before the hydrogen economy begins	High
Atmospheric hydrogen sinks	The magnitude of the soil sink for hydrogen is highly uncertain but it does strongly influence the GWP for hydrogen	Encourage field experiments and budget studies of hydrogen uptake by soils	Medium
Stratospheric ozone depletion modelling	In view of the limited nature of the quantification of the potential impacts of hydrogen on the stratospheric ozone layer, it is important that new studies are commissioned using a range of state-of-the science stratospheric ozone models	Promote studies of hydrogen and stratospheric ozone layer depletion by UK universities and research institutions	High
Hydrogen and climate change	It is important to move forward to obtain a more community-based estimate of the GWP of hydrogen	Promote studies of hydrogen and climate change by UK universities and research institutions	High

1. Introduction to the global atmospheric impacts of hydrogen

Interest in hydrogen as an atmospheric trace gas has recently been revived because of its potential role as an energy carrier in a future low-carbon energy economy. This review summarises the present state of our understanding of the potential global atmospheric impacts of any future increased use of hydrogen. Hydrogen has been little studied and has received little attention from the atmospheric research community. This stems in large part because, between its point of release to the atmosphere and its point of removal, hydrogen causes no direct damage to human health or to target ecosystems, it is therefore not considered to be an atmospheric pollutant. Because hydrogen is a homonuclear diatomic molecule, it possesses no dipole moment, it does not absorb infrared radiation and therefore is not a direct greenhouse gas.

This review has identified two global atmospheric dis-benefits from a future hydrogen economy: stratospheric ozone depletion through its moistening of the stratosphere, and contribution to climate change through increasing the growth rates of methane and tropospheric ozone. These two dis-benefits stem from the consequences of the main atmospheric removal process for hydrogen (H₂), namely the reaction of hydrogen with hydroxyl (OH) radicals in reaction (1):



Although this reaction removes hydrogen from the atmospheric circulation, it has the side-effect of producing water vapour (H₂O). The production of water vapour in the lower atmosphere has few adverse consequences but its production in the upper atmosphere may lead to its moistening. This moistening may cause cooling of the stratosphere. The reaction of hydrogen with OH radicals has a further side-effect of reducing the availability of OH radicals with potential impacts on the build-up of greenhouse gases.

The review summarises what is known about the global atmospheric impacts of hydrogen on the stratospheric ozone layer and on the build-up of greenhouse gases.

2. Methods

This review and assessment has been compiled from the available industrial and academic literature on the potential global atmospheric impacts of hydrogen and of a future hydrogen economy. Candidate research papers were identified through searches on SCOPUS, ScienceDirect, GOOGLE and COOGLE SCHOLAR and through searches on the journals listed in Table 1. To establish the importance of each evidence source to the review and assessment, attention was paid as to whether the research paper was peer-reviewed, whether the conclusions matched the data presented, whether the authors and their institutes had a track record in this subject area and whether there were any likely, potential conflicts of interest from their funding sources.

Table 1. List of journals surveyed for the purposes of identifying evidence sources in the industrial and academic literature on the potential global atmospheric impacts of hydrogen and a future hydrogen economy.

Atmospheric impacts

Atmospheric Chemistry and Physics

Atmospheric Environment

Climatic Change

Environmental Science and Technology

Geophysical Research Letters

Geoscientific Model Development

Global Biogeochemical Cycles

Global Environmental Change

Journal of Atmospheric Chemistry

Journal of Geophysical Research

Science

Tellus

Hydrogen Economy

Energy and Environmental Science

Energy Policy

International Journal of Energy Research

International Journal of Hydrogen Energy

International Journal of Nuclear Hydrogen Production and Application

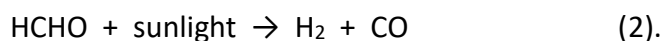
Journal of Fuel Cell science and Technology

3. Early studies of the global hydrogen budget

Hydrogen (H₂) is the simplest of all the molecular gases of the atmosphere. Atmospheric hydrogen and its isotopomers were first systematically investigated following the atmospheric testing of nuclear weapons from the 1950s onwards. Junge (1963) in reviewing these early studies pointed to an average level of 0.51 ppm at Harwell, Oxfordshire which is close to what is considered the modern level using modern instrumentation. However, little of his discussion of hydrogen sources and sinks is now considered relevant because the chosen sources, namely the decomposition of organic matter and the photolysis of water

vapour, have turned out to be inconsequential. Since then, hydrogen has largely been forgotten and it has received little attention from the atmospheric research community.

The role played by hydrogen in tropospheric chemistry was first laid out by Levy (1971). He pointed to an important source of hydrogen from the photolysis of formaldehyde (HCHO),



Formaldehyde is an important product of the oxidation of methane and other organic compounds by hydroxyl (OH) radicals. The main sink identified for hydrogen is oxidation by OH radicals in reaction (2):



Crutzen (1974) then went on to link the tropospheric chemistry of methane, hydrogen, carbon monoxide, ozone, oxides of nitrogen (NO_x) and organic compounds through their reactions with OH radicals. He showed how there is a steady state distribution of tropospheric OH radicals that provides efficient sinks for a range of trace gases. He showed how the life cycles of methane, carbon monoxide, hydrogen and ozone were intimately coupled together to maintain a steady state of OH radicals. In doing so, he laid the foundations for all subsequent descriptions of tropospheric chemistry and our understanding of the build-up of the two most important greenhouse gases after carbon dioxide: methane and tropospheric ozone.

The OH radical steady state proposed by Crutzen (1974) has stood the test of time and his chemical mechanisms have survived more or less unchanged to the present. His work provides the essential core in the global chemistry-transport models used to predict future levels of methane and tropospheric ozone, two of the most important greenhouse gases after carbon dioxide.

Schmidt (1974) provided the first budget assessment of the sources and sinks for hydrogen. The identified sources included:

- man-made sources (13 Tg year^{-1})
- biological processes in the oceans (4 Tg year^{-1})
- biological processes in soils, (0.1 Tg year^{-1}), and
- photochemical production in the troposphere via HCHO ($4.6 - 9.2 \text{ Tg year}^{-1}$).

The identified sinks included:

- soil uptake ($21.6 - 26.2 \text{ Tg year}^{-1}$), and
- photochemical destruction in the troposphere by OH radicals ($3.7 - 7.3 \text{ Tg year}^{-1}$).

Together the sink processes give hydrogen an atmospheric lifetime of 4 – 7 years with the soil uptake being several times stronger than OH radical destruction.

The hydrogen budget study of Schmidt (1974) is crucially important to this review because it demonstrated how hydrogen was in steady state between its sources and sinks. It also highlighted the importance of the two sinks for hydrogen: soil uptake and OH radical

destruction. Hence, if the steady state is perturbed by an additional emission pulse of hydrogen, the pulse decays away over a 4 – 7 year period. During this period, the additional hydrogen depletes the OH radical levels below their steady state levels, weakens the methane sink and so leads to methane build up above the levels without the pulse. The impact on methane resulting from the hydrogen pulse is mitigated by the soil uptake sink for hydrogen, over time. The Schmidt (1974) budget analysis set the scene for this important competition between the soil uptake and OH radical destruction sinks for hydrogen.

At the time of the preparation of the Schmidt (1974) hydrogen budget, the information available on the distribution of the sources and sinks between the hemispheres and on the magnitude of the photochemical source were sparse and subject to considerable uncertainty. More recent hydrogen budget studies find that the Schmidt (1974) study underestimated the photochemical hydrogen source strength by a large factor, 4.6 – 9.2 Tg year⁻¹ versus 40 – 77 Tg year⁻¹ (Pieterse et al., 2013). Modern estimates of the atmospheric lifetime of hydrogen are accordingly much shorter, 1.4 – 2.1 years (Pieterse et al., 2013) versus 4 – 7 years from Schmidt (1974).

Most trace gases with large man-made sources show higher concentrations in the northern hemisphere compared with the southern hemisphere, following the global population distribution. Hydrogen is unusual in having larger atmospheric sinks in the northern hemisphere compared with the southern hemisphere, following the global land surface distribution. The soil uptake sink for hydrogen causes higher concentrations in the southern hemisphere compared with the northern hemisphere, hence the inverted concentration distribution, because of the greater land surface area in the northern hemisphere

Continuous high-frequency hydrogen monitoring carried out at the Mace Head, Ireland Atmospheric Research Station supported by BEIS points to current northern hemisphere baseline levels being 496.5 ppb (Simmonds et al., 2000) over the 1994-1998 period. This makes hydrogen the ninth most abundant atmospheric gas (after nitrogen, oxygen, water vapour, argon, carbon dioxide, neon, helium and methane). The Mace Head observations demonstrated the presence of European regional hydrogen sources, local sinks in the peat bogs surrounding the Mace Head station and the inverted tropospheric distribution when elevated hydrogen levels were advected to the station from tropical latitudes (Simmonds et al., 2000).

Novelli et al. (1999) used the NOAA/CMDL flask sampling network to characterise the surface distribution of hydrogen at 50 remote locations between 1991 and 1996. Average hydrogen mixing ratios increased from northern hemisphere polar to tropical latitudes and reached a maximum in the southern hemisphere tropics, confirming an inverted tropospheric distribution. Hydrogen seasonal cycles were well-defined with maximum levels occurring in late winter/early spring and minimum levels in autumn. The amplitude of the seasonal cycle in high latitudes of the northern hemisphere was about three times that in the low latitudes of the southern hemisphere, confirming the importance of soil uptake as a sink in the northern hemisphere.

The NOAA study (Novelli et al., 1999) and the BEIS-funded AGAGE/GAGE study (Simmonds et al., 2000) provide the main source of observations in use by the global chemistry-transport models to set up their initial conditions and to evaluate model performance for hydrogen.

Grant et al. (2010) analysed 15 years of continuous hydrogen monitoring data for Mace Head, Ireland covering the period from 1994 to 2008 and, in contrast to previous studies, found no overall trend in hydrogen levels. The previously reported increases for 1995 – 1998 (Simmonds et al., 2000) and for 1992 – 1999 (Novelli et al., 1999) were due to the limited time series of observations (< 5 years) then available. Grant et al. (2010) confirmed the importance of European regional sources of hydrogen, southerly transport events and baseline seasonal cycles in the Mace Head hydrogen observational record.

4. Hydrogen and stratospheric ozone depletion

Hydrogen enters the stratosphere through stratosphere-troposphere exchange, primarily in tropical latitudes. The lifetime of hydrogen in the lower stratosphere is long enough for it to be transported through the middle stratosphere to the upper stratosphere where it can be destroyed by reaction with OH radicals:



Consequently, the altitude profile of hydrogen falls off slowly throughout the depth of the stratosphere (Schiller et al., 2002). Hydrogen acts as a source of water vapour in the stratosphere, supplementing the other sources from the oxidation of methane and transport of H₂O itself from the troposphere (Zager et al., 1999).

Increased atmospheric emissions of hydrogen will therefore inevitably lead to increased levels of water vapour in the stratosphere which will in turn lead to increased stratospheric cooling (Forster and Shine 2002). This cooling may change the distribution of polar stratospheric clouds which play an important role in the formation of ozone holes and hence may delay the recovery of the ozone layer (Tromp et al., 2003).

To put the estimates of hydrogen emissions that follow into some form of context, we note that the current levels of hydrogen in the troposphere and stratosphere of about 400 – 500 ppb are supported by an atmospheric source strength of about 75 Tg year⁻¹ (Novelli et al., 1999). If a future hydrogen supply rate of the order of 7.4 Tg H₂ year⁻¹ is considered for the United Kingdom, see section 7 below, and a putative 1% hydrogen leakage rate is assumed, then these assumptions would imply an atmospheric hydrogen emission of 0.074 Tg H₂ year⁻¹ and an increase in atmospheric hydrogen levels of about 0.4 ppb.

Tromp et al. (2003) using the Caltech/JPL 2-D model were the first to attempt to quantify the potential impacts of rising levels of hydrogen and hence water vapour in the stratosphere. Assuming a quadrupled surface hydrogen mixing ratio of 2.3 ppm, an ozone depletion of 3 – 8 % was found. However, in a less extreme scenario, a 0.25 ppm increase in tropospheric hydrogen caused an increase of 0.5 ppm in stratospheric water vapour and cooled the stratosphere by about 0.5°C. Such a cooling would increase the area of the northern polar vortex by 7% and the southern polar vortex by 4%. Polar vortices are thought

to last 5 to 8 days longer when there is a 0.5°C temperature drop. Colder vortices are known to last longer and cause more ozone depletion.

Increased emissions of hydrogen could therefore delay the recovery of the ozone layer that is expected to result from the bans on the use of chlorofluorocarbons and other ozone depleting agents. It was noted by Tromp et al., (2003) that the lower levels of chlorofluorocarbons expected several decades in the future should lead to less ozone destruction for a given level of stratospheric cooling caused by increased hydrogen emissions. So, the impact of a given level of hydrogen emission depends on how far into the future it occurs, whether in the next 10 years, for example, or more than 50 years from now.

Warwick et al. (2004) studied the impact of hydrogen emissions on the troposphere and stratosphere using a 2-D model. They found that by raising surface hydrogen mixing ratios from 0.55 to 2.3 ppm, stratospheric water vapour levels increased by about 20%, which was significantly less than the 35% found by Tromp et al. (2003). They assumed in one of their scenarios that if hydrogen leakage was restricted to 5%, then stratospheric water vapour levels increased by 3.4%. They concluded that this was small in comparison to recent observed trends in water vapour of 10 – 20% for the recent past decades. In all their scenarios, the changes in stratospheric ozone were small and less than 1%, and were not significant in comparison with observed changes over the last two decades. Predicted changes in stratospheric temperatures were also small and ranged from -0.1 K to -0.3 K. The changes in stratospheric water vapour were, however, significantly smaller than those predicted by Tromp et al. (2003).

Jacobson (2008) used the GATOR-GCMOM model to study the impacts of a hydrogen economy on the global environment. The study evaluated the impact of changes in the emissions of a comprehensive suite of ozone precursor gases following the replacing of fossil-fuel motor vehicles and electric power plants with hydrogen fuel cell vehicles and power plants. A sensitivity test with 10% hydrogen leakage isolated the model impact of hydrogen-alone. No adverse impacts on tropospheric pollution or the stratospheric ozone layer were found.

Vogel et al. (2011) used the CLaMS model to study the impact of a potential future hydrogen economy on stratospheric water vapour, stratospheric temperatures and chlorine-induced polar ozone loss. An averaged increase in water vapour concentrations of 0.18 ppm was found to produce a 2.5 Dobson Unit increase in spring-time ozone depletion which amounted to a 4% increase in the accumulated ozone loss over the winter. This study suggested that the potential impact of enhanced water vapour caused by a future global hydrogen economy was of minor importance for stratospheric ozone loss processes and would become even smaller as stratospheric chlorine levels decline.

Vogel et al. (2012) investigated the impact of a possible global hydrogen energy economy on Arctic stratospheric ozone loss. They showed that additional hydrogen emissions brought enhanced water vapour concentrations to the stratosphere which had an impact on stratospheric temperatures and on polar ozone loss. They noted that both stratospheric water vapour and ozone are important drivers of climate change. The potential

environmental risks from the hydrogen economy were found to be small in comparison with the environmental benefits.

Van Ruijven et al. (2013) used the CAM3.5 global 3-D chemistry-transport model to study the impact of large scale hydrogen application on stratospheric chemistry and found a small negative impact on stratospheric ozone concentrations. Stratospheric ozone concentrations would decrease when hydrogen emissions increased. The effect on the total ozone column was found to be rather small because the decrease in the stratospheric ozone was compensated by an increase in tropospheric ozone. In scenarios with high hydrogen emissions, the maximum ozone reduction was found to be approximately 2 Dobson Units in high latitudes, which was less than 1% of the annual mean ozone column. This decrease is much smaller than the observed decrease in the northern hemisphere total ozone column during the 1990s, associated with the increase in man-made chlorine in the stratosphere.

Wang et al. (2013) studied the impact of future hydrogen emissions on stratospheric composition and chemistry using the MOZART global chemistry-transport model. They showed that future hydrogen emissions would perturb stratospheric chemistry in the 2050 atmosphere by affecting the ozone destruction cycles involving, HO_x, NO_x and ClO_x. The impact of the hydrogen scenarios on the stratospheric ozone column was found to be in the range from -0.54% to -0.20%. The largest relative reduction in stratospheric ozone concentrations was found in the lower stratosphere where HO_x cycles dominate ozone loss. In the middle stratosphere, ozone concentrations increased slightly whilst in the upper stratosphere both increases and decreases were found, depending on the hydrogen scenario. They noted that although the hydrogen scenarios brought about ozone depletion, this depletion was considerably less than the ozone recovery by 2050 brought about by the reductions in usage of CFCs. Therefore, the stratospheric ozone depletion due to hydrogen usage in 2050 should not constitute a major concern.

There are a limited number of studies in the peer-reviewed literature of the impact of hydrogen emissions on the stratospheric ozone layer with which to make more than a cursory assessment. Having said that, the few available studies all point to the impact of large potential hydrogen leakages on the stratospheric ozone layer as being small. There appears to be no conflict between the studies reviewed here on this point.

This review and assessment takes the view that the stratospheric ozone layer impacts of hydrogen cannot currently be quantified and but are likely to be small.

In view of the limited nature of the quantification of the potential impacts of hydrogen on the stratospheric ozone layer, it is important that new studies are commissioned using a range of state-of-the-science stratospheric models, using up-to-date information where new model input data are available.

5. Hydrogen and global warming

5.1 The Global Warming Potential (GWP) for hydrogen

The IPCC (1990) in its first scientific assessment of climate change put forward the concept of global warming potential (GWP) to help policy-makers assess the climate consequences

of future emissions of a range of trace gases. The GWP of the emissions of a trace gas is defined as the time integrated commitment to climate forcing from 1 kg of a trace gas expressed relative to that of 1 kg of carbon dioxide. In this way, the GWP concept envisages the instantaneous emission (or pulse) of a quantity of a particular trace gas into the atmosphere. The trace gas concentration then declines with time and whilst it is in the atmosphere, it may generate a greenhouse warming (direct GWP). If its decline is due to atmospheric chemistry processes, then the products of these reactions may generate additional greenhouse warming (indirect GWP).

Indirect greenhouse warming may occur if the trace gas decays by reaction with tropospheric OH radicals as is the case, for example, with methane, carbon monoxide, halocarbons and organic compounds. The trace gas pulse may deplete the tropospheric steady state of OH radicals which will increase the lifetimes of all the other trace gases which have OH oxidation as a main feature of their life cycles, methane included. Increased methane lifetimes will lead to increased greenhouse warming. It was also recognised that the emissions of a number of trace gases, including NO_x, carbon monoxide, methane and other hydrocarbons have the potential to influence the tropospheric concentrations of ozone, an important radiatively-active trace gas. So many trace gases may potentially have important indirect GWPs by virtue of their influences on the tropospheric distributions of methane and ozone.

Over the years, the global chemistry-transport models that were used to estimate direct and indirect GWPs have increased in sophistication and reliability. The IPCC (2001) in their third assessment report reviewed the then current state-of-the-science on tropospheric chemistry and the global chemistry-transport models that describe it. It focussed on the role played by tropospheric OH radicals in linking together the life cycles of methane, carbon monoxide, hydrogen, NO_x, ozone and organic compounds and how this coupling influences the estimates of direct and indirect GWPs. It felt confident enough to identify that in a possible fuel-cell economy, future hydrogen emissions may need to be considered as a potential climate perturbation (pp. 256, IPCC, 2001).

The GWP for hydrogen was first estimated by Derwent et al. (2001) using the Met Office global Lagrangian chemistry-transport model STOCHEM. In response to an emission pulse of hydrogen, a steady rise in methane set in during the first two years before a steady decline then set in. Detailed analysis was hampered by the limited experimental period because of the computational burden of the model. However, experiments with analogous methane, carbon monoxide and NO_x emission pulses were strikingly similar with the 'excess' methane decaying with an e-folding time of about 12 years. This time scale was significantly longer, about 23%, than the steady state methane lifetime. The time-integrated methane 'excess' was estimated to be about 0.81 ppb year when integrated over a 100-year time horizon for a 1 Tg emission pulse of hydrogen. As a result of the increases in the concentrations of methane and other ozone precursors caused by perturbation to the tropospheric OH distribution following the hydrogen pulse, adjustments were found in tropospheric ozone which led to an initial rise to a maximum followed by a steady decline. This decline also had

an e-folding time of 12 years, as with the 'excess' methane. The time-integrated ozone 'excess' was estimated to be 0.010 ppb year over a 100-year time horizon.

Derwent et al. (2001) converted the time-integrated 'excess' methane into a time-integrated radiative forcing using the radiative forcing formulae for methane from IPCC (1990) to estimate 2.1 mW m⁻² year from a 1 Tg emission pulse of hydrogen, over a 100-year time horizon. When compared to the time-integrated radiative forcing from 1 Tg of CO₂, this gave a GWP for hydrogen of 3.4 from the changes to methane alone. To convert the time-integrated 'excess' ozone into a time-integrated radiative forcing, the Edwards and Slingo (1996) radiation code was employed. Stratospheric temperatures were iteratively adjusted until stratospheric heating rates returned to their unperturbed values. This gave a GWP for hydrogen of 2.4 from changes to ozone alone. Summing the impacts on methane and ozone, gave Derwent et al., (2001) a GWP for hydrogen of 5.8. Compared with methane, this value for the GWP for hydrogen is somewhat lower because the tropospheric removal of hydrogen is not dominated by OH oxidation as it is for methane, but by soil uptake.

Hydrogen is thus an indirect greenhouse gas because it interferes with the global chemical reactions which control the methane levels and the formation of ozone (Derwent et al., 2001). Methane and ozone are the second and third most important greenhouse gases after carbon dioxide. The GWP of hydrogen was found to be 5.8 by summing its influence on both methane and ozone. That is to say, the emission of 1 Tg year⁻¹ of hydrogen causes the global warming equivalent to 5.8 Tg year⁻¹ of carbon dioxide when evaluated over a 100 year time horizon (1 Tg = 1 million tonne = 1 megatonne).

In view of the importance of the estimated GWP for hydrogen to this review, it is recommended that the global chemistry-transport model studies of Derwent et al. (2001) are repeated in other models, having been brought up-to-date where new model input data are available.

5.2 Uncertainties in the GWP for hydrogen

In view of the Derwent et al. (2001) being the only published estimate for the GWP for hydrogen, it is important to make some estimate of the likely uncertainties surrounding this estimate. There are a number of critical points in the original estimation procedure that can be used to test the robustness of the Derwent et al. (2001) estimate against current understanding of the hydrogen life cycle and estimate the likely uncertainties surrounding the GWP estimate.

5.2.1 Uncertainties arising from hydrogen sinks

Many assessments of the global hydrogen budget have used assumed global averages of the controlling parameters such as temperature and key reactants to calculate the magnitudes of the two main tropospheric hydrogen sinks: OH oxidation and soil uptake. Simulation of hydrogen using the Met Office global three-dimensional chemistry-transport STOCHEM model and two different soil uptake schemes were compared with surface observations (Sanderson et al., 2003). An improved soil uptake scheme which took into account soil moisture allowed surface observations and their seasonal cycles to be simulated much more

accurately. The study indicated a global mean hydrogen soil uptake deposition velocity of $5.3 \times 10^{-4} \text{ m s}^{-1}$ and an atmospheric lifetime of 2.2 years for hydrogen. The split between oxidation by OH radicals and soil uptake was found to be 17.1 versus 58.3 Tg year⁻¹, significantly different from the split in the STOCHEM version employed for the GWP estimation in Derwent et al. (2001).

In view of the central importance of the soil uptake sink for hydrogen in ameliorating the influence of hydrogen on the tropospheric OH radical distribution, a literature review of this sink is appropriate at this stage and is presented in Table 2. Seven estimates are listed in this Table in comparison with the input parameter value set in the STOCHEM experiments of Derwent et al. (2001). The average of the estimates is found to be $4.0 \pm 3.4 \times 10^{-4} \text{ m s}^{-1}$, where the quoted range is the 2 – σ or 95% confidence interval and central values of the quoted ranges were used when only ranges were provided. The STOCHEM input parameter is not statistically significantly different from the average value of the seven literature estimates in Table 2.

Table 2. Literature estimates of the soil uptake deposition velocity for hydrogen.

Soil uptake deposition velocity, 10^{-4} m s^{-1}	Reference	Comments
0.5 – 9	Steinbacher et al. 2007	Suburban site near Zurich, Switzerland ^a
0 - 10	Yonemura et al. 1999	Suburban field in Tsukuba, Japan
1 - 14	Conrad and Seiler, 1985	Field measurements in Transvaal, Andalusia and Karoo.
2.6	Simmonds et al. 2000	Peat bogs around Mace Head, Ireland
4.8 ± 1.3	Gerst and Quay, 2001	Soil uptake chamber experiments
5.3	Sanderson et al. 2003	Global chemistry-transport model study
3.3	Constant et al. 2008	Upper limit value for rural Quebec, Canada
4.5	Derwent et al. 2001	Input value to STOCHEM for GWP calculation

Note:

a. these low values are considered representative of suburban environments on days with maximum temperatures above 25°C and dry soil conditions.

The mechanism underpinning the indirect global warming impact of hydrogen relies heavily on the depletion of tropospheric OH radical levels following the emission of a pulse of hydrogen. The fate of this pulse depends on the atmospheric lifetime of hydrogen and its

impact on tropospheric OH depends on the flux through the OH + H₂ reaction. The global warming impact then increases with the fraction of the hydrogen sink that goes through the OH + H₂ reaction. A sophisticated global chemistry-transport model is required to describe quantitatively the tropospheric OH radical distribution and the interaction between the tropospheric chemistry of methane, carbon monoxide, hydrogen, NO_x and organic compounds that controls it. Roughly speaking, about one quarter of the hydrogen is destroyed by reaction with OH radicals and the remaining three quarters is taken up by soils. Table 3 presents the fraction of the hydrogen sink that involved oxidation by OH radicals in eight literature global chemistry-transport models. The average value of these eight studies is 0.31 ± 0.16, where the quoted range expresses 95% confidence.

Table 3. Global chemistry-transport model estimates of the fraction of the tropospheric hydrogen sink that involves the OH + H₂ reaction versus soil uptake.

Ratio of OH + H ₂ sink to soil uptake sink	Reference	Comments
0.32	Ehhalt and Rohrer, 2009	Critical review paper.
0.25	Hauglustaine and Ehhalt, 2002	MOZART chemical-transport model. Soil sinks may be overestimated.
0.34	Novelli et al., 1999	Global budget study
0.40	Pieterse et al. 2011	Early TM5 study
0.43	Pieterse et al. 2013	TM5 model study which updates previous studies.
0.22	Rhee et al., 2006	Soil sinks may be overestimated.
0.29	Sanderson et al. 2003	Met Office STOCHEM model employed.
0.21	Xiao et al. 2007	Soil sinks may be overestimated.
0.23 ± 0.12	Derwent et al. 2018	Monte Carlo uncertainty analysis using STOCHEM.

A Monte Carlo uncertainty analysis involving 98 STOCHEM model runs gave 0.23 ± 0.12 (Derwent et al., 2018) for the fraction of the hydrogen sink through reaction with OH radicals. This estimate is significantly lower than the average of the eight studies in Table 3. However, the 2 – σ or 95% confidence limits from the STOCHEM Monte Carlo analysis and from the eight literature studies overlap and so the difference between these two estimates is not statistically significant. Overall, this means that the fraction of the hydrogen sink that involves OH radicals was not well constrained in the various model studies and that

uncertainties are necessarily large. Overall, it is likely that STOCHEM underestimates this fraction and this may mean in turn that the GWP for hydrogen from STOCHEM is also underestimated.

5.2.2 Uncertainties arising from tropospheric chemistry

Schultz et al., (2003) explored the global environmental impacts resulting from the application of hydrogen fuel cell technology to power the surface traffic fleet. They found a decrease in global OH and an increased lifetime of methane, caused primarily by the reduction in the NO_x emissions from current vehicles. They pointed out that a possible rise in atmospheric hydrogen concentrations was unlikely to cause significant perturbation of the climate system without quantifying what these perturbations might be.

Prather (2003) in reviewing the Schultz et al., (2003) study noted that Schultz et al., (2003) did not report their assumed annual usage of hydrogen. This means that it was difficult to estimate their assumed hydrogen leakage rates. For an assumed upper limit leakage rate of 10%, Prather (2003) estimated an additional hydrogen emission rate of 105 Tg year⁻¹ and a consequential increase in atmospheric hydrogen of up to 0.6 ppm. Prather (2003) then went on to estimate an increased OH + H₂ flux of 0.062 ppm year⁻¹ and an increased methane build-up of 0.006 ppm year⁻¹. This latter estimate assumed that the impact of hydrogen and carbon monoxide were equal on a by-molecule basis, when allowance was made for their relative rates of reaction with OH. The amplifying effect of the methane feed-back meant that methane abundances would increase by 0.072 ppm, about 4%, corresponding to a greenhouse forcing of about +0.026 W m⁻². Prather (2003) noted that this climate forcing is a small fraction of that due to methane (+0.5 W m⁻²) and carbon dioxide (+1.5 W m⁻²) since pre-industrial times and is a little larger than the climate forcing due to carbon dioxide emissions from present day aviation.

A summary of Prather (2003) and Schultz et al. (2003) concerning the environmental impacts of hydrogen leakage is that 105 Tg year⁻¹ hydrogen leakage should generate an extra 0.072 ppm methane and +0.026 W m⁻² methane forcing. That is to say, about 0.69 ppb additional methane abundance was produced for each 1 Tg year⁻¹ hydrogen leakage.

This figure is useful because it can be used, in principle, to check the GWP estimate of Derwent et al. (2001). However, the first obstacle to be overcome is that the Schultz et al. (2003) experiments were carried out as 'step-changes'. That is to say, the Schultz et al. (2003) model was set up with the current atmosphere and run until some form of steady state was established. Then an abrupt change was made to the emissions of hydrogen and this situation was maintained throughout the model experiment. The model response to this 'step-change' was then followed until a new steady state was established over a ten-year or so period. In contrast, the GWP concept envisaged by the IPCC (1990) considered the fate of an instantaneous emission pulse which would lead to an initial perturbation, followed by a decline back to the initial steady state again over a ten-year or so period. So, 'step-change' experiments are not immediately suited to the estimation of GWPs.

However, by lining up back-to-back a series of emission pulses, it is possible to simulate a 'step-change'. The emission pulse experiments of Derwent et al. (2001) when lined up,

produced a step-change of 12 Tg year⁻¹ which produced a perturbation to methane which built up over a 10-year period to an excess of about 10.5 Tg or about 3.8 ppb. This is about 0.31 ppb additional methane abundance per 1 Tg year⁻¹ hydrogen leakage, in conflict with the 0.69 ppb methane abundance per 1 Tg year⁻¹ hydrogen leakage estimated from the reinterpretation by Prather (2003) of Schultz et al. (2003). The difficulty with the Prather (2003) estimate of the impact of additional hydrogen on the methane distribution stems from the assumption that the relative impacts of hydrogen and carbon monoxide were equal on a by-molecule basis, when allowance was made for their relative rates of reaction with OH. At the time of the Prather (2003) reinterpretation, there was no way of confirming the validity of this assumption. If this assumption was to have overstated the impact of hydrogen, then the conflict between the two sets of results could be resolved.

The additional flux through the OH + H₂ reaction depletes the tropospheric distribution of OH radicals which in turn leads to a build-up of methane and ultimately tropospheric ozone. Global chemistry-transport models generally show a non-linear relationship between a perturbation in methane and the perturbation in tropospheric ozone that results. The IPCC (1996) Third Assessment Report characterised this non-linear relationship using the equation:

$$\delta O_3 = a \delta \ln CH_4$$

where δO_3 is the perturbation in the global average tropospheric ozone mixing ratio in ppb and δCH_4 is the corresponding perturbation in methane. The slope factor, a , however is not a well-defined quantity and is highly model dependent as is shown in Table 4. The average value of a from the five studies is 8.8 with a range from 2.8 to 21.5. The corresponding value from the STOCHEM study (Derwent et al., 2001) used to estimate the GWP for hydrogen was 21.7 which is just beyond the top of the range of the literature studies in Table 3. On this basis, the GWP estimate from Derwent et al. (2001) may be an overestimate by a factor of close to 2.5.

Table 4. Estimates of the ratios in the responses in global ozone to changes in global methane using the relationship: $\delta O_3 = a \times \delta \ln CH_4$.

$a = \delta O_3 / \delta \ln CH_4$	Source	Comments
2.8 – 14.0	IPCC, 1994	δCH_4 1756 – 2099 ppb
5.0 – 6.7	IPCC, 1996	δCH_4 1745 – 4300 ppb
4.4 – 8.8	Stevenson et al. 2013	δCH_4 791 – 1756 ppb
5.6 – 6.7	Wild et al. 2012	δCH_4 1756 – 2740 ppb
12.4 – 21.5	Young et al., 2013	δCH_4 1756 – 3476 ppb
21.7	Derwent et al. 2001	

5.2.3 Uncertainties arising from the estimation of radiative forcings

In estimating GWPs, the time-integrated forcing due to an instantaneous emission pulse of the trace gas is compared with the time-integrated forcing of an emission pulse of carbon dioxide. At the time of the calculations in Derwent et al. (2001), the GWP calculated for hydrogen was found to be 5.8 over a 100 year time horizon and 24.5 ± 7.5 for methane (IPCC, 1994). Subsequently, the IPCC in its Fifth Assessment Report (IPCC, 2013), noted that previous assessments of the time-integrated forcing from carbon dioxide had not included coupling to a climate model and so had not included climate-carbon cycle feedbacks. If these were included, together with updates to the radiative forcing for methane to allow for increased stratospheric water vapour, then the GWP for methane would rise to 34 over a 100 year time horizon, with a 5 – 95% confidence uncertainty range of -30% to +40%. Since the time-integrated radiative forcing used by Derwent et al. (2001) did not include climate-carbon cycle feedbacks and the recent updates to the radiative forcing for methane to allow for the formation of stratospheric water vapour, their GWP estimate for hydrogen would need to be updated by this same factor of $1.39_{-0.42}^{+0.56}$.

5.2.4 Impacts of hydrogen on radiative forcing through its indirect impacts on vegetation

The suggestion has been made by Collins et al. (2010) that ozone damage to vegetation may impact on the terrestrial storage of carbon. They studied the impact of the additional tropospheric ozone produced by rising level of methane on vegetation productivity using a coupled earth-system climate model. For a 20% change in methane, they found between 3% and 10% effects on climate metrics through changes in the carbon cycle depending on the sensitivity of plants to ozone. In commenting on this study, IPCC, (2013) noted that this effect had only been seen in one climate model. In complex and interconnected systems, feedbacks can become increasingly complex, and uncertainty in terms of both sign and magnitude increases the further from the primary perturbation they are exerted (IPCC, 2013). Following these comments, no allowance for this feedback has been made in this review to the GWP for hydrogen.

5.3 Summary of the global warming impacts of hydrogen

In drawing attention to the uncertainties inherent in the estimation of the global warming potential for hydrogen, a number of issues have surfaced and these have been reviewed in the sections above. The initial estimate of the GWP for hydrogen of 5.8 over a 100-year time horizon was the best estimate of a highly uncertain parameter, though Derwent et al., (2001) made no attempt to quantify the uncertainties at that time. Subsequently, Derwent et al. 2018 performed a Monte Carlo uncertainty analysis using the same global chemistry-transport model in which they randomly sampled the STOCHEM model input parameters in 98 replicate model runs. The ratio of the OH + H₂ to total hydrogen sink gave a first order estimate of the likely uncertainties in the STOCHEM model treatment of the influence of hydrogen on the tropospheric chemistry of methane and ozone. From the 95% confidence range about the central value of the ratio of the OH + H₂ to total hydrogen sink, we can estimate the 95% confidence range of 2.8 – 8.8, surrounding the original estimate of the GWP.

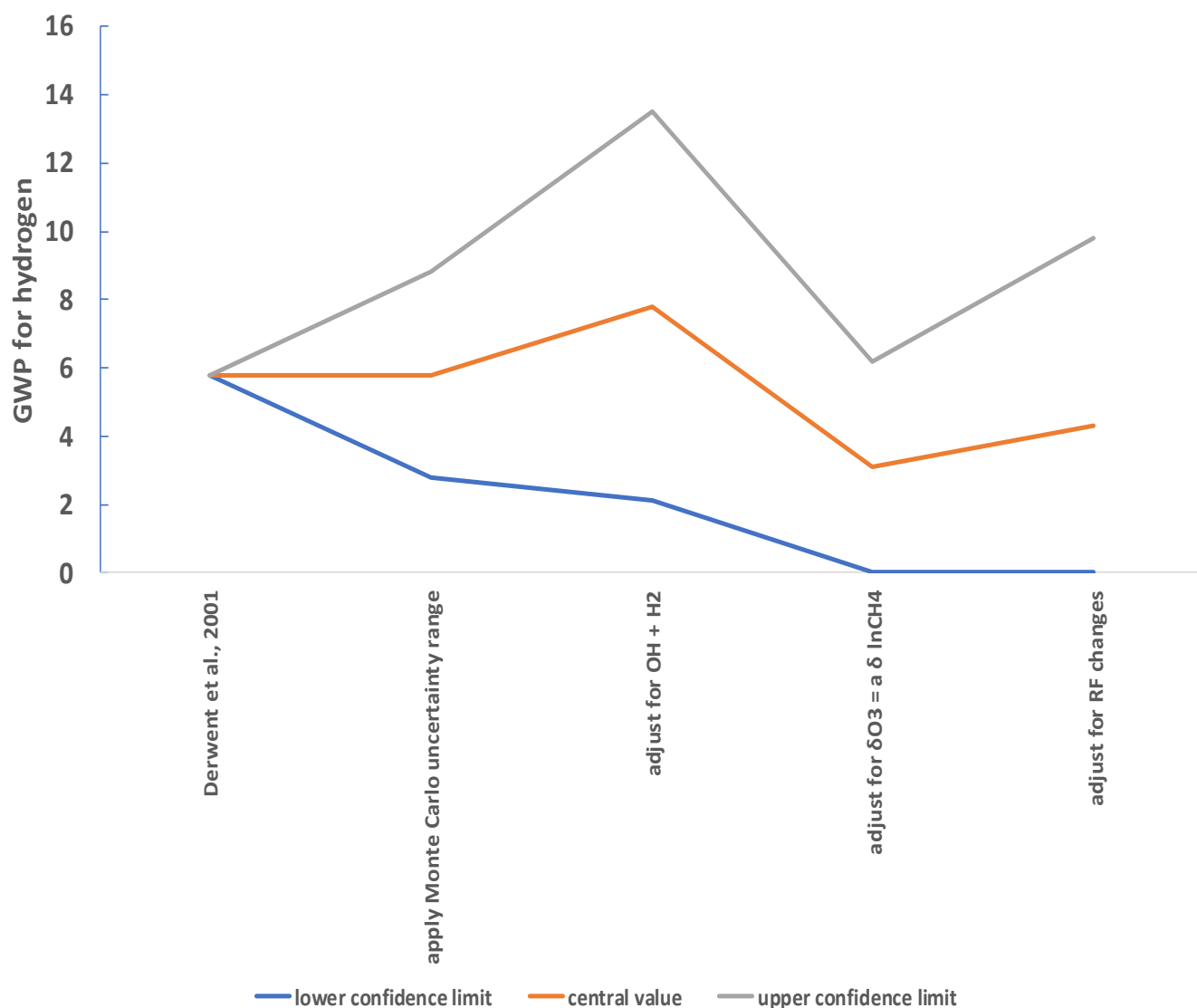


Figure 1. Evolution of the estimated global warming potential for hydrogen over a 100 year time horizon.

The evolution of the GWP for hydrogen and its uncertainties is illustrated in Figure 1, beginning at the left-hand side of this figure with the likely uncertainties in STOCHEM. Figure 1 has then been extended by considering first the adjustments for the ratios of the OH + H₂ to total sinks found in other chemistry-transport models. This adjustment not only increases the central value to 7.8 but widens the 95% confidence range to 2.1 – 13.5. The next consideration is the ratio of the δO_3 to $\delta \ln CH_4$ which was overestimated in STOCHEM. This adjustment brings the central value down to 3.1 but also widens the 95% confidence range to 0 – 6.2. Finally, adjustments are made to account for changes in the radiative forcing calculations for methane to account for the formation of stratospheric water vapour and for climate-carbon cycle coupling from IPCC (2013). These adjustments move the

central value up to 4.3 and widen the 95% confidence range to 0 – 9.8. Overall then, the best estimate for the GWP for hydrogen over a 100-year time horizon is $4.3_{-4.3}^{+5.5}$. This means that it is very unlikely that the GWP is greater than 9.8 and very unlikely that it is negative (cooling influence).

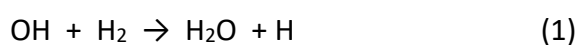
The impact of hydrogen emissions on global climate is very unlikely to be zero and is very likely to be small and warming (positive influence).

Overall, however, the uncertainties in the final estimate are large and encompass zero. The central estimate is based on only one model and on a study published many years ago. STOCHEM like all global chemistry-transport model has its biases and limitations, many of which still remain because of the dearth of observations. The results from STOCHEM, like those from other chemistry-transport models, should be approached critically. The available results are, however, considered adequate to begin an initial policy analysis of the global environmental impacts of hydrogen within BEIS. If at some point in the future the climate change impacts of hydrogen within BEIS begin to look important for policy, then new studies should be commissioned using a range of state-of-the-science chemistry-transport models, using up-to-date information where new model input data are available.

6. Other environmental impacts of hydrogen

Hydrogen has been little studied and has received little attention from the atmospheric research community. This stems in large part because, between its point of release to the atmosphere and its point of removal, hydrogen causes no direct damage to human health or to target ecosystems, it is therefore not considered to be an atmospheric pollutant. Heeb et al. (2006) noted that hydrogen is a well-known reducing agent, with possible effects on atmospheric redox chemistry on a local, regional and global scale. However, Heeb et al. (2006) gave no indication as to what these effects might be and what are atmospheric redox reactions.

Because of the relative inertness and its lack of chemical reactivity with urban pollutants such as NO_x, O₃, SO₂, CO, VOCs and suspended particulate matter, it has no direct influence on urban air quality. However, because of its reaction with hydroxyl radicals:



it plays a weak role in the long-range transport of photochemical ozone by delaying and slowing up the formation of elevated peak ozone levels. Popa et al. (2015) used the LOTOS-EUROS model to assess population exposure to elevated levels of ozone in Europe, with and without additional hydrogen emissions. They concluded that additional hydrogen emissions would not have a significant effect on ground level air pollution in Europe. The depletion of OH radicals in the reaction above is relatively weak and is only felt on the continental scale, consistent with its role in the chemistry of the background troposphere and its influence on the tropospheric OH radical distribution discussed in detail above.

There has been considerable interest in the literature concerning the possible impacts of increased hydrogen levels on stratospheric chemistry, stemming from an increase in stratospheric water vapour levels. This literature is reviewed in some detail in section 3

above and no further comment is required here. However, Tromp et al. (2003) in their study of stratospheric ozone loss, went on to comment on the possible impact of increased hydrogen emissions on mesospheric chemistry. They asserted that an increase in mesospheric water vapour derived from increased hydrogen emissions could lead to an increase in noctilucent clouds, with potential impacts on the Earth's albedo and mesospheric chemistry. However, none of these impacts were quantified or commented on further by Tromp et al. (2003).

The combustion of hydrogen will inevitably lead to the production of water vapour in the troposphere. In this respect, however, hydrogen is no different to methane or petroleum-based fuels. No environmental consequences are anticipated from the release of water vapour into the troposphere from future hydrogen usage.

7. Assessment of the global atmospheric consequences of a theoretical exploratory hydrogen-based energy scenario

In this section, an illustrative scenario is assembled for the purposes of giving a sense of the scale of the potential global climate consequences of hydrogen leakage. The scope of the emissions considered is purposefully narrow and leaves out a number of potential emission sources for hydrogen other than those associated with the fugitive emissions of hydrogen. There are potentially significant emissions associated with the upstream process of getting input fuels for the SMR process, electricity grid emissions and infrastructure commissioning and decommissioning that are beyond the scope of the present review and assessment. Hence, this section is not attempting to make statements about the likely emissions that could be associated with hydrogen use in the UK. It is merely attempting to give some scale to the global warming consequence of hydrogen leakage by comparing them to the UK combustion emissions from natural gas.

The analysis begins by examining the role of natural gas in the UK domestic sector in 2011. This sector accounted for 293,400 GWh of energy consumption (Table 4.1, DUKES, 2013) as natural gas which was equivalent to 1056 PJ, using the conversion factor 3.6×10^{-3} PJ per GWh (pp19, DUKES, 2013)

Using the CO₂ emission factor for natural gas of 0.184 kg CO₂ per kWh (pp. 230, DUKES, 2013), then natural gas consumption in the UK domestic sector in 2011 emitted 54.0 million tonnes CO₂ from the combustion products alone, ignoring the radiative forcing impacts from the methane released from natural gas leakage. Based on the UK Greenhouse Gas Inventory (BEIS, 2017), the radiative forcing impacts of natural gas leakage are estimated to be of the order of 5 million tonnes CO₂ equivalent annually, or about 5% of the radiative forcing from the combustion products. At this stage, any radiative forcing impacts from natural gas leakage have been ignored and attention has been focussed on the radiative forcing impacts of its CO₂ combustion products.

If this 2011 domestic sector energy consumption were to be supplied on some future date by a low-carbon hydrogen system supplying hydrogen with an energy content of 142.18 MJ per kg (Argonne National Laboratory, 2008) instead of natural gas, then 7.43 million tonnes of hydrogen would be required annually.

If this future hydrogen system was a perfectly sealed system with no leakage then it would save the entire 54.0 million tonnes of CO₂ per year, that is to say, the low-carbon hydrogen system offers the potential for generating savings in greenhouse gas emissions of 54.0 million tonnes of CO₂ per year.

If there were to be significant atmospheric leakage of hydrogen from the production, distribution and end-use in the low-carbon system then the indirect global warming from hydrogen would reduce or offset some of the above savings in greenhouse gas emissions. This reduction or offsetting can be estimated using the megatonne equivalence or GWP for hydrogen which is 4.3 megatonnes of CO₂ per megatonne of hydrogen. On this basis, if there were to be a 1% leakage rate by mass, then this hydrogen would have an equivalent global warming of 0.32 million tonnes CO₂, reducing the savings in greenhouse gas emissions from 54.0 to 53.7 million tonnes CO₂ per year, that is by 0.6%.

Despite the uncertainties in the CO₂ equivalence of hydrogen, the available results are, however, considered adequate to begin an initial policy analysis of the global atmospheric impacts of hydrogen within BEIS.

8. Conclusions

Hydrogen is a clean fuel that may well have an important role in future low-carbon energy systems. There is the possibility that increased hydrogen usage may cause damage to the ozone layer and may bring on climate change. Although there are only a few studies and the uncertainties within them are large, the available results show that these global atmospheric impacts are likely to be small. The studies are thought to be adequate enough to begin an initial policy analysis of the global environmental impacts of hydrogen within BEIS.

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