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**Evaluation of the Potential Environmental Impacts from
Large-Scale Use and Production of Hydrogen in Energy and
Transportation Applications**

Final Report

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Table of Contents

Executive Summary	page 3
Acknowledgments	page 10
Emissions Scenario Development	Section 1 (page 11)
Tropospheric Impact Assessment	Section 2 (page 37)
Stratospheric Ozone Impact Assessment	Section 3 (page 91)
Regional Air Quality Impact Assessment	Section 4 (page 127)
H ₂ Microbial Adaptive Soil Sink Assessment	Section 5 (page 161)
Integrated Assessment Model	Section 6 (page 167)
Oxygen Plume Risk Assessment	Section 7 (page 177)
Metal Embrittlement Risk Assessment	Section 8 (page 183)

Executive Summary

Project Objective:

The purpose of this project was to systematically identify and examine possible near and long-term ecological and environmental impacts from the use of hydrogen in future road transportation and power applications. The project involved modeling, data analysis and some field and laboratory experiments. This project was aimed at an end-to-end analysis of the potential ecological and environmental impacts of transitioning to a hydrogen-based road transportation sector.

Background:

There is limited quantitative understanding of the projected market penetration, the changes in emissions avoided or gained upon transitioning to hydrogen-based systems, and on the resulting impacts on the environment. Our project team is composed of scientists, engineers, and economists that have the right blend of expertise and tools to appropriately attack the issues we will face in this assessment.

The specific objectives include analyses to address the following:

- Impact of hydrogen releases on the oxidative capacity of the atmosphere
- Long-term stability of the ozone layer due to changes in hydrogen emissions
- Impact of hydrogen emissions and resulting concentrations on atmospheric chemistry and climate
- Impact on microbial ecosystems involved in hydrogen uptake
- Role of biological impacts in causing indirect effects on the atmosphere and climate

- Criteria pollutants emitted given different scenarios of vehicle market penetration
- Impact of criteria pollutants on human health, air quality, ecosystems and structures under different penetration scenarios

Using a state-of-the-art model of the energy-technology-economy system (MiniCAM) along with other analyses, we evaluated changes in emissions due to hydrogen technologies and uses. We evaluated the effects of hydrogen on all aspects of atmospheric chemistry and composition using state-of-the-art three-dimensional global models of atmospheric chemistry and physics (models used: CAM-chem, CMAQ, MOZART). Through field and laboratory studies, we gained new insights into the relationships affecting soil uptake and the impacts on ecosystems. Analyses were carried out, under various assumptions of hydrogen concentrations, of the effect of the potential of hydrogen to degrade materials and structures.

Summary of Future H₂-Based Road Transportation Sector Impact Assessment Findings

- **High and low 2050 emissions scenarios that bracket possible future emissions were developed.** Emissions scenarios were developed for 2050 based on the IPCC high-emitting A1FI and low-emitting B1 growth scenarios and two hydrogen technology adoption scenarios (fuel cell (FC) and internal combustion engine (ICE) technologies). Our basic assumptions are that the hydrogen for road transportation is produced cleanly and renewably, e.g., with wind, solar, or nuclear power, that all road-based transportation switches to H₂, and that in 2050 the efficiency of fuel cells and internal combustion engines will be comparable. The implications of these assumptions as well as the sensitivity of the emissions to these assumptions are explored in the full

report. With the adoption of an H₂ based road transportation sector H₂ emissions increase due to H₂ leakage (by ~4 times for the A1FI and ~7 times for the B1 scenarios; however, the total H₂ emissions increase only ~1.8 times for the A1FI and ~1.6 times for the B1 scenarios) and fossil fuel combustion related emissions decrease (e.g., CO decreases by 25% and 9% and NO_x decreases by 29% and 24% for the A1FI and B1 scenarios, respectively). Even with the emissions changes the absolute emissions for the B1 scenarios are lower than those for any of the A1FI scenarios. There are still large uncertainties in future H₂ emissions since these depend on many factors with large uncertainties, e.g., leakage rates, fuel cell and internal combustion engine efficiency improvements, and growth in population and energy demand. Our assumptions were conservatively chosen to represent the higher end and larger impact H₂ emissions.

- **There is a general improvement in tropospheric air quality with the adoption of an H₂ fuel cell powered transportation sector.** Annual mean global ozone burdens decrease by 7% and 1% for the A1FI-FC and A1FI-ICE scenarios and 5% and 1% for the B1-FC and B1-ICE scenarios. Summertime ozone concentrations decrease by ~15 ppb over population centers. The annual mean global CO burden decreases by 14% and 18% for the A1FI-FC and A1FI-ICE scenarios by 4% and 7% for the B1 scenarios. There are also substantial decreases in soot and sulfate aerosols. However, H₂ burdens increase by ~40% and ~20% for the A1FI and B1 scenarios respectively. There is also a decrease of ~4% in OH radical concentrations, and hence the oxidizing power of the troposphere, for both the A1FI and B1 fuel cell technology scenarios. OH concentrations actually increase by 7% and 3% for the A1FI-ICE and B1-ICE scenarios, respectively. For the A1FI-FC scenario about one half of the OH decrease is due to the H₂ increase and the other half due to the changes in other fossil fuel combustion emissions and decrease in O₃ concentration. The decrease in the oxidizing capacity of the troposphere

could increase the lifetime of methane, a potent greenhouse gas. However, this trade off must be evaluated against the improvements in air quality and could be somewhat ameliorated by decreasing H₂ leakage emissions. Though the adoption of an H₂ based road transportation sector improves air quality to some degree for both H₂ fuel cell and H₂ internal combustion engine technology in both the A1FI and B1 scenarios, for all of the gaseous pollutants the improvements due to the adoption of H₂ as a fuel are smaller than those achieved by following the lower emitting B1 growth path instead of the higher emitting A1FI growth path.

- **A Future H₂ based road transportation sector may adversely impact stratospheric ozone but total ozone levels would still be higher than current levels due to recovery of CFC induced ozone loss.** The impact of an H₂-based road transportation sector on stratospheric ozone depends on the H₂ scenario examined. Global annual mean stratospheric ozone burdens decrease by 0.5% for the A1FI-FC scenario, 0.2% for the A1FI-ICE and B1-FC scenario and increases by 0.04% for the B1-ICE scenario. The largest relative decreases generally occur in the tropical upper troposphere and lower stratosphere. These changes are caused by a combination of increased HO_x concentrations and decreased NO_x concentrations and the interaction between the HO_x and NO_x ozone chemistry. Put in context, the possible adverse impact on stratospheric ozone (up to 0.5% decrease) is considerably less than the ~3% decrease throughout the 1980s and 1990s due to chlorofluorocarbon (CFC) caused ozone destruction. In addition by 2050 ozone levels likely will have substantially recovered from the CFC induced ozone loss and even with the possible ozone loss from the adoption of an H₂ based road transportation sector, stratospheric ozone levels would be greater than they are today.
- **Substantial improvements in U.S. regional air quality are possible for a future H₂ based road transportation sector.** There are substantial

improvements in all of the key air quality indicators (e.g., O₃, NO_x, PM 2.5, CO, PAN) in a future fuel cell powered H₂ based transportation sector. Most of these improvements occur during times of maximum concern about pollution thereby enhancing the efficacy of improvements in terms of regulatory and health impacts. For example, the largest O₃ reductions occur during summertime when O₃ concentrations are typically highest. Although there are many substantial uncertainties in predicting the future impacts of an H₂ powered road transportation sector in 2050 some inferences appear to be robust. For all H₂-FC scenarios substantial air quality improvements were observed. This robust conclusion is directly due to the emissions reductions and independent of growth scenario and season. The absolute air quality differences between the A1Fi and B1 growth scenarios are typically larger than the differences between technology scenarios, e.g., the air quality in a B1 type scenario is generally better than in any A1Fi scenario regardless of H₂ technology adoption or not. In other words, a societal move away from fossil fuel use to alternative energy and transportation choices is generally better for air quality than remaining heavily fossil fuel intensive. If H₂-ICE technology is adopted there are relatively small improvements in some key air quality species, e.g., O₃, NO_x, PAN, and less improvement in PM 2.5 air quality than in the H₂-FC technology case.

- **Enhanced H₂ soil microbial uptake may mitigate future H₂ concentration increases.** Soil microbes play a major role in the global hydrogen (H₂) cycle, accounting for about 80% of the H₂ removed from the current atmosphere. Our laboratory results suggest there would be a significant stimulatory effect on the H₂ uptake by soils at increased atmospheric H₂ concentrations expected with the adoption of an H₂-based road transportation sector. In our simulations this decreases tropospheric H₂ concentrations by over 20% over the non-enhanced sink. This negative feedback to increasing H₂ concentrations would

also tend to ameliorate the adverse impact of an H₂ based road transportation sector on stratospheric ozone.

- **An H₂ integrated assessment model allows quick scientifically-based assessment of climate impacts.** An integrated assessment model (IAM) has been developed to allow easy estimates of the impact of the adoption of an H₂ powered road transportation sector. The IAM is based on the global model simulations with comprehensive chemistry used for the tropospheric and stratospheric impact analysis. It will allow the emissions, atmospheric chemical concentrations, and radiative forcings to be determined for a user selected market penetration of one of the scenarios examined here (A1FI-FC, A1FI-ICE, B1-FC, B1-ICE). It will output data tables and figures for each of the species of interest (H₂, O₃, CO, NO_x, OH, column O₃, CO₂) as latitude x longitude surface plots, zonal mean altitude x latitude plots, or time series plots. The IAM is based on the distilled science of the sophisticated global chemistry transport models but allows the exploration of H₂ adoption scenarios in minutes instead of the weeks to months necessary for the full chemistry model simulations.
- **Oxygen plumes from H₂ production may increase the risk of fire in close vicinity of the electrolysis facility and should be assessed on a case by case basis.** Oxygen (O₂) is a by-product of the production of hydrogen via water electrolysis. With the large scale production of H₂ it is likely that this oxygen will be released to the atmosphere and these increased oxygen concentrations could increase the risk of fire occurrence and spread. The energy demand for the entire U.S. transportation system in 2002 was estimated to be 26.5 Quads. We assume that future road transportation will be roughly equal to this value. The corresponding O₂ production is $\sim 5 \times 10^4 \text{ kg sec}^{-1}$. Assuming there are 100 H₂ factories with equal production capacities distributed throughout the U.S,

each would release $\sim 500 \text{ kg O}_2 \text{ sec}^{-1}$. This oxygen is assumed to be released from an 80m high stack. A 5% volume increase in oxygen concentration causes a significant increase in fire spread; therefore we take this as a threshold for a significant impact of oxygen from a large-scale electrolyzer. While this threshold is not exceeded under most conditions, under stagnant atmospheric conditions this threshold could be exceeded for up to $\sim 2\text{km}$ downwind of the facility. Though there are many uncertainties and unknowns about the details of the facilities this study points to the necessity of more detailed site and plant specific assessment once the details of future plant design are known.

- **Hydrogen embrittlement of materials and structures not likely a threat.** Analysis of the predicted levels of atmospheric hydrogen combined with an extensive theoretical and experimental analysis of hydrogen embrittlement mechanisms in metals shows that the hydrogen road transportation sector does not represent a threat. The primary concern in a hydrogen economy would be in pressurized storage vessels and pipelines where metals are exposed to high pressures of pure hydrogen for extended times. Knowing this, designs can be adopted and specific metals chosen to reduce or practically eliminate concerns. We therefore conclude that hydrogen embrittlement of metals does not pose a threat to structures or devices under normal circumstances.

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Section 1

Scenarios for Hydrogen and Other Emissions from Hydrogen-Based Transportation Systems

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Introduction

The heavy reliance on fossil fuels in energy and transportation systems have led to a number of environmental issues including impacts on air quality, human health, agriculture, and ecosystems. Hydrogen (H_2) is being considered as the key fuel for energy and transportation systems of the future because it potentially offers a cleaner and more efficient energy carrier than fossil fuels. The vision for a hydrogen economy is based on the expectations that hydrogen can be produced from domestic energy sources in a manner that is affordable and environmentally benign and that H_2 powered vehicle emissions of water and limited amounts of hydrogen would displace fossil fuel combustion byproduct emissions. In order to identify and examine possible near and long-term environmental effects from large-scale use of hydrogen in transportation systems, particularly to evaluate the global atmospheric chemical and climate effects of the switch to a hydrogen economy in the future, we have developed several emissions scenarios for the year 2050 with and without an H_2 based transportation sector. These emissions scenarios were prepared for our atmospheric model simulations to evaluate the atmospheric impact of a possible future H_2 -based transportation sector using the CAM-Chem and MOZART chemistry transport models. Future emissions depend on many highly uncertain factors, for example, population growth, economic growth and technological advances. Given the large uncertainties in these factors (e.g., IPCC SRES 2000) we have chosen to evaluate a range of scenarios encompassing different growth paths and technological options. Two growth paths were selected based on the Intergovernmental Panel on Climate

Change (IPCC) low emitting (B1) and high emitting (A1FI) scenarios for 2050. These scenarios were chosen because they span the range of the IPCC scenarios.

The base case emissions for the year 2000 use the standard CAM-Chem and MOZART emissions files which are based on the well established POET (Precursors of Ozone and their Effects on the Troposphere) emissions database with some additions. We estimate H₂ leakage emissions using a top down approach based on an H₂ leakage rate and the amount of H₂ needed to meet projected transportation energy requirements.

Here we present our method of calculating the emissions scenarios used in our modeling studies, apply this method to current (year 2000), A1FI 2050, and B1 2050 scenarios and compare the resulting H₂ emissions with other published estimates.

Emission Scenarios

Road transportation systems are likely to make the easiest transition to hydrogen power. We focus on two H₂ adoption pathways for each of the IPCC B1 and A1FI growth scenarios: 1) the development and implementation of hydrogen fuel cell engines and 2) the use of hydrogen in internal combustion engines (ICE).

Following the upper-bound market penetration case created by the committee of “The Hydrogen Economy: Opportunities, Costs, Barriers, and R &D Needs” (The Hydrogen Economy, NRC, 2004), hydrogen vehicles are assumed to capture 100% of the fuel light-duty vehicles (cars and light trucks) market for new vehicles in 2038, and to reach 100% fraction of total vehicle miles in 2050, in the United States. The committee focus was on light-duty vehicles, the largest segment of the vehicle market, with the aim of gaining a sense of the potential quantitative significance of a transition to hydrogen. Though hydrogen applications of heavy-duty vehicle, e.g. diesel trucks, are not discussed in this report, it mentions that hydrogen has an optimistic potential for usage in US and Japan over the next few decades and in Europe, although diesel engines will also be used in the next decades. Here we assume all road transportation in the world will switch to hydrogen by year 2050 to examine the maximum potential impact of an H₂ based transportation economy. We examine two cases: 1) all future

road transportation use hydrogen-fueled fuel cells, such that there will be no emissions from fossil fuel combustion byproducts (CO, NO_x, SO₂, VOC, Soot, etc.) from land transportation and 2) all future road vehicles use hydrogen-fueled internal combustion engines, such that while there are no associated CO, VOC, SO₂, or soot emissions, NO_x is still emitted from the high temperature ICE combustion process. As a sensitivity study we also evaluate the impact of H₂ leakage with no concurrent decrease in other emissions. This scenario, though not realistic, allows us to isolate the impact of hydrogen alone on atmospheric chemistry.

Each of these cases is evaluated for the A1FI fossil fuel intensive scenario which contains higher emissions and the B1 technology/environment intensive scenario which contains lower emissions. In this report and the follow up reports that evaluate the impact of these emissions scenarios the scenarios will be referred to as IPCC_scenario Hydrogen_Society_option, where Hydrogen_Society_option is one of: 1) HS0 which refers to the baseline emissions scenario, 2) HS1 which refers to the scenario with additional H₂ leakage emissions from an H₂-based transportation sector, 3) HS2 which refers to the fuel cell technology option and includes H₂ leakage emissions and a corresponding reduction of emissions of all road transportation fossil fuel combustion byproducts, or 4) HS3 which refers to the H₂ internal combustion engine option and includes H₂ leakage emissions and a corresponding reduction of emissions of all road transportation fossil fuel combustion byproducts except NO_x. (Note that in the following reports these scenarios have been renamed as follows: HS0 = Baseline, HS2 = H₂-FC, and HS3 = H₂-ICE.)

Methods

Baseline Emissions

The main global emissions inventory used here for the current (year 2000) atmosphere is POET which is based on version 3 of the Emission Database for Global Atmospheric Research (EDGAR) inventory (Granier et al., 2005, Olivier et al., 2003). Biomass burning emissions are from the Global Fire Emissions Database version 2 (GFED-v2) (Van der Werf GR et al., 2006). The fossil/biofuel SO₂ emissions are

taken from the EDGAR-FT2000 database and volcanic SO₂ emissions are from the Global Emissions Inventory Activity (GEIA) (Graedel et al., 1993) database. Soot emissions including its road transportation fraction are from Tami Bond (personal communication). These emission totals are shown in Table 1 broken down by road transportation, all fossil fuel (which includes transportation), other, and total. Since the road transportation H₂ component is not contained in the POET database we estimated it using the mass emission ratio of H₂:CO (0.03) from fossil fuel combustion and CO road transportation emissions (192.6 Tg/r) from POET. Note that there is a relatively large uncertainty in the H₂: CO mass emission ratio from fossil fuel use including automobile traffic. Estimates range from 0.01 (Simmonds et al., 2000) to ~0.07 (Seiler and Zankl, 1975). Other estimates are 0.025-0.032 (Barnes et al., 2003) and 0.026-0.043 (Vollmer et al., 2007). For this study we have chosen to use a mid-value of 0.03 and assume it remains constant through time.

The future baseline (non H₂ road transportation sector) emissions were calculated by scaling these current fossil fuel emissions by growth factors from the IPCC scenarios.

$$[\text{Future}] = (\text{Future_scale_factor} / \text{Current_scale_factor}) * [\text{Current}]$$

The brackets [] in the above equation indicate an emissions map array for a given specie, e.g., NO_x, CO, SO₂ and several NMVOCs: CH₃COCH₃, C₄H₁₀, C₄H₈, C₁₀H₁₆, C₂H₄, C₂H₅OH, C₂H₆, C₃H₆, C₃H₈, CH₂O, CH₃CHO, CH₃OH, ISOP, MEK, TOLUENE. For H₂ and soot which are not included in the IPCC scenarios, we used the CO scale factors. All other emissions, e.g., from ocean, biogenic emissions, biomass burning, remain at their current (year 2000) levels. Emissions for these scenarios are shown in Tables 2 and 3 for the A1FI and B1 scenarios respectively, and the region dependent fossil fuel emissions scale factors are shown in Tables 4 and 5. Note that for all of our model simulations CAM-Chem and MOZART used the same emissions species with the exception of SO₂ and soot which are not included in MOZART.

Emissions from an H₂ Based Transportation Sector

For the H₂ based transportation sector emissions scenarios we remove the road/land transportation portion of the emissions from fossil fuel combustion, e.g., H₂, CO, VOCs, NO_x, SO₂, and soot for the fuel cell technology and H₂, CO, VOCs, SO₂, and soot for the ICE technology option, and then add in the H₂ emissions due to leakage.

For our assessment we used a leakage rate of 2.5%. However, confidence in the current knowledge of hydrogen leakage rates is low and we are not aware of any real-world measurements of leakage rates. To date, most leakage rate estimates are based on natural gas leakage rates of about 1% and the assumption that since hydrogen is a smaller more diffusive molecule than methane (the primary component of natural gas) its leakage rate will be higher. Current estimates tend to be in the 1% to 4% range (e.g., Schultz et al., 2003, Colella et al., 2005), though much larger rates have been used in some studies (e.g., Tromp et al., 2003). Knowledge of actual leakage rates, their dependence on technological sophistication, and how they will change in the future is one of the key uncertainties in estimating future atmospheric hydrogen emissions.

We assume all road transportation will use hydrogen in the future such that H₂-powered vehicles will consume the same amount of energy as would the year 2050 "business-as-usual" fleet assumed in the IPCC SRES A1FI and B1 scenarios (IPCC, 2000 & 2001).

Transportation energy requirements for the current (year 2000), A1FI, and B1 scenarios (Table 6) were calculated with the MiniCAM energy-technology-economics models (e.g., Edmonds et al., 2004a, b). The MiniCAM model considers population, GNP/GDP, energy use, land use, anthropogenic emissions, and other factors and has been used extensively in IPCC evaluations and other reports (e.g., IPCC 2000, CCSP 2007, WMO 2007). The transportation energy requirements were broken down by liquid, gas, electric fuel, and other types. We assumed a 100% conversion efficiency

between H₂ and liquid and gas fuel types and a 50% transformation efficiency from H₂ to electricity.

The energy density of hydrogen is nearly the same in all fuels (Thomas, 2000). The energy density, also called the energy content of H₂, is 39.4 kWh (higher heating value (HHV)) and 33.3 kWh (lower heating value (LHV)), equal to 142MJ/kg (HHV) and 120 MJ/kg (LHV), respectively. This means that every 1kg of mass of H₂ has an energy value of 142EJ (HHV) and 120 EJ (LHV). Here, we use 120 MJ/kg (Thomas, 2000) for calculation of H₂ demand to achieve an upper limit on the H₂ emission flux.

Thus the total H₂ demand (Table 6) is given by

$$\text{H}_2 \text{ Demand} = (\text{Liquid} + \text{Gas} + \text{Electric}/50\%) / (120 \text{ MJ/kg})$$

where Liquid, Gas, and Electric are the transportation energy requirements in MJ and 50% is the H₂ to electric conversions efficiency. Of this transportation energy demand we assume that 80% is used for road transportation based on current usage (IPCC 2007). Current fuel cell vehicles are nearly 2.5 times more efficient than gasoline powered ICE vehicles (IPCC 2007) while for diesel powered ICE vehicles this value is much lower. There is much room for improvement in ICE efficiencies with technological advances and materials, and in all IPCC scenarios (e.g., A1FI, A1B, B1, etc.) energy efficiency will increase in year 2050, although to different extents. Therefore we assume that in 2050 fuel cell and ICE vehicles will have comparable efficiencies. It should be noted that while we have assumed that H₂ fuel cell and ICE vehicle efficiencies will be equal in 2050 other projections including those from DOE assume that fuel cells will maintain an efficiency advantage over ICE through year 2050, e.g., DOE projections assume an internal combustion engine vehicle efficiency of 40% and fuel cell vehicle efficiency of 60% in 2050. The impact of these different efficiency assumptions, which would decrease our H₂ leakage estimates, is discussed in detail below. Assuming a 2.5% leakage rate the total leakage emissions are shown in Table 6. The total H₂ leakage emissions were distributed

according to the current CO₂ road transportation emissions from the EDGAR 32FT2000 (Granier et al., 2005, Olivier et al., 2003) emissions inventory.

Results and Discussion

In this section we present and examine the H₂ 2050 emissions scenarios developed using the method detailed above focusing particularly on the changes that result from the adoption of the various H₂ usage scenarios. Since there are no published estimates of future emissions changes from the adoption of an H₂-based transportation sector, we then apply the method to year 2000 (current) emissions in order to compare with other estimates and evaluate of how this method performs. Note that the calculation of the impact on current emissions is for comparison only and these scenarios are not evaluated in the impact assessment.

2050 Scenario Emissions

The total speciated emissions for each of the scenarios is then created from the data in Tables 2-3 which describe the baseline HS0 emissions and Table 6 which presents H₂ leakage estimates for the A1FI and B1 scenarios (HS1, HS2, and HS3). For example, total emissions for the HS2 fuel cell adoption scenarios are obtained by removing all of the road transportation emissions from the HS0 baseline scenario and then adding the H₂ leakage emissions while total emissions for the HS3 ICE adoption scenarios are obtained by removing all of the road transportation emissions except NO_x from the HS0 baseline scenario and then adding the H₂ leakage emissions.

The A1FI and B1 scenarios have vastly different total emissions in 2050 due to their somewhat diametrically opposed assumptions about future growth and technology. For every category of emissions the A1FI scenario in 2050 has higher emissions than today while for the B1 scenario in 2050 the emissions of most species are projected to decrease or stay nearly the same as current levels (Figure 1). NO_x total emissions in the A1FI HS2 fuel cell adoption scenario are nearly twice as large as in the B1 HS2 fuel cell adoption scenario.

However there are many common general features in the emissions too. For each specie the emissions distributions in each technology scenario (HS0, HS1, HS2, and HS3) have similar patterns. The geographical distributions of the emissions in the A1FI and B1 scenarios are similar for some species, e.g., H₂ and NO_x, with larger emissions over more densely populated areas such as the eastern United States, western Europe, and parts of India and Eastern China (e.g., Figures 2 and 3). For some other species, e.g., CO (Figure 4) natural emissions from oceans and soils also contribute leading to different distributions of emissions for these species. In the HS2 fuel cell adoption and HS3 ICE adoption scenarios the emissions decrease for most combustion-related species with the adoption of an H₂ powered road transportation sector since the road transportation emissions are removed in an H₂ economy. For example, in 2050, CO global emissions decrease by 25% and 9% for the A1FI, and B1 both HS2 fuel cell and HS3 ICE adoption scenarios respectively and NO_x global emissions decrease by 29% and 24% respectively for the HS2 fuel cell adoption scenario (Table 8, Figure 1). Aerosol precursor emissions also decrease; SO₂ emissions decrease by 3% in both the A1FI and B1 scenarios and soot emissions decrease by 17% for the A1FI scenario and 8% for the B1 scenario (Table 8).

As noted earlier, H₂ leakage emissions depend directly on the assumptions about fuel cell and ICE vehicle efficiencies since these efficiencies determine the amount of fuel needed to power the vehicles and hence impact the amount of H₂ leaked which is a fixed percentage of the required H₂. Assuming equal efficiencies, H₂ emissions from road transportation increase about 4 times from 14.8 TgH₂/yr to 60.8 TgH₂/yr for the A1FI scenario and nearly 8 times from 3.2 TgH₂/yr to 24.0 TgH₂/yr for the B1 scenario (Tables 2-3, 6). Although the relative increase is larger in the B1 scenario the absolute emissions in the B1 scenario are still substantially smaller than in the A1FI scenario. The total H₂ emissions increase by nearly 60% for both the B1 and A1FI scenarios, however the absolute total emissions are nearly twice as large in the A1FI scenario (102.6 TgH₂/yr) than the B1 scenario (53.2 TgH₂/yr).

If we instead adopt a 1.5 ratio of fuel cell to ICE vehicle efficiency (60% / 40%) the H₂ leakage emissions decrease by 33.3% ($1 - 1.0/1.5$) to 40.5 TgH₂/yr and 16

TgH₂/yr for the A1FI and B1 scenarios respectively (Table 7). The total H₂ emissions decrease by ~20% for the A1FI scenario and ~15% for the B1 scenario. On the other hand, if we assume a current fuel cell to ICE efficiency ratio of ~2.9 (Collela et al, 2005) H₂ leakage emissions would decrease by nearly 66%.

An interesting question is at what point H₂ emissions from fossil fuel powered road transportation would equal those from H₂ fuel cell powered road transportation. As discussed earlier H₂ emissions from fossil combustion depend on the emission of H₂ for a given amount of fuel and the amount of fuel consumed, which depends, of course, on efficiency, while the H₂ leakage emissions depend on the leakage rate and amount of hydrogen required which depends directly the ratio of the efficiencies between fossil fuel and fuel cell vehicles and the amount of fuel required. Collela et al (2005) report a break even leakage rate of 3% for the current vehicle fleet but do not directly note the dependence on vehicle efficiency. Thus for converting the current (year 2000) fleet to fuel cell vehicles (with current efficiencies) the break even leakage rate would be 3.1% for the A1FI scenario and 3.5% for the B1 scenario (Table 12). However, for the 2050 scenarios the break even leakage rates are 0.6% and 0.3% for the A1FI and B1 scenarios respectively assuming equal efficiencies and 0.9% and 0.4% assuming a 60% to 40% fuel cell to ICE vehicle efficiency. Note that for each of these the product of the break even leakage rate and the ratio of efficiencies is constant and proportional to the total amount of energy needed for road transportation. While it is interesting to investigate the break even leakage rate for a given scenario, it is important to note its dependence on other factors, e.g., efficiencies, which will change over time. Therefore it is important to realize that the break even leakage percentage will not be constant between different scenarios.

Year 2000 H₂ emissions from fossil fuel combustion

Using the method described above we estimate that current global fossil fuel H₂ emissions are about 14.4 TgH₂/yr. This value is in good agreement with most other estimates (see Table 9 for a comparison of this estimate with other published estimates). Many of these other estimates are based on scaling CO emissions

estimates by measured H_2/CO emission ratios (similar to our method) but have used different CO inventories and emission ratios. These estimates generally fall in the 5-25 TgH_2/yr range (Table 9). Some estimates included more processes such as indirect emissions from residential heating, refineries and fertilizer production as fossil fuel related and have slightly higher estimates than ours, e.g., 20 TgH_2/yr (Sanderson et al., 2003), 15-20 TgH_2/yr (Derwent et al., 2006), and 18.3 TgH_2/yr (Price et al., 2007). Independent estimates based on isotopic methods give similar values, e.g., Rhee et al.'s (2006) estimate of 9-21 TgH_2/yr . The most recent work based on an exhaustive review of the literature estimates that fossil fuel H_2 emissions are in the range of 7-15 TgH_2/yr (Ehhalt and Rohrer, 2009).

Of the 14.4 TgH_2/yr global fossil fuel H_2 emissions we estimate that 6 TgH_2/yr are from road transportation. Though there are fewer estimates of only the road transportation portion of the fossil fuel H_2 emissions to compare with, early estimates suggested a wide range of 5-20 TgH_2/yr (Novelli et al., 1999) while more recent estimates generally fall into the 4-12 TgH_2/yr range (Table 10). The more recent estimates of 5.6 TgH_2/yr (Jacobsen, 2008) and 6 TgH_2/yr from this work both fall at the low end of the range (6-12 TgH_2/yr) given in Ehhalt and Rohrer's (2009) review paper. Ehhalt and Rohrer (2009) also point out that the slightly higher $H_2:CO$ emission ratios measured close to the sources are likely to be more representative of the actual emission ratio and that estimates made from measurements further from the source should be regarded as a lower limit. This applies to both of the more recent estimates.

H_2 emissions from converting the current road transportation sector to H_2 power.

Based on the B1 and A1FI scenarios for the year 2000 we estimate that H_2 emissions from an H_2 -powered transportation would be 12-14 TgH_2/yr for H_2 internal combustion scenarios (Table 6) assuming H_2 ICE and gasoline ICE have comparable efficiencies. For the HS2 fuel cell adoption scenario using current internal combustion engine efficiency (0.14 for gasoline, 0.31 for diesel, and 0.5 for fuel cell) and

assuming that the ratio of gasoline to diesel powered vehicles is 80% to 20%, the H₂ emissions from H₂-powered transportation would be 4.5-5.1 TgH₂/yr, which is less than 50% of the H₂ internal combustion scenarios. Though several studies have published H₂ emissions estimates for current H₂ economies very few have reported the transportation contribution separately (Table 11). In order to compare our estimate with these other estimates we obtain their H₂ road transportation emissions by scaling their H₂ total fossil fuel emissions (Table 11) using the road transportation energy demand fraction (20%~25%) for total fossil fuel energy (IPCC 2007, Evans 2007, Rodrigue et al., 2009) accounting for different H₂ leakage rates and different scenario assumptions (Scenario factor) between the other estimates and ours. This method is far from ideal and has large uncertainties but does allow the different estimates to be compared in a somewhat quantitative manner. Thus we estimate other road transportation emissions as H₂ road transportation emissions = H₂ total fossil fuel emissions * Scenario factor * Our H₂ leakage(2.5%) / H₂ leakage , where the “Scenario factor” is determined from different scenario key assumptions, for example, the fraction of which fossil fuels were converted to H₂ usage and the energy demand fraction used in road transportation.

Using this method we estimate that of the 60-120 TgH₂/yr total H₂ fossil fuel emissions suggested by Tromp et al. (2003) from replacing all oil and gasoline combustion by hydrogen fuel cells with 10~20% H₂ leakage that at least 11.5 TgH₂/yr would be due to road transportation (with a scenario factor of 0.48/0.50*0.8 since more than 48% of world gasoline or oil is used in road transportation today and gasoline accounts for 50% of total transportation energy use, and about 80% of total transport energy from road traffic (IPCC 2007)). We estimate transportation emissions of about 1.1~10.4 TgH₂/yr for the Schultz et al.(2003) scenario assuming a 0.20~0.25 scenario factor since 20%~25% of total fossil fuel energy used in transportation today (IPCC 2007, Evans 2007, Rodrigue et al., 2009). For Warwick et al. (2004) we estimate that 13~16.3 TgH₂/yr of the total fossil 26-312 TgH₂/yr are due to transportation with same scenario factor (0.20~0.25 for energy demand ratio of fossil fuel in transportation today). Similarly we estimate that 12.5~15.6 TgH₂/yr of

the total 25 TgH₂/yr fossil emissions of Derwent et al. (2006) are due to transportation, also using the same scenario factor (0.20~0.25). Thus our estimate of 12 to 14 TgH₂/yr for the H₂ internal combustion scenario appears to agree with these other estimates. In addition we estimate that the 4.8 TgH₂/yr H₂ road transportation emissions for a fuel cell powered fleet from Jacobsen (2008) would be ~4 TgH₂/yr when adjusted our 2.5% leakage rate. Thus our estimate of 4.5-5.1 TgH₂/yr H₂ emissions for the current fuel cell scenario is in fairly good agreement with the 4 TgH₂/yr estimate of Jacobsen (2008).

CO₂ emissions

In addition to reductions in other fossil fuel combustion related byproducts with the adoption on of an H₂ based transportation sector, there will also be large decreases in CO₂ emissions. Based on the energy demand for road transportation from different fossil fuel types (liquid, gas, electricity) (Table 6), and the lower heating value energy density for each fossil fuel type (liquid oil: 43 MJ/kg, gas: 38 MJ/kg, electricity (assuming coal generation): 24 MJ/kg), as well as the CO₂ yield from each fuel type (46/14 for liquid, 46/16 for gas, and 46/12 for electricity), we obtain CO₂ emissions from fossil fuel based transportation sector (Table 13). CO₂ emissions from fossil fuel based road transportation are 22.1 GtCO₂/yr for 2050 A1FI and 10.1 GtCO₂/yr for 2050 B1 scenario. Since we have assumed that H₂ is produced and distributed using non carbon emitting power sources there are no CO₂ emissions associated with hydrogen powered road transportation for both the 2050 A1FI and B1 scenarios. Total 2050 fossil CO₂ emissions decrease by 26.1% for the A1FI scenario and 23.5% for the B1 scenario upon switching to hydrogen powered road transportation.

Conclusions and Implications

We have developed a series of emissions scenarios to be used in model simulation to evaluate the environmental impact of transforming to an H₂ based road transportation sector in year 2050. Due to the large uncertainties inherent in predicting

growth and technology changes over time we have chosen scenarios based on IPCC scenarios that span the range of generally accepted possibilities. While H₂ emissions could increase substantially with the adoption of an H₂ based transportation sector in these scenarios, the emissions of key ozone and aerosol precursors would decrease: NO_x by 24% and 28%, CO by 9% and 25%, NMVOCs by 8% and 14%, and soot by 8% and 17% for the B1 and A1FI HS2 fuel cell adoption scenarios. By year 2050 CO₂ total fossil emissions would decrease by more than 20% in both A1FI and B1 hydrogen powered transportation societies (HS2 fuel cell and HS3 ICE adoption scenarios).

There are relatively large uncertainties in the H₂ emissions. These uncertainties are due to uncertainties in parameters and knowledge of how these parameters will change over time, e.g., H₂:CO emissions ratios, vehicle efficiency, and leakage rates. Uncertainty in growth paths is also a major factor as is evident from the differences between the B1 and A1FI based scenario emissions. In general, for this study we have chosen parameters that should provide a reasonable upper bound to the H₂ emissions. The choice towards the upper bound of the uncertainties was deliberate since increased atmospheric H₂ concentrations may have an adverse impact on stratospheric ozone. If fuel cell vehicles maintain their efficiency advantage into the future these emissions estimates would decrease proportionally to the ratio of efficiencies. There are also uncertainties in the magnitude of the changes in the other non-H₂ emissions. However for all expected possible scenarios emissions of these species decrease (or at worst remain unchanged as for NO_x in the HS3 ICE adoption scenario) which would tend to improve air quality metrics. These uncertainties, though real, are likely not as key to policy considerations since possible adverse impacts are more problematic than knowing precisely how much improvement will occur provided one is confident that improvement will occur.

References

Barnes, D. H., S. C. Wofsy, B. P. Fehrlau and E. W. Gottlieb. (2003), Hydrogen in the atmosphere: observations above a forest canopy in a polluted environment, *J. Geophys. Res.*, Vol.108, No. D6, 4197, doi:10.1029/2001JD001199.

CCSP (2007), Scenarios of Greenhouse Gas Emissions and Atmospheric Concentrations. U.S. CCSP Synthesis and Assessment Product 2.1a.

CCSP (2007), Global-Change Scenarios: Their Development and Use. U.S. CCSP Synthesis and Assessment Product 2.1b.

Colella, W. G., M. Z. Jacobson, and D. M. Golden (2005), Switching to a US hydrogen fuel cell vehicle fleet: The resultant change in emissions, energy use and GHGs, *J. Power Sources*, 150, 150-181.

Derwent, R., P. Simmonds and S. O'Doherty, A. Manning and W. Collins, D. Stevenson (2006), Global environmental impacts of the hydrogen economy. *Int. J. Nuclear Hydrogen Production and Applications*, 1, 1, 57-67.

Edmonds, J., J. Clarke, J. Dooley, S. H. Kim, S. J. Smith (2004a), Stabilization of CO₂ in a B2 World: Insights on The Roles of Carbon Capture and Disposal, Hydrogen, and Transportation Technologies. *Energy Economics*, 26, 517-537.

Edmonds, J. A., J. Clarke, J. Dooley, S. H. Kim, and S. J. Smith (2004b), Modeling greenhouse gas energy technology responses to climate change. *Energy*, 29, 1529-1536.

Ehhalt, D.H. and F. Rohrer (2009), The tropospheric cycle of H₂: a critical review, *Tellus*, 61B, 500-535.

Evans, R.L. (2007), *Fueling our future: an introduction to sustainable energy*, Cambridge University Press, Cambridge, UK.

Graedel, T. F., T. S. Bates, A. F. Bouman, D. Cunnold, J. Dignon, I. Fung, D. J. Jacob, B. K. Lamb, J. A. Logan, G. Marland, P. Middleton, J. M. Pacyna, M. Placet, and C. Veldt (1993) A compilation of inventories of emissions to the atmosphere. *Global Biogeochem. Cycles*, 7: 1-26.

Granier, C., J. F. Lamarque, A. Mieville, J. F. Muller, J. Olivier, J. Orlando, J. Peters, G. Petron, G. Tyndall, S. Wallens (2005), POET, a database of surface emissions of ozone precursors, <http://www.aero.jussieu.fr/projet/ACCENT/POET.php>.

Hauglustaine, D.A., and D.H. Ehhalt(2002) A three-dimensional model of molecular hydrogen in the troposphere, *J. GEOPHYS. RES.*, Vol.107, No.D17, 4330.

IPCC (2001), *Climate Change 2001, The Scientific Basis*. Contribution of Working Group 1 to the Third Assessment Report of the IPCC, Cambridge University Press, Cambridge, UK and New York, USA.

IPCC (2007), *Climate change 2007: Mitigation of Climate Change*. Contribution of Working Group III to the Fourth Assessment Report of the IPCC, Cambridge University Press, Cambridge, UK and NY, USA.

Jacobson, M. Z., W. G. Colella, and D. M. Golden (2005), Cleaning the air and improving health with hydrogen fuel-cell vehicles. *Science*, 308, 1901-1905.

Jacobson, M.Z. (2008), Effects of wind-powered hydrogen fuel cell vehicles on stratospheric ozone and global climate, *Geophys. Res. Lett.*, Vol.35, L19803.

Nakicenovic, N., et al. (2000), *IPCC Special Report on Emissions Scenarios (SRES)*, *Special Report on Emissions Scenarios*. Working Group III, IPCC, Cambridge University Press, Cambridge, 2000.

Novelli, P. C., P. M. Lang, K. A. Masarie, D. F. Hurst, R. Myers (1999). Molecular hydrogen in the troposphere: global distribution and budget. *J. Geophys. Res.* 104, 30 427–30 444.

Olivier J., J. Peters, C. Granier, G. Petron, J.F. Muller, and S. Wallens (2003): Present and future surface emissions of atmospheric compounds, POET report #2, EU project EVK2-1999-00011.

Olivier, J.G.J., J.A. Van Aardenne, F. Dentener, L. Ganzeveld, and J.A.H.W. Peters (2005). “Recent trends in global greenhouse gas emissions: regional trends and spatial distribution of key sources”, in *Non-CO2 Greenhouse Gases (NCGG-4)*, A. van Amstel (coord.), page 325-330. Millpress, Rotterdam, ISBN 90 5966 043 9.

Price, H., L., Jaegle, A. Rice, P. Quay, P. C. Novelli (2007), Global budget of molecular hydrogen and its deuterium content: constraints from ground station, cruise, and aircraft observations. *J. Geophys. Res.* 112, D22108, doi:10.1029/2006JD008152.

Rhee, T. S., C. A. M. Brenninkmeijer, and T. Röckmann (2006). The overwhelming role of soils in the global atmospheric hydrogen cycle. *Atmos. Chem. Phys.* 6, 1611–1625.

Rodrigue Jean-Paul, Claude Comtois, Brian Slack (2009), *The Geography of Transport Systems*, ISBN: 978-0-415-48324-7, Routledge.

Sanderson, M. G., W. J. Collins, R. G. Derwent, and C. E. Johnson(2003). Simulation of global hydrogen levels using a Lagrangian threedimensional model. *J. Atmos. Chem.* 46, 15–28.

Schultz, M., T. Diehl, G. Brasseur, and W. Zittel (2003), Air pollution and climate-forcing 2000.impacts of a global hydrogen economy. *Science*, 302, 624-627.

Seiler, W. and Zank, H. (1975), Die Spurengase CO und H₂ über München. *Umschau* 75(23), 735-736.

Simmonds, P.G., R.G. Derwent, S. O'Doherty, D.B. Ryall, L.P. Steele, R.L. Langenfelds, P. Salameh, H.J. Wang, C.H. Dimmer, L.E. Hudson(2000), Continuous high-frequency observations of hydrogen at the Mace Head baseline atmospheric monitoring station over the 1994-1998 period. *J. Geophys. Res.*, 105(D10), 12105-12121.

Steinbacher, M., A. Fischer, M. K. Vollmer, B. Buchmann, S. Reimann (2007), Perennial observations of molecular hydrogen (H₂) at a suburban site in Switzerland. *Atmos. Env.* 41, 2111-2124.

Thomas George (2000): Overview of Storage Development DOE Hydrogen Program , Hydrogen Program Review, San Ramon, CA.

Tromp, T., R. Shia, M. Allen, J. Eiler, and Y. Yung (2003), Potential environmental impact of a hydrogen economy on the stratosphere. *Science* 300, 1740-1742.

Van der Werf, G.R., J. T. Randerson, L. Giglio, G. J. Collatz, P. S. Kasibhatla, A. F. Arellano(2006), Interannual variability in global biomass burning emissions from 1997 to 2004, *Atmos. Chem. Phys.* 6: 3423-3441 AUG 21.

Vollmer, M.K., N. Juergens, M. Steinbacher, S. Reimann, M. Weilenmann, B. Buchmann (2007), Road vehicle emissions of molecular hydrogen (H₂) from a tunnel study. *Atmos Environ*, 41:8355-69.

Warwick, N. J., S. Bekki, E. G. Nisbet, and J. A. Pyle (2004), Impact of a hydrogen economy on the stratosphere and troposphere studied in a 2-D model. *Geophys. Res. Lett.*, 31, doi:10.1029/2003GL019224.

World Meteorological Organization (WMO) (2007), *Scientific Assessment of Stratospheric ozone: 2006*. WMO Global Ozone Research and Monitoring Project – Report No. 50, Geneva, Switzerland.

Xiao, X., R. G. Prinn, P. G. Simmonds, L. P. Steele, P. C. Novelli(2007), Optimal estimation of the soil uptake of molecular hydrogen from the Advanced Global

Atmospheric Gases Experiments and other measurements. *J. Geophys. Res.* *112*, D07303, doi:10.1029/2006JD007241.

Table 1. Year 2000 emissions for different species based on the POET emissions database with additions as described in the text. Note that total fossil emissions include road transportation emissions. Units are Tg/yr except as noted.

Specie	Road Transportation	Total Fossil	Other	Total
H ₂	6	14.4	24.6	40
CO	204	332	1030	1361
NO _x [TgN/yr]	10.2	27	16.8	43.8
SO ₂ [TgS/yr]	2.5	68.4	7.2	75.6
Black Carbon (Soot)	1.17	2.99	5.26	8.26
Total NMVOCs	45.0	116.4	353.2	469.6
C ₂ H ₄	1.07	1.71	19.09	20.8
C ₂ H ₆	0.17	5.28	9.22	14.5
C ₃ H ₆	0.47	0.86	5.77	6.63
C ₃ H ₈	0.35	6.99	3.41	10.4
C ₄ H ₁₀	23.1	62.7	2.4	65.1
C ₄ H ₈	3.93	5.2	5.2	10.4
CH ₂ O	0.35	0.69	6.31	7
CH ₃ CHO	0.71	1.38	10.62	12
CH ₃ OH	0	0.96	241.8	242.8
C ₂ H ₅ OH	0	2.32	3.65	5.97
CH ₃ COCH ₃	0.01	0.47	28.43	28.9
MEK	0.01	1.32	8.49	9.81
Toluene	14.9	26.5	8.8	35.3

Table 2. H₂ and other related emissions for the 2050 A1FI HS0 baseline scenario. Note that total fossil emissions include road transportation emissions. Units are Tg/yr except as noted.

Specie	Road Transportation	Total Fossil	Other	Total
H ₂	14.8	32	24.6	56.6
CO	461.3	815.1	1029.6	1844.7
NO _x [TgN/yr]	27.1	77.6	16.7	94.3
SO ₂ [TgS/yr]	2.9	76.3	7.2	83.5
Black Carbon (Soot)	2.28	8.48	5.26	13.7
Total NMVOCs	82.4	247.6	353.3	600.9
C ₂ H ₄	1.85	3.42	19.1	22.5
C ₂ H ₆	0.3	13.2	9.2	22.4
C ₃ H ₆	0.79	1.74	5.77	7.51
C ₃ H ₈	0.7	16.7	3.4	20.1
C ₄ H ₁₀	40.8	133	2.4	135.4
C ₄ H ₈	7.18	10.5	5.19	15.7

CH ₂ O	0.62	1.45	6.32	7.77
CH ₃ CHO	1.4	2.97	10.6	13.6
CH ₃ OH	0	2.18	241.8	244
C ₂ H ₅ OH	0	5.07	3.65	8.72
CH ₃ COCH ₃	0.04	1.02	28.5	29.5
MEK	0.02	2.53	8.49	11.02
Toluene	28.7	53.8	8.8	62.7

Table 3. H₂ and other related emissions for the 2050 B1 HS0 baseline scenario. Note that total fossil emissions include road transportation emissions. Units are Tg/yr except as noted.

Specie	Road Transportation	Total Fossil	Other	Total
H ₂	3.2	7.8	24.6	32.4
CO	116.2	193.6	1029.7	1223.3
NO _x [TgN/yr]	11.2	29.3	16.7	46
SO ₂ [TgS/yr]	2.4	63.3	7.1	70.4
Black Carbon (Soot)	0.56	1.97	5.26	7.23
Total NMVOCs	34.2	89.4	353.3	442.7
C ₂ H ₄	0.8	1.29	19.11	20.4
C ₂ H ₆	0.1	4.12	9.18	13.3
C ₃ H ₆	0.35	0.65	5.77	6.42
C ₃ H ₈	0.27	5.7	3.41	9.11
C ₄ H ₁₀	17.3	48.6	2.4	51
C ₄ H ₈	2.98	3.91	5.21	9.12
CH ₂ O	0.26	0.53	6.32	6.85
CH ₃ CHO	0.6	1.06	10.64	11.7
CH ₃ OH	0	0.77	241.8	242.6
C ₂ H ₅ OH	0	1.72	3.65	5.37
CH ₃ COCH ₃	0.004	0.36	28.45	28.8
MEK	0.006	0.95	8.49	9.44
Toluene	11.5	19.8	8.8	28.6

Table 4. Fossil fuel emissions scale factors for IPCC A1FI both world and regions. (OECD90: Organization for Economic Cooperation and Development member states as at 1990; ASIA: Asia excluding the Middle East; ALM: Africa, Latin America and Middle East; REF: Central and Eastern Europe and Newly Independent States of the former Soviet Union.)

World - A1FI	Specie	Unit	2000	2050	2050/2000
	SO _x	MtS	69.0	80.5	1.17
	NO _x	MtN	32	95	2.97
	CO	MtCO	877	2159	2.46

	NMVOC	Mt	141	322	2.28
OECD90					
	SOx	MtS	17.0	5.1	0.30
	NOx	MtN	12	16	1.30
	CO	MtCO	161	250	1.55
	NMVOC	Mt	36	37	1.02
ASIA					
	SOx	MtS	25.3	37.0	1.46
	NOx	MtN	9	44	4.94
	CO	MtCO	270	1030	3.82
	NMVOC	Mt	37	119	3.18
ALM					
	SOx	MtS	12.8	24.7	1.94
	NOx	MtN	8	25	3.20
	CO	MtCO	404	714	1.77
	NMVOC	Mt	55	110	2.00
REF					
	SOx	MtS	11.0	10.7	0.97
	NOx	MtN	3	9	3.20
	CO	MtCO	41	166	4.01
	NMVOC	Mt	13	57	4.38

Table 5. Fossil fuel emissions scale factors for IPCC B1 both world and regions. (OECD90: Organization for Economic Cooperation and Development member states as at 1990; ASIA: Asia excluding the Middle East; ALM: Africa, Latin America and Middle East; REF: Central and Eastern Europe and Newly Independent States of the former Soviet Union.)

World – B1	Specie	Unit	2000	2050	2050/2000
	SOx	MtS	69.0	68.9	0.998
	NOx	MtN	32	39	1.21
	CO	MtCO	877	471	0.54
	NMVOC	Mt	141	116	0.82
OECD90					
	SOx	MtS	17.0	2.5	0.14
	NOx	MtN	12	5	0.39
	CO	MtCO	161	85	0.53
	NMVOC	Mt	36	21	0.58
ASIA					
	SOx	MtS	25.3	21.4	0.85
	NOx	MtN	9	13	1.48
	CO	MtCO	270	245	0.91
	NMVOC	Mt	37	37	1.00
ALM					
	SOx	MtS	12.8	35.6	2.79
	NOx	MtN	8	18	2.28
	CO	MtCO	404	121	0.30
	NMVOC	Mt	55	47	0.86
REF					

	SO _x	MtS	11.0	6.5	0.59
	NO _x	MtN	3	3	0.90
	CO	MtCO	41	19	0.47
	NMVOC	Mt	13	11	0.85

Table 6. Energy demand, hydrogen demand, and hydrogen leakage emissions for the transportation sector for the A1FI and B1 scenarios assuming 120 MJ/kgH₂, a 2.5% leakage rate, and that road transportation accounts for 80% of the total.

A1FI	Transportation Fuel Type	2000	2050
	Liquid	64.4 EJ	266.0 EJ
	Gas	1.0 EJ	5.8 EJ
	Electric	0.6 EJ	8.3 EJ
	H ₂ Demand	0.556 Pg	2.403 Pg
	H ₂ Leakage	14 Tg	60.8 Tg

B1	Transportation Fuel Type	2000	2050
	Liquid	56.2 EJ	123.0 EJ
	Gas	1.0 EJ	2.4 EJ
	Electric	0.6 EJ	3.4 EJ
	H ₂ Demand	0.486 Pg	1.101 Pg
	H ₂ Leakage	12 Tg	24Tg

Table 7. Comparison of H₂ emissions for different sectors for 2050 HS2 scenarios assuming equal vehicle efficiencies and 40% internal combustion engine and 60% fuel cell vehicle efficiencies (Unit: TgH₂/yr).

A1FI	Equal Efficiencies	40% / 60% Efficiencies	Change [%]
Transportation Emissions	60.8	40.5	-33.3
Other Fossil Emissions	17.2	17.2	0
Total Fossil Emissions	78	57.7	-26.0
Other Emissions	24.6	24.6	0
Total Emissions	102.6	82.3	-19.8
	Equal Efficiencies	40% / 60% Efficiencies	Change [%]
B1			
Transportation Emissions	24	16	-33.3
Other Fossil Emissions	4.6	4.6	0
Total Fossil Emissions	28.6	20.6	-28
Other Emissions	24.6	24.6	0
Total Emissions	53.2	45.2	-15

Table 8. Total emissions changes upon adoption of an H₂-based transportation sector for the 2050 A1FI HS2 and B1 HS2 scenarios (Note that brackets contain results assuming 40% ICE efficiency and 60% fuel cell efficiency).

Specie	Change in emissions [%]	
	A1FI	B1
H ₂	+81.3 (+45.4)	+64.2 (+39.5)
NO _x	-28.7	-24.4
CO	-25.0	-9.5
NMVOCS	-13.7	-7.7
SO ₂	-3.4	-3.4
Soot	-16.6	-7.7

Table 9. Estimates of current H₂ emissions from fossil fuel combustion.

	TgH ₂ /yr
This work	14.4
Novelli et al. (1999)	5-25
Hauglustaine et al. (2002)	16
Tromp et al. (2003)	5-25
Schultz et al. (2003)	5-25
Sanderson et al. (2003)	20.0
Derwent et al. (2006)	15-20
Rhee et al. (2006)	9-21
Vollmer et al. (2007)	15
Price et al. (2007)	18.3
Xiao et al. (2007)	5-25
Ehhalt et al. (2009)	7-15
D.Streets, (from Jacobson's DOE Merit Review 2009)	8.4

Table 10. Estimates of current H₂ emissions from road transportation.

	TgH ₂ /yr
This work	6
Novelli et al. (1999)	5-20
Vollmer et al.(2007)	4.2-8.1
Jacobson (2008)	5.58
Ehhalt et al. (2009)	6-12

Table 11. Estimates of H₂ leakage emissions in a current H₂-economy.

	Total H ₂ Fossil Emissions (TgH ₂ /yr)	Key Assumptions	H ₂ Leakage
This work	15.8~17.8	Current (year 2000) total world road transportation switches to H ₂ economy	2.5%
Tromp et al. (2003)	60-120	Hydrogen fuel cells replace all oil or gasoline combustion; Assuming surface H ₂ mixing ratio quadrupled	10-20%
Schultz et al. (2003)	6.8-50	If 100% fossil fuels conversion to H ₂ technology	3% (0-3% plus test at 10%)
Warwick et al. (2004)	26-312	1/3 to complete conversion to H ₂ economy; Assume surface H ₂ mixing ratio 1.4 or 2.3 ppm	1-12 %
Jacobson et al. (2005)	5.68 (U.S. road vehicle emissions)	Switching U.S. vehicles to HFCVs in 1999	10%
Derwent et al.(2006)	25	100% replacement of fossil	1 % (1~10% range)
Jacobson (2008)	4.82 (for world road vehicle emissions)	1995 world road vehicles 100% replaced by H ₂ fuel cells	3%

Table 12. H₂ break even leakage percentage for different cases (Unit: %, other units: TgH₂/yr).

Equal Efficiencies	2050 A1FI	2050 B1	2000_A1FI	2000_B1
H ₂ emissions from fossil transportation	14.8	3.2	6	6
Total H ₂ demand for road transportation	2403.5	1101.3	556	486
H ₂ break even percentage	0.6	0.3	1.1	1.2

40% ICE / 60% Fuel Cell Efficiencies	2050 A1FI	2050 B1	2000_A1FI	2000_B1
H ₂ emissions from fossil transportation	14.8	3.2	6	6
Total H ₂ demand for road transportation	1602.3	734.2	193.5	169.1
H ₂ break even percentage	0.9	0.4	3.1	3.5

Table 13. Year 2050 CO₂ emissions for A1FI and B1 baseline and H₂ powered road transportation sector (GtCO₂/yr).

A1FI	HS0, HS1	HS2, HS3	Change [%]
Road Transportation	22.1	0	-100
Total Fossil	84.7	62.6	-26.1

B1	HS0, HS1	HS2, HS3	Change [%]
Road Transportation	10.1	0	-100
Total Fossil	42.9	32.8	-23.5

Figure 1. Global total emissions for the Current and A1FI and B1 HS0 baseline and HS2 H₂-based fuel cell transportation sector scenarios.

Figure 2. Annual average total H₂ emissions for the 2050 A1FI (HS2) fuel cell adoption scenario. (Contour Units: 10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$)

Figure 3. Annual average total NO_x emissions for the 2050 A1FI (HS2) fuel cell adoption scenario. (Contour Units: 10⁹ molecules cm⁻² s⁻¹)

Figure 4. Annual average total CO emissions for the 2050 A1FI (HS2) fuel cell adoption scenario. (Contour Units: 10⁹ molecules cm⁻² s⁻¹)

Section 2

Impact of a Future Hydrogen-Based Road Transportation Sector on Tropospheric Composition and Chemistry

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1. Introduction

Road traffic burning fossil fuels emits a number of gaseous pollutants, including nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs), which have been long recognized as major pollutants and subject to EPA regulation (<http://www.epa.gov/air/airpollutants.html>), as well as particulate matters (mainly soot, or black carbon). Studies have shown that soot imposes health hazards on respiratory system [e.g., *Dockery et al.*, 1993], and contributes to global warming [e.g., *Bond and Bergstrom*, 2006]. In addition, ground level ozone (O_3), the “bad” ozone (<http://www.epa.gov/air/ozonepollution/>), forms through photochemical reactions involving CO and VOCs in the presence of NO_x and sunlight (see the included Appendix for more information on tropospheric chemistry). Hydrogen (H_2) has been proposed as an alternative energy carrier which is much cleaner than fossil fuel. Vehicles powered by H_2 fuel cells do not emit NO_x , CO, VOCs or soot; the only substances they emit are water vapor and a small amount of H_2 due to leakage during its production, transportation and storage processes. Vehicles powered by H_2 internal combustion engines have no CO, VOC, and soot emissions. Given these reductions in emissions it is reasonably foreseeable that transitioning the world’s road traffic from fossil fuel internal combustion engine (ICE) powered vehicles to H_2 technology based would substantially improve air quality provided that the H_2 is produced by non-polluting methods, e.g., wind or solar power. Such a transition would take some time as substantial changes to energy delivery infrastructure and technology, and industrial H_2 massive production capacity would be required. Here we quantitatively examine

the possible impact of such a transition on tropospheric air quality, composition and chemistry in 2050 for two types of H₂ technology (H₂ fuel cells and H₂ internal combustion engines) in combination with two future growth paths. The future growth paths are based on the IPCC fossil fuel intensive A1FI scenario (high emitting) and the service and information intensive B1 scenario (low emitting) [IPCC, 2000], in order to bracket the possibilities of the world's future. The additional H₂ emission will likely increase its abundance in the troposphere, but it should not raise an environmental concern in the troposphere. Its major tropospheric sink is deposition to soils and by reaction with atmospheric hydroxyl, producing water vapor but in amounts dwarfed by natural levels of water vapor.

2. Method

2.1 Model Description

For this study we use the Community Atmosphere Model with chemistry (CAM-Chem) chemistry climate model [Lamarque *et al.*, 2005; Heald *et al.*, 2008; Pfister *et al.*, 2008]. CAM-Chem was developed primarily at the National Center for Atmospheric Research (NCAR) in cooperation with the National Science Foundation (NSF), the Department of Energy (DoE), the National Aeronautics and Space Administration (NASA), and the University Corporation for Atmospheric Research (UCAR). CAM-Chem's chemistry module is based on the chemical component of the Model for Ozone And Related chemical Tracers (MOZART) [Horowitz *et al.*, 2003]. This mechanism contains a comprehensive tropospheric gas phase and aerosol chemical mechanism and includes 119 species and 300 reactions. For this study, the global atmosphere is divided into grids with a horizontal resolution of 1.9° latitude by 2.5° longitude, and with 26 vertical layers, extending from the surface to 3-millibar level (about 40 km altitude). The meteorology data is prescribed by climate model output data from Community Climate System Model (CCSM) which corresponds to the current climate state. After one year's calculation is completed, the meteorology field is repeated for the next year. This method allows the impact of changes in emissions to be investigated excluding the possible influences of changes in meteorology. The 2050 atmospheric CH₄ concentration is determined by scaling the

2000 atmospheric lower boundary CH₄ concentration (1760 ppb) to the concentration projected by *IPCC*, 2001 (2668 ppb and 1881 ppb for A1FI and B1, respectively). The model is run for eight years and has reached steady state, that is, year-to-year relative difference of key species is less than 1%.

Deposition to soil is an important sink (~80%) of H₂ in the atmosphere. Despite its importance, the controlling factors of this deposition are not well characterized and are subject to large uncertainties. Observations have shown a strong correlation between the H₂ and CO deposition velocities [*Liebl and Seiler*, 1976; *Conrad and Seiler*, 1985; *Yonemura et al.*, 1999 and *Yonemura et al.*, 2000]. Based on these studies we adopt an H₂ deposition velocity equal to two times the CO deposition velocity. Others have proposed calculating H₂ deposition velocities as a function of soil temperature, moisture content, and diffusivity [e.g., *Smith-Downey et al.*, 2006]. However, it is not known if the relationship derived in these studies has global validity given the limited observations providing the basis for this approach. In addition, application of this relationship to the temperature range between 0 and 30°C contradicts the observational findings by *Yonemura et al.*, [1999] and *Yonemura et al.*, [2000]. Therefore, we model H₂ dry deposition velocity (V_d) to soils by using its correlation with CO dry deposition velocity. Based on observations we adopt a $V_d[\text{H}_2]$ equal to two times $V_d[\text{CO}]$, though there remain large uncertainties.

2.2 Emission Scenarios

Future growth scenarios are based on the highest and lowest IPCC emissions scenarios (*IPCC*, 2000), A1FI and B1, respectively. Given the large uncertainties in future projections, these scenarios were chosen since they bracket the possible high and low impacts. In the A1FI scenario, the world is assumed to evolve with rapid economic growth and rely intensively on fossil fuel; whereas in the B1 scenario the world's economic structures are projected to change rapidly toward service-and-information intensive society. For each of these two IPCC growth scenarios four emission scenarios were developed:

- 1) Baseline (BL) scenario: reference scenario for 2050.
- 2) Baseline + H₂ (BL+H₂) scenario: energy demands of the road transportation sector are met by H₂ and leakage of H₂ to the atmosphere is included but other emissions remain the same as in the BL scenario. This scenario, though not realistic, allows the evaluation of the impact of H₂ emission alone on tropospheric composition and chemistry.
- 3) H₂ Fuel Cell (H₂-FC) scenario: energy demands of the road transportation sector are met by H₂ fuel cell technology. In this scenario emissions due to H₂ leakage as well as reductions in combustion-related emissions of NO_x, VOCs, CO, SO₂ and soot are included.
- 4) H₂ Internal Combustion Engine (H₂-ICE) scenario: energy demands of the road transportation sector are met by H₂ using internal combustion technology. In this scenario emissions due to H₂ leakage as well as reductions in combustion-related emissions of VOCs, CO, SO₂ and soot are included, however there are no reductions in NO_x emissions.

These emissions are input to the model as monthly varying maps at the model resolution. Annual global emissions of key species are summarized in Figures 1 and 2. In 2050, for the A1FI scenario an H₂-based transportation sector would decrease global CO, NMVOCs*, NO_x, SO₂ and soot emissions by 25%, 14%, 29% (H₂-FC) or 0% (H₂-ICE), 3% and 17% whereas increase H₂ emissions by 81%. For the B1 scenario an H₂-based transportation sector would decrease global CO, NMVOCs NO_x, SO₂ and soot emissions by 10%, 8%, 24% (H₂-FC) or 0% (H₂-ICE), 3% and 8% while increase H₂ emissions by 64%. For more details about the emission changes, please refer to our companion report on emissions.

3. Results

Our modeling studies suggest that in the experimental scenarios assuming only added H₂ emission without related emissions changes (BL+H₂ scenarios) the added H₂ alone

* NMVOCs: non-methane volatile organic compounds

has little impact on tropospheric chemistry except for a significant rise in atmospheric H₂ concentration. Air quality improves significantly (significant reductions in concentrations of O₃, CO, NO_x and particulate matters) in H₂-FC scenarios. Air quality improves considerably (significant reductions in concentrations of CO and particulate matters) in H₂-ICE scenarios.

The projected mean tropospheric concentrations of chemical species of interest in the BL scenarios and the projected changes of concentrations in the H₂ scenarios relative to those in the corresponding BL scenarios are summarized in Tables 1 and 2. For the A1FI scenarios, tropospheric H₂ burden (total H₂ in the troposphere) would be about 40% higher in the H₂ scenarios than that in the BL (Table 1). Concentrations of gaseous species and particulate matters of air quality concern decrease significantly. Tropospheric O₃, CO, NO_x, soot, sulfate aerosols and secondary organic aerosols burdens decrease by 7%, 14%, 16%, 17%, 4% and 12% in the A1FI H₂-FC scenario. Tropospheric O₃, CO, soot, sulfate aerosols and secondary organic aerosols burdens decrease by 1%, 18%, 17%, 3% and 18% in the A1FI H₂-ICE scenario. The BL+H₂, H₂-FC and H₂-ICE scenarios change the tropospheric OH abundance by -2%, -4% and +7%, respectively.

For the B1 scenarios, tropospheric H₂ burden would be increased by approximately 20% in the H₂ scenarios (Table 2). Tropospheric O₃, CO, NO_x, soot, sulfate aerosols and secondary organic aerosols burdens decrease by 5%, 4%, 11%, 7%, 4% and 3% in the B1 H₂-FC scenario. Tropospheric O₃, CO, soot, sulfate aerosols and secondary organic aerosols burdens decrease by 1%, 7%, 7%, 3% and 9% in the B1 H₂-ICE scenario. The BL+H₂, H₂-FC and H₂-ICE scenarios change the tropospheric OH abundance by -1%, -4% and +3%, respectively. The magnitudes of relative changes in the B1 scenarios are less than those in the A1FI scenarios because B1 is a service and information intensive society in which energy demands by transportation sector are smaller than those in A1FI.

In the following section individual atmospheric species of interest will be discussed in detail.

3.1 H₂

In the H₂ scenarios (BL+H₂, H₂-FC and H₂-ICE) the projected tropospheric mean H₂ concentrations are around 1150 ppb* (A1FI) and 740 ppb (B1), which are equivalent to an increase from the BL scenarios by 40% and 20%, respectively. In other words, compared with today's atmosphere, tropospheric H₂ concentration would be 2.2 (A1FI) or 1.5 (B1) times the current value (around 500 ppb). The increase in molecular hydrogen abundance would not cause much environmental concern because of H₂'s low chemical reactivity in the troposphere.

In the 2050 A1FI BL scenario ground-level annual-mean H₂ mixing ratio over the world would be around 800 ppb (Figure.3), with maxima in highly urbanized and/or industrialized regions like northeastern U.S., southern California, Western Europe, Korean peninsula, Japan and eastern China. Lowest H₂ mixing ratios (about 700 ppb) would appear over mid-latitude continents of the southern hemisphere, reflecting both small human H₂ source and large H₂ soil sink in those regions.

Because of its long chemical lifetime in the troposphere, the patterns of ground H₂ concentrations, primarily determined by its human source, resemble each other much in the H₂ scenarios. This similarity allows us to examine the H₂-FC scenario as an example of the H₂ societies. The projected inter-hemispheric [H₂]** gradient is opposite to that for today's atmosphere – higher background H₂ abundance (around 1.2 ppm) is observed in the northern hemisphere, comparing with some 1.15 ppm in the southern hemisphere. This reflects the larger forcing of H₂ emission from human activities (more intensive in the northern hemisphere) on hemispheric H₂ concentrations. The background surface H₂ mixing ratio increases at least 40% in the

* ppb: parts per billion by volume.

northern hemisphere and 35% in the southern hemisphere. Highest mixing ratio (more than 1.6 ppm) occurs in eastern China and Korea, corresponding to a more than 75% increase from the BL scenario (Figure. 3). In northeastern U.S., $[H_2]$ increases by 50%.

In the B1 BL scenario, ground-level annual-mean H_2 mixing ratio over the world is projected to be around 600 ppb in 2050 (Figure. 4), showing no regions with significantly high value. In the H_2 -FC scenario, a representative of the H_2 scenarios, ground-level H_2 mixing ratio is projected to be around 700 ppb in both hemispheres. The background surface H_2 mixing ratio would increase from the BL scenario by more than 20% in the northern hemisphere and by more than 16% in the southern hemisphere (Figure.4). Maximum mixing ratio (more than 860 ppb) appears in eastern Asia, corresponding to a more than 40% increase from the BL. The pattern of relative increase of zonal mean H_2 mixing ratio in H_2 societies relative to the non- H_2 society is similar to that in the corresponding A1FI scenarios, except that the magnitude of increase is smaller.

From a zonal mean perspective, $[H_2]$ is increased throughout the troposphere in the H_2 scenarios (Figures.5 and 6). In the A1FIBL scenario, inter-hemispheric $[H_2]$ gradient would have already reversed from today's with higher $[H_2]$ in the northern hemisphere (NH) since enhanced human activities in the NH would place a larger forcing on atmospheric $[H_2]$ (Figure.5). An H_2 -based road transportation sector would even sharpen the inter-hemispheric $[H_2]$ gradient by increasing $[H_2]$ more in the NH. The largest increase ($\sim 45\%$) occurs near surface in the mid-latitudes of the NH (Figure. 5), demonstrating intensive human activities there.

Whereas in the B1 BL scenario, inter-hemispheric $[H_2]$ gradient would be the same with today's with higher $[H_2]$ in the southern hemisphere (SH) since enhanced human

** $[X]$ represents species X's mixing ratio.

activities in the NH would place a forcing strong enough on atmospheric $[H_2]$ (Figure.6). However, in the B1 H_2 scenarios, this gradient would be reversed as a result of enhanced H_2 emission.

3.2 Ozone

Tropospheric ozone is an air pollutant and a greenhouse gas. Addition of H_2 alone to the atmosphere does not directly affect tropospheric ozone abundance. However, significant ozone mitigation can be achieved if an H_2 -based road transportation sector is implemented in combination with CO , NO_x and NMVOCs emissions reduction.

In the three H_2 scenarios, H_2 -FC would achieve the most ozone reductions, whereas there is almost no change in ozone mixing ratio in BL+ H_2 , and ozone is slightly reduced in H_2 -ICE.

In the A1FI BL scenario, annual mean surface ozone concentration over land in 2050 is projected to be mostly above 30 ppb (Figure.7). Higher ozone mixing ratios, resulting from NO_x , NMVOCs and CO emissions due to fossil fuel combustion, are seen in densely populated areas. In the H_2 -FC scenario, ozone mixing ratios 5~10 ppb lower than those in BL are seen over these areas. Ozone reductions are most effective in summertime, when ozone pollution is most severe. In terms of relative change, ozone decreases by more than 6% over the world, with as much as 20% decrease in Latin America and Southeast Asia. However, there is increased ozone in some extremely populated areas such as New York, London and South Korea (Figure. 7). This is because in these regions NO_x -VOC ratio belongs to VOC limited scheme (Figure.8), i.e., decreasing both NO_x and VOC emission is not effective in ozone mitigation, because VOC mixing ratio is the limiting factor. In the A1FI H_2 -FC scenario, the annual, zonal average ozone mixing ratios are generally decreased by more than 5% (Figure. 9) in the lower troposphere. Peak decrease (more than 10%) appears near surface at the low latitudes of northern hemisphere.

In the A1FI H₂-ICE scenario surface ozone concentration decline compared with the base scenario is generally not as apparent as in the A1FI H₂-FC scenario (Figure.7). In contrast to the A1FI H₂-FC scenario, in those regions where ozone reduction is not apparent in H₂-FC, [O₃] decreases considerably, suggesting that in these regions VOC emission reductions are more effective in ozone pollution mitigation. The zonal mean ozone concentrations do not change significantly except in the lower troposphere of the northern middle latitudes, where ozone decreases by ~5% (Figure. 9).

For the B1 BL scenario, the distribution pattern of annual mean near surface ozone concentrations over the world is similar to that for the corresponding A1FI scenarios, but as can be expected from B1's lower emissions, the absolute concentrations are lower (Figure. 10). In the B1 H₂-FC scenario, annual mean near surface ozone decreases significantly (more than 10%) in the southern part of the U.S. and along the East Coast. Ozone reductions in the B1 H₂-ICE scenario are not as apparent (Figure. 11).

3.3 OH radicals

A major concern over the potential impact of an H₂-based road transportation sector on tropospheric chemistry is that the added molecular hydrogen in the atmosphere would titrate OH radicals so as to impair the oxidizing power of the atmosphere. Model simulations show that adding only H₂ to the atmosphere would only reduce OH abundance in the troposphere by 2%. Greater impact is seen when combined with concomitant reductions of ozone precursors (NO_x, CO and NMVOCs) emissions – [OH] decreases by 4% in both the A1FI and B1 H₂-FC scenarios. When only reducing CO and NMVOCs emissions as in the H₂-ICE scenarios, tropospheric OH abundance would increase (by 7% for A1FI and by 3% for B1) instead of decrease, because there are less VOC sinks for OH.

H₂ itself does not significantly impact on the abundance of OH in the troposphere. In the experimental simulation in which only additional H₂ emission is considered (A1FI

BL+H₂ scenario), tropospheric OH concentrations are decreased by as much as 3% (Figure.12). The largest decrease is observed in the lower troposphere of the southern hemisphere.

In the more realistic H₂ scenario (A1FI H₂-FC), OH decrease is more apparent than in BL+H₂ as a consequence of decreased ozone concentration (Figure.12). The maximum OH concentration decline (more than 20%) would be predicted in the lower troposphere of the southern mid-latitudes. Around 10% OH increase is observed in the free troposphere at northern high-latitudes in boreal spring. However, this is not important since the base OH concentration is low in this region.

In the A1FI H₂-ICE scenario, OH concentrations in most of the troposphere increases by more than 5% (Figure. 12). The troposphere OH burden increases by 7%. OH increases by over 30% in the middle troposphere at 60°N, as a result of almost unchanged ozone concentrations and significantly decreased VOCs (OH sinks) abundances.

For the B1 scenarios the patterns of OH concentration changes are similar to those of the corresponding A1FI scenarios but the magnitude of impact is smaller (Figure. 13).

3.4 NO_x

NO_x concentration does not change if only atmospheric H₂ concentration increases (BL+H₂ scenarios). When CO, NO_x and NMVOCs emissions are mitigated (H₂-FC scenarios), [NO_x] are reduced significantly. However, model predicts that tropospheric [NO_x] increases if only CO and NMVOCs emissions are reduced while NO_x emissions keep unchanged (H₂-ICE scenarios).

Regions with intense human activities are polluted with high concentrations of NO_x. In the H₂ scenario with NO_x emission mitigation (H₂-FC), those high [NO_x] regions would benefit from substantial [NO_x] reduction. Annual mean ground level [NO_x] is

reduced considerably along coasts of North and South Americas, Western Europe, North Africa, the Middle East and Japan (Figure.14). Relative reduction can be as high as 60%, such as in California. The relative reduction is most obvious in wintertime. From zonal mean perspective, NO_x concentrations decline throughout the lower troposphere (Figure.15). Maximum reductions appear in the boundary layer between 30°S and 60°S and between 0° and 60°N. In the A1FI H_2 -ICE scenario, near surface NO_x concentration change is not apparent, showing that the internal combustion engine type of H_2 society is not effective in ground level NO_x mitigation. In the middle and upper troposphere there is a $[\text{NO}_x]$ increase because its sink against VOCs is reduced since NMVOC emissions are reduced.

For the B1 scenarios, we see similar annual mean ground level NO_x mixing ratio relative change pattern in the H_2 -FC scenario, but the reductions are to a lesser extent than in the counterpart of the A1FI scenarios (Figure.16 and 17).

3.5 CO

Atmospheric H_2 concentration increase has little impact on CO (BL+ H_2 scenarios). In the H_2 -FC and H_2 -ICE scenarios tropospheric CO burden decreases by 14~18% for A1FI, and by 4~7% for B1. H_2 -ICE scenarios are generally more efficient in CO reduction than H_2 -FC.

For the A1FI scenarios, CO concentrations in remote areas of the northern hemisphere decreases by more than 20% (Figure.18). Relative $[\text{CO}]$ reductions in the H_2 -FC scenario are most apparent in urbanized and/or industrialized regions, such as northeastern U.S., California, central and western Europe, the Middle East, South Korea and Japan. New York City can have as much as 80% less $[\text{CO}]$ in the air. The $[\text{CO}]$ reduction is perennial but is most pronounced in winter. In the H_2 -ICE scenario ground level $[\text{CO}]$ reduction pattern is similar to that in the A1FI H_2 -FC scenario, but the magnitude of reduction is even larger, demonstrating that H_2 internal combustion engines are more effective than H_2 fuel cells in terms of CO mitigation.

From the zonal mean perspective, [CO] reduction patterns are similar in H₂ scenarios, with increasing magnitude of reduction from the south to the north (Figure.19). We see more reduction in H₂-ICE than in H₂-FC. This is because there is more OH in the troposphere in H₂-ICE than in H₂-FC. And reaction against OH is the major sink of atmospheric CO.

In the B1 H₂-FC and H₂-ICE scenarios, CO concentrations at remote sites in the northern hemisphere decrease by more than 10~20%. The maximum reduction appears over northeastern U.S. (Figure.20), but not as significant in magnitude as in the A1FI corresponding scenario. The zonal mean [CO] reductions in B1 H₂ scenarios are smaller than those in the corresponding A1FI scenarios (Figure.21).

3.6 Aerosols

Our model simulations show that merely increasing atmospheric H₂ concentration (BL+H₂ scenarios) has little impact on aerosols. For the H₂-FC and H₂-ICE scenarios, tropospheric aerosols, especially soot, sulfate aerosols and secondary organic aerosols concentrations are significantly reduced as a result of emissions mitigation. H₂-FC scenarios have similar soot and SO₄ reductions efficiency with that of the H₂-ICE scenarios. Hereby we take the H₂-FC scenario as a representative of an H₂-based road transportation sector scenario for detailed soot and SO₄ analysis.

3.6.1 Soot

Mass concentration of soot decreases by around 17% for the A1FI scenarios, and by 7% for the B1 scenario (Tables.1 and 2). Since soot is a product of fossil fuel combustion its pollution is highly localized. Its concentrations in remote atmosphere near the surface are rather low, whereas there are high soot concentrations in regions where human activities are intensive (Figure. 22). If the world evolves along the A1FI scenario, in 2050 soot pollution would be most severe in eastern China. Considerable

soot pollution would also be seen in India, Europe. In the Midwest and eastern U.S. annual mean near surface soot concentration would be around $2\mu\text{g}/\text{m}^3$.

In the A1FI H₂-FC scenario (as above-mentioned the A1FI H₂-ICE scenario is very similar to H₂-FC scenario in terms of soot pollution), ground level soot can be significantly reduced in most regions of the U.S., Europe and Japan (Figure. 22). In interior U.S. regions and Western Europe, the reduction can be as much as more than 50% in comparison with the A1FI BL scenario. Reduction of soot in eastern Asia is not apparent. The soot pollution mitigation is most obvious in wintertime.

From the zonal mean view, soot concentration decrease is predicted at high latitudes of both hemispheres (Figure. 23) in the H₂-FC scenario, with the largest decline in the northern hemisphere.

In the B1 scenarios soot reductions in the H₂-FC and H₂-ICE scenarios are less in magnitude but still significant than in the corresponding A1FI scenarios (Figures.24 and 25).

3.6.2 SO₄

Sulfate aerosols (SO₄) decreases by 4% by mass for both the A1FI and B1 H₂-FC scenarios; it decreases by 3% for both the A1FI and B1 H₂-ICE scenario (Tables.1 and 2). In the A1FI H₂-FC scenario, there is around 10%-15% decrease in SO₄ mass concentration comparing with the A1FI BL scenario over most Eurasia, North Africa, western and southern U.S., Mexico, and South America (Figure. 26). Zonal mean SO₄ concentration decreases more in the NH (Figure. 27). SO₄ mass concentrations are also decreased, but to a lesser extent, in the B1 H₂ scenarios (Figures.28 and 29).

3.6.3 SOA

Secondary organic aerosols (SOA) contribute to a significant part of ambient tropospheric aerosols. There would be declines in SOA concentrations in the

scenarios with an H₂-base road transportation sector: tropospheric SOA mass concentration decreases by around 12~18% for the A1FI scenarios and by 3~9% for the B1 scenarios (Tables.1 and 2). Here the lower-end decline represents the H₂-FC scenarios whereas the higher-end decline represents the H₂-ICE scenarios. H₂-based road transportation sector with H₂ internal combustion engines application is more efficient in SOA reduction than that with H₂ fuel cells.

In the A1FI H₂-FC scenario, there is a significant decrease in SOA mass concentration (more than 30%) over a broad band at northern mid-latitudes (Figure. 30). Whereas in the A1FI H₂-ICE scenario, its decrease is even more than the H₂-FC scenario (more than 40% in the northern hemisphere). SOA mass concentrations are decreased by a smaller magnitude in B1 H₂ societies than in A1FI (Figures.32 and 33).

4. Comparison with other studies

Because of diverse scenario assumptions, it is hard to directly compare with other studies. Nevertheless, it would provide helpful comparisons if we assume linear tropospheric chemical response and use scaling method. In our study, 2% OH concentration decrease results from 40% of H₂ concentration increase. Using a two-dimensional model to carry out a somewhat ideal modeling experiment, *Warwick et al.* [2004] find quadrupling atmospheric H₂ concentrations leads to 10% decrease in OH concentrations, which is in good agreement if scale our study. They also obtain 2.2% decrease of tropospheric ozone in *current* atmosphere if converted to H₂ society. While the divergence of the emission scenarios in their study from ours nulls direct comparison, it would be helpful noting that ozone is predicted to be 2.2% less in H₂ society according to *Warwick et al.*

Assuming half of current fossil fuel combustion changed to H₂ technology, *Schultz et al.* [2003] find 5% decrease in tropospheric ozone, in a 3-D modeling study. Their predicted regions with most ozone reductions overlap those predicted by our study. Just as shown in our study, they have also captured the increase in surface ozone near London, New York City, and Korea.

Jacobson et al. [2005] find substantial ozone decrease in southeastern U.S. in a natural gas type H₂ society. However, there is discrepancy in prediction of soot reduction. We predict most apparent reductions appear in interior U.S. while *Jacobson et al.* find largest decline in southeastern U.S. This discrepancy is likely to arise from the different scenarios used in the two studies. In a subsequent study *Jacobson [2008]* shows similar characteristics of air quality improvement in H₂ society with our study.

Ignoring H₂'s impact on troposphere chemistry (its impact has been shown to be small in our study), the environmental effect of H₂ society is much like that of removal of traffic emissions. A number of studies [*Mattes et al.*, 2007; *Niemeier et al.*, 2006; *Hoor et al.* 2009] examine the impact of road traffic emissions on troposphere chemistry, by comparing the atmosphere chemistry with and without road traffic emissions. The abatement of air pollution in H₂ society in our study is at the opposite sign of air quality degradation when adding road emissions in the above-mentioned studies, although we are doing simulations about the future while these studies focus on the current atmosphere. This suggests our results are consistent with these studies.

5. Conclusions

A set of numerical simulations using a three-dimensional global atmospheric chemistry and transport model have been carried out in order to study potential impact of a future (year 2050) H₂-based road transportation sector on tropospheric composition and chemistry. The assumptions in the modeling studies include high- and low-emitting future scenarios to bracket possible growth paths, and a set of H₂ technology option scenarios.

Atmospheric simulations assuming only H₂ emission without related emissions change (BL+H₂ scenarios) show that H₂ by itself has little impact on tropospheric chemistry except for significant rise in tropospheric H₂ concentration, which should

raise no environmental concern as it is not toxic (however, it does lead to questions about effects on the stratosphere addressed in a separate report).

Air quality would improve significantly with application of an H₂ fuel cell type road transportation sector (H₂-FC scenarios). Primary gaseous (CO, NO_x) and particulate (soot) pollutants are mitigated as fossil fuel combustion process is replaced with H₂ oxidization process which only generates H₂O. Ozone, a major secondary pollution gas now still often found exceeding air quality standard in some U.S. regions, would be reduced to a significant extent since its precursors, CO, NO_x and VOC emissions are mitigated. Meanwhile, secondary aerosols, including sulfate aerosols and secondary organic aerosols, would also be reduced.

Air quality would also improve with application of an H₂ internal combustion engine type road transportation sector (H₂-ICE scenarios). Emissions of primary gaseous and particulate pollutants (CO and soot) are mitigated. Ambient ozone concentrations would decrease slightly as its precursors (CO and VOC) emissions by fossil fuel combustion from road transportation sector is eliminated. Ozone mitigation in the H₂-ICE scenarios is especially effective in VOC limited regions. Sulfate aerosols and secondary organic aerosols would also be reduced.

In conclusion, by using a comprehensive atmospheric chemistry-transport model that represents key physical and chemical mechanisms of the atmosphere, we show that transitioning to an H₂-based road transportation sector would be beneficial in reducing concerns about air quality.

References

1. Bond, T.C. and R.W. Bergstrom, Light absorption by carbonaceous particles: An investigative review, *Aerosol Science and Technology*, Volume 40, Issue 1, pp.27-67, 2006.
2. Conrad, R., and W. Seiler, Influence of Temperature, Moisture, and Organic Carbon on the Flux of H₂ and CO Between Soil and Atmosphere: Field Studies in Subtropical Regions, *J. Geophys. Res.*, 90(D3), 5699–5709, 1985.
3. Dockery, D.W., C.A. Pope, X.P. Xu, J.D. Spengler, J.H. Ware, M.E. Fay, B.G. Ferris, F.E. Speizer, An Association between Air-Pollution and Mortality in 6 United-States Cities, *New England Journal of Medicine*, Volume 329, Issue 24, pp. 1753-1759, 1993.
4. Heald, C. L., D. K. Henze, L. W. Horowitz, J. Feddema, J.-F. Lamarque, A. Guenther, P. G. Hess, F. Vitt, J. H. Seinfeld, A. H. Goldstein, and I. Fung, Predicted change in global secondary organic aerosol concentrations in response to future climate, emissions, and land use change, *J. Geophys. Res.*, 113, D05211, doi:10.1029/2007JD009092, 2008.
5. Hoor, P., The impact of traffic emissions on atmospheric ozone and OH: results from QUANTIFY, *Atmos. Chem. Phys.*, 9, 3113–3136, 2009.
6. Horowitz, L. W., et al., A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res.*, 108(D24), 4784, doi:10.1029/2002JD002853, 2003.
7. IPCC, *Special Report on Emissions Scenarios*. Working Group III, IPCC, Cambridge University Press, Cambridge, 2000.
8. IPCC, Climate Change 2001, *The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the IPCC*, Cambridge University Press, New York, 2001.
9. Jacobson, M. Z., W. G. Colella, and D. M. Golden, Cleaning the air and improving health with hydrogen fuel-cell vehicles. *Science*, 308, 1901-1905, 2005.

10. Jacobson, M.Z., Effects of wind-powered hydrogen fuel cell vehicles on stratospheric ozone and global climate, *Geophys. Res. Lett.*, Vol.35, L19803, 2008.
11. Lamarque, J.-F., J. T. Kiehl, P. G. Hess, W. D. Collins, L. K. Emmons, P. Ginoux, C. Luo, and X. X. Tie, Response of a coupled chemistry-climate model to changes in aerosol emissions: Global impact on the hydrological cycle and the tropospheric burdens of OH, ozone, and NO_x, *Geophys. Res. Lett.*, 32, L16809, doi:10.1029/2005GL023419, 2005.
12. Liebl. K.H., and W. Seiler. CO and H₂ destruction at the soil surface, in *Microbial Production and Utilization of Gases*, edited by H.G. Schlegel, G. Gottschalk, and N. Pfenning, Goltze, Gottingen, Germany, pp. 215-229, 1976.
13. Matthes, S., V. Grewe, R. Sausen, and G.-J. Roelofs, Global impact of road traffic emissions on tropospheric ozone, *Atmos. Chem. Phys.*, 7, 1707–1718, 2007.
14. Niemeier, U., C. Granier, L. Kornblueh, S. Walters, and G. P. Brasseur (2006), Global impact of road traffic on atmospheric chemical composition and on ozone climate forcing, *J. Geophys. Res.*, 111, D09301, doi:10.1029/2005JD006407.
15. Pfister, G. G., P. G. Hess, L. K. Emmons, P. J. Rasch, and F. M. Vitt (2008), Impact of the summer 2004 Alaska fires on top of the atmosphere clear-sky radiation fluxes, *J. Geophys. Res.*, 113, D02204, doi:10.1029/2007JD008797.
16. Schultz, M., T. Diehl, G. Brasseur, and W. Zittel, Air pollution and climate-forcing impacts of a global hydrogen economy. *Science*, 302, 624-627, 2003.
17. Warwick, N. J., S. Bekki, E. G. Nisbet, and J. A. Pyle, Impact of a hydrogen economy on the stratosphere and troposphere studied in a 2-D model. *Geophys. Res. Lett.*, 31, doi:10.1029/2003GL019224, 2004.
18. Yonemura, S. et al., Continuous measurements of CO and H₂ deposition velocities onto an andisol: uptake control by soil moisture, *Tellus*, Volume 51 Issue 3, Pages 688 – 700, 1999.

19. Yonemura, S., S. Kawashima, and H. Tsuruta, Carbon monoxide, hydrogen, and methane uptake by soils in a temperate arable field and a forest, *J. Geophys. Res.*, 105(D11), 14,347–14,362, 2000.

Tables and figures

Table 1. Tropospheric burdens and changes of relevant species in A1FI.

	A1FI-BL	A1FI-BL+H ₂	A1FI-H ₂ -FC	A1FI-H ₂ -ICE
H ₂	839 ppb	41%	40%	38%
O ₃	44 ppb	0%	-7%	-1%
OH	9.1x10 ⁵ molecules/cm ³	-2%	-4%	7%
CO	133 ppb	1%	-14%	-18%
NO _x	100 ppt	0%	-16%	10%
soot	0.01 µg/m ³	0%	-17%	-17%
SO ₄	0.34 µg/m ³	0%	-4%	-3%
SOA	0.04 µg/m ³	0%	-12%	-18%
PAN	197 ppt	0%	-23%	-14%
NMV	9.9 ppb	1%	-11%	-18%
ISOP	41.0 ppt	0%	24%	-1%

Table 2. Tropospheric burdens and changes of relevant species in B1.

	B1-BL	B1-BL+H₂	B1-H₂-FC	B1-H₂-ICE
H₂	621 ppb	20%	20%	19%
O₃	37 ppb	0%	-5%	-1%
OH	10.1x10⁹molecules/cm³	-1%	-4%	3%
CO	90 ppb	0%	-4%	-7%
NO_x	60 ppt	0%	-11%	3%
soot	0.01 µg/m³	0%	-7%	-7%
SO₄	0.33 µg/m³	0%	-4%	-3%
SOA	0.03 µg/m³	0%	-3%	-9%
PAN	110 ppt	0%	-16%	-10%
NMV	5.1 ppb	0%	-7%	-13%
ISOP	47.7 ppt	0%	19%	0%

Figure 1. A1FI based total emission scenarios.

Figure 2. B1 based total emission scenarios.

Figure 3. Change of annual-mean ground-level H_2 mixing ratio between A1FI-BL and A1FI H_2 scenarios.

Figure 4. Similar to Figure 3 except that these figures are for the B1 scenarios.

Figure 5. Change of annual, zonal mean H_2 mixing ratio between A1FI-BL and A1FI H_2 scenarios.

Figure 6. Similar to Figure 5 except that these figures are for the B1 scenarios.

Figure 7. Change of annual-mean ground-level O_3 mixing ratio between A1FI-BL and A1FI H_2 scenarios.

Figure 8. Annual mean emissions of NO_x and VOC ($10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$) in A1FI BL scenario.
Upper left: NO_x. Upper right: VOC. Lower left: VOC-NO_x. Lower right: VOC/NO_x.

Figure 9. Change of annual, zonal mean O_3 mixing ratio between A1FI-BL and A1FI H_2 scenarios.

Figure 10. Similar to Figure 7 except that these figures are for the B1 scenarios.

Figure 11. Similar to Figure 9 except that these figures are for the B1 scenarios.

Figure 12. Change of annual, zonal mean OH concentration between A1FI-BL and A1FI H₂ scenarios.

Figure 13. Similar to Figure 12 except that these figures are for the B1 scenarios.

Figure 14. Change of annual mean ground level NO_x mixing ratio between A1FI-BL and A1FI H_2 scenarios.

Figure 15. Change of annual, zonal mean NO_x mixing ratio between A1FI-BL and A1FI H_2 scenarios.

Figure 16. Similar to Figure 14 except that these figures are for the B1 scenarios.

Figure 17. Similar to Figure 15 except that these figures are for the B1 scenarios.

Figure 18. Change of annual mean ground level CO mixing ratio between A1FI-BL and A1FI H₂ scenarios.

Figure 19. Change of annual, zonal mean CO mixing ratio between A1FI-BL and A1FI H₂ scenarios.

Figure 20. Similar to Figure 18 except that these figures are for the B1 scenarios.

Figure 21. Similar to Figure 19 except that these figures are for the B1 scenarios.

Figure 22. Change of annual mean ground level soot mass in 1m^3 between A1FI-BL and A1FI H₂ scenarios.

Figure 23. Change of annual, zonal mean soot concentration between A1FI-BL and A1FI H₂ scenarios.

Figure 24. Similar to Figure 22 except that these figures are for the B1 scenarios.

Figure 25. Similar to Figure 23 except that these figures are for the B1 scenarios.

Figure 26. Change of annual mean ground level sulfate aerosol mass in 1m³ between A1FI-BL and A1FI H₂ scenarios.

Figure 27. Change of annual, zonal mean sulfate aerosol concentration between A1FI-BL and A1FI H₂ scenarios.

Figure 28. Similar to Figure 26 except that these figures are for the B1 scenarios.

Figure 29. Similar to Figure 28 except that these figures are for the B1 scenarios.

Figure 30. Change of annual mean ground level SOA mass in 1m^3 between A1FI-BL and A1FI H₂ scenarios.

Figure 31. Change of annual, zonal mean SOA concentration between A1FI-BL and A1FI H₂ scenarios.

Figure 32. Similar to Figure 30 except that these figures are for the B1 scenarios.

Figure 33. Similar to Figure 32 except that these figures are for the B1 scenarios.

Appendix: Tropospheric ozone formation from CO and VOCs with the help of NO_x

Below is the main chemical mechanism of ozone formation during CO oxidation process:

If we add reactions 1 to 5 up, we can get the following reaction as the net reaction:

Ozone formation during VOCs oxidation processes is more complicated, but we may see a simple example as the following:

The generated NO₂ can go through reactions 4 and 5 and form ozone. On the other hand RO can be further oxidized and more NO₂ is generated during its oxidation, leading to even more ozone formation via reactions 4 and 5.

Section 3

Impact of a Future Hydrogen-Based Road Transportation Sector on Stratospheric Composition and Chemistry

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Introduction

Hydrogen (H_2) is being considered as a key fuel for energy and transportation systems of the future because it potentially offers a cleaner and more efficient energy carrier than fossil fuels. The large-scale adoption of H_2 fuel in the road transportation sector could impact tropospheric and stratospheric* atmospheric chemistry through leakage of H_2 and reduced emissions of fossil fuel combustion byproducts. Our companion tropospheric and air quality impact study suggests that the emissions changes associated with the adoption of an H_2 based road transportation sector could result in considerable air quality improvements in the troposphere, though the magnitude of the improvements would depend on the details of the technology adopted. The greatest air quality improvement would occur with the adoption of a fuel cell powered road transportation sector where the H_2 is produced with non-polluting technologies. Here we evaluate the impact of these possible emissions changes on the composition and chemistry of stratospheric ozone.

Stratospheric ozone (O_3) is known as “good” ozone since it shields the biosphere from the Sun’s ultraviolet radiation (UV), which can adversely affect the physiological well-being of humans, plants, and animals. The stratospheric ozone layer has previously been adversely impacted by the unforeseen consequences of emissions of compounds that were once believed to be ‘safe’. Chlorofluorocarbons (CFCs) were widely used as refrigerants, propellants, and solvents. Their widespread use was due in part to their stability in the troposphere and long lifetimes (some CFCs have lifetimes of order 100 years). However due to their long atmospheric lifetimes these compounds are transported

* Stratosphere: the atmospheric layer situated between approximately 10km to 50km altitude, in which temperature increases with altitude.

to the stratosphere where they degrade when exposed to intense sunlight (photolyze) releasing Chlorine (Cl) and Bromine (Br) compounds that actively destroy ozone. As a result stratospheric ozone levels have been decreasing since the 1980s with an average global decrease of 3% (1997-2001 average relative to 1980) [WMO, 2002]. In order to avert a catastrophic decline in ozone *The Montreal Protocol on Substances that Deplete the Ozone Layer* was signed in 1987. The Montreal Protocol and its amendments are credited for the decrease in ozone destroying gases in recent years. The stratospheric ozone layer and the Antarctic ozone hole are currently projected to recover in the 2060 to 2070 timeframe [e.g., Newman, et al., 2006].

Given this past experience of unintended consequences of CFCs it is imperative to quantitatively assess the possible impact of an H₂ based road transportation sector on stratospheric ozone. The chemical impact on the stratosphere could come from the change in emissions of H₂ and fossil fuel combustion byproducts (the related chemical mechanisms are discussed in the stratospheric chemistry section). Here we evaluate the impact using emissions scenarios (described in the companion Emissions Scenario Report) based on the high and low emissions scenarios from Intergovernmental Panel on Climate Change (IPCC) future growth projections and atmospheric chemistry transport models.

Method

Model description

In this study, we used a chemistry transport model (CTM), Model for OZone And Related chemical Tracers (MOZART) version 3.1 [Kinnison et al., 2007], which has been developed by the National Center for Atmospheric Research (NCAR), and widely utilized in a number of studies by the atmospheric chemistry and climate community [e.g., Lamarque et al., 2008; Liu, et al., 2009a; Liu, et al., 2009b; Ordóñez et al., 2010; Park et al., 2009; Youn et al., 2009]. The model simulates the atmosphere from the surface to 0.001 Pa level (~115km) by dividing it vertically into 60 layers. Horizontally the globe is partitioned into 96 grids on latitude and 144 grids on longitude, corresponding to a resolution of 1.9° x 2.5° (latitude x longitude). It simulates in a detailed fashion the physical and chemical processes of the troposphere and stratosphere.

It models 108 species, 71 photochemical reactions, 218 gas phase reactions and 18 heterogeneous reactions including heterogeneous chemistry in the stratosphere and polar stratospheric cloud processes. The model meteorology field is from a year of simulation of the Whole-Atmosphere Community Climate Model version 3 (WACCM3) [Garcia *et al.*, 2007], which represents the mid-1990s atmosphere. This meteorology is repeated for each year of our multiyear simulations. We have chosen to use this meteorology since in this study we focus on emissions changes' impacts on photochemistry and because predicting meteorological changes in 2050 with any confidence is highly uncertain (in addition, previous studies [e.g., Lin *et al.*, 2008] have shown that emissions changes will likely be more important than changes in climate on atmospheric composition and chemistry in the future). For more details about the model, see Kinnison *et al.* [2007].

Scenarios description

As mentioned earlier we evaluate the possible impact of an H₂-based road transportation sector in the 2050 atmosphere based on the highest and lowest IPCC emissions scenarios, A1FI and B1, respectively. Given the large uncertainties in future projections, these scenarios were chosen to bracket the possible high and low impacts. In the A1FI scenario, the world is assumed to evolve with rapid economic growth and rely intensively on fossil fuel; whereas in the B1 scenario the world's economic structures are projected to change rapidly toward service-and-information intensive. For each of these two IPCC growth scenarios three emission scenarios were developed: 1) a Baseline emissions scenario without an H₂-based road transportation sector, 2) an H₂ fuel cell technology scenario (H₂-FC) which utilizes H₂ fuel cell powered transportation and includes H₂ leakage emissions and reductions in fossil fuel combustion byproducts, e.g., CO, NO_x, NMVOCs*, and 3) an H₂ internal combustion engine scenario (H₂-ICE) in which the H₂ is burned in conventional internal combustion engines such that there are H₂ leakage emissions and decreases in CO and NMVOCs emissions as in scenario 2) but no decrease in NO_x emissions. In 2050, for the A1FI scenario an H₂-based transportation sector would decrease global CO, NMVOCs and NO_x emissions by 25%, 14%, and 29% (H₂-FC) or 0% (H₂-ICE) whereas increase H₂ emissions by 81%. For the B1 scenario an H₂-based transportation sector would decrease global CO, NMVOCs and NO_x emissions by 10%,

* NMVOCs is a collective term referring to non-methane volatile organic compounds.

8%, and 24% (H₂-FC) or 0% (H₂-FC) while increase H₂ emissions by 64%. The annual-mean global emissions for key species, H₂, CO, NO_x and NMVOCs are listed in Table. 1. For more details see the detailed description in the companion Emissions Scenario Report. Note that the emissions of related species (CO, NO_x, NMVOCs) are the same as those used in the tropospheric impact assessment except for carbonaceous particles and sulfur dioxide, which are not used in the MOZART model. Latitude dependent monthly varying lower boundary conditions for longer lived species (N₂O, CFCs, CH₄) are taken from the appropriate IPCC scenario projections [IPCC, 2001]. The model was run for twelve years so as to reach an annually repeating steady state. Here we present results based on these scenarios.

Results and discussion

Our modeling studies suggest that the combined effect of increased H₂ emissions and other emission changes in an H₂-based road transport sector would tend to decrease ozone concentrations in the stratosphere in all scenarios except for the B1 H₂-ICE one. The overall effects on annual-, global-mean stratospheric column ozone are -0.54%, -0.23%, -0.20% and +0.04% for A1FI H₂-FC, A1FI H₂-ICE, B1 H₂-FC and B1 H₂-ICE scenarios, respectively. Since interpretation of the stratospheric impact involves knowledge of stratospheric chemistry, please refer to the *Appendix* for background information.

Baseline Scenarios

The baseline 2050 atmospheres for IPCC A1FI and B1 scenarios (with fossil fuel transportation sector) are used as baselines in this study. The model simulations show that in the 2050 Baseline scenarios stratospheric ozone would recover to a significant extent compared with today's atmosphere (Figure. 1), as would be expected from future decline of atmospheric halogen concentrations. For the 2050 A1FI Baseline scenario there would be ~13 DU more ozone in the stratosphere than that for today (Figure. 1b), in terms of column ozone*. Whereas for the 2050 B1 Baseline scenario atmosphere, the stratospheric column ozone would be ~11 DU higher than that for today (Figure. 1c). The Antarctic

* Column ozone, often expressed in Dobson unit, refers to the amount of ozone in the atmospheric column under study. 1 DU is the amount of ozone that would be one thousandth of a centimeter thick at standard temperature and pressure, or 2.69×10^{16} O₃ molecules/cm².

ozone hole would have recovered to a significant extent. The minimum total column ozone would be around 220 DU at the southern polar region in October for both the A1FI and B1 Baseline scenarios, in contrast to the 150 DU minimum ozone column today (Figure. 1a).

Hydrogen Fuel Cell Scenarios

The annual-, global-mean stratospheric column ozone for the A1FI H₂-FC scenario would be reduced by -0.54%, or 1.5DU. The reduction ranges from 0.4% to 1%, or 1DU to 2.5DU, depending on latitude and time of a year (Figures. 2a and 2b). For the B1 H₂-FC scenario the mean stratospheric column ozone would be reduced by -0.20%, or 0.5DU. The reduction ranges from 0.2% to 1%, or 0.2DU to 1DU (Figures. 3a and 3b).

The relative reduction in ozone concentration is generally more pronounced at lower altitudes in the upper troposphere/lower stratosphere (UT/LS) region (Figure. 4b and 5b), partly due to the reduced ozone production in the underlying troposphere due to reduced [NO_x]*. (For more background information on tropospheric ozone chemistry, please refer to the companion tropospheric impact report.)

The most pronounced relative O₃ reduction (up to 12% for the A1FI H₂-FC scenario and up to 6% for the B1 H₂-FC) appears at approximately 13 km altitude around 15 °N (Figures. 4b and 5b). This maximum relative [O₃] decrease in the UT/LS region coincides with a strong relative reduction of [NO_x] there (up to 16% for A1FI and up to 10% for B1) (Figures. 6b and 7b), which slows down local ozone production. Meanwhile, as will be elucidated later, [NO_x] decrease would lead to enhancement of HO_x catalyzed cycles, which results in faster ozone loss (NO_x/HO_x coupling).

In the lower stratosphere where tropospheric origin ozone has relatively small impact (altitudes > 15km at 35°N, for example), catalytic cycles involving HO_x overwhelm ozone destruction. Our model results confirm the overwhelming role of HO_x cycles in ozone destructions in the lower stratosphere (Figures. 8b,c and 9b,c). HO_x concentrations

* The species in bracket represents its concentration.

are predicted to increase by up to 6% and 4% for both the A1FI and B1 scenarios, respectively (Figures. 10b and 11b). This $[\text{HO}_x]$ increase enhances the HO_x -catalyzed ozone loss cycles (Figures. 12c,d and 13c,d). At the same time, as discussed in the appendix, the concomitant $[\text{NO}_x]$ reduction (Figures. 6b and 7b) would impact the HO_x cycles* via reactions (14) and (17), affecting $[\text{HO}_x]$ as well as the HO_2/OH ratio. In this case, $[\text{HO}_2]$ would increase due to decreased availability of NO in reaction (14), leading to enhanced ozone loss via reactions (7) and (15). Meanwhile, the rate of reaction (17) would fall as $[\text{NO}]$ decreases, making reaction (17) a smaller HO_x sink. Both of these effects tend to further enhance the HO_x -catalyzed ozone destruction cycle. The HO_x cycles intensify by up to 3% and up to 2% for the A1FI and B1 H_2 -FC scenarios, respectively (Figures. 12c and 13c). In addition, a decrease in $[\text{NO}_x]$ would also lead to halogen cycles enhancement (Figures. 12c,d and 13c,d) via NO_x /halogen cycles coupling. This enhancement would have a smaller impact on ozone concentrations since halogen cycles are only responsible for a few percent of ozone destruction in the lower stratosphere (Figures. 8b,c and 9b,c). To summarize, in the lower stratosphere O_3 loss is dominated by HO_x catalyzed O_3 destruction cycles and the decrease in ozone concentration in the A1FI and B1 H_2 -FC scenarios is due to an intensification of these cycles.

In the middle stratosphere (25-35km altitude in the tropics, somewhat lower at higher latitudes), there exists a slight ozone increase (less than 0.4%) for both A1FI and B1 H_2 -FC scenarios (Figures. 4b and 5b). Even though ozone loss from HO_x catalytic cycles increases due to $[\text{HO}_x]$ increase, the overall ozone loss is alleviated because NO_x cycles dominate ozone loss in the middle stratosphere (Figures. 8b,c and 9b,c) and $[\text{NO}_x]$ is reduced there (Figures. 6b,c and 7b,c). The major source of NO_x in the stratosphere is the reaction of N_2O against $\text{O}(^1\text{D})$. In this region where $[\text{N}_2\text{O}]$ and $[\text{O}(^1\text{D})]$ are not significantly affected by the perturbation of an H_2 -FC sector, $[\text{NO}_x]$ decrease is due to enhancement of reaction (17), through which increased $[\text{HO}_x]$ makes this reaction a larger NO_x sink and, likely due to decreases in $[\text{NO}_x]$ in the underlying atmosphere. Changes in $[\text{NO}_x]$ in the troposphere typically do not impact its concentrations in the stratosphere owing to its short lifetime. However, it is proposed that reactive nitrogen

* “ HO_x cycles” is short for “ HO_x -catalyzed ozone loss cycles”. This also applies to other cycles hereafter.

(NO_y) in the upper troposphere over tropical regions can significantly impact on the lower stratosphere [NO_y] [Ko *et al.*, 1986] due to NO_y's longer lifetime. This is supported by observations [e.g., Murphy *et al.*, 1993]. In this study, [NO_y] in the UT/LS region is about 1 ppb (parts per billion by volume) in all scenarios (Figures. 14 and 15), exceeding the threshold mixing ratio suggested by Murphy *et al.* [1993], which is 0.6 ppb. Therefore, [NO_y] in the underlying atmosphere are likely to be significant enough to impact on stratospheric NO_y abundance. In the H₂-FC scenarios, [NO_y] in the UT/LS region is significantly reduced (~15% for A1FI and 8% for B1) (Figures. 14b and 15b), resulting in [NO_x] declines in the above stratosphere. The NO_x catalyzed ozone destruction cycle is reduced throughout most of the stratosphere (Figures. 12c and 13c), however, its impact on ozone concentrations is only apparent where NO_x cycles dominate ozone destruction (Figures 8b,c and 9b,c). Therefore, slight ozone concentration increase is seen in the middle stratosphere in both of the H₂-FC scenarios (Figures. 4b,c 5b,c 12a,b and 13a,b) due to an attenuation of NO_x catalyzed ozone destruction cycle (Figures. 12c,d and 13c,d).

In the upper stratosphere, HO_x catalyzed cycles again dominate ozone loss cycles (Figures 8b,c and 9b,c). The [HO_x] increase from enhanced H₂ abundance and the decline in the rate of reaction (17) as a result of the [NO_x] decrease leads to enhancement of HO_x catalyzed cycles (Figures. 12c,d and 13c,d). The resulting [O₃] decline in this region is up to 1% for A1FI and B1 H₂-FC scenarios (Figures. 4b and 5b), but the impact on total column ozone is relatively small owing to the low number concentrations there (Figures. 8a and 9a).

Hydrogen Internal Combustion Engine Scenarios

The impact of the H₂-ICE road transportation sectors on stratospheric ozone concentration is relatively modest compared with the corresponding H₂-FC scenarios. The annual-, global-mean stratospheric column ozone for the A1FI H₂-ICE scenario would be reduced by -0.23%, or 0.5DU. The perturbation on mean stratospheric column ranges from -0.8% to +1%, or -2DU to +2.5DU, depending on latitude and time of a year (Figures. 2c and 2d). For the B1 H₂-ICE scenario the mean stratospheric column ozone

would be increased by 0.04%, or 0.1DU. The reduction ranges from -0.2% to +1%, or -0.5DU to +2.5DU (Figures. 3c and 3d).

One prominent feature distinguishing the H₂-ICE scenarios from the H₂-FC scenarios is that the [NO_x] decrease in the stratosphere is not as significant in the H₂-ICE scenarios as that in H₂-FC. For the H₂-ICE scenarios, [NO_x] increases in the lower and upper stratosphere for A1FI (Figures. 6d and 6e), and increases throughout the stratosphere for B1 (Figures. 7d and 7e). In the lower stratosphere [NO_x] increases because of [NO_x] increase throughout the troposphere since in the H₂-ICE scenarios NO_x is still emitted as combustion byproduct of internal combustion engines. In addition, HO_x concentrations decrease in the troposphere due to the reduced NMVOCs emissions (NMVOCs oxidation provides a HO_x source in the upper troposphere). The decrease in [HO_x] decreases the NO_x loss due to reaction (17), which in turn enhances [NO_x].

For the A1FI H₂-ICE scenario the relative perturbation on the catalytic ozone loss cycles is about half of that for the A1FI H₂-FC scenario (Figures. 12g and 12h). The combined impact is a smaller in magnitude but more spatially dispersed [O₃] increase in the middle stratosphere (Figures. 4d and 4e). However, this widespread [O₃] increase would not fully compensate the [O₃] decrease in the lower stratosphere because ozone is denser in terms of molecular number concentration there (Figure. 8a). The global-mean column ozone in the stratosphere would still be 0.23% less than that in the A1FI Baseline atmosphere.

For the B1 H₂-ICE scenario there would be negligible impact on all cycles except for the halogen catalyzed ones (Figures. 13g and 13h). The ozone loss rate of halogen catalyzed cycles decreases by about 2%, resulting in a slight [O₃] increase. The impact of increased NO_x catalyzed cycles on ozone in the lower stratosphere is “buffered” by decrease in halogen catalyzed cycles. (Increased [NO_x] leads to slower halogen catalyzed cycles via halogen/NO_x coupling, like a buffer, see *Nevison et al.*, 1999.) In the upper stratosphere, enhanced HO_x catalyzed cycles are compensated by alleviated halogen cycles. The resulting ozone loss rate is decreased throughout the stratosphere (Figure. 13h). Zonal mean [O₃] increases slightly throughout the middle and upper stratosphere (Figures. 5d and 5e). In the lower stratosphere, [O₃] decreases in the tropics and northern hemisphere

due to tropospheric impact, but increases in the southern high latitudes, where halogen catalyzed ozone loss cycles dominate (Figure. 16), and halogen cycles are slowed down there as $[\text{NO}_x]$ increases. The overall effect of B1 H_2 -ICE scenario is minimal on stratospheric ozone column (+0.04%). However, the total column ozone, the amount of ozone overhead, would still be 0.06% less than that in the B1 Baseline scenario since tropospheric ozone is reduced.

Comparison with other studies

There have been several studies of a hydrogen society's impact on the atmosphere. *Tromp et al.* [2003] used the Caltech/JPL 2-D CTM to study the impact of quadrupling atmospheric H_2 concentration on the stratosphere. They did not consider the changes of related emissions (CO , NO_x , NMVOCs) associated with the replacement of fossil fuel with hydrogen technology. They found major ozone loss of up to 8% during polar spring, however, their modeling results did not capture subtle ozone features at non-polar latitudes, while better representation of dynamical and transport processes in our three-dimensional modeling work allowed us to do so. Despite of these major differences, we may take a comparison of projected stratospheric water vapor concentration with Tromp et al. They predicted 0~35% water vapor increase due to 300% increase of H_2 concentration. Our study shows about 30% increase of H_2 mixing ratio would result in 0~5% increase in stratospheric H_2O . These results are in general agreement if we scale the concentration change.

Tromp et al. [2003] predicted maximum column ozone change rather differently from our study: they predicted that maximum reduction occurs at poles during spring. This discrepancy may arise because their simulations were based on the current atmosphere, in which atmospheric Cl_y and Br_y (Cl_y and Br_y are important in ozone hole chemistry) burdens are still large, whereas our simulations are based on the 2050 atmosphere, in which $[\text{Cl}_y]$ and $[\text{Br}_y]$ are reduced as a consequence of the implementation of the Montreal Protocol.

Taking into consideration of associated changes in CO , NO_x , NMVOCs emissions when using H_2 fuel and using a 2-D model, *Warwick et al.* [2004] found no significant change

in stratospheric ozone (it slightly increased by ~0.1% according to their study). What is worth noting is that another experiment in the same paper showed four-fold increase in atmospheric H₂ concentration would increase stratospheric ozone. Warwick et al. attributed this to that in their model H₂ is not completely converted to water vapor in the stratosphere. They found up to 20% stratospheric water vapor increase if H₂ concentration quadrupled. This number is significantly lower than that found by *Tromp et al.* [2003].

Conclusions

In this study possible impact of a future H₂-based road transportation sector on stratospheric composition and chemistry is investigated by modeling simulations of the 2050 atmosphere based on different assumed scenarios on emissions, in which, to bracket the possible lower and higher ends, the world is projected to evolve along either a fossil fuel intensive (A1FI) pathway or a service and information intensive (B1) pathway, and H₂-based road transportation sector is assumed to be implemented with two different technological choices: H₂ fuel cell and H₂ internal combustion engine.

The modeling studies suggest that future implementation of an H₂-based road transportation sector would perturb stratospheric chemistry, by means of affecting catalytic ozone destruction cycles involving O_x, HO_x, NO_x, ClO_x and BrO_x. The magnitude of the impact depends on the future growth path as well as the H₂ utilization technology adopted. The overall impact ranges from a 0.54% decrease (A1FI H₂-FC) to a very slight increase (0.04%, B1 H₂-ICE), depending on different scenarios and technological options, on a global mean total column ozone basis. The overall effect on stratospheric column ozone is considerable for the A1FI scenarios (-0.54% for H₂-FC and -0.23% for H₂-ICE) and for the B1 H₂-FC scenario (-0.20%). The largest relative reduction of ozone concentration takes place in the lower stratosphere where impact from the underlying troposphere is prominent. In the middle stratosphere ozone concentration slightly increases. At higher altitude it either slightly decreases or slightly increases depending on scenarios, but this change has little impact on column ozone since ozone at this level only takes up a few percent in terms of column ozone, due to the low ozone number concentration there. It is important to note that in developing the H₂ emissions

our assumptions were chosen to represent the maximum possible impact and thus these estimates likely represent the maximum possible ozone loss.

Our modeling studies suggest that the impact of an H₂-based road transportation sector on stratospheric ozone depends on technological options. The combined effect of changes in catalytic cycles would result in more ozone loss for the H₂-FC scenarios than in the H₂-ICE scenarios. Meanwhile, the impact on stratospheric ozone depends also on which scenario the world would evolve along in the future. Our studies suggest that with the same technological option, there would be less impact on stratospheric ozone if the world evolves along B1 scenario than A1FI.

It is also worth noting that even though an H₂-based road transportation sector is likely to decrease stratospheric ozone, this reducing effect is projected to be less than the ozone recovery effect due to removal of ozone depleting substances from the atmosphere as of 2050. In terms of total column ozone, there would be still 4%~7% more ozone in the 2050 atmosphere with an H₂-based road transportation sector than that in today's atmosphere. Therefore, the ozone reduction due to an H₂-based road transportation sector might not constitute a major concern on increased UV radiation at the surface in 2050.

References:

1. Chapman, S., A theory of upper atmospheric ozone, *Mem. Roy. Meteorol. Soc.* 3, 103-125, 1930.
2. Garcia, R. R., D. R. Marsh, D. E. Kinnison, B. A. Boville, and F. Sassi, Simulation of secular trends in the middle atmosphere, 1950–2003, *J. Geophys. Res.*, 112, D09301, doi:10.1029/2006JD007485, 2007.
3. IPCC, *Climate Change 2001, The Scientific Basis. Contribution of Working Group 1 to the Third Assessment Report of the IPCC*, Cambridge University Press, Cambridge, UK and New York, USA, 2001.
4. Kinnison, D. E., G. P. Brasseur, S. Walters, et al., Sensitivity of chemical tracers to meteorological parameters in the MOZART-3 chemical transport model, *J. Geophys. Res.*, 112, D20302, doi:10.1029/2006JD007879, 2007.
5. Ko, M. K. W., M. B. McElroy, D. K. Weisenstein, and N. D. Sze, Lightning: A possible source of stratosphere odd nitrogen, *J. Geophys. Res.*, 91, 5395-5404, 1986.
6. Lamarque, J.-F., D. E. Kinnison, P. G. Hess, and F. M. Vitt, Simulated lower stratospheric trends between 1970 and 2005: Identifying the role of climate and composition changes, *J. Geophys. Res.*, 113, D12301, doi:10.1029/2007JD009277, 2008.
7. Lin, J.T., K.O. Patten, K. Hayhoe, X.-Z. Liang and D.J. Wuebbles, Effects of future climate and biogenic emissions changes on surface ozone over the United States and China, *Journal of Applied Meteorology and Climatology* **47** (7), pp. 1888–1909, 2008.
8. Liu, C., Y. Liu, Z. Cai, S. Gao, D. Lu, and E. Kyrola, A Madden–Julian Oscillation-triggered record ozone minimum over the Tibetan Plateau in December 2003 and its association with stratospheric “low-ozone pockets,” *Geophys. Res. Lett.*, 36, L15830, doi:10.1029/2009GL039025, 2009.
9. Liu, Y., C. X. Liu, H. P. Wang, X. X. Tie, S. T. Gao, D. Kinnison, and G. Brasseur, Atmospheric tracers during the 2003–2004 stratospheric warming event and impact of ozone intrusions in the troposphere, *Atmospheric Chemistry And Physics*, Volume 9, Issue 6, Pages: 2157-2170, 2009.

10. McElroy, M. B., R. J. Salawitch and K. Minschwaner, The changing stratosphere. *Planet. Space. Sci.*, 40:373-401, 1992.
11. Minschwaner, K., R. J. Salawitch, and M. B. McElroy, Absorption of Solar Radiation by O₂: Implications for O₃ and Lifetimes of N₂O, CFCl₃, and CF₂Cl₂, *J. Geophys. Res.*, 98(D6), 10, 543–10, 561, 1993.
12. Murphy, D. M., D. W. Fahey, M. H. Proffitt, S. C. Liu, K. R. Chan, C. S. Eubank, S. R. Kawa, and K. K. Kelly, Reactive Nitrogen and Its Correlation With Ozone in the Lower Stratosphere and Upper Troposphere, *J. Geophys. Res.*, 98(D5), 8751–8773, 1993.
13. Nevison, C. D., S. Solomon, and R. S. Gao (1999), Buffering interactions in the modeled response of stratospheric O₃ to increased NO_x and HO_x, *J. Geophys. Res.*, 104(D3), 3741–3754, doi:10.1029/1998JD100018.
14. Newman, P. A., E. R. Nash, S. R. Kawa, S. A. Montzka, and S. M. Schauffler (2006), When will the Antarctic ozone hole recover?, *Geophys. Res. Lett.*, 33, L12814, doi:10.1029/2005GL025232.
15. Ordonez, C., N. Elguindi, O. Stein, et al., Global model simulations of air pollution during the 2003 European heat wave, *Atmospheric Chemistry and Physics*, Volume 10, Issue 2, Pages 789-815, 2010.
16. Park, M., W. J. Randel, L. K. Emmons, and N. J. Livesey, Transport pathways of carbon monoxide in the Asian summer monsoon diagnosed from Model of Ozone and Related Tracers (MOZART), *J. Geophys. Res.*, 114, D08303, doi:10.1029/2008JD010621, 2009.
17. Seinfeld, J. H. and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 1997.
18. Tromp, T., R. Shia, M. Allen, J. Eiler, and Y. Yung, Potential environmental impact of a hydrogen economy on the stratosphere. *Science* 300, 1740-1742, 2003.
19. Warwick, N. J., S. Bekki, E. G. Nisbet, and J. A. Pyle, Impact of a hydrogen economy on the stratosphere and troposphere studied in a 2-D model, *Geophys. Res. Lett.*, 31, L05107, doi:10.1029/2003GL019224, 2004.
20. World Meteorological Organization. *Scientific Assessment of Ozone Depletion: 2006*, Geneva, 2006.

21. Youn, D., K.O. Patten, J.-T. Lin and D.J. Wuebbles, Explicit calculation of indirect global warming potentials for halons using atmospheric models, *Atmospheric Chemistry And Physics*, Volume 9, Issue 22, Pages: 8719-8733, 2009.

Appendix: A brief survey of stratospheric chemistry

Ozone plays a central role in stratosphere chemistry. Local ozone concentrations are determined by photochemical production and loss as well as transport. In the stratosphere, ozone is produced through a series of reactions involving O_2 in the presence of sunlight with wavelength less than 242 nm [e.g., *Chapman*, 1930]:

The key step in this sequence is generation of oxygen atoms formed when oxygen molecules are photochemically dissociated into oxygen atoms (reaction 1). These oxygen atoms quickly combine with oxygen molecules in the presence of a third body (M, typically N_2 or O_2) to form ozone (reaction 2). The rates of reactions (2) and (3) are substantially larger than those of reactions (1 and 4), thus O and O_3 are quickly interconverting. Because of this quick cycling O and O_3 are collectively referred to as odd oxygen (O_x), and ozone loss can be expressed as destruction of O_x .

Ozone (or O_x) is destroyed through several pathways including odd oxygen only chemistry and through catalytic ozone destruction cycles involving NO_x , HO_x , ClO_x , and BrO_x . Reaction (4) represents the ozone loss through oxygen only chemistry and together with reactions (1)-(3) make up the Chapman mechanism which laid the foundation of our current understanding of stratospheric ozone [e.g., *Chapman*, 1930; *Seinfeld and Pandis*, 2006]. A typical catalytic ozone destruction cycle involving $X = NO, OH, H, Cl$, or Br may be written

During this cycle the X consumed in reaction (5) is regenerated in reaction (6) and available to repeat the cycle while two odd oxygens are destroyed in the cycle. Since it is regenerated, X acts as a catalyst for ozone destruction. In the catalytic cycles there is typically fast cycling between reactions X and XO such that they are referred to as XO_x, e.g., NO_x, HO_x, ClO_x, BrO_x. (HO_x may be defined to include H, OH, and HO₂). For NO_x and HO_x the XO₂ reactions may also be important, e.g.,

For NO_x there is a competing reaction for NO₂.

Note that reactions (8) and (9) represent a null cycle in which no ozone is destroyed since the O quickly reacts via reaction (2) to reform O₃.

The catalytic destruction cycles do not operate in isolation from each other but are coupled, for example

For X = Cl or Br in reactions (15) and (16).

Ozone destruction through these catalytic cycles will continue until the catalyst is converted to a more stable form referred to as a reservoir species. A reservoir species may react to regenerate the catalyst or may leave the stratosphere via transport to the troposphere. The major reservoir species include HNO₃, HCl, and ClONO₂ and are formed via reactions between the reactive families.

The impact of coupling of the catalytic ozone destruction cycles is complex and depends on location in the stratosphere. In the mid latitude lower stratosphere overall catalytic ozone destruction is inversely correlated with NO_x concentrations since the balance of the relative importance of reactions (7) and (14) depends on NO_x concentrations as does the balance of reaction (6) with $\text{X} = \text{Cl}$ and reaction (19) [e.g., Wennberg *et al.*, 1994; Seinfeld and Pandis, 2006].

The relative importance of each cycle varies with altitude in the stratosphere. HO_x cycles are found to be the biggest mechanism of ozone destruction in the stratosphere below 22 km altitude [McElroy *et al.*, 1992]. The HO_x cycle (reactions 5 with $\text{X} = \text{OH}$ and 7) is found to be responsible for 30~50% of ozone destruction in the lower stratosphere [Seinfeld and Pandis, 1997]. The HO_x cycles dominate the loss of O_x in the lower and upper stratosphere but has little impact in the mid-stratosphere (~35 km) while the NO_x cycle dominates loss in the middle stratosphere but has a relatively small direct impact in the lower and upper stratosphere (Figures 3b,c and 4b,c). In the upper stratosphere, the rate of ozone destruction resulting from HO_x cycles is again more than that from NO_x cycles [Minschwaner *et al.*, 1993]. The most important catalytic cycle responsible for ozone destruction above 40km consists of reactions (5) and (6), where in both reactions X represents H. The increasing importance of the HO_x cycle above with altitude comes from increasing O and H concentration with altitude. The impacts of the O_x and halogen cycles are more uniform and play a less significant role throughout the stratosphere than either the HO_x or NO_x impact [e.g., Seinfeld and Pandis, 2006].

As mentioned in the introduction, a future hydrogen-based road transportation sector could perturb the stratospheric composition and chemistry by altering emissions of fossil fuel combustion byproducts and leaking H_2 into the atmosphere. H_2 's atmospheric lifetime is around two years, which is longer than the time required for H_2 to make its way to the stratosphere. Therefore a portion of H_2 emitted at the surface will penetrate

into the stratosphere, where it is oxidized and becomes a source of HO_x (reactions 20 and 21). One H₂ molecule can produce two HO_x radicals via the following reactions

where O(¹D) is the excited state of oxygen atom. In such a way, increased H₂ concentration can lead to more HO_x in the stratosphere (Figures. 10 and 11).

Tables and Figures

Table 2. Annual-mean global emissions for key species.

Species	H ₂	CO	NO	NMVOCs
Unit	Tg/yr	Tg/yr	TgN/yr	Tg/yr
A1FI Baseline	56.6	1844.7	94.3	600.9
A1FI H ₂ -FC	102.7	1383.4	67.2	518.5
A1FI H ₂ -ICE	102.7	1383.4	94.3	518.5
B1 Baseline	32.4	1223.3	46.0	442.7
B1 H ₂ -FC	53.2	1107.1	34.8	408.5
B1 H ₂ -ICE	53.2	1107.1	46.0	408.5

Figure 1. Simulated stratospheric column ozone as a function of latitude and year for (a) current (year 2000) atmosphere, (b) 2050 A1FI Baseline scenario and (c) 2050 B1 Baseline scenario.

Figure 2. Change of stratospheric column O_3 in a year at different latitudes in H_2 road transportation sectorscenarios relative to the A1FI Baseline scenario. (a): relative change (%) for A1FI H_2 -FC; (b): absolute change (DU) for A1FI H_2 -FC; (c): relative change (%) for A1FI H_2 -ICE; (d): absolute change (DU) for A1FI H_2 -ICE.

Figure 3. Change of stratospheric column O_3 in a year at different latitudes in H₂ road transportation sector scenarios relative to the B1 Baseline scenario. (a): relative change (%) for B1 H₂-FC; (b): absolute change (DU) for B1 H₂-FC; (c): relative change (%) for B1 H₂-ICE; (d): absolute change (DU) for B1 H₂-ICE.

Figure 4. (a) O₃ concentration for A1FI Baseline; (b) Relative change of O₃ concentration in A1FI H₂-FC relative to Baseline; (c) Absolute change of O₃ concentration in A1FI H₂-FC relative to Baseline; (d) Relative change of O₃ concentration in A1FI H₂-ICE relative to Baseline; (e) Absolute change of O₃ concentration in A1FI H₂-ICE relative to Baseline. All figures are zonal, annual-mean.

Figure 5. The same as in Figure.4 except that these figures are for the B1 scenarios.

Figure 6. The same as in Figure 4 except that these figures are for NO_x .

Figure 7. The same as in Figure 6 except that these figures are for the B1 scenarios.

Figure 8. (a): Model calculated O₃ profile;
(b): Model calculated contributions to total O₃ loss rate by different catalytic cycles;
(c): profile of relative contributions (%) by different catalytic cycles to the O₃ loss rate.
All figures are daily averaged values for fall equinox at 35°N for the A1FI Baseline scenario.

Figure 9. The same as in Figure 8 except that these figures are for the B1 scenarios.

Figure 10. The same as in Figure 4 except that these figures are for HO_x .

Figure 11. The same as in Figure 10 except that these figures are for the B1 scenarios.

Figure 12. Changes of O_3 profiles and contributions of different catalytic cycles to total O_3 loss. The upper row of figures is for H_2FC -Baseline; lower row for H_2ICE -Baseline. (a) and (e): absolute O_3 number concentration; (b) and (f): relative change (%) in O_3 number concentration; (c) and (g): change (%) of different catalytic O_3 destruction cycles compared to its contribution in Baseline; (d) and (h): change (%) of different catalytic O_3 destruction cycles compared to the total O_3 loss rate in Baseline. All figures are daily averaged values for fall equinox at $35^\circ N$ for the A1FI scenarios.

Figure 13. The same as in Figure 12 except that these figures are for the B1 scenarios.

Figure 14. The same as in Figure 4 except that these figures are for NO_y .

Figure 15. The same as in Figure 14 except that these figures are for the B1 scenarios.

Figure 16. Percentage contribution to total ozone loss by halogen catalyzed cycles at fall equinox.

Section 4

Assessment of the Impact of a 2050 H₂-based Transportation Sector on Air Quality in the Continental United States

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Introduction

The quality of the air at the surface of the Earth is vitally important to the health of humans, agriculture, and ecosystems. Measures of air quality are typically related to the ground level concentrations of key gaseous and particulate pollutants. These concentrations depend in a complicated manner on the emissions of the pollutants or their precursors and atmospheric photochemistry and transport processes. The impacts of these pollutants are varied. For example, increased ground level ozone (O₃) can cause airway irritation, coughing, wheezing and breathing difficulties, aggravation of asthma and increased susceptibility to respiratory illnesses like pneumonia and bronchitis, and, with repeated exposure, permanent lung damage. Increased ozone can also adversely affect ecosystem health and crop yields. When breathed, carbon monoxide (CO) is absorbed into the bloodstream where it displaces oxygen and bonds with the hemoglobin in blood depriving the body of oxygen. Airborne particulate matter less than 2.5 microns in diameter (PM_{2.5}) is able to travel deeply into the respiratory tract and lungs where it can cause short-term health effects such as eye, nose, throat and lung irritation, coughing, sneezing, runny nose and shortness of breath. Long term exposure may be associated with increased rates of chronic bronchitis, reduced lung function and increased mortality from lung cancer and heart disease. Other components of smog, e.g., peroxyacetyl nitrate (PAN) are also irritants with adverse health impacts.

It has been known since the early 1950s that one of the primary components of photochemical smog is ozone [Haagen-Smit 1952]. Ozone is not emitted directly by car engines or by industrial operations, but formed by the reaction of volatile organic compounds (VOC) and nitrogen oxides (NO_x=NO+NO₂, where NO is nitric oxide and NO₂ is nitrogen dioxide) in air exposed to sunlight and warm temperatures [see, for example, textbooks such as Seinfeld and Pandis (2006) or Jacob (1999), as well as the

companion report to this one on tropospheric impacts]. VOC and NO_x are known as ozone precursors because they are necessary for and typically lead to the production of tropospheric ozone. The predominant source of these ozone precursors is emissions from the incomplete combustion of fossil fuels, for example from automobiles. In many countries concerns about air quality have led to regulatory controls on the emissions of these ozone precursors. The Clean Air Act of 1963 was the first federal legislation regarding air pollution control and has been followed by further legislation aimed at improving ground level air quality particularly in large cities. This legislation has been largely successful with emissions reductions of ~50% (VOC) and 30% (NO_x) between 1980 and 2007 even though vehicle miles traveled more than doubled and energy consumption increased by 30% (US EPA 2008, Weaver et al. 2009).

Though efforts are ongoing to improve air quality through controls on automobile emissions there has been less emphasis on moving away from fossil fuels and internal combustion engine (ICE) technology to other energy technologies. However, there are possibly large benefits to moving towards hydrogen (H₂) as a transportation energy carrier and to H₂ powered fuel cell engines. Hydrogen fuel cell systems emit limited amounts of water and these emissions would displace fossil fuel combustion emissions of NO_x, VOC, CO, and particulate matter, all of which contribute to the environmental problems inherent with fossil fuel combustion. Additionally, if the H₂ is made from renewable non-polluting energy sources, e.g., wind or solar power, there will be an associated reduction in the emissions of carbon dioxide (CO₂), and in the case of coal combustion, sulfur dioxide (SO₂). Although there would undoubtedly be some leakage of H₂ to the environment, it is postulated that the environmental benefit of the decrease in fossil fuel related emissions would more than outweigh the possible adverse impact of the emitted H₂. The complete conversion to an H₂-powered transportation sector would certainly take some time as it would require a large-scale change in delivery infrastructure and an entirely new fleet of automobiles worldwide.

Here we evaluate the possible impact on United States air quality of converting to an H₂-powered transportation sector in 2050. Since future changes in transportation are exceedingly difficult to project and highly uncertain we evaluate several growth and technology scenarios chosen to bracket the possible future paths. Two growth paths were selected based on the Intergovernmental Panel on Climate Change (IPCC) low emitting

(B1) and high emitting (A1Fi) scenarios for 2050. The A1FI scenario represents a future where the world is assumed to evolve with rapid economic growth relying intensively on fossil fuel; whereas in the B1 scenario the world's economic structures are projected to rapidly transform to a service-and-information based society with minimal reliance on fossil fuels. For each of these growth scenarios two technology adoption scenarios were chosen, the first assumes fuel cell technology with its corresponding decrease in NO_x, VOC, CO, and aerosol precursor emissions, and the second assumes H₂ burning internal combustion engines in which VOC, CO, and aerosol precursors are reduced but NO_x emissions are not reduced. These scenarios currently represent the range of the best available evaluation of future emissions from human related activities for the extent of this century. This report is a companion report to the emissions report and the tropospheric and stratospheric impact reports.

Methods

We are using the Community Multiscale Air Quality Modeling System (CMAQ) version 4.6 [see www.cmaq-model.org] to evaluate the regional air quality impacts of an H₂ economy. The CMAQ model was initially released to the public by U.S. Environmental Protection Agency (EPA) in 1998 and has undergone many revisions and improvements since [e.g., Appel 2007, 2008]. The CMAQ modeling system was designed to approach air quality as a whole by including state-of-the-science capabilities for modeling multiple air quality issues, including tropospheric ozone, fine particles, toxics, acid deposition, and visibility degradation. In this way, the development of CMAQ involves the scientific expertise from each of these areas and combines the capabilities to enable a community modeling practice. CMAQ was also designed to have multi-scale capabilities so that separate models were not needed for urban and regional scale air quality modeling. The CMAQ model is used for research and regulatory applications by the EPA, states, and other researchers and has been extensively evaluated against observations [e.g., most recently, Appell 2007, 2008; Sarwar, et al, 2008; Mathur et al., 2008, Roy, et al., 2007; Eder and Yu, 2006; Tong and Mauzerall, 2006]. As the EPA recommended model for use in air quality evaluation the source code and algorithms also undergo a regular peer-review process. The results of which are available from www.cmaq-model.org.

For this study the model horizontal resolution is 30 km by 30 km with 22 vertical layers from the surface to 13km. It has a relatively good resolution in the boundary layer with 5 layers in the first km. The meteorological data to drive CMAQ is from a climate version of the MM5 model [CMM5; e.g., Liang et al., 2001] for the year 1995. We have chosen to use 1995 meteorology since here our focus is on air quality and photochemistry influenced impacts due to changes in emissions and because predicting meteorological changes in 2050 with any confidence is fraught with uncertainty (in addition, previous studies [e.g., Lin et al., 2008] have shown that future climate changes will likely have less effect on air quality than the future changes in emissions). For this study CMAQ uses the Carbon Bond 5 gas phase photochemistry package [Luecken, et al., 2008; Sarwar, et al., 2008] with 56 species and 156 reactions. The aerosol chemistry package is coupled to the gas phase chemistry package and contains 34 transported aerosol modes. The aerosol package represents the particle size distribution as the superposition of three lognormal modes. The processes of coagulation, particle growth by the addition of new mass, and particle formation are included. Time stepping is done utilizing an analytical solution to the differential equations for the conservation of number and species mass conservation. The simulation was carried out with a 12 minute dynamical timestep and the chemistry package using a 2.5 min sub-timestep. Detailed descriptions of the mechanisms, algorithms, and implementation are available in the CMAQ scientific documentation (see www.epa.gov/asmdnerl/CMAQ/CMAQscienceDoc.html).

Boundary conditions for the CMAQ model simulations are based on the corresponding global tropospheric model simulations. The global tropospheric simulations were carried out with the Community Atmospheric Model with chemistry (CAMchem). CAMchem development is led by the National Center for atmospheric Research with considerable contributions from the community including the National Science Foundation, the Department of Energy, the National Aeronautics and Space Administration, and the University Corporation for Atmospheric Research. For the tropospheric simulations CAMchem was run with a horizontal resolution of 1.9° latitude by 2.5° longitude and 16 vertical levels and a comprehensive tropospheric chemistry package. For details on CAMchem and the tropospheric simulation see the companion report on possible future H₂ impacts on tropospheric composition and chemistry.

Here we evaluate the impact of a future H₂-based transportation sector for two technology options following two growth paths for a total of six simulations (a Baseline simulation and two technology option simulations for each growth scenario). The base emissions for the regional simulations are based on emissions from the Sparse Matrix Operator Kernel Emissions (SMOKE) emissions processor [see www.smoke-model.org] using the U.S. National Emissions Inventory (NEI) for 2002. These emissions (NO_x, CO, speciated VOC, etc.) were developed at a time resolution of one hour. Due to the large difference between the CAMchem global model resolution and the CMAQ regional horizontal resolution (30km x 30km) and temporal resolutions and in order to keep changes in the regional emissions consistent with changes in the global emissions inventories, the 2002 SMOKE-based emissions were scaled for the future scenarios using scaling factors calculated from changes in emissions on the global grid. These scaling factors are species specific for the major species, e.g., NO_x, CO, some VOC and are mapped to the closest species in the lumped mechanism where there is not a direct correspondence. A detailed description of the emissions are presented in the companion Emissions Report.

The two technology options for H₂ utilization in road transportation evaluated here are Fuel Cell technology (H₂-FC) and Internal Combustion Technology (H₂-ICE). The two technologies differ in their related emissions. In the fuel cell technology option background atmospheric H₂ concentrations are higher due to H₂ leakage and emissions of all combustion related byproducts including CO, NO_x (=NO+NO₂), soot, SO₂, and volatile organic compounds (VOC) are greatly reduced. In the ICE scenario background atmospheric H₂ concentrations are higher due to H₂ leakage and emissions of all combustion related byproducts except NO_x are greatly reduced. NO_x emissions are not reduced since they are created from air driven high temperature combustion in the internal combustion engine while CO, VOC, SO₂, and soot emissions are still reduced since H₂ is not a hydrocarbon.

Monthly mean lateral boundary conditions are taken from the corresponding global CAMchem simulations. Monthly varying background concentrations of methane (CH₄) and hydrogen (H₂) were also taken from the CAMchem simulations. Annual average CH₄ and H₂ concentrations are shown in Table 1. Seasonal variations were typically relatively small with peak to peak amplitudes less than 5% of the mean

concentration. While CH₄ and H₂ are important to tropospheric background chemistry, they have a relatively small impact on urban air quality due to their low chemical reactivity. Although the total atmospheric lifetime of H₂ is ~2 years, the atmospheric chemical lifetime is ~9 years, similar to the CH₄ lifetime [e.g., Novelli et al. 1999; Ehhalt and Rohrer 2008, IPCC 2007]). The model was spun up for one month to eliminate the impact of the initial chemical atmospheric state which typically takes a few days (e.g., Tong and Mauzerall 2007) and then a one year simulation was run. One hour average model data was archived and used for this analysis.

Results

This impact assessment focuses on the continental United States in 2050 and evaluates the H₂ fuel cell (H₂-FC) and H₂ internal combustion engine (H₂-ICE) technology adoption scenarios for the A1Fi and B1 IPCC future growth scenarios. The H₂-FC scenario represents the adoption of H₂ fuel cell technology with reduced NO_x and VOC emissions while the H₂-ICE scenario represents a transitional scenario in which H₂ is burned in internal combustion engines such that VOC emissions are reduced but NO_x emissions are not. We focus on EPA National Ambient Air Quality Standards (NAAQS) criteria pollutants including O₃, CO, PM_{2.5}, and NO_x as these are among the most important species in terms of air quality. Relevant NAAQS standards are 75 ppb 8-hour average concentration for O₃, 9 ppm 8-hour average and 35 ppm 1-hour average for CO, 53 ppb annual average and 100 ppb 1-hour average for NO₂, and 15 micrograms/m³ annual average for PM 2.5.

For all scenarios and seasons, ozone concentrations are higher near population centers and along the west and east coasts with a plume extending off of the east coast during summer (Figures 1 and 2). Both the A1Fi and B1 scenarios have higher concentrations during summer than in winter. Over the southwestern U.S. and parts of the East Coast, baseline monthly average 8-hour average maximum concentrations are projected to exceed the EPA standard of 75 ppb over much of the summertime for the A1Fi scenario while during the winter it typically remains below ~55 ppb. Concentrations are below the standard the vast majority of the time for the B1 Baseline scenario, below ~56 ppb and ~48 ppb in summer and winter respectively. Simulated ozone changes depend critically on the assumed growth scenario, technology scenario

and season (Figures 1 and 3). Relatively large decreases in O₃ concentrations are noted with the adoption of the H₂-FC scenario. For both the A1Fi and B1 scenarios the decreases are largest over population centers. Summertime decreases are nearly 18 ppb for A1Fi and 12 ppb for the B1 scenario respectively. In stark contrast with these decreases for the H₂-FC scenario there is little decrease in summertime O₃ concentrations for the H₂-ICE scenario over the vast majority of the U.S. (Figures 1 and 3). There are some relatively small reductions over the Los Angeles and San Francisco regions of California and a few very localized points in the Midwest but these reductions are much smaller than for the H₂-FC scenario.

In wintertime there are generally smaller decreases in O₃ concentrations over much of the U.S. Reductions for the H₂-ICE scenarios are still much smaller than for the H₂-FC scenario but the difference is not as stark. Interestingly, for the A1Fi H₂-FC scenario in the wintertime, O₃ concentrations actually increase slightly (<~5 ppb) for some localized areas in Midwest and Northeast and on the west coast. In general there are substantial decreases in O₃ concentrations for the H₂-FC scenarios while there are only small decreases in summertime O₃ for the H₂-ICE scenarios.

Examining the distribution of daily 8-hour maximum ozone concentrations over the year there is a large shift towards lower O₃ impact for the H₂-FC scenario for both the A1Fi and B1 scenarios (Figures 2 and 4). In the A1Fi scenario much of the high tail above 80 ppb is reduced thus achieving the EPA standard much more frequently (Figure 2). While the improvement for the A1Fi scenario is quite impressive, the H₂-ICE scenario improvements are much more modest with small improvements in the >80 ppb tail. In the B1 scenarios (Figure 4) the standard is rarely exceeded in any scenario but there are still substantial improvements with the adoption of a fuel cell powered road sector. In the scenarios examined here summertime O₃ over the continental U.S. is predominantly NO_x controlled and emphasizes the importance of the utilization of non-combustion technology, e.g., fuel cells, in a future H₂ economy in terms of O₃ air quality.

Baseline CO concentrations are generally highest over the east coast in wintertime with monthly average wintertime concentrations of greater than 150 ppb and 400 ppb over much of the Eastern part of the U.S. for the B1 and A1Fi scenarios respectively (Figures 5 and 7). For each scenario examined here there are large decreases in CO

concentrations due to the decrease in CO emissions. The largest decreases occur over areas with the highest emissions in the Baseline case and in contrast to some other pollutants there are only slight differences between the fuel cell and H₂-ICE scenarios. Wintertime CO decreases are nearly 100 ppb and 280 ppb for the B1 and A1Fi scenarios over polluted regions, corresponding to decreases over much of the east coast of greater than 60%. Summertime decreases are nearly half as large as wintertime decreases because the wintertime planetary boundary layer is shallower, there is less vigorous vertical mixing, and chemical loss is lower.

Overall there are significant decreases in CO concentrations throughout the year for all scenarios examined here (Figures 6 and 8). The daily 8-hour maximum CO distributions are shifted to substantially lower levels. The changes are most pronounced in the A1Fi scenarios and the decreases are somewhat larger for the H₂-ICE scenarios than the H₂-FC scenarios but the differences between technological scenarios are not as significant as the differences between the Baseline and either H₂ scenario and both are well below the 8-hour maximum standard for CO.

For the Baseline A1Fi and B1 cases PM_{2.5} concentrations are generally highest along the Ohio River Valley and the East Coast of the US and are typically higher in winter than in summer (Figures 9 and 11). Wintertime concentrations peak at roughly 9 microgram/m³ for the A1Fi scenario and around 8 microgram/m³ for the B1 scenario. As with O₃, improvements in PM 2.5 air quality depend on the technology adoption scenario. PM 2.5 reductions are greatest with the H₂-FC scenarios' NO_x and VOC emissions reductions while the reductions are much more modest with the VOC only emissions reductions of the H₂-ICE scenario. While the areas of largest absolute decrease correspond to the areas of highest initial concentrations the areas of largest relative decrease are typically over areas with lower initial concentrations in the Midwest and west coast. For the H₂-FC scenario there are reductions of ~1 microgram/m³ and 1.5 microgram/m³ for the B1 and A1Fi scenarios in winter over the regions of high concentration in the Midwest. For the H₂-ICE scenario reductions are much more modest at around 1 and 0.5 microgram/m³ for the A1Fi and B1 winter scenarios, respectively, and more concentrated on the eastern seaboard. The smaller PM 2.5 reduction in the H₂-ICE scenario is due to the impact of nitrate aerosol PM 2.5 production from the NO_x emissions, whereas in the H₂-FC scenario there are reductions in soot, sulfate, and nitrate

aerosols as well as secondary organic aerosol formation from decreases in VOC emissions. There are relatively small shifts in the PM 2.5 distributions (Figures 10 and 12). Compared to the other species there are modest improvements for all of the scenarios examined here with slightly larger improvements for the H₂-FC scenarios than the H₂-ICE scenario.

Baseline PAN distributions display a highly seasonal nature with summertime maxima along the East Coast and wintertime maxima in the Southwest, Texas, and Oklahoma (Figures 13 and 14). In both seasons maximum concentrations are nearly two times larger for the A1Fi scenario than the B1 scenario with peaks of ~1.4 ppb and 0.7 ppb for the A1Fi summertime and wintertime respectively. Summertime peak concentrations are typically nearly two times larger than found in wintertime. With the adoption of an H₂ fuel cell powered road transportation sector, PAN concentrations decrease considerably with the largest summertime absolute decreases over the East and West coasts. Although the absolute decrease is larger over the east coast, the relative decrease is greater over the west coast (~70%) than over the east coast (~40%) for both the A1Fi and B1 scenarios. Summertime PAN decreases for the H₂-ICE scenario are nearly negligible compared to the H₂-FC scenario.

NO_x is primarily of interest because of its importance as an ozone precursor and because one of its components (NO₂) is a NAAQS criteria pollutant. NO_x concentration peaks tend to be highly localized for both the A1Fi and B1 scenarios, particularly in summertime (Figures 15 and 17). Peaks are concentrated in the northeast U.S. and in locations in the west, e.g., Los Angeles and Bay areas of California. Wintertime concentrations are higher than summertime concentrations and concentrations are higher in the A1Fi than B1 scenarios. There are large decreases in NO_x concentrations with the adoption of an H₂ fuel cell transportation sector, up to ~13 ppb (~50%) in winter over the northeast U.S. for the A1Fi scenario (Figure 15). However, for the H₂-ICE scenario there is almost no change in NO_x concentrations evident in the figures. The NO_x decreases in the H₂-FC scenarios are substantial through out the seasons (Figures 16 and 18). Figures 16 and 18 are broken into two panels to cover the wide range of NO_x concentrations. From the distributions it is evident that there are relatively small increases in NO_x concentrations in the H₂-ICE scenario relative to the Baseline scenario.

Comparison with Other Work

Although there have been no other studies of the future air quality impact of an H₂ based road transportation sector, several studies as discussed below have investigated the possible impacts of a present day hydrogen based economy. Our results are broadly consistent with these other findings. Schultz et al [2003] found large improvements in air quality with the present day adoption of a hydrogen powered economy using a three dimensional global chemistry model. As found here for the future scenarios, they noted large decreases in surface O₃, CO, and NO_x concentrations, mostly due to the large NO_x, CO, and VOC emissions reductions. As with our findings they also noted that the reduced NO_x emissions are responsible for the majority of the O₃ reductions and that at few areas in the Northern Hemisphere near major pollution sources the reduced NO_x emissions actually led to higher O₃ concentrations in wintertime. These findings are also consistent with Jacobson et al [2005] who reported large air quality improvements with the adoption of H₂ fuel cell powered vehicles in the current fleet.

Conclusions

Overall the analyses presented here suggest that there are potentially substantial air quality improvements associated with a future H₂ based transportation sector. However, the findings also highlight the advantages of utilizing H₂ with a non-combustion technology, e.g., H₂ fuel cells. If H₂-ICE technology is used in an H₂ transportation sector there are relatively small improvements in some key air quality species, e.g., O₃, NO_x, PAN, and less improvement in PM 2.5 air quality than in the H₂-FC technology case. Conversely, these results suggest that there are substantial improvements in all of the key air quality indicators (e.g., O₃, NO_x, PM 2.5, CO, PAN) in a future fuel cell powered H₂ based transportation sector. For the H₂-FC scenarios most air quality improvements occur during times of maximum adverse impact thereby enhancing the efficacy of improvements in terms of regulatory and health impacts. For example, the largest O₃ reductions occur during summertime when O₃ concentrations are typically highest and thus seasonal peak O₃ concentrations are reduced. Likewise the largest CO concentration reductions occur in wintertime when they are typically highest. Although there are many substantial uncertainties in predicting the future impacts of an H₂ powered road transportation sector in 2050 including technology changes, growth

changes, changes in emissions characteristics, changes in engine efficiencies, and climate changes, some inferences appear to be robust. For all H₂-FC scenarios substantial air quality improvements were observed. This robust conclusion is directly due to the emissions reductions and independent of growth scenario and season. Conversely, it should be noted that the absolute air quality differences between the A1Fi and B1 growth scenarios are typically larger than the differences between technology scenarios, e.g., the air quality in a B1 type scenario is generally better than in any A1Fi scenario regardless of H₂ technology adoption or not. In other words, a societal move away from fossil fuel use to alternative energy and transportation choices is generally better on air quality than remaining heavily fossil fuel intensive.

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References

- Appel, W., A. Gilliland, G. Sarwar, and R.C. Gilliam, Evaluation of The Community Multiscale Air Quality (CMAQ) Model Version 4.5: Uncertainties and Sensitivities Impacting Model Performance: Part I – Ozone, *Atmos. Environ.*, 41(40):9603-9613, (2007).
- Appel, W., P. Bhawe, A. Gilliland, G. Sarwar, and S.J. Roselle, Evaluation of The Community Multiscale Air Quality (CMAQ) Model Version 4.5: Uncertainties and Sensitivities Impacting Model Performance: Part II - Particulate Matter, *Atmos. Environ.*, 42(24):6057-6066, (2008).
- Eder, B. K. and S. Yu, A Performance Evaluation of the 2004 Release of Models-3 CMAQ, *Atmos. Environ.*, 40(26):4811-4824, (2006).
- Ehhalt, D. H. and F. Rohrer, The tropospheric cycle of H₂: a critical review, *Tellus*, 61B, 500-535, (2009).
- IPCC, Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, N.Y., U.S.A., 996 pp., (2007).
- Jacob, D. J., Introduction to Atmospheric Chemistry, Princeton University Press, Princeton, N. J. U.S.A., (1999).
- Jacobson, M., W. Colella, and D. Golden, Cleaning the air and improving health with hydrogen fuel-cell vehicles, *Science*, 308, 1901-1905, (2005).
- Liang, X.-Z., K.E. Kunkel, and A.N. Samel, Development of a regional climate model for U.S. Midwest applications. Part 1: Sensitivity to buffer zone treatment, *J. Climate.*, 14, 4363-4378, (2001).
- Lin, J., K. O. Patten, K. Hayhoe, X. Liang, and D. Wuebbles, Effects of future climate and biogenic emissions changes on surface ozone over the United States and China, *J. Appl. Met. Clim.*, 47 (7), 1888-1909, DOI: 10.1175/2007JAMC1681.1, (2008).

- Luecken, D. J., A. S. Phillips, G. Sarwar, and C. Jang, Effects of using the CB05 vs. SAPRC99 vs. CB4 chemical mechanism on model predictions: Ozone and gas-phase photochemical precursor concentrations, *Atmos. Environ.*, 42, 5805–5820, (2008).
- Mathur, R., S. Yu, D. Kang, and K. L. Schere, Assessment of the Winter-Time Performance of Developmental Particulate Matter Forecasts With the Eta-Cmaq Modeling System, *J. Geophys. Res.*, 113(D02303):1-15, (2008).
- Novelli, P. C., P. M. Lang, K. A. Massaie, D. F. Hurst, R. Myers, and J. W. Elkins, Molecular hydrogen in the troposphere: Global distribution and budget, *J. Geophys. Res.*, 104, D23 30,427-30,444, (1999).
- Roy, B., R. Mathur, A. Gilliland, and S. Howard, A Comparison of CMAQ-Based Aerosol Properties With Improve, Modis, and Aeronet Data, *J. Geophys. Res.*, 112(D14):1-17, (2007).
- Sarwar, G., D. J. Luecken, G. Yarwood, G. D. Whitten, and W. P. Carter, Impact of An Updated Carbon Bond Mechanism on Predictions from the CMAQ Modeling System: Preliminary Assessment, *J. Appl. Met. Clim.*, 47(1):3-14, (2008).
- Schultz, M., T. Diehl, G. Brasseur, and W. Zittel, Air pollution and climate-forcing impacts of a global hydrogen economy, *Science*, 302, 624-627, (2003).
- Seinfeld, J. H. and S. N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, second edition, John Wiley and Sons, Hoboken, N.J., U.S.A. (2006).
- Tong, D. and D. Mauzerall, Spatial variability of summertime tropospheric ozone over the continental United States: Implications of an evaluation of the CMAQ model, *Atmos. Environ.* 40, 3041-3056, (2006).
- U.S. EPA, National air quality: Status and trends through 2007, U.S. EPA EPA-454/R-0806, 48pp., (2008).
- Weaver, C. P., et al, A preliminary synthesis of modeled climate change impacts on U.S. regional ozone concentrations, *BAMS*, 1843-1863, Dec., (2009).

Table 1. Annual average CH₄ and H₂ concentrations and relative seasonal variation (peak to peak amplitude (PTP) divided by the mean) over the continental U.S. model domain.

	CH ₄		H ₂	
	Annual [ppm]	Average PTP/mean [%]	Annual [ppm]	Average PTP/mean [%]
A1Fi Baseline	2.66	2.0	0.84	3.3
A1Fi H ₂ -FC	2.66	2.0	1.20	3.7
A1Fi H ₂ -ICE	2.66	2.1	1.21	4.1
B1 Baseline	1.90	2.3	0.56	4.1
B1 H ₂ -FC	1.90	2.2	0.73	3.7
B1 H ₂ -ICE	1.90	2.3	0.74	4.2

Figure 1. Monthly averages of the maximum daily 8-hour-average O_3 concentrations for July (top) and Feb (bottom) for the A1Fi scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H_2 -FC scenario (center), and difference between the Baseline and H_2 -ICE scenario (right). Data are averaged over the lowest three model levels (~ 250 m). Note that the scales are different between panels.

Figure 2. Normalized probability distribution [#/ppb] of simulated surface daily 8-hour average maximum O₃ concentrations over 1 year for the A1FI Baseline, H₂-ICE, and H₂-FC scenarios across the model domain.

Figure 3. Monthly averages of the maximum daily 8-hour-average O_3 concentrations for July (top) and Feb (bottom) for the B1 scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H_2 -FC scenario (center), and difference between the Baseline and H_2 -ICE scenario (right). Data are averaged over the lowest three model levels (~ 250 m). Note that the scales are different between panels.

Figure 4. Normalized probability distribution [#ppb] of simulated surface daily 8-hour average maximum O_3 concentrations over 1 year for the B1 Baseline, H₂-ICE, and H₂-FC scenarios across the model domain.

Figure 5. Monthly average CO concentrations for July (top) and Feb (bottom) for the A1Fi scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 6. Normalized probability distribution [#/ppb] of simulated surface daily 8-hour average maximum CO concentrations over 1 year for the A1FI Baseline, H₂-ICE, and H₂-FC scenarios across the model domain.

Figure 7. Monthly average CO concentrations for July (top) and Feb (bottom) for the B1 scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 8. Normalized probability distribution [#/ppb] of simulated surface daily 8-hour average maximum CO concentrations over 1 year for the B1 Baseline, H₂-ICE, and H₂-FC scenarios across the model domain.

Figure 9. Monthly average PM 2.5 concentrations for July (top) and Feb (bottom) for the A1Fi scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 10. Normalized probability distribution [$\#/\text{ug m}^{-3}$] of simulated surface daily average PM_{2.5} concentrations over 1 year for the A1FI Baseline, H₂-ICE, and H₂-FC scenarios across the model domain.

Figure 11. Monthly average PM 2.5 concentrations for July (top) and Feb (bottom) for the B1 scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 12. Normalized probability distribution $[\#/\mu\text{g m}^{-3}]$ of simulated surface daily average PM_{2.5} concentrations over 1 year for the B1 Baseline, H₂-ICE, and H₂-FC scenarios across the model domain.

Figure 13. Monthly average PAN concentrations for July (top) and Feb (bottom) for the A1Fi scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 14. Monthly average PAN concentrations for July (top) and Feb (bottom) for the B1 scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 15. Monthly average NO_x concentrations for July (top) and Feb (bottom) for the A1Fi scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 16. Distribution of simulated surface daily average NO_x concentrations over 1 year for the A1Fi Baseline, H₂-ICE, and H₂-FC scenarios across the model domain. Top

panel shows distribution from 0-500 ppt and the bottom panel shows the distribution from 0.5 to 40 ppb. Vertical axis in both panels is #/ppt. Note the difference in scales.

Figure 17. Monthly average NOx concentrations for July (top) and Feb (bottom) for the B1 scenario across the contiguous United States. Each row contains the Baseline Case (left), difference between the Baseline and H₂-FC scenario (center), and difference between the Baseline and H₂-ICE scenario (right). Data are averaged over the lowest three model levels (~250 m). Note that the scales are different between panels.

Figure 18. Distribution of simulated surface daily average NO_x concentrations over 1 year for the B1 Baseline, H₂-ICE, and H₂-FC scenarios across the model domain. Top

panel shows distribution from 0-500 ppt and the bottom panel shows the distribution from 0.5 to 40 ppb. Vertical axis in both panels is #/ppt. Note the difference in scales.

Section 5

1) The Effect of Long Term H₂ Enrichment on H₂ uptake by Soils

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Introduction

Soil microbes play a major role in the global hydrogen (H₂) cycle, accounting for about 80% of the H₂ removed from our current atmosphere. If leaks and fugitive emissions from a future H₂ economy increase the atmospheric hydrogen concentration [H₂] above the current level (0.55 ppm H₂), the soil microbes would be expected to respond by increasing their number or capacity for H₂ consumption. Previous studies from our laboratory have shown that a five-fold increase in [H₂] (2.75 ppm H₂) causes an immediate 4 to 5 fold stimulation in the H₂ deposition (i.e. uptake) rate (i.e. a first order relationship). However, after long-term (3-5 months) exposure to the higher [H₂], the H₂ deposition rate increased to 7 to 12 times higher than that of soils exposed to air with current levels of H₂.

To use this information in H₂ cycle models, it will be important to understand the nature of the relationship between long term exposure to elevated [H₂] and the rate of H₂ deposition in soils. This could be a linear, concave or convex relationship.

Experimental Design:

Twelve soil chambers were designed and built so that the [H₂] could be controlled in the gas space over the soil. Each of the rectangular plastic chambers held 2900 cm³ of soil with a surface area of 320 cm² and 9 cm of soil depth. The soil was taken from a corn (*Zea mays*) field at the Ottawa Research Station of Agriculture and AgriFood Canada in Ottawa, Ontario.

The chambers were allocated into the following three H₂ treatments with four chambers per treatment:

Ambient: 0.47 ± 0.02 ppm H₂

Medium: 1.38 ± 0.03 ppm H₂

High: 2.48 ± 0.04 ppm H₂

The H₂ concentrations in the inflow and exhaust gas streams for each chamber were monitored over the 243 days of treatment and the results combined with information on the flow rate to calculate the rate of H₂ deposition. Every few days during the treatment period, the chambers were weighted and water added to bring the weight (and the soil water content) back to its initial value.

Results:

After 67 days of soil exposure to air with 0.47, 1.38 or 2.48 ppm H₂, a linear relationship was found between the H₂ concentration and the rate of H₂ uptake by the soil (Fig 1.1). However, after 114 or 243 days of exposure, a clear convex relationship was observed (Fig 1.1). When the results were expressed in terms of the relative H₂ uptake rate, a similar pattern emerged (Fig. 1.2).

Discussion / Conclusion

The results reported here have important implications for modeling the role of soils in the feedback control over the atmospheric H₂ concentration in a future H₂ economy.

The convex relationship shown in Fig. 1.1 suggests that even a small enrichment in the atmospheric H₂ concentration above ambient (say from 0.5 to 1.4 ppm), there would be a significant stimulatory effect on the H₂ uptake by soils. However, above 1.4 ppm H₂, the effect of H₂ enrichment on H₂ uptake by soils will be less than the effect of a similar pH₂ increment below 1.4 ppm.

While these studies do not provide any evidence on the underlying mechanism, a number of simple explanations are possible. The most obvious is the potential for a limiting factor affecting the rate of H₂ uptake in soil at H₂ concentrations above 1.4 ppm.

Fig 1.1 The effect of long term exposure of soils to a head space concentration of hydrogen on the rate of H₂ uptake by the soil. 67days (Grey), 114 days (red), 243 days (Green)

Fig 1.2 The effect of long term exposure of soils to a head space concentration of hydrogen on the relative rate of H₂ uptake by the soil. 67days (Grey), 114 days (red), 243 days (Green)

2) Impact of adaptive H₂ soil sink on atmospheric H₂ concentrations in a future society with an H₂-based road transportation sector

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It is not well understood how soil microbes, which are the most important sink of atmospheric H₂, will respond to increased atmospheric H₂ concentrations in a future society with a hydrogen-based road transportation sector. Recent laboratory studies as part of this project support the hypothesis that soil microbes will adapt to elevated atmospheric H₂ concentration by increasing their H₂ uptake non-linearly. Based on these laboratory results, we have carried out model simulations to evaluate the impact of this adaptation on atmospheric H₂ concentrations in a future H₂ society.

Our laboratory studies indicate that microbial adaptation to higher ambient H₂ levels could have a large impact on the magnitude of the H₂ soil sink in the future. Examining the impact of this adaptation is critical as it could have a large affect on future atmospheric H₂ concentrations particularly for the high-emissions scenarios. Current results suggest that at the concentrations simulated for the A1FI 2050 Baseline scenario uptake would be approximately 2.5 times current values and roughly 4 times higher for the 2050 A1FI H₂-FC and H₂-ICE scenarios (Figure 2.1). This increase in the H₂ soil sink could provide a strong negative feedback to increasing atmospheric H₂ concentrations and could possibly mitigate some of the adverse stratospheric impacts of an H₂ economy.

Figure 2.1, Laboratory study results of H₂ uptake relative to the current value as a function of H₂ ambient concentration.

This adaptive uptake mechanism has been incorporated into the CAMChem tropospheric model and its impact on atmospheric concentrations will be evaluated for the A1FI H₂-FC 2050 scenario.

In the MOZART atmospheric chemistry transport model the H₂ soil sink is represented by deposition velocity (V_d) to the surface. In the standard configuration $V_d(\text{H}_2)$ is assumed to be two times the CO deposition velocity ($V_d(\text{CO})$), a value supported by observations under current conditions. To simulate the enhanced H₂ soil sink $V_d(\text{H}_2)$ is assumed to be dependent on the near-surface H₂ concentration as well as $V_d(\text{CO})$. The H₂ dependence is implemented by scaling the original $V_d(\text{H}_2)$ by a factor determined from the laboratory studies (Table 2.1). The model simulation was carried out for the A1FI-FC scenario which has the largest increase in atmospheric H₂ concentration.

Table 2.3. Deposition velocity scale factor

Range of [H ₂] [ppm]	Scale factor
H ₂ ≤ 0.5	2.0 * H ₂
0.5 < H ₂ ≤ 1.3	6.6 * (H ₂ - 0.5) + 1.0
H ₂ > 1.3	2.1 * (H ₂ - 1.3) + 6.28

Preliminary results indicate that soil microbe adaptation to elevated ambient H₂ concentrations will decrease tropospheric H₂ concentrations by more than 0.2 ppm (~20%) relative to the non-adaptation case (Figure 2.2). The H₂ concentration decrease extends into the stratosphere through the tropical upwelling, resulting in a pattern with a larger decrease in the tropics and a smaller decrease in higher latitudes at each altitude level in the stratosphere (Figure 2.2). The reduction in the Northern Hemisphere is larger than that in the Southern Hemisphere, with the largest absolute reduction appearing in the boundary layer in the northern mid-latitudes. This asymmetry reflects the overwhelming impact of soils on the continents of the northern hemisphere on global H₂ budget.

Figure 2.2 Absolute [ppb] (left) and relative [%] (right) reduction of atmospheric H_2 concentration with soil microbe adaptation compared to that without adaptation for the A1FI H_2 -FC scenario.

Section 6

Integrated Assessment Model for a Hydrogen-Based Road Transportation Sector

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Introduction

The goal of the integrated assessment model (IAM) presented here is to facilitate the quick and easy assessment of the potential impacts of a transition to a H₂-based transportation sector. Additionally, it will allow further analysis of the likely H₂, greenhouse gases and criteria pollutant concentration changes (increases and/or decreases) arising from a developing global H₂ infrastructure, including the ability to quantify the potential impacts of different market penetration scenarios. The IAM is based on a combination of results from detailed simulations of the impact of the emissions scenarios we developed (presented in a companion report) and other simplified models to assess other specific impacts. The outputs of the set of models and simulations are united, refined, and simplified to distill their essence to present the user with a single text file interface from which to make selections to create customized H₂ scenarios. The user-defined variables includes information on depth of adoption of hydrogen as well as changes in the character of emissions. The IAM calculates the atmospheric perturbations of criteria pollutants and greenhouse gases and their impacts. The IAM focuses on changes in key atmospheric constituents that are of interest for this project including H₂, CO₂, column O₃, tropospheric O₃, OH, and CO, though the model could be expanded to include some other species or budget terms if necessary. The box-model IAM will synthesize our comprehensive modeling results as look up tables with interpolation. It will capture the nonlinearities in physics and chemistry to guide policy. However, it does not include dynamical feedbacks from climate change and larger scale regional air-pollution. Additional detailed climate –chemistry modeling would be required to address those interactions.

Methods

The core model flows and computational modules of the IAM are depicted in Figure 1. There are core databases (emissions and concentrations). These are connected by three computational modules depicted by the numbered arrows: 1) calculates the atmospheric concentration changes of hydrogen and other species for the selected hydrogen penetration scenario; 2) calculates the radiative forcings (RF) from these concentration changes, and finally 3) calculates the temperature change from these RF changes. Each of these steps is described in more detail below. In this version, there is no active feedback capability for changes in air quality or climate to then affect concentrations further.

The atmospheric changes for the user-defined scenario for all gases except CO₂, (e.g., H₂, O₃, OH, CO, aerosols) are estimated by interpolation from archived results from our detailed simulation scenarios. The case libraries were developed using our state-of-the-art atmospheric chemistry-transport models CAM-Chem and MOZART and encompass a wide range of emissions scenarios as described in the companion emissions scenario report. Using these results as a basis, the atmospheric concentrations for the user-determined scenario are calculated assuming a linear atmospheric response. The output from this calculation are available as changes in zonal annual means rather than changes in global means since many of these species are not uniformly distributed in the atmosphere. Regional concentration changes are output as annual averages at the surface. All of this data are then output as figures as well as data files. The linearized response assumption imposes certain restraints on the possible input scenarios. The requested scenario must be based on one of the core adoption scenarios from the emissions scenarios, e.g., a combination of A1FI, or B1 and FC or ICE. Additionally the requested adoption scenario must be reasonably within the span of input scenarios used as a basis for the linearization in order to obtain scientifically justifiable results. Additionally the user scenario selection does not allow for regional variations. For most cases the restriction of this limitation is more than offset by the computational cost (weeks to months of computer run time) of a full atmospheric chemistry calculation.

The change in global mean CO₂ concentration is calculated from estimates of the hydrogen-displaced CO₂ emissions using the Bern carbon cycle model. The Bern carbon cycle model is a simplified parameter fit to a detailed terrestrial-ocean carbon cycle model (Plattner *et al.*, 2001; Joos *et al.*, 2001) and has been used extensively in the Intergovernmental Panel on Climate Change (IPCC) assessments (e.g., IPCC 2001). The radiative forcing change estimated from radiative efficiency factors and formulas relating atmospheric perturbations to their radiative forcings derived from complex models (e.g., IPCC 2001, IPCC 2007, Myhre *et al.*, 1998). Finally, the temperature change response is calculated using the Shine *et al.* (2005) energy balance model that relates radiative forcing and climate sensitivity to global mean temperature response. It incorporates an upwelling-diffusion model for the ocean and resolves land and oceans separately in each hemisphere.

The tropospheric ozone radiative forcing is estimated directly from the ozone burden changes in the model and the specific radiative forcing. The aerosol radiative forcings are estimated from the current reported aerosol radiative forcings from IPCC [2007] for sulfate, nitrate, and black carbon (including the black carbon on snow albedo impact). From these current global average radiative forcings and the current model simulated aerosol burdens a specific forcing is calculated and this value is then scaled to the future aerosol burdens. Using relative changes in the radiative forcings in this manner reduces the significant uncertainties associated with calculations of absolute aerosol radiative forcing. It must be noted that there are large uncertainties associated with the aerosol radiative forcing estimates. The uncertainties associated with each forcing are often nearly as large as the value, e.g., the current RF for BC is $0.2 \pm 0.15 \text{ W/m}^2$ and $0.1 \pm 0.1 \text{ W/m}^2$ for the BC snow albedo effect [IPCC, 2007]. The IPCC currently assigns a low level of scientific understanding to the aerosol RF, medium to the ozone RF, and high to CO₂ RF. The stratospheric ozone specific RF is estimated from the current IPCC estimated RF due to stratospheric ozone loss (-0.05 ± 0.1) and the change in

stratospheric ozone column ($\sim -10\text{DU}$) for the same time period [WMO, 2006]. The methane (CH_4) concentration changes are estimated as in IPCC [1999] based on changes in the CH_4 lifetime calculated from the CAM-Chem tropospheric impact simulations (Table 1.) with an amplification factor of 1.4 [e.g., IPCC 2001]. The small positive feedback of CH_4 changes on global background tropospheric O_3 is also included.

The time evolution of adoption is assumed to increase linearly from zero at the beginning of adoption, here taken to be 2005, to the end point of the user input percent adoption in 2050. Thus the non- CO_2 RFs increase linearly from zero in the start year (2005) to their maximum absolute value in 2050. The CO_2 changes and RFs are calculated from the more detailed carbon cycle model. All of the timeseries are plotted as differences from the Baseline scenario. Radiative forcing and temperature changes are the differences from the Baseline scenario and not absolute values and thus represent the changes from the Baseline path due to the adoption of H_2 technology.

The model is designed in a modular fashion such that the addition of new or updated modules and cases in the library will be relatively straightforward. This capability is particularly important since the simplified RF and temperature response modules will likely be updated as scientific understanding and computational power increase.

Overview of Results for Scenarios

Although the emphasis of the integrated assessment model is to provide a tool to allow DOE to evaluate scenarios of their choosing, here we present a short summary of the climate impact of the A1FI-FC, A1FI-ICE, B1-FC, and B1-ICE scenarios from the companion tropospheric assessment study.

For all scenarios there is a decrease in global average radiative forcing and temperature with the adoption of an H_2 based road transportation scenario (Figures 2-5). The majority of the impact is caused by the decrease in atmospheric CO_2 concentrations due to the displacement of fossil fuel usage for transportation. This benefit is only realized for H_2 produced by non- CO_2 emitting means, e.g., wind, solar, nuclear. The total 2050 radiative forcing changes are nearly -0.6 W/m^2 (A1FI-FC), -0.65 W/m^2 (A1FI-ICE), -0.25 W/m^2 (B1-FC), and -0.27 W/m^2 (B1-ICE). For comparison the total RF change from 2005 to 2050 is estimated to be 3.2 W/m^2 for the A1FI scenario and 1.77 W/m^2 for the B1 scenario [IPCC, 2001]. The corresponding total 2050 temperature changes are nearly -0.34 (A1FI-FC), -0.37 (A1FI-ICE), -0.09 (B1-FC), and -0.15 (B1-ICE). For comparison the total temperature change from 2005 to 2050 is estimated to be 1.62°C for the A1FI scenario and 0.96°C for the B1 scenario [IPCC, 2001].

The largest single contribution to the changes is from CO_2 (the CO_2 contribution is at least 4 times larger than any other contribution (Figures 2-5)). For all scenarios the sulfate (SO_4) RF change is positive (a warming effect) but small due to the decrease in sulfate aerosols. The stratospheric ozone RF change is small and negative (a cooling effect) and the nitrate aerosol contribution is small and positive. While the relative contribution of the other species is mostly independent of the scenario, the CH_4 depends critically on the technology scenario. For the fuel cell technology scenarios the CH_4 RF

change is positive due to the increased CH₄ lifetime while for the internal combustion engine (ICE) scenarios the CH₄ RF change is negative due to the decrease in CH₄ lifetime in those scenarios. The dependence of the CH₄ RF change on scenario causes the overall decrease in RF to be larger for the ICE scenarios than for the FC scenarios. While this is desirable from a climate perspective it must be emphasized that air quality improved much more in the FC scenarios than in the ICE scenarios. The RF changes for soot and tropospheric ozone are negative for all scenarios though the decreases are larger for the FC scenarios.

Conclusions: Overall, the adoption of H₂ as an energy carrier for road transportation will have a beneficial impact on climate reducing global average radiative forcings and surface temperature provided the hydrogen is produced without emitting CO₂ to the atmosphere. This study indicates that there are some trade-offs to be addressed, e.g., the scenarios with the largest improvement from a climate perspective (ICE) and the scenarios with the largest improvement from an air quality perspective (FC) are not the same. It should also be emphasized that, as with the air quality improvements, the future growth scenario has a larger impact on future climate than adopting a H₂ based road transportation sector with either FC or ICE technology. For example, even though the climate improvements are greater for the A1FI scenarios with the adoption of an H₂ based road transportation sector, future climate change is still lower for any of the B1 future growth scenarios regardless of H₂ adoption.

IAM Scenario Selection and Use

Here we describe the use of the model in detail and results for a sample scenario. Most of the scenario selection parameters for the IAM are located in the H2_IAM.py file. Editing of these files on Windows is easiest with wordpad or the idle editor with python. These are the parameters discussed here (see the technical documentation in the README file for additional details on modifying additional parameters). The base scenario is selected based on the 'Growth_Scenario' and 'Tech_Scenario' parameters. These parameters determine the base or starting point for the penetration scenario selection. The 'Growth_Scenario' may be either 'B1' or 'A1FI' and the 'Tech_Scenario' may be either 'FC' or 'ICE'. The 'Scenario_Scale' parameter determines the penetration of hydrogen as a road transportation fuel as a percentage and must be between 0 and 1.0. Note that if Scenario_Scale is 0.5 then it is assumed that 50% of the fuel is supplied as H₂ and 50% is supplied traditional fossil fuel. Additional optional parameters are 'Scenario_Prefix' which will be used as a prefix for all output files in order to make it easier to differentiate different runs with different scenarios and 'OutDir' which is the directory in which to store the output files (this directory will be created if it does not already exist). 'SaveData' and 'SavePlots' are flags to determine whether the data and plots will be written to files. Since plotting the data requires some (though not much) additional time. For this example we have chosen Growth_Scenario=A1FI, Tech_Scenario=FC, ScenarioPrefix='A1FI_FC', and Scenario_Scale=1.0 with the SaveData and SavePlots flags set to 'True'.

When the model is run the following files are written to the output directory.

A1FI_FC_emissions.txt: which contains the emissions of H₂, CO, NO, SO₂, BC, and NMVOC for this scenario.

A1FI_FC_CO_latlon.png A1FI_FC_O3_col_latlon.png A1FI_FC_O3_zonal.png
A1FI_FC_CO_zonal.png A1FI_FC_O3_col_strat_latlon.png A1FI_FC_OH_zonal.png
A1FI_FC_H2_latlon.png A1FI_FC_O3_col_trop_latlon.png
A1FI_FC_PM25_latlon.png
A1FI_FC_H2_zonal.png A1FI_FC_O3_latlon.png A1FI_FC_RF.png
A1FI_FC_dT.png

These files contain plots of the resulting baseline scenario and differences between the Baseline and selected scenario.

A1FI_FC_CO_latlon_base.txt	A1FI_FC_O3_col_trop_latlon_base.txt
A1FI_FC_CO_zonal_base.txt	A1FI_FC_O3_latlon_base.txt
A1FI_FC_H2_latlon_base.txt	A1FI_FC_O3_zonal_base.txt
A1FI_FC_H2_zonal_base.txt	A1FI_FC_OH_zonal_base.txt
A1FI_FC_O3_col_latlon_base.txt	A1FI_FC_PM25_latlon_base.txt
A1FI_FC_O3_col_strat_latlon_base.txt	
A1FI_FC_CO_latlon_diff.txt	A1FI_FC_O3_col_trop_latlon_diff.txt
A1FI_FC_CO_zonal_diff.txt	A1FI_FC_O3_latlon_diff.txt
A1FI_FC_H2_latlon_diff.txt	A1FI_FC_O3_zonal_diff.txt
A1FI_FC_H2_zonal_diff.txt	A1FI_FC_OH_zonal_diff.txt
A1FI_FC_O3_col_latlon_diff.txt	A1FI_FC_PM25_latlon_diff.txt
A1FI_FC_O3_col_strat_latlon_diff.txt	A1FI_FC_RF.txt
A1FI_CO2_dT.txt	A1FI_FC_CO2.txt

These files contain the data used to make the plots described above and a description of the grid.

References

IPCC 1999: Aviation and the Global Atmosphere, Prepared in collaboration with the Scientific Assessment Panel to the Montreal Protocol on Substances that Deplete the Ozone Layer, J.E.Penner, D.H.Lister, D.J.Griggs, D.J.Dokken, M.McFarland (Eds.), Cambridge University Press, UK. pp 373.

IPCC 2001: Climate Change 2001: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) J. T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P. J. van der Linden and D. Xiaosu (Eds.) Cambridge University Press, UK. pp 944.

IPCC, 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp.

Joos, F., I. Prentice, S. Sitch, R. Meyer, G. Hooss, G. Plattner, S. Gerber, K. Hasselmann, Global warming feedbacks on terrestrial carbon uptake under the IPCC emission scenarios, *Global Biogeochemical Cycles*, 15, 891– 907, 2001.

Myhre, G., E.J. Highwood, K.P. Shine, and F. Stordal: New estimates of radiative forcing due to well mixed greenhouse gases. *Geophysical Research Letters*., **25**, 2715-2718, 1998.

Plattner, G.-K., F. Joos, T.F. Stocker, and O. Marchal, Feedback mechanisms and sensitivities of ocean carbon uptake under global warming, *Tellus*, 53B, 564-592, 2001 .

Shine, K., J. Fuglestvedt, K. Hailemariam, N. Stuber, Alternatives to the Global Warming Potential for Comparing Climate Impacts of Emissions of Greenhouse Gases, *Climatic Change*, 68, 3, 281-302, 2005.

WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project—Report No. 50, 572 pp., Geneva, Switzerland, 2007.

Table 1. CH₄ lifetimes [years] for the CAM-Chem 2050 H₂ based road transportation sector impact assessment model simulations.

	A1FI	B1
2050 Baseline	9.1	8.3
2050 FC	9.7	8.8
2050 ICE	8.7	8.1

Figure 1. Schematic diagram of the hydrogen Integrated Assessment Model. The boxes represent the levels of data and the numbered arrows represent the computational modules that calculate the next level of data from the previous one as described in the text.

Figure 2. Radiative forcing (left) and temperature (right) changes due to the adoption of an H_2 powered road transportation sector for the A1FI-FC scenario.

Figure 3. Radiative forcing (left) and temperature (right) changes due to the adoption of an H_2 powered road transportation sector for the A1FI-ICE scenario.

Figure 4. Radiative forcing (left) and globally-averaged temperature (right) changes due to the adoption of an H_2 powered road transportation sector for the B1-FC scenario.

Figure 5. Radiative forcing (left) and globally-averaged temperature (right) changes due to the adoption of an H_2 powered road transportation sector for the B1-ICE scenario.

Section 7

H₂ Production Oxygen Plume Risk Assessment

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In a hydrogen economy, oxygen (O₂) can be a by-product of molecular hydrogen (H₂) production, if H₂ is generated from electrolysis of water. The produced oxygen, if not collected for other use is expected to be released to the atmosphere. Increased oxygen concentration can facilitate fire spread. Thus it is of interest to examine the expected increase in oxygen content around a large-scale electrolysis facility. Here we analyze this potentially hazardous effect by estimating the increased O₂ concentration near an H₂ plant with an assumed emission rate using a Gaussian plume model.

Estimated emission rate

As a “worst-case” scenario the O₂ release rate from 100 large H₂ plants. It is assumed that all energy needed by the U.S. for road transport is provided by H₂. The energy demand by total U.S. transportation system for year 2002 was estimated to be 26.5 Quads [LLNL]. The future *road* transportation part is assumed to be roughly equal to this value. To meet such a demand, 890GJ (1GJ= 1×10^9 Joules) must be stored in the form of H₂ per second. Taking the energy density of H₂ (142 MJ/kg, Bossel, Ulf and Eliasson [2003]) into account, 6200 kg sec⁻¹ H₂ must be produced. The corresponding O₂ production is $\sim 5 \times 10^4$ kg sec⁻¹. Assuming there are 100 H₂ factories with equal production capacities distributed throughout the U.S, each will release 500 kg sec⁻¹ O₂. This oxygen is assumed to be released from an 80m high stack.

There is no specific threshold for a major increase in fire spread. As oxygen concentration increases fire spread increases both because more oxidizer is available and because a fuel/oxidizer mixture closer to stoichiometry is more readily achieved so the fire burns hotter near the surface, accelerating pyrolysis of the surface. A significant increase in fire spread can be expected from a 5 volume % increase in oxygen concentration, therefore we take this as a threshold for a significant impact of oxygen from a large-scale electrolyzer. Under standard temperature and pressure conditions, a 5 volume % increase in oxygen concentration is equal to 70 g m⁻³. This constitutes our expected zone of fire safety risk around an electrolyzer.

Gaussian plume model

Snap-shot O_2 plume concentrations downwind of an O_2 source in a realistic atmosphere are difficult to predict precisely in a timely fashion because of instantaneous turbulence, ubiquitous in the mixing-layer atmosphere (Fig. 1, left). However, according to observations, the time-averaged pollutant concentration generally obeys a Gaussian distribution in the horizontal and vertical directions in the plane normal to the prevailing wind direction (Fig. 1, right). Thus the Gaussian plume model (Fig. 2) has been developed, and has been widely used since the 1940s.

Figure 2. Instantaneous (left) and time-averaged (right) plume shape.
Source: Blade et al., Meteorology and Atomic Energy, 1968

Based on a Gaussian distribution, concentrations of a pollutant in the stack plume can be described by the following equation,

$$C = \frac{Q}{2\pi u \sigma_y \sigma_z} \cdot \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \cdot \left[\exp\left(-\frac{(z-H)^2}{2\sigma_z^2}\right) + \exp\left(-\frac{(z+H)^2}{2\sigma_z^2}\right) \right]$$

Where C is the oxygen concentration, Q is the oxygen emission rate, u is the background wind speed, H is the stack height, and σ_y and σ_z are horizontal and vertical standard deviations of the emission distribution.

Figure 2. A visualization by Milton Beychok of a buoyant Gaussian air pollutant dispersion plume. The oxygen plume is not expected to be buoyant but the general shape is expected to be the same in form but closer to the ground.

σ_y and σ_z are functions of distance to the emission source and stability classes (Table 1). The main mechanisms to dilute the pollutant plume are entrainment and mixing of fresh ambient air into the plume. The intensity of these processes is determined by the amount of atmospheric turbulence present in the mixing layer. Thus, classifying atmospheric stability is helpful in describing intensity of atmospheric dispersion. The judging criteria for Pasquill stability classes are listed in Table 2.

Table 1. The Pasquill stability classes

Stability class	Definition
A	Very unstable
B	Unstable
C	Slightly unstable
D	Neutral
E	Slightly stable
F	Stable

When there are inversions present, which act like a lid aggravating the concentration in the mixing layer, the Gaussian equation can be modified as the following,

$$C = \frac{Q}{2\pi u \sigma_y \sigma_z} \cdot \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \cdot \sum_{m=-\infty}^{+\infty} \left[\exp\left(-\frac{(z-H+2mL)^2}{2\sigma_z^2}\right) + \exp\left(-\frac{(z+H+2mL)^2}{2\sigma_z^2}\right) \right]$$

where L is the bottom height of the lowest inversion layer. Treatment of the problem with an assumed inversion layer both presents a “worst-case” condition and simply handles the non-buoyant plume.

Table 2. Classifying criteria for Pasquill stability classes

Surface wind speed	Daytime incoming solar radiation			Nighttime cloud cover	
m/s	Strong	Moderate	Slight	>50%	<50%
<2	A	A-B	B	E	F
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

Model results and discussion

Emitted O₂ plume concentrations were calculated for various combinations of stability classes, background wind speeds and inversion layers present. Detailed O₂ concentrations are plotted in the horizontal plane at stack height and vertical cross-section in Appendices I and II.

When inversion layers are present, the O₂ plume cannot disperse into the atmosphere and is confined in the mixing layer. Thus, the O₂ concentration is larger than without inversions. The effect of inversions is apparent by comparing Appendices I and II.

Under each specific stability class, the O_2 plume concentration decreases with increasing background wind. This is easy to understand because dispersion is stronger with larger wind speed. In the extreme case, under stability class F with a background wind speed of 1 m s^{-1} , the 70 g m^{-3} critical concentration extends to 1600 meters downwind of the source. When inversion layer is at 100m aloft, this value can be as far as 1800 meters.

At the same background wind speed, the O_2 concentration increases with increasing stability. Meanwhile, the horizontal dimension of increased fire risk increases significantly. The effect of atmospheric stability on O_2 plume dispersion is illustrated in Figures 3 and 4.

Figure 3. Stack height level O_2 plume concentration with different background wind speed under different stability classes. The x-axis is along the prevailing wind direction.

The O_2 plume concentration from an H_2 plant in a future H_2 society estimated based on the series of assumptions and simplifications described above produces typical behaviors as described above. The productivity of an individual H_2 plant may be quite different from the case we are studying here. However, one can easily get the desired O_2 concentration from this study by scaling the Q term in the Gaussian plume equation and rescaling the concentrations in each of the plots described for higher or lower values. For example, provided that stability class and background wind speed are the same, if in a real case an H_2 plant is emitting 100 kg s^{-1} O_2 instead of the 500 kg s^{-1} assumed in this study, then the O_2 concentrations in the plots would be reduced by a factor of five.

Figure 4. Vertical cross-section O₂ plume concentration with different background wind speed under different stability classes. The x-axis is along the prevailing wind direction.

As mentioned before, the Gaussian plume equation is designated to describe a time-averaged plume. In real case the instantaneous concentration might fluctuate due to atmospheric disturbances. Therefore, the fire hazardous area may be larger than the area bound by the critical lines in this study. Safety regulation makers must bear this in mind. Likewise in a completely stagnant air mass with a velocity of zero the oxygen concentration could easily build up to dangerous levels at the electrolyzer plant itself.

References:

- Energy & Environment Directorate, Lawrence Livermore National Laboratory, <http://eed.llnl.gov/flow/02flow.php>, June, 2004.
- Bossel, Ulf & Eliasson, Baldur. [Energy and The Hydrogen Economy](#). January 2003.

Section 8

Impact of an H₂-Based Road Transportation Sector on Materials and Structures

Angus Rockett

The incorporation of elemental hydrogen into almost all metals decreases their ductility greatly and can be a cause of fracture in high hydrogen environments. Therefore the adoption of a hydrogen economy with consequent increases in atmospheric hydrogen is a concern. While any amount of hydrogen represents a potential threat to an engineering/structural metal alloy a key question is whether the level of hydrogen predicted here to be associated with the hydrogen economy, including in localized areas, represents a threat to metal structures.

Analysis of the predicted levels of atmospheric hydrogen combined with an extensive theoretical and experimental analysis of hydrogen embrittlement mechanisms in metals shows that the hydrogen economy does not represent such a threat. Under normal conditions, even were hydrogen concentrated in a local area, the incorporation rate of hydrogen into structural alloys is too slow to degrade their properties. This is because metals include a surface oxide layer that is typically somewhat protective for hydrogen incorporation and further that hydrogen in its typical diatomic configuration is relatively unreactive. The necessary decomposition of the diatom as a first step to incorporation in and embrittlement of a metal is slow. Therefore unless a combination of metals is used that can simultaneously catalyze decomposition of the hydrogen molecules and promote incorporation of the resulting atoms into a strongly embrittleable metal, it is highly unlikely that atmospheric hydrogen would represent a threat. Such a catalytic combination is relatively rare and elevated temperatures are normally needed in any case to incorporate hydrogen at a sufficient rate to cause trouble.

The primary concern in a hydrogen economy would be in pressurized storage vessels and pipelines where metals are exposed to high pressures of pure hydrogen for extended times. Knowing this, designs can be adopted and specific metals chosen to reduce or practically eliminate concerns.

We therefore conclude that hydrogen embrittlement of metals does not pose a threat to structures or devices under normal circumstances.