Max-Planck-Institut für Meteorologie
Max Planck Institute for Meteorology

MAX-PLANCK-GESELLSCHAFT

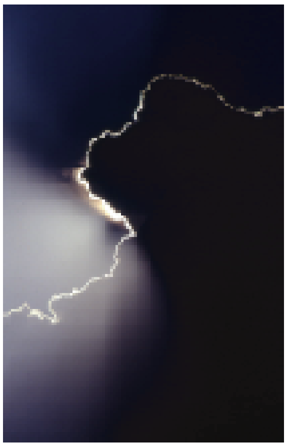
HyCARE

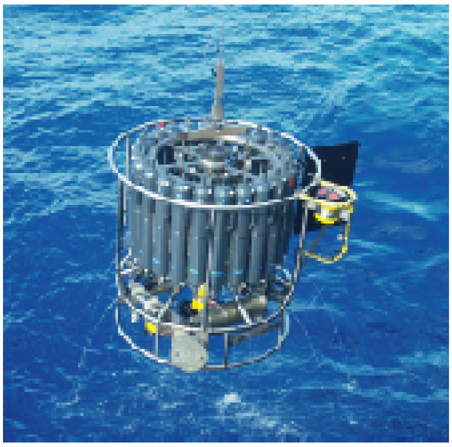
Hydrogen Energy
Chances and Risks for the Environment

Proceedings of the first HyCARE meeting,

Hamburg, 16-17 December 2004

Edited by Martin G. Schultz





Berichte zur Erdsystemforschung 5/2005

Reports on Earth System Science

Hinweis

Die Berichte zur Erdsytemforschung werden vom Max-Planck-Institut für Meteorologie in Hamburg in unregelmäßiger Abfolge herausgegeben.

Sie enthalten wissenschaftliche und technische Beiträge, inklusive Dissertationen.

Die Beiträge geben nicht notwendigerweise die Auffassung des Instituts wieder.

Die "Berichte zur Erdsystemforschung" führen die vorherigen Reihen "Reports" und "Examensarbeiten" weiter.

Notice

The Reports on Earth System Science are published by the Max Planck Institute for Meteorology in Hamburg. They appear in irregular intervals.

They contain scientific and technical contributions, including Ph. D. theses.

The Reports do not necessarily reflect the opinion of the Institute.

The "Reports on Earth System Science" continue the former "Reports" und "Examensarbeiten" of the Max Planck Institute.

Anschrift / Address

Max-Planck-Institut für Meteorologie
Bundesstrasse 53
20146 Hamburg
Deutschland

Tel.: +49-(0)40-4 11 73-0
Fax: +49-(0)40-4 11 73-298
Web: www.mpimet.mpg.de

Layout:

Bettina Diallo, PR & Grafik

Titelfotos:
vorne:
Christian Klepp - Jochem Marotzke - Christian Klepp
hinten:
Katsumasa Tanaka - Christian Klepp - Clotilde Dubois

HyCARE

Hydrogen Energy
Chances and Risks for the Environment

A forum to discuss the European research strategy concerning the environmental impacts of a future hydrogen economy

Proceedings of the first HyCARE meeting, Hamburg, 16-17 December 2004
Edited by Martin G. Schultz

Published as report No. 5 of the series
Berichte zur Erdsystemforschung – Reports on Earth System Science
Max Planck Institute for Meteorology
Hamburg, Germany, January 2005
ISSN 1614-1199

In order to discuss the most pressing research needs and structure the research activities regarding the environmental impact of large-scale hydrogen use in Europe, a workshop was held at the Max Planck Institute for Meteorology, Hamburg, Germany on Dec. 16 and 17, 2004. Thirty-two internationally recognized experts in atmospheric chemistry, soil microbiology, fuel cell technology, and scenario development came to Hamburg for two days of exchange of knowledge. This report summarizes the meeting presentations and discussions and is intended to support governments and funding agencies in structuring their agenda with respect to hydrogen impact research. All presentations from the workshop are also available as pdf documents on the HyCARE web pages:
http://www.mpimet.mpg.de/en/depts/dep1/acc/hycare/HyCARE_index.html (English) or
http://www.mpimet.mpg.de/en/depts/dep1/acc/hycare/HyCARE_de.html (German).

Table of Contents

Executive Summary

Thirty-two internationally recognized experts in atmospheric chemistry, soil microbiology, fuel cell technology, and scenario development participated in a workshop in Hamburg, Germany in December 2004 in order to

- conduct a survey of what is known about hydrogen in the environment,
- define and structure research needs regarding the environmental impacts of a future hydrogen economy,
- establish contacts between interested parties,
- create a topical structure for research proposals, and
- communicate research needs to policy makers and funding agencies.

This report summarizes the presentations and discussions from this first "Hydrogen Energy: Chances and Risks for the Environment" (HyCARE) meeting and makes several specific suggestions for further research activities in this area. The participants express their hope that this report will be considered in further planning of European research activities on the national and community level, and that funding will be made available in order to carry out the interesting and important work that is needed to assess the consequences of the anticipated major changes in our energy supply chains due to the introduction of hydrogen technology.

It is generally believed that the use of hydrogen technology will lead to reductions in greenhouse gas and air pollutant emissions and will thus be beneficial for human health and the environment. While this is generally true for the end-use of hydrogen energy, it becomes less clear when the complete energy chain is evaluated. In particular the method chosen to generate hydrogen will have a large impact on the achievable reductions in pollutant and greenhouse gas emissions. Potential problems also arise from the anticipated changes in the global atmospheric budget of hydrogen, although there is no need to ring the alarm bells as it happened in fall 2003 when a study from California found that rising hydrogen concentrations in the atmosphere could lead to enhanced ozone destruction in the stratosphere.

Hydrogen energy will not be able to solve all environmental problems, but it could reduce some of them, albeit at significant costs. Research into the environmental consequences of hydrogen use in specific energy sectors can help to make the right decisions as to where and how hydrogen should be employed, and it might prevent the build-up of new environmental problems before they cause serious damage or large costs.

This report may serve as a guide to define what is known about hydrogen in the atmosphere, what is available in Europe to study the environmental impacts of future hydrogen use, and what needs to be studied. It has become very clear during the workshop that successful research requires the collaboration of several groups working in the different fields of Earth System science, and technology and scenario development. Furthermore, a strong integration of observational activities and modeling studies is needed. We hope that the HyCARE workshop has contributed to forming strong research consortia, and that funding will be made available to carry out the research proposed by these groups.

The workshop was quite successful in bringing together the major actors in environmental hydrogen research and establishing links to the industry that is developing hydrogen technology. As it is very important to ensure communication between these different groups and to structure the various research activities in this field, the workshop organizers plan to establish HyCARE as a lasting communication platform. As a first step, a web site has been established, where all presentations from the workshop and this report can be found. It is planned to establish a small but effective management structure and to initiate communication with other hydrogen energy related programmes and platforms in Europe and elsewhere. HyCARE could thus evolve into a general platform for issues related to the environmental impacts of a hydrogen economy including a clearinghouse function for new scientific studies and an information center for news media and the general public.

Background

Air pollution, climate change, and the diminishing resources of oil and gas require a fundamental restructuring of our energy systems in the near future. Besides a necessary increase in the shares of wind power, solar energy, and geothermal energy for electricity generation, molecular hydrogen is often regarded as a key component in the future energy supply chain. With hydrogen powered vehicles, air pollution from direct traffic emissions could be a story of the past in a few decades from now, and air quality in European cities might be considerably improved. However, a large-scale hydrogen economy is also not without risks for the environment. Recent studies disagree about the potential environmental benefits and risks, largely due to the fact that the current atmospheric budget of molecular hydrogen remains poorly understood. More research in this area is urgently needed. Plausible scenarios must be developed and their consequences for the Earth system must be assessed.

Research on molecular hydrogen in the atmosphere was initiated around 1920, when the first measurements of the atmospheric hydrogen content were made (reported by Parneth, 1937). The atmospheric budget of hydrogen received some interest in the 1960s and 1970s, when it was discovered that atomic bomb explosions released tritium, the radioactive isotope of hydrogen. Around that time, the potential use of hydrogen as energy carrier of the future was also explored, and research into the infrastructure of a hydrogen economy began. During the 1980s and early 1990s, there was very little interest in atmospheric hydrogen research, and few publications on the subject appeared (see bibliography at the end of this report). Long-term measurements of atmospheric hydrogen were made since the early 1990s, mostly as a by-product of routine carbon monoxide observations (Novelli et al., 1999; Simmonds et al., 2000). Few analyses of the global budget of atmospheric hydrogen were made based on observations and three-dimensional chemistry transport models (Table 1), and it was generally found that sources and sinks are approximately balanced, although very large uncertainties remained due to insufficient understanding and quantification of hydrogen emissions and the uptake of hydrogen by soil microorganisms or –enzymes (Novelli et al., 1999; Hauglustaine and Ehhalt, 2002; Sanderson et al., 2003).

Scientists recognized the potential role of hydrogen as an indirect greenhouse gas, and this was noted in the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC, 2001). Interest in atmospheric hydrogen has grown again recently after several governments and the European Commission intensified their support of the development of hydrogen technology and infrastructure, and after an alarming report on potential damage by hydrogen to the stratospheric ozone layer was published in Science magazine (Tromp et al., 2003). Even though this report was heavily criticized for unrealistic assumptions and exaggerated conclusions, it nevertheless demonstrated the need for assessing the environmental consequences of a future hydrogen economy including the complex feedbacks between emission trading, air pollution, and climate change. The scientific community immediately reacted with two further modeling studies (Schultz et al., 2003; Warwick et al., 2004), and the obvious need to structure further research into this topic led to the organization of two international meetings in December 2004: the HyCARE meeting in Hamburg, and a special session at the Fall Meeting of the American Geophysical Union in San Francisco.

Table 1: Summary of global budget studies of atmospheric H_2 (TgH_2/year).

	Sanderson *et al.* (2003)	Hauglustaine and Ehhalt (2002)	Novelli *et al.* (1999)	Ehhalt (1999)	Warneck (1988)	Seiler and Conrad (1987)
Sources						
Oxidation of CH_4 and VOC	30.2	31	40±16	35±15	50	40±15
Fossil fuel combustion	20	16	15±10	15±10	17	20±10
Biomass burning	20	13	16±11	16±5	15	20±10
N_2 fixation	4	5	3±1	3±2	3	3±2
Ocean release	4	5	3±2	3±2	4	4±2
Volcanoes	-	-	-	-	0.2	-
Total	78.2	70	77±16	71±20	89	87
Sinks						
Deposition	58.3	55	56±41	40±30	78	90±20
Oxidation by OH	17.1	15	19±5	25±5	11	8±3
Total	74.4	70	75±41	65±30	89	98

The HyCARE meeting was initiated with the intention to bring together experts from different fields related to hydrogen research: while the majority of participants were Earth System scientists, there were also representatives from the automobile industry, energy systems and environmental consultants, and economists attending. The objectives of HyCARE were formulated as follows:

- Survey of what is known about hydrogen in the environment
- Define and structure research needs
- Establish contacts between interested parties
- Create a topical structure for research proposals
- Communicate research needs to policy makers and funding agencies

In order to meet these objectives, the meeting participants were asked to prepare brief reviews about their previous scientific work regarding hydrogen in the Earth system, and to formulate research questions for the future and identify their own research interests.

The meeting was structured into a general introduction, and two topical sessions focusing on

1. Results and Research Needs Regarding Measurements and Modeling of the Present-Day Budget of Hydrogen, and
2. Future Hydrogen Emissions (and Hydrogen-related Emission Changes), Scenario Development and Implications

Summaries of the individual sessions were prepared by designated rapporteurs and served as a basis for further discussion. This report provides a summary of the discussions and meeting conclusions and contains extended abstracts of all presentations. The complete presentation slides can be found as pdf documents on the HyCARE web pages:
http://www.mpimet.mpg.de/en/depts/dep1/acc/hycare/HyCARE_index.html (English) or
http://www.mpimet.mpg.de/en/depts/dep1/acc/hycare/HyCARE_de.html (German).

Session 1: Results and Research Needs Regarding Measurements and Modeling of the Present-Day Budget of Hydrogen

Summary of available H_2 observations and measurement needs

At present, no systematic observations of H_2 are made in Europe. Sporadic observations and snap shot measurements were presented by A. Engel (University of Frankfurt) and M. Steinbacher (EMPA). Data on the D/H isotopic ratio are available from T. Röckmann (MPI-K Heidelberg). These data can provide valuable constraints on the global budget of hydrogen. Further observations were made at Mace Head, Ireland, and Mte. Cimone, Italy. Most concentration measurements are in-situ observations and rely on the HgO method (Schmidt and Seiler, 1970).

In order to evaluate past trends of the atmospheric hydrogen concentration, some sporadic data from the 1970ies can be used, and only very little data from the 1980ies (Figure 1). The NOAA/CMDL time series (Novelli et al., 1999) starts around 1990. Archived air samples may open the possibility to also get isotope information on atmospheric hydrogen in the past, but long-term stability of hydrogen has to be ascertained.

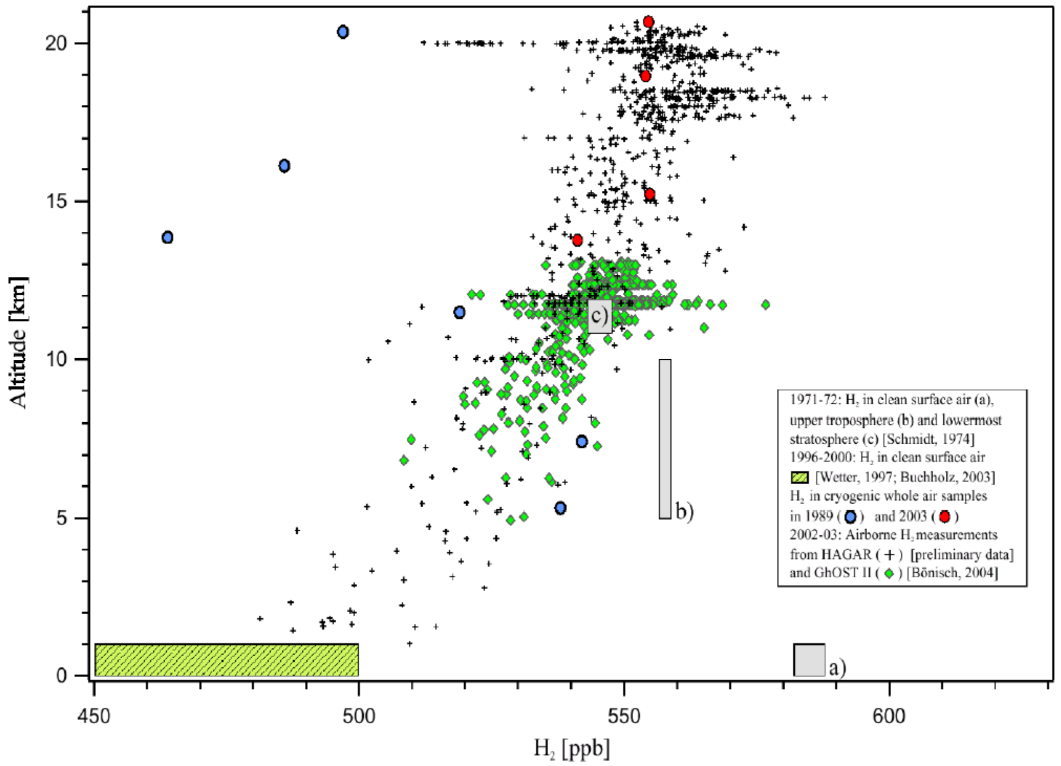


Figure 1: Secular changes in the vertical H_2 distribution since 1971 (unpublished data by U. Schmidt, A. Engel, and T. Wetter, Univ. Frankfurt)

Remote tropospheric H_2 concentrations range from about 450 to 550 ppb with a seasonal cycle of about 50 ppb. Maximum values in moderately polluted rural sites are around 800 ppb, higher values are observed in the vicinity of combustion sources. In tunnel measurements near Zürich up to 6 ppm were observed. At the locations listed above, peaks in H_2 time series are always mirrored in the CO time series. The tunnel measurements by EMPA show a rather good correlation between CO and H_2 with a slope of 0.54 ppm H_2 / ppm CO, providing a good estimate of the emission ratio from fossil fuel combustion (Novelli et al., 1999, cite emission ratios of 0.035 to 0.071 $kgH_2/kgCO$). A diurnal cycle has been observed near the sources (street measurements by EMPA), but not at more remote sites (Taunus Observatory measurements by Univ. FFM). The southern hemisphere has higher H_2 mixing ratios than the northern hemisphere, probably due to the domination of the soil sink in the NH.

Stratospheric H_2 is controlled by the production from methane oxidation and the destruction due to the OH reaction. In addition, H_2 is exchanged with the troposphere. Currently, the lower NH stratosphere has somewhat higher H_2 values than the troposphere. Thus, the stratosphere apparently acts as a small source of H_2 to the troposphere. There are indications of a long-term increase in stratospheric H_2 due to increasing CH_4 mixing ratios (IPCC, 2001). Stratospheric hydrogen has a higher deuterium content than tropospheric H_2, due to a strong isotope fractionation in the oxidation chain of CH_4. This isotope fractionation is important in explaining the isotopic composition of tropospheric H_2.

Upper stratospheric air has lower values of H_2, because there is less CH_4 to produce H_2. Much higher H_2 concentrations occur again in the mesosphere, where the dominant source is assumed to be H_2O photolysis. The low deuterium content of mesospheric H_2 supports this hypothesis. Mesospheric air can penetrate down into the lower stratosphere as has been observed during one occasion with very high H_2 values around 23 km altitude (see text by A. Engel et al. in this report). Hydrogen is an important component in stratospheric "total water" (i.e. the sum of hydrogen-containing molecules, which can be converted into each other through photochemical reactions). An increase in the total water content is related to the observed stratospheric cooling, which influences the dynamics in the stratosphere and possibly even in the troposphere.

Even though there are presently no systematic observations of atmospheric hydrogen in any of the European Union member states, Europe is in a good position to establish a strong observational network within a short time frame. Experienced researchers and instruments for measuring atmospheric H_2 are available at several laboratories. The isotopic composition measurements initiated by T. Röckmann (MPI-KP, Heidelberg) could easily be included in such a network. We suggest to set-up a loose network of about 12 stations throughout Europe (Figure 2) and to perform targeted measurements at or near the different emission sources in order to better constrain hydrogen emission ratios. Funding would be required mostly for setting-up the instrumentation and for personnel to operate the instruments and analyse the data.

Figure 2: Proposed network of European stations measuring atmospheric hydrogen (from draft CHESAI proposal ["Changing to a hydrogen economy: Study of atmospheric impact"] with additions marked in yellow)

Additional measurements of hydrogen should be performed from airborne platforms. H_2 measurements are part of the instrument payload of the CARIBIC programme ("Civil aircraft for the regular investigation of the atmosphere based on an instrument container", C. Brenninkmeijer, MPI-CH, Mainz), and the University of Frankfurt also has observational capabilities for airborne observations during targeted field campaigns. Such data should be augmented by trajectory analyses and inverse modeling approaches in order to provide additional information on hydrogen source signatures, particularly in data sparse regions. For example, it appears possible that measurements from CARIBIC could be used to improve the characterization of the biomass burning source of hydrogen.

R. Conrad (MPI-TMB Marburg), P. Ambus (Risø, Kopenhagen), and T. Laurila (FMI) demonstrated their experience in performing H_2 flux measurements and expressed their interest to further broaden these studies in order to better characterize the dominant sink term of atmospheric hydrogen due to soil deposition.

Besides an urgent need to perform more systematic observations of atmospheric H_2 concentrations, and to better characterize its sources and sinks, additional work should be performed on the existing data sets. There is a need for better inter-calibration of measurement standards, and the data should be further analyzed across the measuring institutions with the help of numerical models. Specific research questions comprise the following:

- Can the seasonal cycles of hydrogen in the Northern and Southern hemisphere be explained with the current knowledge on H_2 sources and sinks?
- How robust are the observed trends in the tropospheric and stratospheric hydrogen concentration?
- What are the constraints on the different emission source and sink terms imposed by their isotopic signature?
- What are the impacts of vehicle catalysts and of the shift from gasoline to diesel vehicles on hydrogen emissions?
- What are the potential changes in the soil uptake of hydrogen under changing climate conditions (including effects from changing soil humidity, desertification, and land-use)?

Summary of modeling studies and further research needs

At present there are only few modeling studies, which have investigated the global budget and photochemical behaviour of hydrogen in the atmosphere. Generally, the global chemistry transport models used for this purpose are able to qualitatively reproduce the seasonal cycle and inter-hemispheric difference of tropospheric hydrogen concentrations as well as the mean concentration (e.g. Hauglustaine and Ehhalt, 2002). However, due to the large uncertainties of hydrogen emission sources (see Table 1) and the lack of a robust parameterization of the soil uptake of hydrogen, the agreement between model and observations may be somewhat fortuitous, and it is unclear to what extent the models can be trusted for assessments of the consequences of future atmospheric hydrogen levels.

As indicated by Figure 1, there appears to be a downward trend of tropospheric hydrogen levels between the 1970s and now. It has been speculated that this trend is largely due to the introduction of catalysts in road vehicles, which has also been made responsible for the observed decrease in hemispheric background CO concentrations (cf. Novelli et al., 2003). Thus far, no model study exists, which has linked past emission changes to possible trends in tropospheric hydrogen concentrations. Addressing this problem also requires to take into account the observed meteorological changes between the 1970s and now, and their potential impacts on natural emissions of volatile organic compounds and methane, which both act as hydrogen precursors.

The increasing tropospheric methane concentrations throughout the 20th century should also have led to elevated hydrogen concentrations in the stratosphere, because methane acts as the major source of hydrogen in this region. However, the available data on stratospheric H_2 are too sparse to allow a robust trend estimate (Figure 1). Additional constraints on the robustness of model results in the troposphere and stratosphere could come from the isotopic composition measurements. So far, no model has attempted to simulate the isotopic composition of hydrogen.

Specific research questions related to the use of numerical models for understanding the present-day hydrogen budget are:

- Can numerical models reproduce the observed hydrogen trends based on present knowledge of methane and VOC trends and changes in the emissions from fossil fuel and biomass combustion?
- Can numerical models reproduce the isotopic signature of atmospheric H_2?
- What are the potential impacts of desertification and land-use change on hydrogen emissions from and uptake by soils?
- How would the atmospheric hydrogen budget change in a changing climate?
- What is the role of hydrogen in the feedback cycles between stratospheric water vapour, temperature, polar stratospheric clouds, ozone, and climate?
- How do changes in hydrogen influence the dynamics and energy budget in the upper stratosphere and mesosphere compared to changes in CO_2 and methane?

In order to address these questions, coupled chemistry climate models covering a wide range of atmospheric conditions must be further developed and parameterizations of hydrogen emissions and deposition must be improved. Funding should be made available for model intercomparison and sensitivity studies, and the modeling activities need to be co-ordinated with the gathering of new observational data, in particular with respect to obtaining more robust emission factors.

Session 2: Hydrogen Emissions (and Hydrogen-related Emission Changes), Scenario Development and Implications

Regarding the potential impacts of a future hydrogen economy, one must distinguish between the possible effects caused directly or indirectly through changes in the global hydrogen budget, and the effects that are related to the changes in greenhouse gas and air pollutant emissions, which are associated with the transformation of the energy and transportation systems. Present modeling studies indicate, that a globally significant impact of increased hydrogen emissions appears unlikely due to the following reasons:

- leak rates of hydrogen production, storage, and transportation systems will be limited to a few percent because of economic and safety reasons, and atmospheric hydrogen concentrations will at most double present values (in fact, global emissions of hydrogen may even decrease below present levels if the average overall leak rate can be limited to 1% or less),
- although hydrogen acts as an indirect greenhouse gas (by lengthening the lifetime of methane in the atmosphere), its impact is small compared to other factors perturbing the global oxidizing capacity: H_2 constitutes only about 5% of the average OH sink, and OH reacts much stronger to changes in reactive nitrogen emissions compared to changes in H_2 emissions (Schultz et al., 2003),
- the amount of water vapour produced from increased hydrogen release and hydrogen combustion is negligible compared to the natural evaporation of water vapour (Zittel and Altmann, 1996; see also the article by W. Zittel in this report). A possible exception would be cryoplanes, which could lead to additional cirrus formation (and therefore cooling of the upper troposphere). Preliminary results indicate, however, that the increased release of water vapour from cryoplanes would be balanced by the reduced emission of condensation nuclei (Marquart et al., 2001; see presentation by C. Zerefos).
- Changes in the stratospheric water vapour concentration due to increased hydrogen emissions would be less than the observed changes during past decades. While the implications of these changes for the cooling of the lower stratosphere and the potential reduction of stratospheric ozone levels are still unclear, they are certainly much smaller than the stratospheric ozone changes that have occurred as a consequence of CFC use, and it appears unlikely that the anticipated stratospheric ozone recovery will be halted or even reversed as a consequence of increased hydrogen use.

In spite of these generally optimistic perspectives, further research into this topic is needed, because the large uncertainties of the present-day hydrogen budget may have led to some important consequences escaping notice, and because the available model studies are not detailed enough to allow for a robust assessment of regional impacts of future hydrogen emissions. For example, it is conceivable that the NH polar vortex may be more sensitive to increasing hydrogen and water vapour concentrations than current models suggest. Furthermore, increased hydrogen levels in the troposphere (and resulting changes in stratospheric "total water") could lead to perturbations in the mesospheric energy budget with potential feedbacks on the dynamics of the middle and upper atmosphere and perhaps even the troposphere. Clearly, addressing these questions requires further development of coupled chemistry climate models, which include a detailed description of tropospheric and stratospheric chemistry and dynamics.

Perhaps of even greater relevance than the potential changes in the atmospheric hydrogen budget itself may be the consequences of a future hydrogen economy for global, regional, and local air pollution and the impacts of related emission changes on the global and regional climate. Preliminary analyses suggest that the hydrogen economy bears some potential to reduce the global burden of key pollutants such as ozone, volatile organic compounds (VOC), and NO_x (Schultz et al., 2003; Warwick et al., 2004). However, these studies were made under the assumption that hydrogen could be generated pollution-free (which is only a long-term perspective), and they neglected the time-scale of the hydrogen market penetration and the concurrent changes in energy demand and other technological developments.

Technology developers have begun to analyse the energy demands, greenhouse gas reduction potentials, and costs of various hydrogen pathways (see for example the presentation from H. Hass, and the recent Risø energy report, 2004), and there is a clear need to extend such studies for estimating the consequences with respect to air pollutant emissions. Chemistry transport models and coupled chemistry climate models rely on suitable emission scenarios for assessing the consequences of a future hydrogen economy on global and regional air pollution and climate change. On the local scale, a relocation of emission sources from the vehicle tailpipe to centralized reforming facilities in the urban outskirts may lead to drastic changes in air pollution levels, their geographical distribution, and their diurnal and seasonal pattern. Different technologies for production, storage, transport, and use of hydrogen may lead to very different air pollution effects. While one might generally expect a reduction in local and regional air pollution levels from the use of hydrogen technology, it will be important to estimate the reduction potential of the different technology options and pathways in order to find the most efficient and cost-effective solution.

European research institutions are well positioned to undertake a comprehensive analysis of the different environmental impacts of a future hydrogen economy. In particular, there is a strong need for:

- Realistic emission scenarios for air pollutants (gases and aerosols), and greenhouse gases. These are a prerequisite for modeling the impact of future hydrogen use.
- Optimization and further development of current chemistry climate models (chemistry modules, soil uptake parameterization, coupling of Earth system model components, numerical efficiency),
- Standardisation of model evaluation and inter-comparison of model simulations of the present and future atmospheric hydrogen budgets,
- Finer resolution emission inventories in particular for traffic emissions. These should ideally be resolved on a street-level (for urban-scale pollution studies) and contain detailed temporal and species information.

Specific research questions are for example:

- How would a future hydrogen economy affect air quality (in particular ozone and particles) on the urban scale, in Europe, and globally?
- What is the influence of changes in the global hydrogen budget compared to reductions (or changes) in NO_x and VOC emissions?
- What is the impact of replacing specific pollution sources with hydrogen technology (e.g. vehicle traffic, ships)?
- What is the impact of hydrogen on the global oxidizing capacity of the atmosphere and the lifetime of greenhouse gases?
- Are there any meteorological influences of potentially increased H_2O emissions (in particular on local scale)?
- How would a future hydrogen economy impact the chemistry in the stratosphere and mesosphere, and could this lead to dynamical changes which may influence the troposphere?

- What are the environmental benefits of hydrogen use compared to other fuel alternatives in different energy sectors?

Targeted research activities addressing these questions require the strong collaboration of Earth System scientists with technology developers, system analysts, and economists developing the scenarios. Numerical models need to be further developed and integrated among different scales. The models must be evaluated with observed concentrations of hydrogen and atmospheric pollutants, and the uncertainties in hydrogen and air pollution emission sources and sinks must be assessed.

European researchers are on the forefront in many of these activities, but the links between the different institutions and activities need to be strengthened in order to utilize the potential and accomplish credible assessments of the possible impacts of a future hydrogen economy. Funding is needed for strengthening of the environmental modeling infrastructure in Europe and to carry out specific research regarding the development of future emission scenarios and their application in global, regional-scale, and urban-scale numerical models.

References

Hauglustaine, D.A. and D.H. Ehhalt, (2002). A three-dimensional model of molecular hydrogen in the troposphere, Journal of Geophysical Research 107, 4330, doi:10.1029/2001JD001156.

IPCC, (2001). *Climate Change 2001: The scientific basis* (Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change), Cambridge University Press, Cambridge, UK, and New York, USA.

Marquart, S., R. Sausen, M. Ponater, V. Grewe, (2001). Estimate of the climate impact of cryoplanes, Aerospace Science & Technology, 5, 73-84.

Novelli P. C., P.M. Lang, K.A. Masarie, D.F. Hurst, R. Myers, J.W. and Elkins, (1999). Molecular hydrogen in the troposphere: Global distribution and budget, Journal of Geophysical Research, 104 (D23), 30427-30444.

Novelli, P.C., K.A. Masarie, P.M. Lang, B.D. Hall, R.C. Myers, and J.W. Elkins, (2003). Reanalysis of tropospheric CO trends: Effects of the 1997-1998 wildfires, Journal of Geophysical Research, 108 (D15), doi: 10.1029/2002JD003031.

Schmidt, U. and W. Seiler, (1970). A New Method For Recording Molecular Hydrogen In Atmospheric Air, Journal Of Geophysical Research, 75/9, 1713ff.

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

Warwick N. J., S. Bekki, E. G. Nisbet, J. A. Pyle, (2004). 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.

Zittel, W. and M. Altmann, (1996). Molecular Hydrogen and Water Vapour Emissions in a Global Hydrogen Energy Economy, Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, June 1996. Schön & Wetzel, Frankfurt am Main, Germany, pp. 71-82.

Extended abstracts

Well-to-Wheels analysis of alternative fuels and powertrains in the European context

Heinz Hass, Ford Forschungszentrum Aachen GmbH, Süsterfeldstr 200, 52072 Aachen
(On behalf of the JRC, EUCAR, CONCAWE consortium)

Introduction

A consortium of the EU Commission's JRC, EUCAR and CONCAWE has carried out a Well-to-Wheels analysis of a wide range of automotive fuels and powertrains. The study gives an assessment of the energy consumption and greenhouse gas emissions (CO_2, CH_4, N_2O), for a wide range of automotive fuels and powertrains relevant to Europe in 2010 and beyond. It also considers macroeconomic costs and the market potential of alternative fuels.

For the reference fuels, gasoline and diesel, only technologies with the potential for mass market series production by 2010 were considered, while for alternative fuels also technologies with the potential for market entry by 2010 were accepted.
The three main primary energy sources considered at present for road transport fuels are: Crude oil as a source for gasoline and diesel; Natural gas, used as CNG or for the production of synthetic liquid fuels or hydrogen; Biomass for production of biodiesel, ethanol, hydrogen and a range of synthetic fuels namely diesel, Di-Methyl-Ether (DME) and methanol.

A common vehicle platform and a common set of performance criteria measured on the New European Driving Cycle (NEDC) was used in order to ensure a sound comparison between the different options. All vehicles had to meet the criteria irrespective of the fuel/powertrain combination. It was also ensured that the benefit of technology improvements was allocated consistently to all fuel/powertrains, wherever relevant. Table 1 summarises the fuel/powertrain options.

Well-Wheels Summary

Figure 1 shows for all pathways the green house gas (GHG) emissions against the total energy used, regardless of its origin, be it fossil or renewable. Each point of the graph represents a different pathway by combining Well-to-Tank data with the appropriate vehicle option (Tank-to-Wheels). The results cluster on trend lines representing the different fuel sources, with a large range of variation along the trend lines – depending on how the fuel is produced and used. The box in the lower left corner of the chart highlights the performance of current gasoline vehicle technology.

Table 1: Fuel/powertrain combinations. PISI: port injection spark ignition; DISI: direct injection spark ignition; DICI: direct injection compression ignition; FC: fuel cell

Powertrains **Fuels**	PISI	DISI	DICI	Hybrid PISI	Hybrid DISI	Hybrid DICI	FC	Hybrid FC	Ref. + hyb. FC
Gasoline	2002	2002		2010+	2010+				2010+
Diesel Fuel			2002 2010+			2010+			2010+
CNG Bi-Fuel	2002 2010+								
CNG (dedicated)	2002 2010+			2010+					
Diesel/FAME Blend 95/5			2002 2010+			2010+			
Gasoline/Ethanol Blend 95/5	2002 2010+	2002 2010+			2010+				
FAME			2002 2010+			2010+			
DME			2002 2010+			2010+			
FT Diesel Fuel			2002 2010+			2010+			
Methanol									2010+
Naphtha									2010+
Compressed Hydrogen Gas	2010+			2010+			2010+	2010+	
Liquid Hydrogen	2010+			2010+			2010+	2010+	

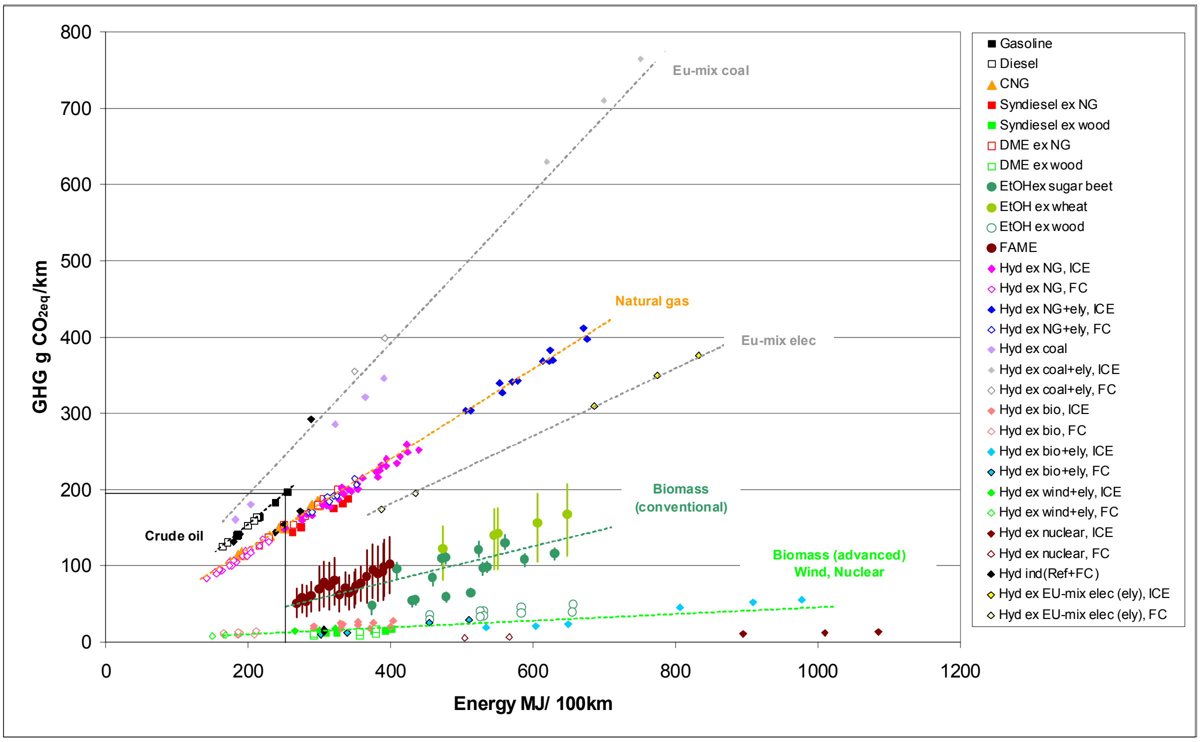


Figure 1: There are many routes to automotive fuels. The square indicates the 2002 baseline gasoline results.

From Figure 1 it clearly appears that many of the possible pathways produce more GHG emissions than today's conventional pathways. Alternative fuels from biomass produce less GHG emissions but are more energy intensive than the conventional products. In general, GHG emissions can be reduced but very often at the expense of energy.

Hydrogen as automotive fuel

Figure 2 shows the results for all considered hydrogen pathways. This variety of hydrogen production is one of its attractions, however, the energy required and the GHG emissions vary also considerably. Among the different hydrogen options shown, fuel cell vehicles have the lowest WTW energy consumption and GHG emissions.

Focussing on natural gas, there is a four-fold difference between producing hydrogen by gas reforming and using it in a fuel cell compared to electrolysing water with electricity generated from gas and burning the hydrogen in an IC engine.

Hydrogen from non-fossil sources (biomass, wind) offers low overall GHG emissions. However, renewable resources have currently a limited potential and can be used to produce electricity, often with higher benefits. Indirect hydrogen through on-board reforming offers little benefits compared to advanced conventional powertrains or hybrid systems.

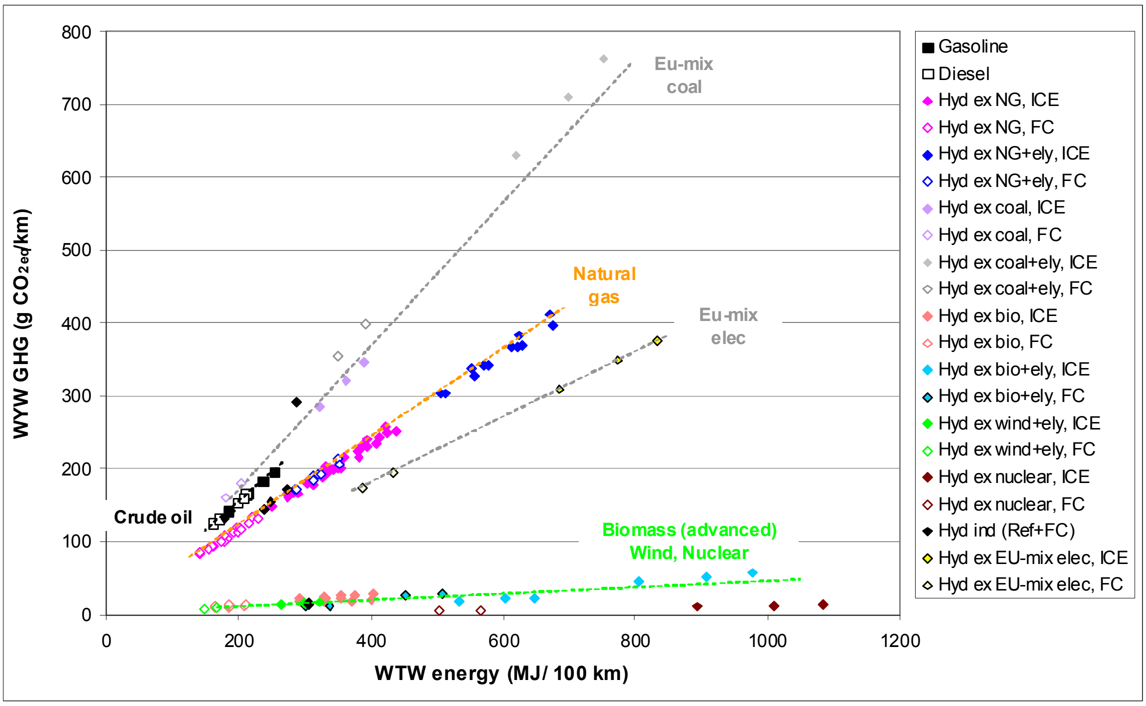


Figure 2: WTW energy requirement and GHG emissions for hydrogen pathways

Summary

A Well-to-Wheels analysis is the essential basis to assess the impact of future fuel and powertrain options.

- Both fuel production pathway and powertrain efficiency are key to GHG emissions and energy use.
- A common methodology and data-set has been developed which provides a basis for the evaluation of pathways. It can be updated as technologies evolve.

A shift to renewable/low fossil carbon routes may offer a significant GHG reduction potential but generally requires more energy. The specific pathway is critical.

Results must further be evaluated in the context of volume potential, feasibility, practicality, costs and customer acceptance of the pathways investigated.

A shift to renewable/low carbon sources is currently expensive.

- GHG emission reductions always entail costs but high cost does not always result in large GHG reductions

Optimum use of renewable energy sources such as biomass and wind requires consideration of the overall energy demand including stationary applications.

The complete report can be downloaded from http://ies.jrc.cec.eu.int/Download/eh.

Measurements of molecular hydrogen at the Institute for Atmosphäre und Umwelt of the J.W. Goethe University Frankfurt.

Andreas Engel, Thomas Wetter, Ute Buchholz, Michael Volk, Harald Bönisch and Ulrich Schmidt, Institut für Atmosphäre und Umwelt, Johann Wolfgang Goethe Universität Frankfurt, Frankfurt am Main, Germany.

The Institute for Meteorology and Geophysics at the J.W. Goethe University Frankfurt performs measurements of molecular hydrogen on different platforms, using gas chromatography with a Reduction Gas Detector (RGD) and doped Electron Capture Detection (ECD). Ground-based measurements have been performed at the Taunus Observatory on the top of the Kleiner Feldberg near Frankfurt during the winter 1996/1997 and the summer of 2000. Airborne observations are available for the UT/LS from the SPURT project with the in-situ GC GhOST II (Wetter, 2002) and for the stratosphere up to 20 km altitude from the in-situ GC HAGAR (Riediger et al. 2000) on board the high flying M55 Geophysika aircraft. Information on the vertical distribution of molecular hydrogen up to altitudes of about 33 km is further available from a number of balloon borne observations using the cryogenic whole air sampler BONBON (Schmidt et al., 1987). The combination of these observations allows to derive a picture of the vertical distribution and seasonal variability of molecular hydrogen in the middle to high latitudes of the northern hemisphere, although this picture is far from complete, due to the sparse data coverage. Especially seasonal variations have only been characterised at the ground. The global distribution and budget of molecular hydrogen has recently been reviewed by Schmidt and Wetter (2002). They note that while molecular hydrogen was higher in the northern hemisphere in the early 1970ies by about 6% in comparison to the southern hemisphere, the situation is reversed now with slightly higher mixing ratios of H_2 in the southern hemisphere, indicating a change in the atmospheric budget of H_2.

At the ground rather constant mixing ratios of molecular hydrogen are found in the middle latitudes of the northern hemisphere, which averaged at about 510 ppb during summer and 540 ppb during winter. Values down to about 420 ppb were observed during both seasons at the Taunus Observatory, while maximum values in polluted air, which is influenced by the city of Frankfurt, are on the order of 750 ppb. The Taunus Observatory is located at about 25 km North of Frankfurt at an altitude of 825 m. At this site no diurnal cycle in molecular hydrogen can be detected, like it is observed in the urban centres, where mixing ratios peak during the rush hours. The values of molecular hydrogen are usually well correlated with simultaneous CO observations. Changes in air masses or the build up of an inversion layer, as observed e.g. on December 13, 1996, are marked by sharp changes in the mixing ratios of both trace gases.

In the free troposphere a slight increase with altitude is observed, with values increasing to about 550 ppb at the tropopause. This increase is probably due to the fact that the most important source of H_2 is the oxidation of methane in the atmosphere, whereas its most important sink, the fixation by soils, is situated at the ground. In the lowermost stratosphere values on the order of 530 to 560 ppb are observed, which tend to be slightly higher than tropospheric values during the same period. The molecular hydrogen in the stratosphere is a mixture of hydrogen of tropospheric origin and hydrogen produced in the stratosphere from the oxidation of methane. As molecular hydrogen is produced in the stratosphere, it is also removed by reaction with the OH radical, yielding water vapour. It is expected that further away from the tropopause, where more aged air is observed, the fraction of molecular hydrogen which originates from the troposphere is reduced, whereas the fraction of molecular hydrogen produced in the stratosphere increases. In the lower stratosphere, H_2 is mostly anti-correlated with N_2O, which can be used as a proxy the age of air (Figure 1; e.g.

Engel et al., 2002). This explains why older stratospheric air has slightly higher molecular hydrogen values of about 560 ppb, indicating a higher equilibrium value than in the troposphere, due to absence of the soil sink.

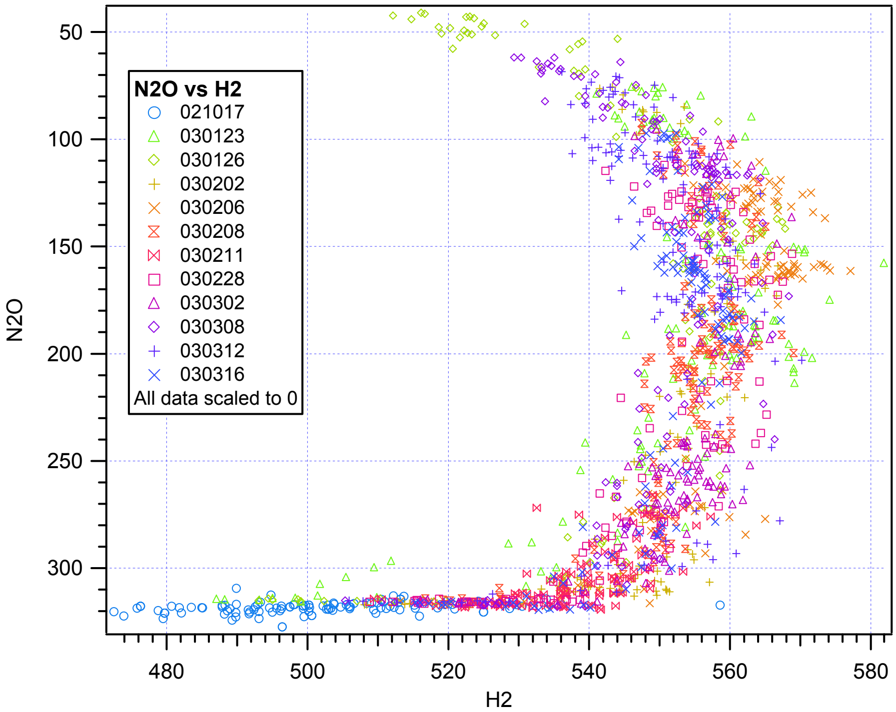


Figure 1: Tracer correlation between N_2O and H_2 observed during the EUPLEX campaign in winter 2003. Explanation see text.

During high latitude winter air originating from the upper stratosphere and from the mesosphere is transported downwards to the middle stratosphere. In air masses originating from the upper stratosphere, low levels of N_2O, CH_4 and also low values of molecular hydrogen (down to about 400 ppb) are observed. These low values of molecular hydrogen can be explained by the fact that these air masses are depleted in methane, therefore the hydrogen source from the oxidation of CH_4 is reduced in comparison to the sink reaction with OH, resulting in lower overall mixing ratios of H_2. On the contrary mesospheric air is characterised by very low levels of CH_4 and N_2O concurrent with high mixing ratios of H_2, as in the mesosphere the photolysis of water vapour by short wavelength UV radiation constitutes an important source of molecular hydrogen.

During a balloon observation on March 6, 2003 from Kiruna in Northern Sweden, a highly structured vertical profile of H_2 was observed, which showed minimum values of about 400 ppb around 23 km altitude, whereas enhanced values with a peak of more than 800 ppb were observed at about 26 km altitude. Only very little variation in other tracers like e.g. CH_4 or N_2O was observed in this altitude range. The variation is explained by a layer of air of mesospheric origin (and thus high in molecular hydrogen) centred around 26 km, which was surrounded by upper stratospheric air with low mixing ratios of molecular hydrogen.
Molecular hydrogen is an interesting tracer of atmospheric chemistry and transport. In the troposphere it can, in conjunction with CO, be used to observe urban plumes and in the stratosphere it is a good tracer of atmospheric dynamics, in particular of air mass origin under polar winter conditions. H_2 can not be observed from satellites, so in-situ observations are necessary to understand the temporal evolution of H_2, as wells as its seasonal and spatial variability throughout the atmosphere.

References

Engel, A., Strunk, M., Müller, M., Haase, H.-P., Poss, C., Levin, I., and U. Schmidt., The temporal development of total chlorine in the high latitude stratosphere based on reference distributions of mean age derived from CO_2 and SF_6, *J. Geophys. Res. 107*, 10.1029/2001JD000584, 2002.

Riediger, O., C. M. Volk, M. Strunk, and U. Schmidt, HAGAR - A new in situ tracer instrument for stratospheric balloons and high altitude aircraft, *Eur. Comm. Air Pollut. Res. Report 73*, 727-730, 2000.

Schmidt, U., Kulessa, G., Klein, E., Röth, E.-P., Fabian, P., and Borchers, R., Intercomparison of balloon-borne cryogenic whole air samplers during the MAP/GLOBUS 1983 campaign, *Planet. Space Sci. 35*, 647-656, 1987.

Wetter, T. Spurengasmessungen in der Tropopausenregion zur Charakterisierung von Stratosphären-Troposphären-Austauschprozessen, PhD Thesis, Johann Wolfgang Goethe Universität Frankfurt, Frankfurt, Germany, 2002.

Schmidt, U. and T. Wetter, Tropospheric chemistry and composition: H_2, In: *Encyclopedia of Atmospheric Sciences* (J. Holton, J. Pyle and J.A. Curry, Eds.), Vol 6, p. 2397 - 2402, Academic Press, 2002.

Continuous measurements of H_2 for the estimation of anthropogenic sources – research needs and future activities

M. Steinbacher, A. Fischer, M. K. Vollmer, K. Stemmler, S. Reimann,
Materials, Science & Technology Institute (EMPA), Air Pollution/ Environmental Technology Laboratory, Ueberlandstrasse 129, CH - 8600 Dübendorf, Switzerland

Introduction

Molecular hydrogen (H_2) is one of the most abundant trace gases in the atmosphere. However, only little attention has been paid until now to investigate the sources and sinks as well as the role of H_2 in atmospheric chemistry. At present, more and more ideas evoke that praise the hydrogen economy (the use of hydrogen to store and carry energy) for replacing the fossil fuel energy system. Before the hydrogen economy becomes reality, the impact of the different emissions on the atmosphere should be investigated in detail.

Accomplished Measurements

Since November 2002, continuous measurements of H_2 and carbon monoxide (CO) are performed at a road site near Zurich (Dübendorf, Switzerland). The aim of this study is to obtain a reliable data set for the modelling of actual emissions related to fossil fuel burning and especially road traffic. A commercial gas chromatograph (Reduction Gas Analyzer RGA3 from Trace Analytical, Inc.) is used to measure H_2 and CO by hot mercuric oxide reduction and UV absorption detection. The instrument is located at one of the sampling sites of the Swiss National Air Pollution Monitoring Network (Nabel) that is operated by Empa in co-operation with the Swiss Agency for the Environment, Forests and Landscape (Saefl). Every 6 minutes, a sample is injected onto the columns. Every fifth measurement is used for quality control by measuring a working standard based on NOAA/CMDL standards. Figure 1 shows the time series of H_2 and CO for 4 days in January 2003. The mixing ratios of H_2 and CO are correlated, reflecting similar sources (predominantly traffic) at this sampling site.

The diurnal cycle of H_2 shows a bimodal pattern with peaks during the morning and evening rush hours. The seasonal cycle shows lowest values in autumn in agreement with published data from the eastern USA [*Barnes et al.*, 2003]. Remarkably low data were measured in autumn 2003 after an exceptionally dry summer. As soils are the strongest H_2 sinks and enhanced uptake rates were observed under dry conditions [*Schuler and Conrad,* 1991] this effect could be probably related to more pronounced sink strengths. The role of the soil has to be still investigated in more detail.

In October and November 2002, H_2 and CO were measured in a highway tunnel near Zurich (Gubrist tunnel). Close correlations of H_2 and CO have been detected (which is in a good agreement with the data recorded at Duebendorf. First chassis dynamometer measurements of fuel cell cars were already performed in collaboration with a European car company.

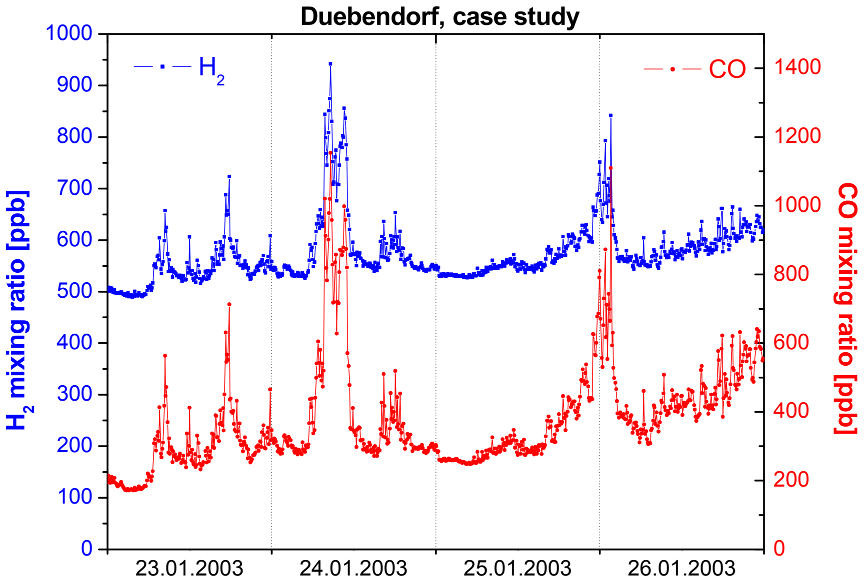


Figure 1: Road-side measurements of CO and H_2 near Dübendorf, Switzerland

Research Needs / Future Activities at EMPA

For a better understanding of the recent H_2 budget and a quantification of the sources and sinks, it is essential to address the following topics:

- long-term monitoring of atmospheric H_2 concentrations at remote stations, for observing the background trend, allocating strong emission sources (similar to already published methodologies for halocarbons [*Reimann et al.*, 2004b], [*Reimann et al.*, 2004a]), and providing input data and validating model outputs for inverse models and CTM. We plan to install continuous hydrogen measurements at the Jungfraujoch (3580 m asl), in order to estimate European emissions, the behaviour of hydrogen during transport and to obtain present climatology of hydrogen in the free troposphere over Europe.
- long-term monitoring of atmospheric H_2 at polluted European boundary layer stations, for discerning different sources and sinks. We aim to obtain a baseline data set from the polluted boundary layer near Zurich (Duebendorf) by continuing the time series, for comparison with future emission related to a potential hydrogen economy.
- emission factor determinations by means of tunnel studies and chassis dynamometer tests for traffic related emissions and flux chamber studies for the determination of sink strengths. We aim to perform short-term studies in road tunnels to obtain a better insight in the temporal evolution of H_2 emissions of the recent vehicle fleet. Evaporative and the tail-pipe emissions of fuel cell cars can be performed at the chassis dynamometer facility of the Empa to estimate the potential of future emissions factors of fuel cell vehicles.

References

Barnes, D.H., S.C. Wofsy, B.P. Fehlau, E.W. Gottlieb, J.W. Elkins, G.S. Dutton, and P.C. Novelli, Hydrogen in the atmosphere: observations above a forest canopy in a polluted environment, *Journal of Geophysical Research*, *108* (D6), art.-nr.: 4197, 10.1029/2001JD001199, 2003.

Reimann, S., A.J. Manning, P.G. Simmonds, D.M. Cunnold, R.H.J. Wang, J. Li, A. McCulloch, R.G. Prinn, J. Huang, R.F. Weiss, P.J. Fraser, S. O'Doherty, B.R. Greally, K. Stemmler, M. Hill, and D. Folini, Low European methyl chloroform emissions inferred from long-term atmospheric measurements, *Nature*, *accepted*, 2004a.

Reimann, S., D. Schaub, K. Stemmler, D. Folini, M. Hill, P. Hofer, B. Buchmann, P.G. Simmonds, B.R. Greally, and S. O'Doherty, Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580m asl): continuous measurements and their use for regional European source allocation, *Journal of Geophysical Research*, *109*, D05307, 10.1029/2003JD003923, 2004b.

Schuler, S. and Conrad, R., Hydrogen Oxidation Activities in Soil as Influenced by Ph, Temperature, Moisture, and Season, Journal of Biology and Fertility of Soils, 12(2), 127-130, 1991.

Isotope information about the global H_2 cycle

Thomas Röckmann, Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

A central requirement for estimating the impact of a future hydrogen economy on the atmosphere is a thorough understanding of its present global cycle. However, research on the global H_2 cycle has been very limited over the past decades despite the strong efforts in atmospheric research in general. Thus, the global H_2 cycle is not well understood. Figure 1 shows that significant uncertainties exist for all relevant terms in the budget, in particular the soil sink. Clearly, a better understanding of the global H_2 cycle is required. The few long time series that exist for H_2 [*Novelli et al.*, 1999] reveal several peculiar characteristics, which need to be understood, e.g.

- H_2 is one of the few trace gases with higher mixing ratios in the southern hemisphere (SH) compared to the northern hemisphere (NH)
- There are clear seasonal variations in both hemispheres, which have higher amplitudes in the NH
- There are significant interannual variations
- The seasonal cycles in NH and SH are not shifted by 6 months

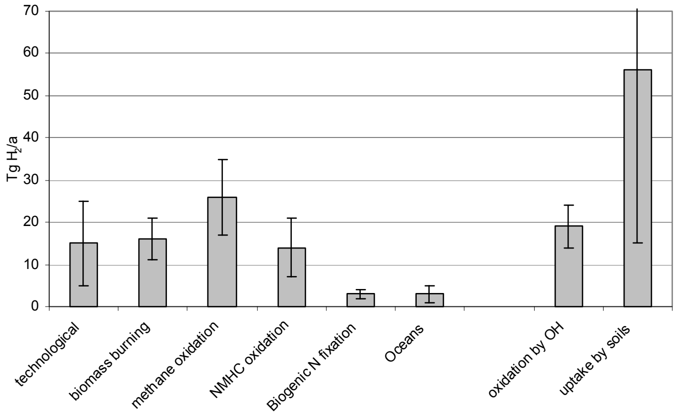


Figure 1: Estimates of the global H_2 budget after [*Novelli et al.*, 1999]. The main sources are combustion processes (industry and biomass burning) and oxydation processes in the atmosphere (CH_4 und NMHC). The dominant sinks are oxidation in soils and to a lesser degree oxidation by OH in the atmosphere. The uncertainties for the individual terms are at least 1/3 of the estimated values.

Isotope measurements are a useful method to derive additional independent information about global trace gas cycles, because individual sources usually emit a trace gas with a characteristic isotopic composition for that source, and also removal processes are often associated with isotope fractionation. Thus, isotope measurements can be used to better quantify the individual source and sink strengths. This is also true for molecular hydrogen, and in this case isotope measurements promise to be particularly valuable since the known signatures from the various sources and sinks span a very wide range. Deuterium (D), the heavy stable isotope of hydrogen, has a mean terrestric abundance of merely 1.5×10^{-4}, but is not equally distributed throughout the hydrogen bearing materials. As isotope fractionation for the light hydrogen atoms are strong, the D/H ratio varies by up to a factor of 4 between individual sources (Figure 2). The D content of atmospheric H2 is quantified by the $\delta D.=([D/H]_{sa}/[D/H]_{st}-1)*1000$‰, where$[D/H]_x$ denotes the D/H ratio in a sample (x=sa) and the international standard material VSMOW (x=st).

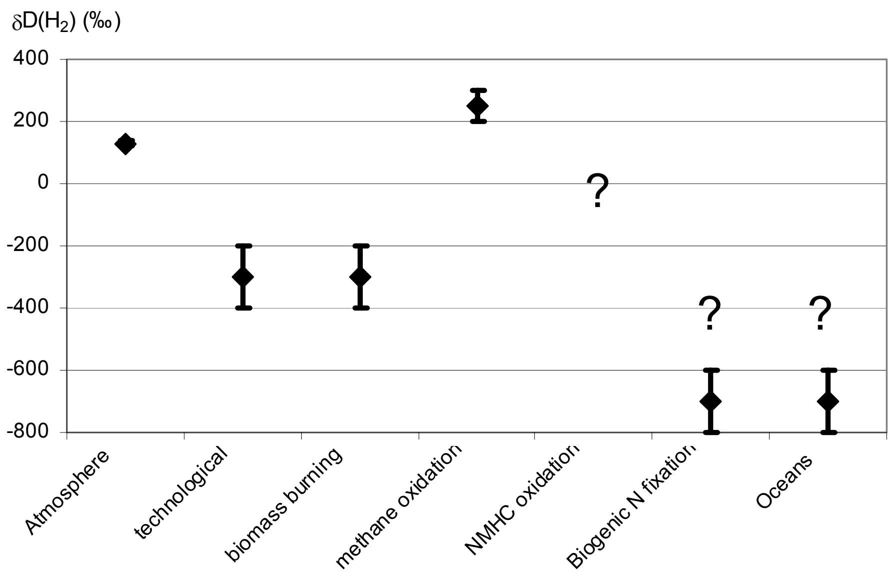


Figure 2: Isotope infor-mation about the major H_2 sources and sinks based on [*Gerst and Quay*, 2000; 2001; *Rahn et al.*, 2002a; 2002b] show a very large dynamic range. Estimates about biogenic fixation and oceanic emissions are uncertain.

Atmospheric H_2 in remote regions has a δ value of ~+130‰ and is thus isotopically enriched compared to emissions from biomass burning and industrial processes (~ - 200 bis -400‰ [Gerst and Quay, 2000; 2001; Rahn et al., 2002a; 2002b]). Only recently measurements on stratospheric air samples have shown that H_2 produced in the oxidation of CH_4 is isotopically heavy (~+250‰, [Rahn et al., 2003; Röckmann et al., 2003]).The isotopic composition of H_2 from NMHC oxidation is not yet known. On the sink side, the fractionation in the reaction with OH is very strong ($\alpha_{OH}=k(H_2+OH)/k(HD+OH)=0.6$) [Ehhalt et al., 1989; Talukdar et al., 1996]. The fractionation in the soil sink is much smaller, the available measurements indicate a value of von α_{soil}~0.94.

Research needs:

A research strategy using measurements of the isotopic composition of H_2 should focus on two points:

- Determination of annual cycles and extended time series of H_2 concentration and isotopic composition at several observing stations in both hemispheres, including the tropics. This will enable to investigate in more detail the reasons for
    - the seasonal variability of H_2
    - the latitudinal gradients
    - and the interannual variability
- Better constraints on the isotope signatures of sources and sinks of H_2, in particular
    - the soil sink
    - the NMHC oxidation source
    - biomass burning

Isotope measurements have a great potential to contribute significantly to improving our understanding of the global atmospheric H_2 cycle. In fact, such measurements have been suggested repeatedly in recent years for this purpose. However, traditional analysis methods were not adequate for a large-scale use of this method. With the new development of continuous-flow methods for quick high-precision isotope measurements [Rhee et al., 2004, Rahn et al., 2002b], this is now possible. Interpretation of the data can be done in an initial phase with simple box models, but if the source and sink signatures are known in sufficient detail, it is also be desirable to include the rare isotopes in atmospheric models.

References:

Ehhalt, D.H., J.A. Davidson, C.A. Cantrell, I. Friedman, and S. Tyler, The kinetic isotope effect in the reaction of H_2 with OH, *JGR*, *94 D*, 9831/6, 1989.

Gerst, S., and P. Quay, The deuterium content of atmospheric molecular hydrogen: Method and initial measurements, *J. Geophys. Res.*, *105* (D21), 26433-26445, 2000.

Gerst, S., and P. Quay, Deuterium component of the global molecular hydrogen cycle, *J. Geophys. Res.*, *106* (D5), 5021-5031, 2001.

Novelli, P.C., P.M. Lang, K.A. Masarie, D.F. Hurst, R. Myers, and J.W. Elkins, Molecular hydrogen in the troposphere: Global distribution and budget, *J. Geophys. Res.*, *104* (D23), 30427-30444, 1999.

Rahn, T., J.M. Eiler, K.A. Boering, P.O. Wennberg, M.C. McCarthy, S. Tyler, S. Schauffler, S. Donnelly, and E. Atlas, Extreme deuterium enrichment in stratospheric hydrogen and the global atmospheric budget of H_2, *Nature*, *424* (6951), 918-921, 2003.

Rahn, T., J.M. Eiler, N. Kitchen, J.E. Fessenden, and J.T. Randerson, Concentration and dD of molecular hydrogen in boreal forests: Ecosystem-scale systematics of atmospheric H_2, *Geophys. Res. Lett.*, *29* (18), doi:10.1029/2002GL015118, 2002a.

Rahn, T., N. Kitchen, and J.M. Eiler, D/H ratios of atmospheric H_2 in urban air: Results using new methods for analysis of nano-molar H_2 samples, *Geochim. Cosmochim. Acta*, *66* (14), 2475-2481, 2002b.

Rhee, T.S., J.E. Mak, C.A.M. Brenninkmeijer, and T. Röckmann, Continuous-flow isotope analysis of the D/H ratio in atmospheric hydrogen, *Rap. Commun. Mass Spectrom.*, *18*, 299-306, 2004.

Röckmann, T., T.S. Rhee, and A. Engel, Heavy hydrogen in the stratosphere, *Atmos. Chem. Phys.*, *3*, 2015-2023, 2003.

Talukdar, R.K., T. Gierczak, L. Goldfarb, Y. Rudich, B.S.M. Rao, and A.R. Ravishankara, Kinetics of hydroxyl radical reactions with isotopically labeled hydrogen, *J. Phys. Chem.*, *100* (8), 3037-3043, 1996.

Observations of NO_x in 'background' air at a North Sea coastal location (Weybourne Atmospheric Observatory, UK)

W.T. Sturges, S.A. Penkett, B.J. Bandy and C.E. Reeves, University of East Anglia, Climate Research Unit, Norwich NR4 7TJ, United Kingdom

One of the immediate benefits of the widespread use of hydrogen as an alternative fuel in vehicles would be a reduction in anthropogenic NO_x emissions to the atmosphere. This would result in improvements to urban and regional air quality, and a reduction in photochemically-formed ozone in regional and background atmospheres. The latter effect could at least partly offset the potential positive indirect radiative term arising from the reaction of fugitive hydrogen emissions with hydroxyl radicals, which could lengthen the atmospheric lifetime of the important greenhouse gas methane.

The projected benefits of reduced NO_x emissions might not, however, be fully realised if NO_x emissions from marine vessels are not also curtailed. It has been suggested that by year 2010 NO_x emissions from European road traffic should have fallen to 6.5 Mtons yr^{-1}, whilst that from shipping in European waters will have reached an almost equivalent amount (6.0 Mtons yr^{-1}) even for a modest 2% yr^{-1} growth rate (presentation of C. Ågren at http://www.seaat.org/public/harmofemissionsagren.ppt).

We have observed evidence for such a significant contribution to NO_x from measurements of NO and NO_2 at the Weybourne Atmospheric Observatory on the North Sea coast of Norfolk, England (Figures 1 and 2). During April and May of 2004, for example, during flow of polluted air from populous regions of the UK, NO_2 levels typically reached 10 to 30 ppb, and midday NO typically peaked at 5 to 10 ppb. During flow from the North Sea, and notably from the northwest, background NO_2 dropped to below 1 ppb indicative of very clean air, and NO was almost undetectable even at midday. These periods, however, were punctuated by frequent 'spikes' of NO_2 of 15 to 35 ppb occurring both day and night. It is considered that these 'spikes' are due to ship stack plumes, from vessels in the sea lanes some miles offshore, crossing the observing site. Although not as sustained as the NO_x levels observed in city plumes, the peak levels were at least as large, suggesting a significant contribution of marine combustion NO_x to background levels in rural areas bordering the North Sea.

These observations will be subject to more rigorous analysis to more clearly identify the origin of these apparent plumes, and also to quantify the corresponding flux on NO_x across the North Sea coastline at this location. Weybourne provides an excellent site for long term observations of this type.

Figure 1: The Weybourne Atmospheric Observatory, Norfolk, located at the North Sea coast of Norfolk, England, at 1.7°E, 53.7°N

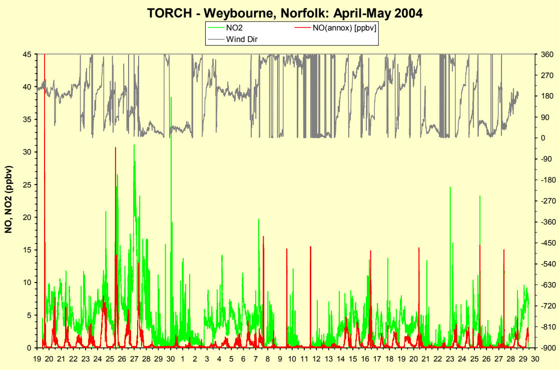


Figure 2: NO_x concentrations and wind direction measured at Weybourne during April and May 2004. High NO_x concentrations during north-westerly flow are indicative of ship emission plumes

Soil enzymes and microorganisms involved in the uptake of atmospheric hydrogen

Ralf Conrad, Max-Planck-Institute for Terrestrial Microbiology, Karl-von-Frisch-Str., 35043 Marburg, Germany

The budget of atmospheric hydrogen has recently been reviewed (Ehhalt, 1999; Novelli et al., 1999). Soils contribute about 75% to the total sink strength, the remainder being due to oxidation by OH. The flux of H_2 between soil and atmosphere is due to biological activities that have been reviewed by Conrad (1988; 1995; 1996; 1999). The net flux of H_2 is the result of simultaneous production and consumption processes, which normally result in deposition of atmospheric H_2. Emission of H_2 from terrestrial ecosystems is only rarely observed. One example is legume fields, where H_2 is produced during biological N_2-fixation (Conrad and Seiler, 1980). Another example is waterlogged soil (e.g. rice fields), where H_2 is produced during anaerobic decomposition of organic matter (Schütz et al., 1988). Finally, H_2 may be produced by fermentation processes in the gut of termites and released into the soil atmosphere (Zimmerman et al., 1982). The rates of gross production and consumption of H_2 in soil can be determined from the flux kinetics and the compensation concentration, which is due to the equilibrium between production and consumption reactions (details see: Conrad, 1994). Figure 1 shows as example the gross rates of H_2 production and H_2 deposition in a clover field, exhibiting a seasonal peak of net H_2 emission due to biological N_2 fixation.

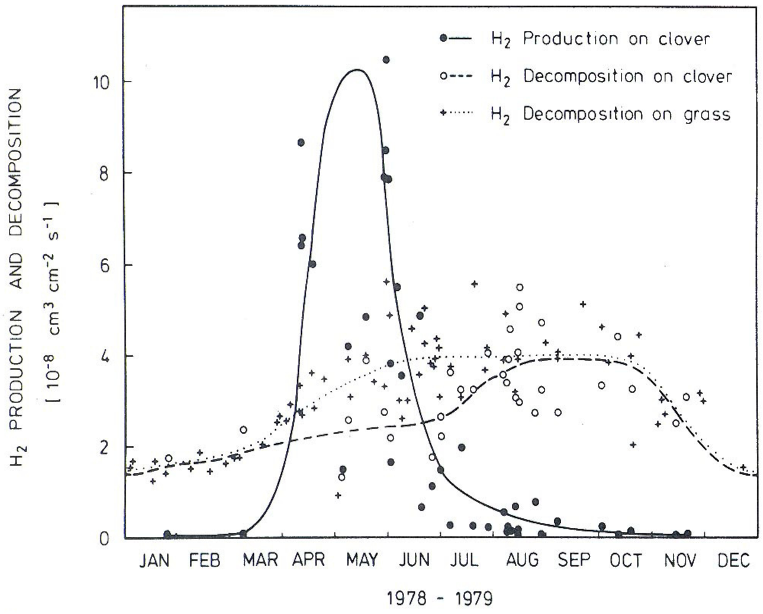


Figure 1: Seasonal change of gross rates of production and decomposition of H_2 in a glover field (for comparison, H_2 decomposition rates in a grass field. Data are taken from Conrad and Seiler (1980)

Early studies of Seiler and coworkers have shown that atmospheric H_2 is consumed within the top soil layers (Liebl and Seiler, 1976; Seiler et al., 1977; Seiler, 1978). Similar results were obtained from studies of uptake of tritium by soil (Fallon, 1982; McFarlane et al., 1978). The localization of H_2 uptake by the top soil layers is in contrast to that of CH_4 uptake, which is usually localized in somewhat deeper soil layers (reviewed by Conrad, 1996). Recent measurements by Yonemura and coworkers (1999; 2000a; 2000b) confirmed that H_2

consumption activity is localized in the top soil, but also showed that the diffusion process can nevertheless be critically important, at least when soil moisture is high or when the potential consumption activity is large.

Consumption of H_2 in soil is biological, but it is not completely clear which type of activity is responsible for it. Based on various circumstantial evidence, Conrad (1988) hypothesized that consumption of H_2 is due to abiontic soil enzymes rather than soil microorganisms. In fact, microorganisms responsible for utilization of H_2 at low atmospheric mixing rations have so far not been identified (Conrad, 1995; 1996; 1999; Klüber et al., 1995). Although soils do contain H_2-oxidizing microorganisms (so-called Knallgas bacteria), these bacteria only oxidize H_2 at elevated but not at atmospheric mixing ratios, and exhibit kinetic parameters that are not consistent with those observed by genuine soil (Häring and Conrad, 1994; Schuler and Conrad, 1990; 1991). Thus, it is possible to distinguish two different activities of H_2 consumption in soil based on different kinetic parameters, i.e. the threshold below which H_2 is no longer consumed and the H_2 mixing ratio (the K_m value) at which consumption reaches half-maximum velocity (Table 1). The activity with low K_m and low threshold is believed to be due to abiontic soil enzymes (hydrogenase), the other with high K_m value and high threshold to be due to Knallgas bacteria (Conrad, 1995; 1996).

Table 1: Characteristic kinetic parameters of the two different H_2 uptake activities that are typically found in soil

H_2 uptake activity	Km (ppmv)	Threshold (ppmv)	Target
High affinity	20-120	< 0.02	Atmospheric H_2
Low affinity	800-1500	> 0.5	Biological H_2

Whereas Knallgas bacteria can be isolated from soil or can be identified using molecular techniques (Klüber et al., 1995; Lechner and Conrad, 1997), abiontic soil hydrogenases are so far enigmatic. By definition, abiontic soil hydrogenases would be enzymes existing in free state, bound to the soil matrix or dead microbial cells. The H_2 consumption activity was found localized at an intermediate-sized soil particle fraction, with only weak correlation to microbial biomass (Gödde et al., 2000; Häring et al., 1994). Attempts to extract this activity from the soil matrix were so far not successful. The activity of these putative enzymes was found in soils from various ecosystems but without preference for a particular one (Figure 2).

Even desert soils consume atmospheric H_2 after addition of water (Conrad and Seiler, 1985). Recently, King (2003) observed uptake of atmospheric H_2 on recent volcanic deposits older than 26 years. However, this author concluded from inhibition studies that the activity in the young volcanic soils is due to intact microbial cells and accounts for up to 25% of total microbial activity (CO_2 production as proxy). In conclusion, the molecular nature of the soil activity that is responsible for 75% of the global sink strength of atmospheric H_2 is still unknown.

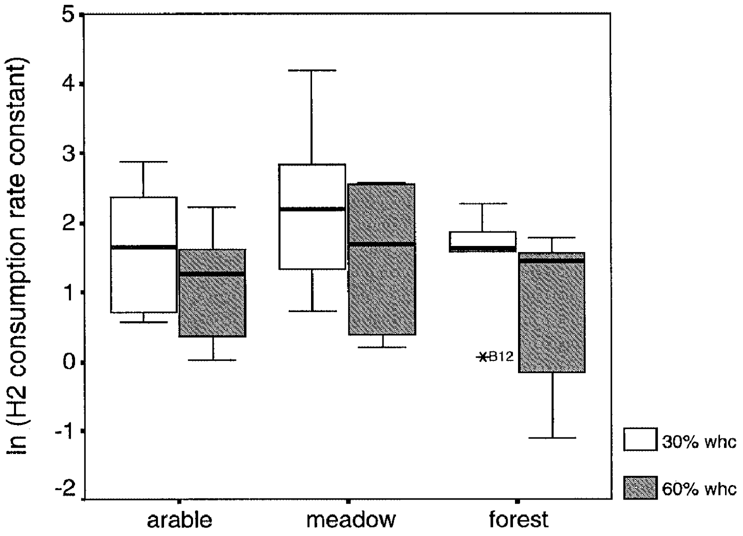


Figure 2: Overview of uptake rate constants for atmospheric H_2 observed in soils (n = 20) sampled from different ecosystems in Germany. Data are from Gödde et al. (2000).

References

Conrad, R. (1988) Biogeochemistry and ecophysiology of atmospheric CO and H_2. *Adv. Microb. Ecol.* **10:** 231-283.

Conrad, R. (1994) Compensation concentration as critical variable for regulating the flux of trace gases between soil and atmosphere. *Biogeochem.* **27:** 155-170.

Conrad, R. (1995) Soil microbial processes involved in production and consumption of atmospheric trace gases. *Adv. Microb. Ecol.* **14:** 207-250.

Conrad, R. (1996) Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O, and NO). *Microbiol. Rev.* **60:** 609-640.

Conrad, R. (1999) Soil microorganisms oxidizing atmospheric trace gases (CH_4, CO, H_2, NO). *Ind. J. Microbiol.* **39:** 193-203.

Conrad, R. and Seiler, W. (1980) Contribution of hydrogen production by biological nitrogen fixation to the global hydrogen budget. *J. Geophys. Res.* **85:** 5493-5498.

Conrad, R. and Seiler, W. (1985) Influence of temperature, moisture and organic carbon on the flux of H_2 and CO between soil and atmosphere. Field studies in subtropical regions. *J. Geophys. Res.* **90:** 5699-5709.

Ehhalt,D.H. (1999) Gas phase chemistry in the troposphere. In *Global Aspects of Atmospheric Chemistry*. Zellner, R. (ed). New York: Springer, 21-109.

Fallon, R. D. (1982) Molecular tritium uptake in Southeastern U.S. soils. *Soil Biol. Biochem.* **14:** 553-556.

Gödde, M., Meuser, K., and Conrad, R. (2000) Hydrogen consumption and carbon monoxide production in soils with different properties. *Biol. Fertil. Soils* **32:** 129-134.

Häring, V. and Conrad, R. (1994) Demonstration of 2 different H_2-oxidizing activities in soil using an H_2 consumption and a tritium exchange assay. *Biol. Fertil. Soils* **17:** 125-128.

Häring, V., Klüber, H. D., and Conrad, R. (1994) Localization of atmospheric H_2-oxidizing soil hydrogenases in different particle fractions of soil. *Biol. Fertil. Soils* **18:** 109-114.

King, G. M. (2003) Contributions of atmospheric CO and hydrogen uptake to microbial dynamics on recent Hawaiian volcanic deposits. *Appl. Environ. Microbiol.* **69:** 4067-4075.

Klüber, H. D., Lechner, S., and Conrad, R. (1995) Characterization of populations of aerobic hydrogen-oxidizing soil bacteria. *FEMS Microbiol. Ecol.* **16:** 167-175.

Lechner, S. and Conrad, R. (1997) Detection in soil of aerobic hydrogen-oxidizing bacteria related to Alcaligenes eutrophus by PCR and hybridization assays targeting the gene of the membrane-bound (NiFe) hydrogenase. *FEMS Microbiol. Ecol.* **22:** 193-206.

Liebl,K.H. and Seiler,W. (1976) CO and H_2 destruction at the soil surface. In *Microbial Production and Utilization of Gases*. Schlegel, H. G., Gottschalk, G., and Pfennig, N. (eds). Göttingen: E. Goltze, 215-229.

McFarlane, J. C., Rogers, R. D., and Bradley, J. (1978) Environmental tritium oxidation in surface soil. *Environ. Sci. Technol.* **12:** 590-593.

Novelli, P. C., Lang, P. M., Masarie, K. A., Hurst, D. F., Myers, R., and Elkins, J. W. (1999) Molecular hydrogen in the troposphere: global distribution and budget. *J. Geophys. Res.* **104:** 30427-30444.

Schuler, S. and Conrad, R. (1990) Soils contain two different activities for oxidation of hydrogen. *FEMS Microbiol. Ecol.* **73:** 77-84.

Schuler, S. and Conrad, R. (1991) Hydrogen oxidation activities in soil as influenced by pH, temperature, moisture, and season. *Biol. Fertil. Soils* **12:** 127-130.

Schütz, H., Conrad, R., Goodwin, S., and Seiler, W. (1988) Emission of hydrogen from deep and shallow freshwater environments. *Biogeochem.* **5:** 295-311.

Seiler,W. (1978) The influence of the biosphere on the atmospheric CO and H_2 cycles. In *Environmental Biogeochemistry and Geomicrobiology. Volume 3: Methods, Metals and Assessment*. Krumbein, W. (ed). Ann Arbor, MI: Ann Arbor Science Publ., 773-810.

Seiler, W., Liebl, K. H., Stöhr, W. T., and Zakosek, H. (1977) CO- und H_2-Abbau in Böden. *Z. Pflanzenernaehr. Bodenkd.* **140:** 257-272.

Yonemura, S., Kawashima, S., and Tsuruta, H. (1999) Continuous measurement of CO and H_2 deposition velocities onto an andisol: uptake control by soil moisture. *Tellus* **51B:** 688-700.

Yonemura, S., Kawashima, S., and Tsuruta, H. (2000a) Carbon monoxide, hydrogen, and methane uptake by soils in a temperate arable field and a forest. *J. Geophys. Res.* **105:** 14347-14362.

Yonemura, S., Yokozawa, M., Kawashima, S., and Tsuruta, H. (2000b) Model analysis of the influence of gas diffusivity in soil on CO and H_2 uptake. *Tellus* **52B:** 919-933.

Zimmerman, P. R., Greenberg, J. P., Wandiga, S. O., and Crutzen, P. J. (1982) Termites: A potentially large source of atmospheric methane, carbon dioxide, and molecular hydrogen. *Science* **218:** 563-565.

Fluxes of hydrogen between soil and atmosphere

Per Ambus, Plant Research Department, Risø National Laboratory, Frederiksborgvej 399, 4000 Roskilde, Denmark.

Soils are believed to constitute the major, global sink for molecular hydrogen with a sink strength in the order of 70% of the global consumption, equivalent to 56 Tg yr-1 (Table 1). However, current estimates are very uncertain ranging from 20 to 90 Tg yr, which suggests an urgent need to achieve more knowledge on the exchange rates of hydrogen between soil and atmosphere.

Hydrogen is produced and consumed by several different biological processes in the soil (Conrad 1995). The hydrogen consuming processes include methanogenesis, respiratory processes of anaerobic bacteria, oxidation by 'Knallgas' bacteria and, probably most importantly, oxidation by free hydrogenase enzymes found in soils worldwide. Production of hydrogen is linked to fermentation processes in oxygen free environments such as wetlands and local hot spots in upland soils. Hydrogen is also produced during the activity of the nitrogenase enzyme complex of nitrogen fixing legume plants. Overall, the sum of all these processes most frequently results in a net uptake of atmospheric hydrogen in the soil resulting in a downward flux. However, under certain soil conditions such at temporary or permanent water saturation, hydrogen may be released to the atmosphere.

Table 1: Strengths of global hydrogen sources and sinks and their isotopic characteristics.

	Strength	Isotopic signature
Sources		
Fossil fuel combustion	15±10 Tg/yr	-196±10‰
Biomass burning	16±5 Tg/yr	-290±60‰
Photochemical reactions	46±19 Tg/yr	nd
Other (ocean, N-fix.)	6±2 Tg/yr	nd
Sinks		
Soil uptake	56±41Tg/yr	0.943
OH oxidation	19±9Tg/yr	0.595 - 0.606
H_2 in the troposphere	155 Tg	+130±4‰

After Guerst & Quay, 2001

Very little is known on the controls of soil hydrogen uptake. However, comparative studies have shown differences among different ecosystems suggesting that hydrogen uptake is under environmental control (Khalil and Rasmussen 2000). More research is needed in this area to further characterize the nature of soil hydrogen turnover. Relevant research questions include the extent of diurnal and seasonal variability, control by soil chemical and physical conditions (e.g. aeration, temperature, moisture, acidity) and characterization of the microbial community / biotic enzyme systems that are involved in the production and consumption of hydrogen. Future work is also needed to characterize the isotopic fractionation associated with soil hydrogen uptake and production that can provide information in the global budgeting of hydrogen cycling. Current knowledge indicates imbalance in the global deuterium budget, however data are incomplete (Table 1).

Quantification of the exchange rate between soil and atmosphere can be done by application of conventional static flux chamber techniques combined by GC analysis (Ambus et al. 1993). Protocols for flux chamber measurements range from low cost manually operated systems that can be deployed in remote locations to fully automated systems integrated with on-line detection instruments, which require relatively sophisticated infrastructure and thus offers limited applicability.

References

P. Ambus, H. Clayton, J.R.M. Arah, K.A. Smith, K.A., S. Christensen 1993 Similar N_2O flux from soil measured with different chamber techniques. Atm. Environ. 27A:121-123.

R. Conrad 1995 Soil microbial processes involved in production and consumption of atmospheric trace gases. In J.G. Jones (ed.) Advances in Microbial Ecology, 14, 207-250. Plenum Press, NY.

S. Gerst, P. Quay 2001 Deuterium component of the global molecular hydrogen cycle. J Geophys Res, 106, D5, 5021-5031.

M.A.K. Khalil, R.A. Rasmussen 2000 Soil-atmosphere exchange of radiatively and chemically active gases. Envrion. Sci. Pollut. Res., 7, 79-82.

Case study on regional impact of traffic emission reduction

Heinke Schlünzen[1], David Grawe[1,2], Elke Meyer[1], Alfred Trukenmüller[1,3]
[1] Meteorological Institute, ZMAW, University of Hamburg, Bundesstr. 55, 20146 Hamburg, Germany
[2] Division of Environmental Health and Risk Management, University of Birmingham, UK
[3] Umweltbundesamt, Postfach 33 00 22, 14191 Berlin, Germany

Introduction

Traffic is currently the main contributor to NO_x concentrations in North-West Europe. For Germany, in year 2000 more than 53% of the NO_x–$NO_2$and about 18% of the NMVOC emissions are from traffic. Thus, traffic considerably contributes to the concentrations of primary pollutants. In addition, traffic emissions are a main source for the development of secondary pollutants in the atmosphere.

Results for current emissions / emission reduction

A case study on the impact of "zero -traffic-emission" is performed with the numerical model system M-SYS (Trukenmüller et al., 2004). M-SYS consists of meteorology models METRAS (Schlünzen, 1990) and MITRAS (Schlünzen et al., 2003), which simulate meteorological fields in different scales, and of consistent chemistry models MECTM and MICTM (Lenz et al., 2000; Grawe 2005). The models are nested in each other, with the outermost model domain covering most of western Europe (Figure 1) and the innermost model domain covering an area of only 1 km^2, but resolving traffic emissions and influences of buildings on street canyon flow directly. Emission data were provided by IER Stuttgart (Germany).

Current emissions show highest concentrations close to emitters (e.g. mostly in agglomerations) for primary pollutants and downwind of agglomerations for secondary pollutants (e.g. ozone). In the reduction scenario ("zero-traffic-emission)" the NO_x area emissions are reduced by 75%. The NMVOC emissions are reduced by 25%. The results show – as expected – considerable reductions for NO and NO_2 concentrations. For the secondary pollutant ozone the reduction is only relevant downwind of the agglomerations; no impact is found in remote areas. Within agglomerations an increase of ozone is found due to the reduced emission of NO, which currently reduces ozone concentrations. Concerning nitrogen deposition a reduction is found everywhere (Figure 1).

Traffic emissions are most pronounced close to roads and other traffic routes. In general, the concentrations close to emitters are higher for smaller grid sizes than for larger grid sizes. However, chemical reactions might alter this relation. For example, ozone is rapidly reduced at traffic influenced areas and NO_2 is formed (Figure 2). Due to complex flow features within the urban canopy layer concentrations can differ by a factor 3 or more at the same height (Figure 2a). The emission from street canyons to the air aloft shows much smaller concentrations than those found in the street canyon, but the impact of NO_2 formation is still visible (Figure 2b). Thus, concentrations above an urban canopy layer cannot be calculated as pure dilution of the emitted pollutants.

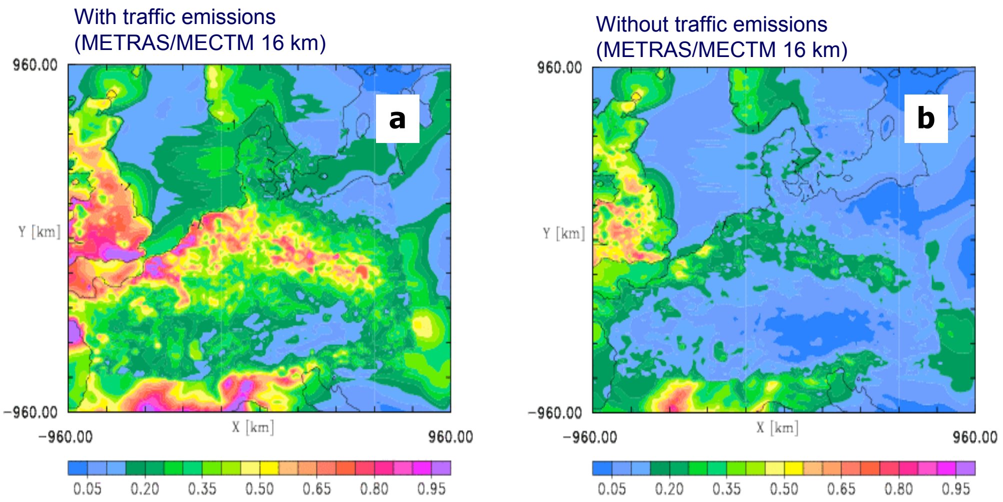


Figure1: HNO_3 deposition in mg N m^{-2} d^{-1} for 09.05.2000 with (a) and without (b) traffic emissions.

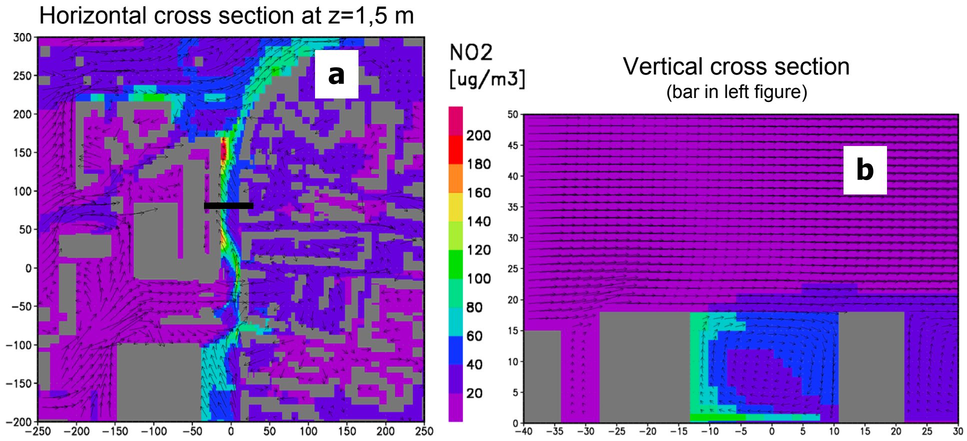


Figure 2: NO_2 concentration for 11.04.2003, 7-7:30 a.m. within the urban canopy layer at 1.5m above ground (a) and within a street canyon (b).

The obstacle resolving model components of M-SYS used for the current investigation can be applied to study chemical reactions close to sources not only above but also within the urban canopy layer, thereby including the complex impacts of buildings on the flow, temperature and radiation field.

Necessary research

Models to study the impact of hydrogen emissions on the urban and regional atmosphere are already available. However, some improvements are necessary: The models need to be further optimized with respect to the numerical solvers and to be adjusted to new computer technologies. Extensions are to be made with respect to the chemistry module (effect of H_2 reaction). Some adjustments to new application regions might also be necessary.

To perform thorough studies of the local impact of hydrogen emissions, emission data need to be available. These could be either emission data for single vehicles and traffic fleets with a high temporal resolution or an emission module that calculates the actual emission in dependence of meteorological data and time of day (on-line emission calculation). Emissions of the different organic compounds and of H_2 need to be included.

Using the emission data in the frame of adjusted models the following results can be achieved:

- Urban „emissions" (i.e. canopy emissions from street canyons) by using high resolution street canyon resolving models with inclusion of chemical reactions.
- Estimation of the impact of hydrogen energy on air quality in agglomerations and remote regions by using regional model systems like M-SYS.

References

Grawe D. (2005): Verknüpfung von Modellen und Daten für die Konzentrationsvorhersage. PhD thesis, *Faculty of Earth Sciences, University of Hamburg (in preparation).*

Lenz C.-J., Müller F. and Schlünzen K.H. (2000): The sensitivity of mesoscale chemistry transport model results to boundary values. *Env. Monitoring and Assessment,* 65, *287 -298.*

Schlünzen K.H. (1990): Numerical studies on the inland penetration of sea breeze fronts at a coastline with tidally flooded mudflats, Beitr. Phys. Atmosph., 63, 243-256.

Schlünzen K.H., Hinneburg D., Knoth O., Lambrecht M., Leitl B., Lopez S., Lüpkes C., Panskus H., Renner E., Schatzmann M., Schoenemeyer T., Trepte S. and Wolke R. (2003): Flow and transport in the obstacle layer - First results of the microscale model MITRAS. J. Atmos. Chem., 44, 113-130.

Trukenmüller A., Grawe D. and Schlünzen K. H. (2004): A model system for the assessment of ambient air quality conforming to EC directives. *Meteorol. Zeitschrift, Vol.13, No.5, 387-394.*

Hydrogen Related Activities at PSI (General Energy) and Air Quality Modeling to Assess the Impacts of a Hydrogen Economy on the Environment

Johannes Keller, Sebnem Andreani-Aksoyoglu, André Prevot
Laboratory of Atmospheric Chemistry (LAC)
Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

The main hydrogen related activities at the General Energy department (ENE) of the Paul Scherrer Institute (PSI, http://www.psi.ch/) take place in the following projects:

- solar production of hydrogen: a two-step water splitting cycle using the Zn / ZnO redox system is being developed at the 45 kW solar furnace (http://solar.web.psi.ch/index.html).
- hydrogen from fluidized bed biomass gasification and reforming (http://lem.web.psi.ch/)
- fuel cells: development of single single cells, cell stacks and their integration in vehicles. The most recent project is the hydrogen car Hy-LIGHT (http://ecl.web.psi.ch/).
- comprehensive assessment of energy systems: full chain analysis including life cycle assessment, environmental impact assessment, energy economics and risks (http://gabe.web.psi.ch/).

In the Laboratory of Atmospheric Chemistry (LAC, http://lac.web.psi.ch/) we are currently using the model package MM5 / CAMx, which allows the simulation of the air quality on a European and regional scale. Examples of studies are:

- the NOx / VOC sensitivity of ozone: In urban areas and their plumes, ozone is controlled by the availability of hydrocarbons. In rural regions with less NOx, however, ozone is sensitive to nitrogen oxides (Figure 1)
- particulate matter: CAMx is capable of simulating size distribution and speciation of particulate matter. First simulations were done for northern Italy and southern Switzerland.
- effect of emission scenarios on air quality: the maximum speed limit on Swiss freeways (currently 120 km/h) was reduced to 80 km/h. Due to this measure the Swiss NOx emissions decreased by about 4%. The reduction of VOC emissions was negligible. The peak ozone mixing ratio decreased by less than 1% (Fig.2). During morning hours there is even an increase along the freeways.

The use of MM5/CAMx model system can contribute to answer the basic question: how does a H_2 economy affect the regional and European ozone and aerosols concentrations? In particular:

- What is the primary influence of increased H_2 emissions (e.g. leakage) on the production of air pollutants (decrease / increase of the OH concentration)?
- What is the secondary influence of a H_2 economy on the production of air pollutants (change in emissions of primary pollutants due to changes in traffic, industry, etc.)?

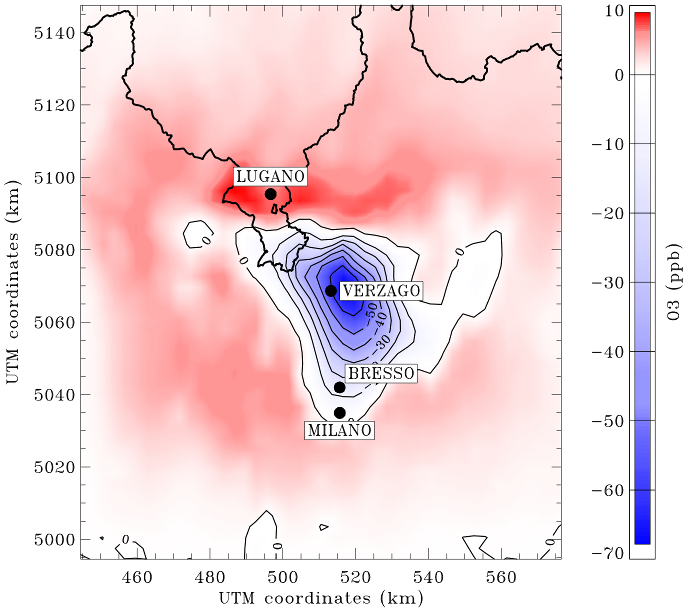


Figure 1: Sensitivity of ozone to NOx and VOC emissions. blue: VOC-sensitive (high NOx/VOC ratio), red: NOx-sensitive (low NOx/VOC ratio).

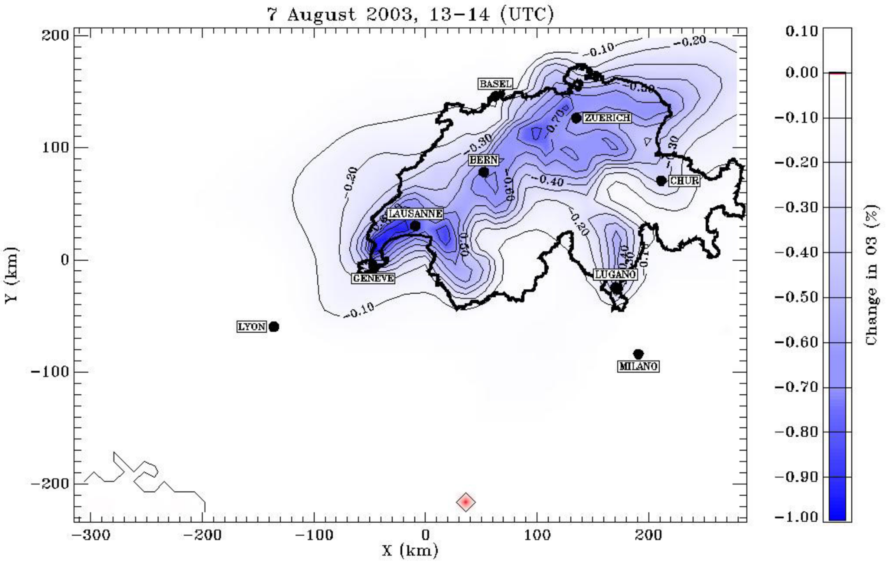


Figure 2: Relative change in ozone mixing ratio if the maximum speed limit on Swiss freeways is reduced to 80 km/h. August 7, 2003, 13-14 h UTC.

Hydrogen-Infrastructures: Feedbacks to Climate and Atmosphere

Martin Kaufmann[1], Martin Riese[1], Rolf Mueller[1], Manfred Fischedick[2], Thomas Feck[3], Thomas Grube[4], Jaco Reijerkerk[5], Martin Schultz[6]
[1] Juelich Research Center, Institute for Chemistry and Dynamics of the Geosphere: Stratosphere (ICG I), D-52425 Jülich
[2] Wuppertal Institute for Climate, Environment and Energy, Döppersberg 19, D-42103 Wuppertal
[3] Juelich Research Center, Fuel Cell Project
[4] Juelich Research Center, Institute for Materials and Progressive Energy Systems: Energy Process Engineering (IWV-3)
[5]Linde AG, Linde Gas Division
[6]Max Planck Institute for Meteorology, Bundesstr. 53, D-20146 Hamburg

Recent studies (e.g. Tromp et al., 2003) demonstrated that a hydrogen based energy economy may affect Earth's atmosphere, especially the stratosphere, seriously. Leakages in the hydrogen transport and fueling system are supposed to increase the mixing ratio of hydrogen in the troposphere from about 0.5 ppm in present days to about 2 ppm or even more after the substitution of fossil fuels by hydrogen. For the troposphere the method of energy generation is most important (Schultz et al., 2003). The conversion of fossil fuels to renewable energy carriers will result in a substantial improvement of air quality. The release of H_2 will decrease the number of OH molecules and therefore the self purification of the troposphere. However, this effect is comparatively small.

An increase in tropospheric H_2 will affect the stratospheric H_2 load significantly since H_2 can pass the tropopause without being frozen out. Here, H_2 will be oxidized to water vapour, which is essential for the energy balance and the ozone budget of the stratosphere. An increase of H_2O will cause a temperature decrease, and in consequence increase the number of polar stratospheric clouds (PSCs). More PSCs cause a decrease of stratospheric ozone, especially during polar spring conditions.

To investigate the consequences of a hydrogen-based energy economy for the atmosphere it is essential to improve our knowledge of possible infrastructures and emission scenarios. For this reason, we introduced the draft of a project dealing with the two most important questions relevant in this context:

1. Definition of reasonable scenarios for the spatial and temporal evolution of hydrogen usage as an energy carrier and related H_2 emissions: Current H_2 emissions from traffic, industry and further sources will be analyzed, evaluated, and global infrastructure scenarios will be developed. The different infrastructures are investigated with respect to energy sources and H_2 emissions. This working package will be settled by the Wuppertal Institute for Climate, Environment, and Energy, Linde AG - Linde Gas Devision, and the Juelich Research Center, Institute for Materials and Progressive Energy Systems: Energy Process Engineering (IWV-3) in cooperation with the Fuel Cell Project.
2. Detailed modeling of the different emission scenarios by means of climate and chemistry transport models (CTMs) of the troposphere and stratosphere: In the previous working package a unique and very extensive database of possible emissions will be generated.

Since detailed modeling with up-to-date climate models is computationally expensive, we propose the following scheme for evaluating the various scenarios: Flexible and very fast chemistry transport models will utilize the dynamical fields of climate models, which will be generated for a few baseline conditions. Detailed chemistry studies will be performed by means of the CTMs. The MAECHAM model of the Max Planck Institute for Meteorology, Hamburg will be used for the generation of the dynamical fields and the MOZART and ROSE models for tropospheric and stratospheric chemistry, respectively. These studies will be performed by the Juelich Research Center, Institute for Chemistry and Dynamics of the Geosphere: Stratosphere (ICG I), and the Max Planck Institute for Meteorology, Hamburg.

References

Schultz M; Diehl T, Brasseur GP, Zittel W: "Air Pollution and Climate-Forcing Impacts of a Global Hydrogen Economy", Science, Vol. 302, 2003.

Tromp TK, Shia RL, Allen M, Eiler JM, Yung YL: "Potential Environmental Impact of a Hydrogen Economy on the Stratosphere", Science, Vol. 300, 2003.

Hydrogen in the middle and upper atmosphere

Hauke Schmidt, Max Planck Institute for Meteorology, Bundesstr. 53, 20146 Hamburg, Germany

Introduction

If a hydrogen economy is to be realized this may have an influence on the amount of atmospheric hydrogen not only close to possible emission regions in the troposphere and lower stratosphere (airplanes) but, due to transport phenomena, with some years of delay also in the middle (stratosphere and mesosphere, ~15 to 90 km) and upper atmosphere. Indirect effects of a hydrogen economy might include a change in the emission of pollutants (see Schultz et al., 2003) and greenhouse gases. The latter should have an influence on the entire atmosphere. A few studies have addressed the stratospheric impact of an increased emission of molecular hydrogen. Tromp et al. (2003) estimate that a quadrupling of tropospheric molecular hydrogen concentrations (which is based on a maybe unrealistically high assumption for hydrogen leakage rates) would lead in general to a small decrease of stratospheric ozone and temperature but via changes in polar stratospheric clouds to a considerable deepening of the ozone hole. The influence of a hydrogen economy on the atmospheric regions above the stratosphere has not been studied, so far.

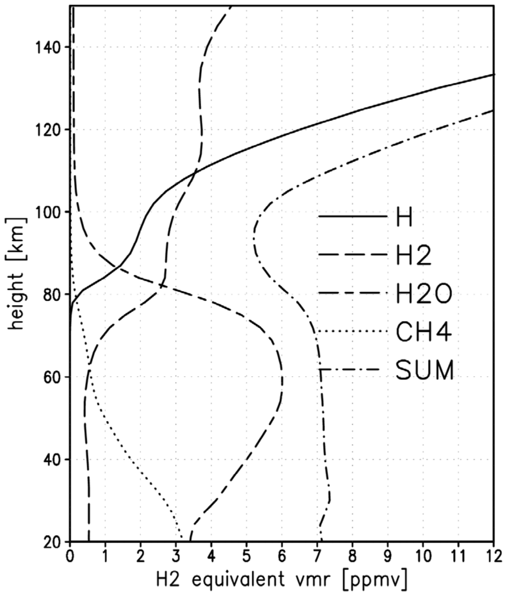


Figure 1: Volume mixing ratios of the main hydrogen containing chemical compounds in ppmv (H_2 equivalent) from 20 to 150 km. Values are annual global means as simulated by HAMMONIA (see text).

Hydrogen containing compounds in the middle and upper atmosphere

Figure 1 shows the current volume mixing ratios of the major hydrogen containing compounds at heights from 20 to 150 km. Methane and water vapour are dominating up to the mid-mesosphere. While methane is decreasing monotonically with altitude, water vapour peaks at around 60 km with a mixing ratio of about 6 ppmv. When molecular diffusion and gravitational separation of compounds become important above ~ 90 km, molecular and in particular atomic hydrogen are by far the most important carriers of hydrogen. The total amount of hydrogen is of about 7 ppmv (H_2 equivalent) throughout the stratosphere, reaches a minimum (named total hydrogen mixing ratio anomaly, THYMRA, by Sonnemann and Körner, 2003) around 90 km, and increases with altitude in the thermosphere. An increase of surface hydrogen would lead for example to an increase of atmospheric water vapour. As shown by Tromp et al. (2003) for the stratosphere, this increase would become stronger with height. Changing water vapour would have an influence on the OH concentration and subsequently on the global atmospheric chemistry, e.g. on mesospheric ozone. The water vapour content influences also the polar mesospheric clouds which occur around the summer mesopause when temperatures reach values below 150 K. An ozone change would directly influence the energy balance via a change in solar heating. However, in the mesopause region, the major heating term in the energy balance is due to exothermic chemical reactions. One of the dominant reactions for this chemical heating is the reaction of ozone with atomic hydrogen. Thus, changes in hydrogen may have a significant influence on mesospheric chemistry, on the energy balance and on dynamics, which are all closely linked. The study of hydrogen change effects in these altitude regions therefore requires a model which treats all these processes interactively and covers a sufficiently large part of the atmosphere.

Entire atmosphere modeling at MPI-Met

During the last years, at the Max Planck Institute for Meteorology, a general circulation and chemistry model has been developed that resolves the atmosphere from the Earth's surface up to about 250 km. This HAMburg Model Of the Neutral and Ionized Atmosphere (HAMMONIA) combines the 3d dynamics from the ECHAM5 model (Röckner et al., 2003, 2004) with the MOZART3 chemistry scheme and some extensions to account for important processes in the upper atmosphere: solar heating in the UV and EUV wavelength regime (down to 5 nm), a non-local thermodynamic equilibrium long-wave radiative scheme, heating and mixing due to parameterized gravity waves, vertical molecular diffusion and conduction, and a simple parameterization of electromagnetic forces in the thermosphere (ion drag and Lorentz forces). A more detailed description of the model is given by Schmidt et al. (2004). So far, it has been applied to study the effects of the 11-year solar cycle and of CO_2 doubling with a focus on the mesosphere and lower thermosphere region. It would be well suited to study the possible direct and indirect effects of a hydrogen economy on chemistry and dynamics of the atmosphere from the surface to the thermosphere.

References

Röckner, E. et al., The atmospheric general circulation model ECHAM 5. PART I: Model description, Rep. 349, MPI for Meteorology, Hamburg, Germany, 127 pp, 2003.

Röckner E., et al., The atmospheric general circulation model ECHAM 5. PART II: Sensitivity of Simulated Climate to Horizontal and Vertical Resolution, Rep. 354, MPI for Meteorology, Hamburg, Germany, 56 pp, 2004.

Schmidt, H., G. P. Brasseur, M. Charron, E. Manzini, M. A. Giorgetta, V. Fomichev, D. Kinnison, D. Marsh, The HAMMONIA Chemistry Climate Model: Sensitivity of the Mesopause Region to the 11-year Solar Cycle and CO2 Doubling, J. of Climate, submitted, 2004.

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

Sonnemann, G. R., U. Körner, Total hydrogen mixing ratio anomaly around the mesopause region, J. Geophys. Res., 108(D22), 4692, doi :10.1029/2002JD003015, 2003.

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

Hydrogen, methane and ozone in the atmosphere – New challenges for atmospheric pollution studies in a changing society

Tuomas Laurila, Tuula Aalto, Juha Hatakka, Marko Lallo, Virpi Tarvainen and Mika Aurela, Finnish Meteorological Institute, Climate and Global Change Research, Sahaajankatu 20E, 00880 Helsinki, Finland

The concentrations, sources and sinks of atmospheric molecular hydrogen have remained one of the least studied issues in the atmospheric chemistry in spite of the fact that hydrogen concentration in the atmosphere is relatively high, about 0.5 ppm. The most important sources are the oxidation products of atmospheric methane and volatile organic compounds (VOC), and the combustion of fossil fuels and biomass. The main sink of hydrogen is deposition to soils where hydrogen is consumed by microbes and enzymes. Hydrogen is also oxidised by the hydroxyl radical in the atmosphere.

Hydrogen economy may change the atmospheric hydrogen concentrations because, on the other hand, the direct hydrogen emissions will increase and, on the other hand, the emissions from the combustion of fossil fuels, at least from the traffic fleet, will probably decrease. Moreover, the emissions of VOCs may decline when gasoline powered automobiles are replaced by hydrogen powered vehicles. Generally, the changing atmospheric composition, including the methane concentrations, affects the concentrations of the hydroxyl radical, which is responsible for the main atmospheric sink reaction. We may foresee that a widespread transition to hydrogen economy will alter the photochemical state of the atmosphere, resulting in changes in many traditional pollutants, including ozone. This stresses the need to initiate both the monitoring of atmospheric hydrogen concentrations and studies of the sources and sinks of hydrogen to better understand and model the hydrogen budget before major changes occur.

For this purpose, the Finnish Meteorological Institute begins in 2005 a project to measure the atmospheric concentrations as well as the anthropogenic sources and natural sinks of hydrogen.

The atmospheric concentration measurements will be conducted at the Pallas-Sodankylä monitoring station belonging to the Global Atmosphere Watch (GAW) network of the World Meteorological Organization (WMO). The station is in the northern boreal zone close to the tree line about 150 km north of the Arctic Circle. The site for atmospheric concentration measurements is on a fjell top, 300 m above the surrounding terrain. At this site a wide spectrum of greenhouse gases, including carbon dioxide, methane and nitrous oxide, and air pollutants (ozone, nitrogen oxides, sulphur dioxide, carbon monoxide and the concentrations and the size spectrum of aerosols) are measured continuously. Continuous measurements of methane were initiated as part of the MethMoniteur-project. The measurement programme will be expanded to molecular hydrogen which will be measured by a gas chromatograph using standards from the Climate Monitoring and Diagnostics Laboratory (CMDL) of NOAA, Boulder.

The variation of the concentrations will be analysed together with the other greenhouse gases, air pollutants, and radon to study the sources and the atmospheric dispersion of hydrogen. Air mass trajectories, routinely calculated for the site, and meteorological parameters which describe the local mixing conditions will be used as tools.

Micrometeorological fluxes of carbon dioxide between the atmosphere and a spruce forest are measured within 5 km from the fjell site. In a close by wetland, an aapa mire, also methane emissions will be measured using the eddy-covariance technique. At these sites, the uptake and possible emission of hydrogen will be measured using the chamber technique. At the forest the mineral soil is covered by a thin humus layer, offering a good setting for the deposition studies. The wetland vegetation is mostly sedges, with air tubes in their stems providing oxygen to the roots. This route also transfers methane directly to the atmosphere. If there is hydrogen production in the anoxic soil layers, it may be emitted directly through these plants.

Additionally we will conduct hydrogen concentration measurement campaigns in southern Finland in the Helsinki area. These data will be used to analyse the present levels of hydrogen in the urban environment. Using statistical analysis and including the concentrations of the other air pollutants we will search for the most important source sectors. This study will also produce an urban air pollution source profile, including all categories of VOCs, nitrogen oxides and hydrogen, to be used in the simulations of photochemical processes responsible for e.g. ozone production. Simulated concentrations in the urban plume of Helsinki will be compared to the measured concentrations in Pallas some 800 km to the north.

Changes in the air pollution composition and the photochemical processes in the long-run will be estimated using the SRES emissions scenarios for the 21st century produced by the Intergovernmental Panel on Climate Change (IPCC). Some of these scenarios assume a widespread change to the hydrogen economy. This part of the study reveals what kind of changes in the oxidising capacity and concentrations of air pollutants may be expected in the boreal region.

Environmental REsearch Laboratory (EREL) / National Centre for Scientific Research "Demokritos" (NCSRD)

Spiros Andreanopolous, NCSRD, Demokritos, 15310 Aghia Paraskevi Attikis, Greece

This presentation aims at presenting the activities and potentials of EREL/NCSRD in view of its possible participation in the consortium for preparing a research proposal on "Hydrogen Energy: Chances and Risks for the Environment".

About NCSRD

NCSRD was founded in the early 60s. Its present staff amounts to1000 employees of whom 450 on research contracts. The covered scientific research areas are: Energy, New Materials, Solid State Physics and Microelectronics, Informatics and Telecommunications, Health, Environment and Cultural Heritage.

NCSRD consists of 8 Institutes, each functioning as an independent unit: Biology, Informatics and Telecommunications, Materials Science, Microelectronics, Nuclear Physics, Physical Chemistry, Radioisotopes and Radio-diagnostic Products, Nuclear Technology Radiation Protection Institute. The Environmental Research Laboratory (EREL) is part of the Institute for Nuclear Technology Radiation Protection.

EREL has a long-standing experience in coordinating more than 10 EU projects and participating in more than 30 EU projects under the 4th, 5th and 6th Framework Programmes. The Laboratory staff consists of 25 persons (researchers, PhD candidates, technicians and administrative staff). EREL has strong links with universities, research institutes and private/public enterprises throughout Europe. The main research activities of the Laboratory, related to the subject of the considered proposal are:

- Atmospheric Transport of Pollutants and Chemical Modelling
- Sorption And Transport In Porous Materials
- Hydrogen Technology (storage, safety and certification)

Topics and Applications related to Emissions / Transport of atmospheric pollutants

EREL has developed or uses a set of numerical codes for the prediction of atmospheric transport and chemistry of pollutants in domains of complex topography. The Laboratory has established and applies a quality system for Software design and development for atmospheric applications according to ISO-9001, certified by TUV.

- Modelling of long-range atmospheric dispersion of pollutants
- Modelling of photochemical pollutants – transport and chemical evolution
- Modelling of atmospheric dispersion of denser-than-air gases
- Modelling of mesoscale atmospheric flows and pollutants dispersion over complex terrain
- Aerosol/photochemical modelling: development, validation and application
- Compilation of *emission inventories* for several air pollutants (NO_X, SO_2, CO, CO_2, PMs, NMVOC, CH_4, H_2O etc) following bottom-up and top-down methodologies

Research areas and Applications related to Hydrogen

The following topics related to hydrogen technology are currently pursued by EREL:

- Modelling and calculations related to hydrogen safety and certification
- Hydrogen storage in solid materials
- Mathematical Modelling and Optimization of Hydrogen Storage in Metal Hydride Beds
- Fuel cells applications
- Hydrogen production

Chemical measurements and analysis laboratory

EREL operates a fully-equipped analytical chemistry laboratory for organic pollutant measurements (GC/FID/FPD, GC/MS with Thermal Desorption Unit, HPLC), as well as a fully equipped unit for sampling and analysis of conventional and unconventional atmospheric pollutants (with emphasis on VOCs, PAHs, sulfur compounds, PMs, etc.). Measurements of meteorological parameters are also performed.

Materials development laboratory

EREL has full access to the following equipment aiming for H_2 storage materials preparation and characterisation:

- Materials preparation: arc-melting, melt-spinning, ball-milling, furnaces
- Materials characterization: X-Ray diffractometer, vibrating sample magnetometers and squid, high-resolution transmission electron microscope and conventional scanning electron microscope

Conclusions

EREL intends to exploit and extend the abovementioned capabilities to contribute to the objectives of the considered proposal. Based on its current activities and expertise EREL can contribute in the areas of compilation of emissions inventories and air-quality studies (measurements and computational simulations) from meso- to regional scales.

Publications related to hydrogen safety, storage and fuel cells

J.C. Statharas, A.G. Venetsanos, J.G. Bartzis, J. Würtz, U. Schmidtchen, (2000), "Analysis of data from spilling experiments performed with liquid hydrogen", Journal of Hazardous Materials 77 (1-3), pp 57-75.

A.G. Venetsanos, T. Huld, P. Adams, J.G. Bartzis, "Source, dispersion and combustion modeling of an accidental release of hydrogen in an urban environment", Journal of Hazardous Materials, A105, 1-25, 2003.

Makridis, S.S; Konstantakou, M.; Steriotis, Th.A.; Efthimiadis, K.G.; Pavlidou, E.; Kikkinides, E.S. and Stubos, A.K.: Structural and Magnetic properties of Rare Earth – Transition Metal Compounds for Hydrogen Storage Materials. Accepted for publication in the Journal of Alloys and Compounds.

Kikkinides, E.S.; Georgiadis, M.C. and Stubos, A.K.: On the Optimization of Hydrogen Storage in Metal Hydride Beds. Submitted to the Int. Journal of Hydrogen Energy.

S. Douvartzides, F.A. Coutelieris, A.K. Demin and P. Tsiakaras, J. Hydrogen Energy, 29 (2004) 375

F.A. Coutelieris, S. Douvartzides and P. Tsiakaras, J. Power Sources, 123 (2003) 200

Atmospheric Impact of a Future Hydrogen Economy and Proposal for Hydrogen Emission Scenario Calculations

Werner Zittel, Ludwig-Bölkow-Systemtechnik GmbH

Today's fossil fuel use has to stop some day because it is not sustainable. The question is not if this will happen but when this will be and which forces will drive the transition to alternatives: resource or sink restrictions or commerical competitiveness of the alternative technologies.

In a post fossil fuel area hydrogen has the potential to become the fuel of choice for mobile applications and storage. In the following the most important atmsopheric emissions of an economy which bases its energy supply partially on hydrogen are sketched briefly. Finally, a proposal is sketched how to takle the problem of identifying environmentally sound energy scenarios.

Water vapour emissions of a hydrogen economy [1]

Carbon dioxide is the final combustion product of fossil fuels and can be calculated from the chemical composition of the fuels. Similarily, the burning of hydrogen unavoidably produces water vapour. Since the emitted water vapour amount depends solely on the fuels throughput, the relevant emissions are easily calculated from the reaction formula $C_xH_y + (x+y/4)\ O_2 \rightarrow x\ CO_2 + 0.5y\ H_2O$, where x=1 and y=0 stands for coal, y=2 for oil, y=4 for methane/natural gas and x=0, y=1 for pure hydrogen. The following table gives specific emissions of carbon dioxide and water vapour.

Table 1: Specific emissions of water vapour and carbon dioxide of fossil fuels, electricity production and hydrogen

fuel type	1 kWh corresponds to	CO_2-emissions g/kWh	H_2O-emissions g/kWh
coal	~0.1 – 0.4kg1)	330-4001)	~502)
oil	~0.1 litre	~270	~110
gas	~0.1 m^3	~200	~160
hydrogen	~0.33 m^3	0 depending on primary energy	~270
electricity	depending on storage	0 depending on primary energy	0-5,0003) depending on technology

The bandwidth is given by the various qualities of hard coal and lignite

Depending on the coal quality, 50 g correspond to a water content of 8wt%; low quality lignite can emitt up to 400g per kWh

The water emissions are due to the cooling requirement. The evaporation energy of water is 1.6 kg/kWh_{th}. About 5 kg water vapour are emitted if the electricity is produced in a heat converting power plant with 30% efficiency and the heat is removed by water evaporation which is the case where only limited amounts of cooling water are available. Heat removal by fresh water increases the water demand by a factor of 50, if a temperature increase of the river of 10 degrees is allowed [2, 3].

The burning of fossil fuels already today emits more than 20,000 Tg of water vapour. Based on a commerical energy consumption of 12 TW*yr (~10^{14} kWh) - of which the share of oil is 37%, of coal is 26% and of natural gas is 24% - , about 10,000 Tg are due to the combustion of fossil fuels [4]. At least another 10,000 Tg are produced for cooling requirements of the electricity production of 16,000 TWh_{el}, taking care of that about 85% are produced from heat converting power plants with huge water requirements for cooling.

If in a future hydrogen economy all oil applications are substituted by hydrogen another 10,000 Tg are emitted which substitute the 4,000 Tg of oil leaving an addition of 6,000 Tg of water vapour. At the other hand, cooling water requirements will be considerably reduced the more electricity is produced either from renewables like water, wind and photovoltaics or from fuel conversion via low temperature fuel cells.

The overall water vapour emissions of a future hydrogen economy will be in the same range as from today's conventional energy supply system. Compared to natural cylces which emitt each year about 525,000,000 Tg anthropogenic additions are in the range of 0.005% and can be neglected [5].

Regional emissions can be estimated at the example of the rush hour traffic in Munich. Each day, about 500,000 passenger cars travel about 20 km within the 20x20 km^2 area of Munich. The average oil consumption is about 1 kWh/km (corresponding to 10 l gasoline per 100 km). This adds up to 0.4 Tg water vapour per year which are emitted, corresponding to a specific emission of about 1 kg/m^2. If these cars are completely converted to hydrogen fueled internal combustion engines these emissions would increase to 1 Tg or 2.5 kg/m^2 annually. This has to be compared with the annual precipitation which amounts 950 mm or 950 kg/m^2, leaving today's and future anthropogenic emissions far below 1 percent. Again, this might be seen as negigible impact.

Furtheron it is expected that hydrogen fueled vehicles will predominantly be based on fuel cell drive systems which are twice as efficient as internal combustion engines in inner city driving situations. Therefore the water vapour emission will be in the same range of todays transport. However, the exhaust temperature of fuel cell vehicles will be much lower than from internal combustion engines possibly giving rise to enhanced condensation. This might lead to increased fog situations at certain days in certain locale areas. This topic needs futher investigations, eventually leading to concepts in which the water vapour must be liquified before leaving the exhaust pipe.

Though most of the water emissions from a hydrogen economy will be harmless, an eventual serious point of concern could be aircraft emissions in the upper troposphere/lower stratosphere. The present emissions of about 100-150 Tg/yr have an influence on contrail formation (which enhance the radiative forcing), life time of hydroxyl radicals and polar stratospheric clouds (which act as catalysts for ozone destructive reactions). These emissions might be increased by a factor of 2.5 if jet fuels are substituted by liquid hydrogen. State-of-the art research shows that the influence of contrail formation on the radiative forcing will presumably not be enhanced by hydrogen fuel. Today the sulfur content of the fuel and unburned hydrocarbons act as seed for contrail formation. In the absence of these species pure water vapour emissions show less tendency to contrail formation and these contrails show less radiative forcing in the infrared regime though more vapour is injected into the critical atmospheric layer.[6]

Hydrogen emissions of a hydrogen economy [7,8]

Unless water vapour emissions which cannot be avoided, pure hydrogen emissions are due to the technological and structural development of the infrastructure and also depend on the willingness (=cost) to take avoidance measures. Therefore, depending on the scenario assumptions almost any emission budget can be constructed, either leading to an environmentally sound hydrogen economy with almost negligible hydrogen emissions (in addition with almost negligible carbon dioxide emissions if based on a pure renewable energy strategy) or to a disastrous scenario increasing hydrogen and carbon dioxide emissions to harmful levels (if based on electrolysis from coal power plants and high emission rates from the infrastructure). The following paragraphs are addressed to illuminate these aspects.

Hydrogen emission can result from production, long distance transport, distribution, storage and application. When talking about hydrogen emissions, two aspects are usually emphasised: Emissions from parking cars and emissions through fittings or leaks in pipelines.

A positive aspect is that hydrogen emissions are highly localised. This makes it easy to take avoidance measures, either in preventing the emission, or in converting the emitted hydrogen into harmless water vapour catalytically or by means of a small fuel cell with the benefit of producing electricity. Presumable, not any mass produced car will be accepted by local authorities if it does not fulfill these requirements, otherwise it would be of permanent public concern with its hazard potential not being allowed to enter tunnels or parking garages.

Boil-off rates in the order of 1% daily from parking liquid hydrogen cars are often misenterpreted as emission to the atmosphere. Correct is that the evaporating liquid hydrogen accumulates in the gas cap of the storage device unless a critical boil-off pressure is reached. Only when this critical pressure (~ 8 bar) is exceeded, boil-off starts. However, in most cases, the pressure will be released by the fuel consumption during driving before boil-off starts. And even, if the critical pressure is exceeded, the released hydrogen will be converted to water vapour with one of the above mentioned measures.

Potential pipeline emissions are usually estimated from comparisons with existing natural gas infrastructure. For instance, for the 5,000 km long distance pipeline between Siberia and Western Europe, natural gas emission below 1 percent are reported [9-12]. However, most of these emissions are due to gas drying measures at compressor stations, and blow outs during repair work. And with respect to the length of the pipeline system it becomes obvious that total emissions will be affected by scenario specific aspects: For instance, the hydrogen emissions from the regional hydrogen grid in Western Germany with approximately 50 km length which connects suppliers and producers are reported far below 0.1% of throughput [7].

Refuelling of liquid hydrogen containers might result in emissions of 5 – 10% or even above if done unprofessional with air contact, or might result with zero emission, as has been planned for the long distance transport between production sites in Western Canada and the final end use position in Germany within the „Euro-Quebec- Hydro-Hydrogen Pilot Project" already in 1991 [13].

Hydrogen emissions will strongly depend on scenario specific aspects: First, the fraction of end use energy which is delivered in form of hydrogen is of interest. Second, the fraction of liquid or gaseous hydrogen is of influence. Third, the strategy, if hydrogen is transported over long distances in liquid or gaseous form or its decentralized use and long distance transport predominantly by electricity considerably influence these emissions.

Therefore its seems adequate at the present state of knowledge, not to calculate the atmospheric impact of a specific energy scenario straight forward but to split the different tasks in order to gain transparency and sketch regimes of „acceptable" emissions.

Proposal for Scenario calculations

Calculating the atmospheric impact of a future hydrogen economy includes three subtasks:

- To calculate one or several scenarios with detailed infrastructure and end use applications
- To estimate the hydrogen emissions of these scenarios
- To estimate the atmospheric impact of these emissions

Each of these subtasks has its specific uncertainties: Scenario predictions depend on a forecast of technological realities as well as human behaviour (e.g. time horizon for special milestones, centralized vs. decentralized use, share of hydrogen in end use applications etc). The specific and total emissions will depend on these scenarios and further uncertanties regarding technological maturity and implantation measures.

Taking these emissions as input for atmospheric calculations allows to assess their impact on atmospheric chemistry and climate. However, these predictions are based on additional uncertainties which come from incomplete understanding of atmospheric trace gas budgets and their evolution.

At the present stage of understanding it seems appropriate to separate the different steps in order to gain some insight instead of increasing confusion: The emission budget might be used as well defined interface which separates the uncertainties of the these tasks.

Climate modelling might be based on a parametric change of input variables of hydrogen emissions and related emissions (e.g. reduced carbon dioxide, NO_x or other relevant trace gases or particulates). The outcome of such simulations can be used to sketch the field of acceptable emission scenarios and to formulate basic restrictions on a future hydrogen economy which have to be fulfilled. Based on these „acceptable‟ budgets, energy scenarios can be identified which are in line with the restrictions given from climate modelling.

The separation of these two completely different kinds of simulations seems mandatory since it allows to discuss uncertainties in the appropriate frame: Results from atmospheric chemical simulations can be checked against the sensitivity of uncertain parameters which still existing. Results from scenario calculations can be checked against their sensitivity on infrastructure developments and specific emission factors.
Once a better understanding of these fundamental parameters and processes has gained, the process can be reversed again and a „reasonable‟ scenario under discussion can be checked with respect to its atmospheric chemical impact.

References

[1] W. Zittel, M. Altmann, Der Einfluß von Wasserdampf auf das Klima, Energie 1994, Seite 25-29
[2] J.D. Peschke, elektrische Energieerzeugung, Teubner Verlag Stuttgart, 1993, S 62 f
[3] K.-H. Ahlheim, Die Energie – Erzeugung, Nutzung, Versorgung, Bibliographisches Institut Mannheim, 1983, S. 284 f
[4] BP Statistical Review of World Energy 2004
[5] Dritter Bericht der Enquete-Kommission des 11ten deutschen Bundestages „Vorsorge zum Schutz der Erdatmosphäre, S. 146/147 und S. 174/175 (english edition)
[6] Marquart, S., Sausen, R., Ponater, M., and Grewe, V., Estimate of the climate impact of cryoplanes, Aerosp. Sci. Techn., 2001, 5, 73-84.

[7] W. Zittel, M. Altmann, Molecular Hydrogen and Water Vapour Emissions in a Global Hydrogen Energy Economy, Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, 1996, pp. 71-81

[8] W. Zittel, Molekularer Wasserstoff in der Atmosphäre, LBST, Ottobrunn,1990

[9] W. Zittel, Zur Problematik der Methanemissionen, in „Erarbeitung von Vorschlägen zur Verminderung umweltschädlicher Auswirkungen im Erdöl- und Erdgassektor in Rußland, Untersuchung im Auftrag des Bundesministeriums für Umwelt, Naturschutz und Reaktorsicherheit, ed. by DIW, 1995, pp. 168-208

[10] W. Zittel, Untersuchung zum Kenntnisstand über Methanemissionen beim Export von Erdgas aus Rußland nach Deutschland, Studie im Auftrag der Ruhrgas AG, Ludwig-Bölkow-Systemtechnik GmbH, Ottobrunn, 1997

[11] J. V. Dedikov, G.S. Akopova, N.G. Gladkaja, A.S. Piotrovskij, V.A. Markellov, S. S. Salichov, H. Kaesler, A. Ramm, A. Müller von Blumencron, J. Lelieveld, Estimating methane releases from natural gas production and transmission in Russia, Atmospheric Environment 33(1999), pp. 3291-3299

[12] M. Fischedick et al. Methanemissionsmessungen an russischen Exportpipelines, Dezember 2004.

[13] Euro-Quebec Hydro-Hydrogen Pilot-Project, Phase II: Feasibility Study, Technical Report, Hydro-Quebec and Ludwig-Bölkow-Systemtechnik GmbH, Ottobrunn, 1991

Atmospheric Impact of a Hydrogen Economy - Research Needs of the Automotive Industry

Dr. Stefan Berger, Adam Opel AG, Fuel Cell Activities, IPC MK-01, D-65423 Rüsselsheim

The development of hydrogen driven Fuel Cell Vehicles has always been based on the idea of hydrogen being produced from renewable energies. Progressively replacing fossil fuels, hydrogen is supposed to achieve a substantial environmental benefit.

In June 2003, Tracey K. Tromp et al. called this benefit into question and raised an impulsive debate with their publication on the potential stratospheric impact of hydrogen. Renowned climate research teams have participated in this discussion, which has thoroughly been observed by the automotive industry. Unanimously, the involved scientists agreed that Tromp et al. had overestimated hydrogen losses of a future hydrogen economy, and built up unrealistic scenarios.

The automotive industry has a vested interest to foster an accurate estimation of anticipated rates of hydrogen release and expected effects on the global environment. Therefore, it seems inevitable to establish a close contact between research teams and involved industry partners in order to develop sound standing scenarios.

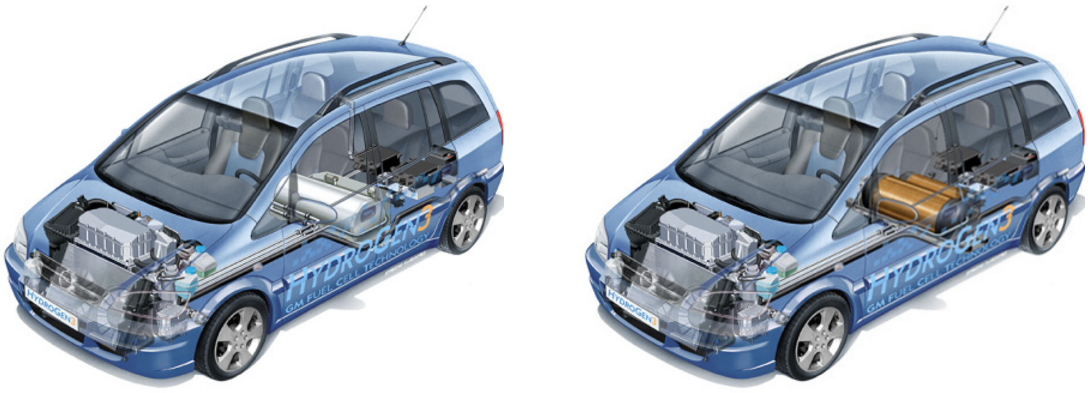


Figure 1: Opel's prototype hydrogen cars HydroGen3. Left: vehicle with liquid hydrogen tank, right: vehicle with compressed hydrogen gas tank (700 bar)

Simulating the Adoption of Fuel Cell Vehicles

Malte Schwoon, International Max Planck Research School on Earth System Modelling, Research Unit Sustainability and Global Change, Hamburg University and Centre for Marine and Atmospheric Science, Bundesstr. 55, 20146 Hamburg, Germany

The path into a *Hydrogen Society*, where hydrogen is used as the main energy carrier and storage medium, will be dominated by the adoption of hydrogen technologies in the automobile sector. To date scenario studies of infrastructure build up and vehicle sales on a regional or global level are mainly driven by cost estimates and technological feasibility assumptions. Furthermore, there seems to be a general notion of a "hen and egg problem", which implies that car producers are not willing to offer fuel cell vehicles (FCVs) as long as there are no gas stations providing hydrogen. But on the other hand a hydrogen infrastructure will not be set up unless there is a noticeable demand generated by a significant number of FCVs on the road. This hen and egg problem is usually raised to argue in favor of a major (public) infrastructure program. These studies neglect that the automobile market is highly competitive and car producers, consumers, and gas station operators form an interdependent dynamic system, where taxes play a major role in technology choice.

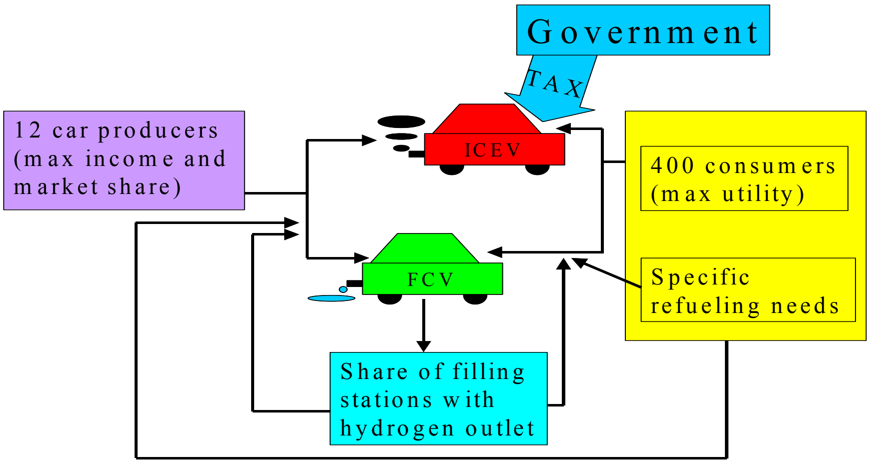


Figure 1: Model structure

I developed a model that captures the main interdependencies to simulate possible diffusion paths of hydrogen vehicles. *Figure 1* shows the structure of the model. There are 12 car producers who decide in every period (a quarter of a year) whether to offer conventional internal combustion engine vehicles (ICEVs) or whether to switch to the production of FCVs. They maximize an objective function, which includes expected income and market share given that the government taxes ICEVs. There are 400 (representative) consumers in the model with different preferences for certain car characteristics. Furthermore, the consumers are heterogeneous in their refueling needs. Thus, beside the after tax price, refueling possibilities (approximated by the share of filling stations with a hydrogen outlet) have an important impact on the individual's buying decision. The number of FCVs on the road determines the share of filling stations offering hydrogen. Finally, this infrastructure as well as the preferences of the consumers feed back on the decisions of the producers.

The model is calibrated so as to roughly approximate the German compact car market. *Figure 2* shows the simulated penetration of the market by FCVs under different tax and infrastructure conditions. It is assumed that by the year 2010 the government introduces either a "fast tax" on ICEVs that shocks the system (a value added tax of 40%) or a "slow tax" that gradually increases by 1% each quarter over a period of 10 years ending up at 40%. Furthermore, the government increases the number of filling stations with hydrogen outlets at a low or a high growth rate (or in the "no growth" case refrains from infrastructure build up

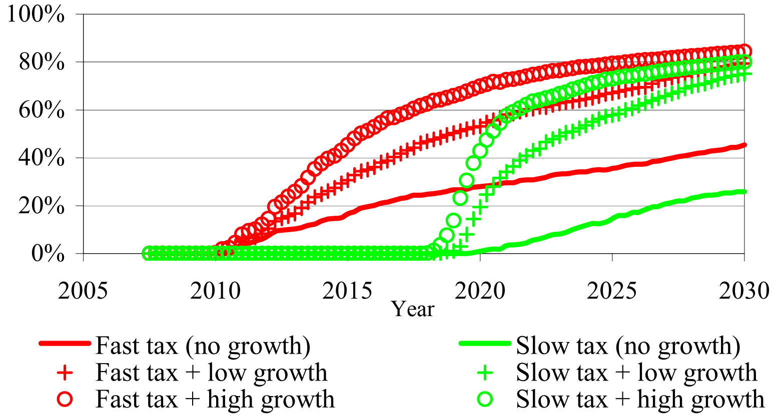


Figure 2: Total share of FCVs sold (in compact car segment). Each graph represents the average of 100 simulations runs with different random initializations.

and leaves it to the market). The results suggest that both tax regimes can successfully promote the diffusion of FCVs even without a major infrastructure program, i.e. the hen and egg problem is not prohibitive. However, if the tax is also covered by public infrastructure built up, FCVs gain high market shares much faster.

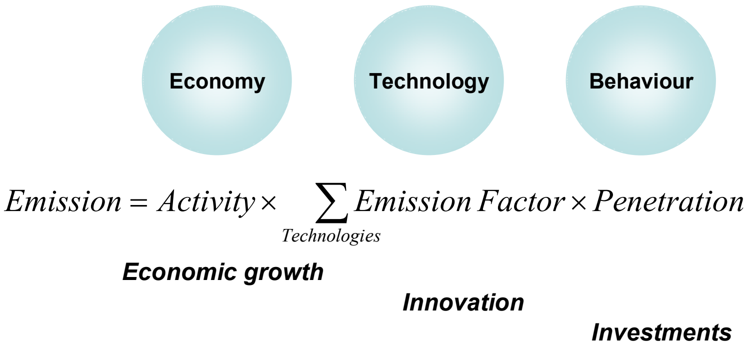
But the government will evaluate tax/infrastructure policies not only according to the speed of change to FCVs but also according to their impacts on consumers and industry. The model helps to understand how the perturbation of the system due to the policy affects consumers, large producers and small producers differently; indicating that differently strong resistance towards the tax/infrastructure combinations should be anticipated. Finally, there is evidence that some producers might benefit from cooperation with gas station operators to generate a faster build up of infrastructure.

The quantitative results crucially depend on how consumers trade off car prices against fuel availability. Empirical studies (in the public domain) are rare for the US and to the best of my knowledge absent for European countries. Thus, future research in this issue is indicated.

The TNO Emission Model

Tinus Pulles, Maarten van het Bolscher and Roel Brand, TNO Environment and Geosciences, Laan van Westenenk 501, NL-7300 AM Apeldoorn

TNO has recently developed a new approach for emission inventorying, in which the penetration of (new) technologies is explicitly modelled. The approach is schematically presented in Figure 1. In this approach the penetration $P_{activity,technology}$ of a certain technology, applied for each specific activity, is introduced into the equation. The penetration is modelled as the percentage of the activity that is performed by applying the relevant technologies. Penetration obviously is dependent upon the activity and the technology. The emission factors for the different pollutants are a property or characteristic of the technology and not of the activity. Every technology could in principle be applied for different economic activities. Examples of these are combustion technologies that can be essentially the same in public power generation, oil refineries and many industrial manufacturing industries.



$$Emission = Activity \times \sum_{Technologies} Emission\ Factor \times Penetration$$

Figure 1: The three aspects of estimating emissions: economy, technology and behaviour

Emissions now are calculated from

- Activity data, derived from (international) economic and energy statistics
- A database of technologies and associated emission factors
- The selection of one or more technologies to each of the activities

The technological developments now are modelled by a gradual replacement of one technology by another, as is demonstrated in Figure 2 for the case of heavy fuel oil combustion in energy industry (power plants and refineries). One technology (the yellow one) has been used for the full time period, whereas the light blue, the red and the dark blue technologies have replaced each other between 1971 and 1975 or 1976 and 1985 respectively. The NOx emission factors for these technologies decreased from 240 via 170 to 150 g/TJ. The graph presents the development of the resulting NOx emissions from this source between 1960 and 2000. The effects of the two oil price shocks in the 1970s are also clearly visible.

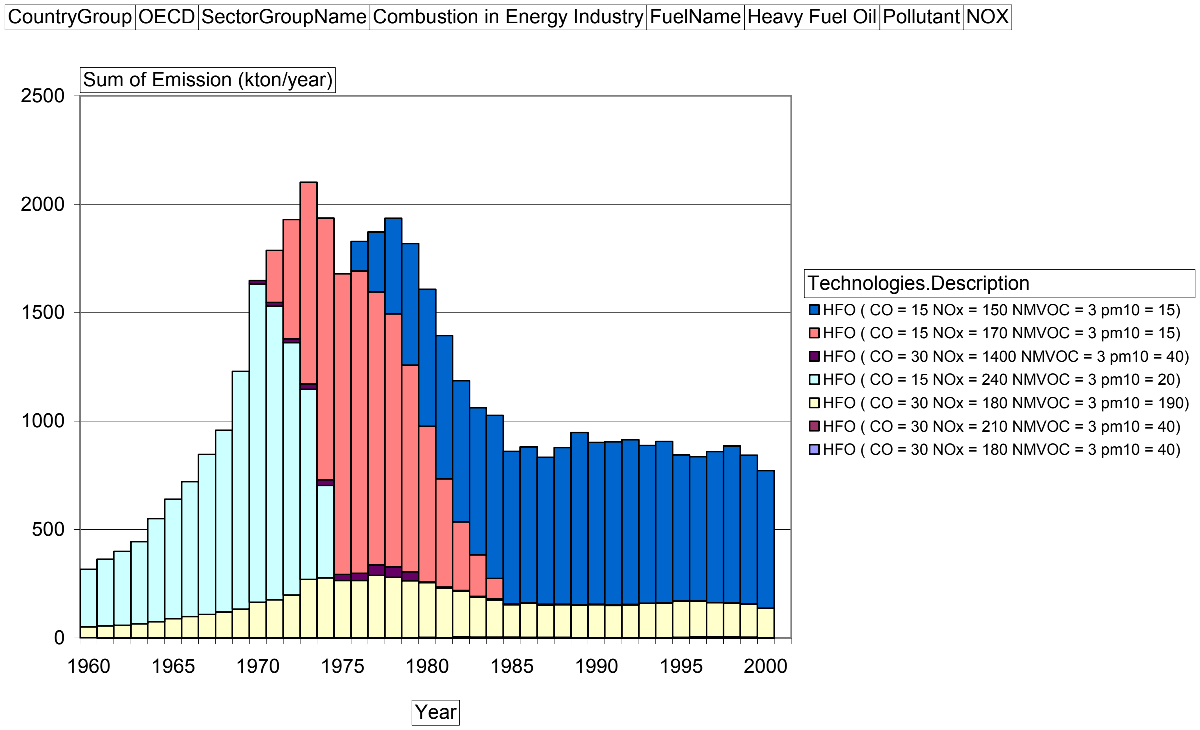
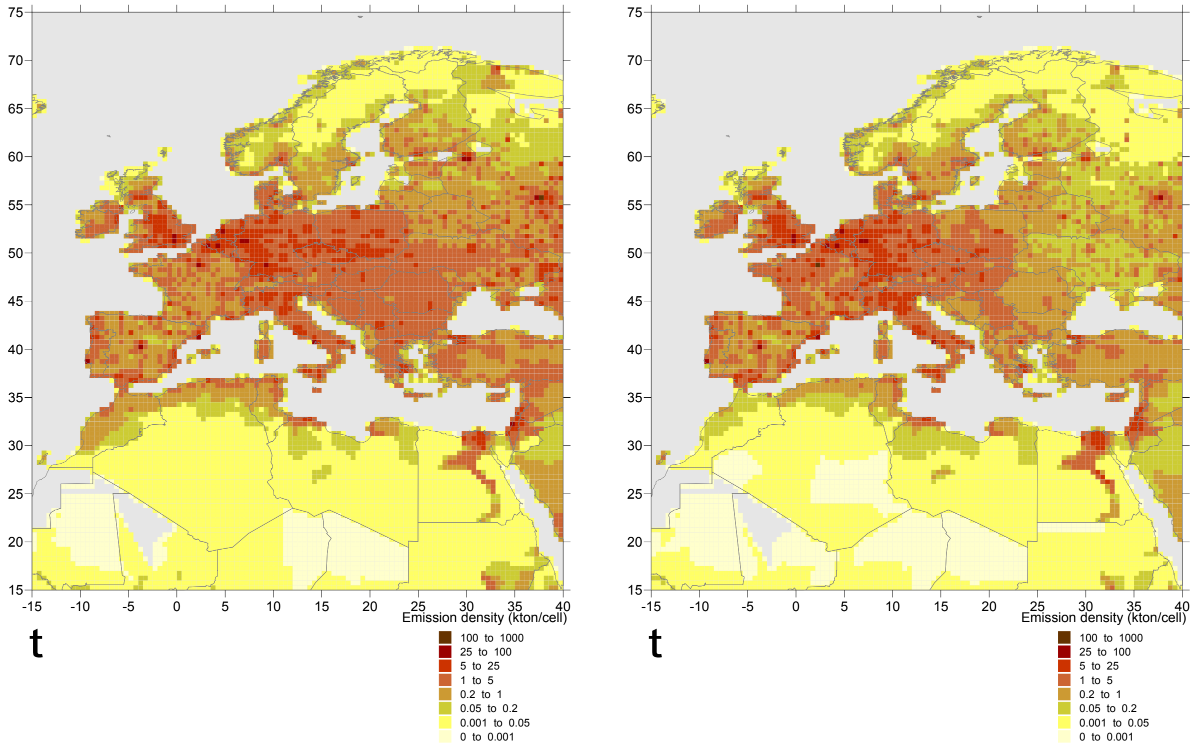


Figure 2: Emissions of NO_x from successive technologies for the combustion of heavy fuel oil in energy industries in the OECD member states.

This approach could be used

- In retrospective studies to analyse the contribution of different economic activities and related emissions to the present composition of the atmosphere to
    - identify the most important sources for certain air pollutants or other trace gases
    - compare with other possibilities (what if the world had decided to implement nuclear energy at a much higher rate?)
- In prospective studies to assess the consequences of emissions of alternative assumptions of the development of the world's energy supply, by either
    - a hydrogen economy or
    - any other alternative.

The TNO Emission Model explicitly models the introduction of (new) technologies and therefore is very well prepared for these type of studies. The model can in principle be developed to any level of detail in all three basic dimensions of an emission model: the pollutant (e.g. speciation of NMVOC emissions), the activity or technology and the location. As an example Figure 3 shows the emissions of NOx from stationary and mobile combustion sources in 2000 in Europe and Northern Africa. It clearly shows that mobile sources are relatively more important in Western Europe as compared to Central and Eastern Europe.



Stationary sources

Mobile sources

Figure 3: Spatially resolved emissions of NO_x in Europe and Northern Africa in 2000 from stationary combustion (left) and mobile sources (right).

Possible Environmental Impacts of a Hydrogen Economy

N. J. Warwick[1], S. Bekki[2], E. G. Nisbet[3] and J. A. Pyle[1],
[1] Centre for Atmospheric Science, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom
[2] Service d'Aeronomie, IPSL/CNRS/UPMC, Universite Paris VI B.102, 4 Place Jussieu, 75252 Paris Cedex 05, France
[3] University of London, Royal Holloway, Egham, Surrey TW20 0EX, United Kingdom

Changing from a fossil fuel to a hydrogen-based energy system will cause significant changes in the magnitude and composition of man-made emissions. These changes in emissions could have both positive and negative environmental impacts. For example, a significant reduction in carbon gases and NO_x could improve urban air quality, whereas a rise in H_2 emissions could increase the atmospheric lifetimes of greenhouse gases and raise stratospheric water vapour concentrations, thus influencing stratospheric ozone. To investigate the potential impact of these changes in emissions on atmospheric chemistry, a 2D model of the atmosphere is run for a selection of hydrogen economy emission scenarios (Warwick et al., 2004). The model has been used previously for a variety of atmospheric studies (e.g. see Law et al., 1993), and extends from pole to pole and from the ground to 60km. The model contains detailed representations of atmospheric chemistry (including heterogeneous reactions on sulphuric acid aerosols), transport and emissions of CH_4, CO, NO_x, and NMHCs. Atmospheric circulation is calculated from forcing terms which include solar heating in the stratosphere by O_2 and O_3 and longwave heating in the stratosphere by CO_2, H_2O, CH_4 and N_2O. Tropospheric heating rates and surface temperatures are specified.

Emission Scenarios

The hydrogen economy emission scenarios used in the model simulations are designed to assess the influence of various trade-offs in fossil fuel and hydrogen emissions on atmospheric composition (see Table 1). Each emission scenario is run for a 20 year period to allow the model to reach equilibrium (results taken from final year). In the first hydrogen scenario, H_2 mixing ratios at the surface level of the model are increased from 0.55 ppmv to 2.3ppmv. This quadrupling of H_2 mixing ratios is the expected effect of highly enhanced H_2 emissions resulting from a hydrogen energy economy equivalent to today's total fossil fuel energy (assuming $2.3x10^{15}$g H_2 will deliver sufficient energy for a global hydrogen economy (Zittel and Altmann, 1996; Tromp et al., 2003)) and a relatively high H_2 leakage rate (e.g. ~12%). Such a high leakage rate should be considered extreme and is unlikely to occur on a large scale, because it is both unsafe and expensive (Schultz et al., 2003). The absence of trade-offs in this experiment (fossil fuel emissions remain unchanged) makes it unreasonable to consider it as a plausible worst-case scenario. The results of Scenario 1 therefore correspond to an extreme.

In the second model scenario, hydrogen mixing ratios at the surface are raised to 1.4 ppmv, based on a smaller leakage rate of 5%. This scenario seems much more plausible than the first one. Further hydrogen economy scenarios (Experiments 3 to 6) include reductions in emissions of CO, NO_x, CH_4 and NMHCs. These emission reductions represent the maximum emission trade-off expected from the complete removal of the fossil fuel industry. Again, we regard these scenarios as extreme end-members of possible scenarios, designed to assess the sensitivity of the model to a range of changes in surface emissions. As production of hydrogen, at least in part, is likely to be from fossil fuels (although nuclear or renewable power represent viable alternatives), no scenario should be considered a complete representation of emissions in a future hydrogen economy.

Table 1: Surface emission variables in the base-line emission scenario and the six hydrogen emission scenarios (taken from Warwick et al., 2004). All emissions have prescribed geographical and seasonal variations except for hydrogen which has a prescribed global mixing ratio in the surface level.

Emission Scenario	H_2 / ppmv (set at surface)	CO (Tg/yr)	NO_x (Tg/yr)	CH_4(Tg/yr)	NMHCs (Tg/yr)
Base	0.55	680	51.4	525	160
1	2.3	680	51.4	525	160
2	1.4	680	51.4	525	160
3	1.4	380	51.4	525	160
4	1.4	380	18.4	525	160
5	1.4	380	18.4	440	160
6	1.4	380	18.4	440	90

Impacts on Atmospheric Composition

Changes in atmospheric composition between the base emission scenario (typical of today) and each of the hydrogen economy scenarios are summarised in Table 2. The model predicts an increase in stratospheric water vapour in all H_2 scenarios. These increases are, however, modest in comparison to those reported from balloon and satellite observations which suggest recent increases in H_2O of about 10-20% for the past couple of decades (Nedoluha et al., 1998; Oltmans and Hofmann, 1995; Rosenlof et al., 2001). It is already acknowledged that even these possible large changes in H_2O are a minor factor in the ozone depletion problem compared to the chlorine loading issue (Chipperfield and Pyle, 1998). In all model experiments, the changes in stratospheric ozone resulting from the recorded changes in emissions are small (less than 1%) and not significant compared to the magnitude of the ozone changes observed in the last two decades. Changes in global average stratospheric temperatures are also small (e.g. see Figure 1) and range from -0.1K to -0.3K in the six model scenarios. Below 40km, the changes in temperature are negligible and the greatest cooling (-1.5K in Scenario 1) occurs in a very limited region at 60km.

Table 2: Percentage changes in global mean mixing ratios in the troposphere (T) and stratosphere (S) for each of the hydrogen economy scenarios relative to the base-line scenario (adapted from Warwick et al., 2004).

Model Scenario	H_2O		OH		O_3	
	T	S	T	S	T	S
1	0	6.9	-10.1	9.9	5.1	0.6
2	0	3.4	-5.5	5.1	2.7	0.3
3	0	3.0	1.4	4.3	-1.7	0.1
4	0	4.0	-10.3	6.1	1.8	0.6
5	0	2.3	-5.3	3.1	-1.8	0.1
6	0	2.3	-5.0	3.1	-2.2	0.1

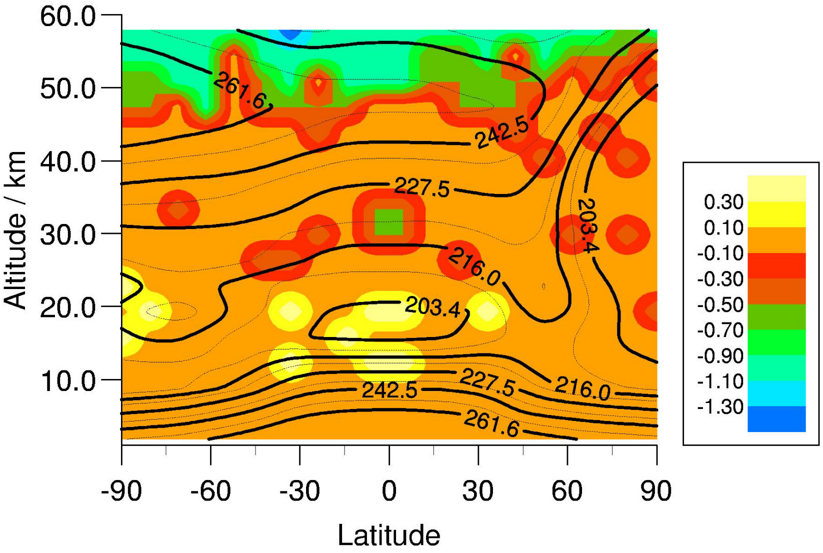


Figure 1: Simulated temperatures (K) in January for the base-line emission scenario (given by black contours) and the absolute temperature changes (K) resulting from a 160% increase in H_2 (surface level) and a reduction in CO and NO_x emissions in Scenario 4 (colour shading).

The potential impact of the removal of fossil fuel use and consequent strong reductions in CO and NO_x is most apparent in the troposphere. A decrease in tropospheric OH of 5 to 10% is calculated for Scenarios 4-6 (see Table 2). A decrease of this magnitude has important implications for the lifetime of methane and possibly other greenhouse gases. The model also calculates a slight net increase in global mean tropospheric ozone, which is the averaged result of local decreases in O_3 throughout much of the Southern and Northern Hemispheres and some model-calculated increases in O_3 and OH in latitudes north of 40°N, the result of strong NO_x reductions in the polluted model chemical regime there.

Summary

We conclude that a move from a fossil fuel-based energy industry to a hydrogen-based industry would most plausibly have little effect on the concentrations of stratospheric ozone. However, we find that switching to a hydrogen economy could significantly influence the chemical composition and oxidation capacity of the troposphere, depending on the magnitude of the trade-offs. Our results highlight the need for further investigation both by modeling (assuming a wide range of hydrogen economy simulations) and by improvements in global efforts to monitor atmospheric hydrogen. Future model studies should include 3D simulations with a radiative feedback and also scenarios where CO_2 is varied. A reduction in fossil fuel burning would lead to reduced atmospheric CO_2 levels which would have a further radiative impact on the stratosphere. This change, and the subsequent impact of temperature changes on stratospheric ozone chemistry, might indeed be the most important factor for the stratosphere of the change to a H_2 economy and needs to be assessed.

References

Chipperfield, M. P. and J. A. Pyle, Model sensitivity studies of Arctic ozone depletion, J. Geophys. Res., 103, 28,389-28,403, 1998.

Law, K. S. and J. A. Pyle, Modeling trace gas budgets in the troposphere 2. CH_4 and CO, J. Geophys. Res., 98, 18401-18412, 1993.

Nedoluha, G. E., R. M. Bevilacqua, R. M. Gomez, D. E. Siskind, B. C. Hicks, J. M. Russell III and B. J. Connor, Increases in middle atmosphere water vapour as observed by the

Halogen Occultation Experiment and the ground-based water vapour millimeter-wave spectrometer from 1991-1997, J. Geophys. Res., 103, 3531-3543, 1998.

Oltmans, S. J. and D. J. Hofmann, Increase in lower stratosphere water vapour at a mid-latitude Northern Hemisphere site from 1981 to 1994,Nature, 374, 146-149,1995.

Rosenlof, K. H., S. J. Oltmans, D. Kley, J. M. Russell III, E.-W. Chiou, W. P. Chu, D. G. Johnson, K. K. Kelly, H. A. Michelsen, G. E. Nedoluha, E. E. Remsberg, G. C. Toon and M. P. McCormick, Stratospheric water vapour increases over the past half-century, Geophys. Res. Lett., 28, 1195-1198, 2001.

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

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

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.

Zittel, W. and M. A. Altmann, Molecular hydrogen and water vapour emissions in a global hydrogen energy economy, Proceedings of the 11th World Hydrogen Energy Conference, T. N. Veziroglu et al., Eds. (Schön & Wetzel, Frankfurt, Germany, 1996) (available at www.hydrogen.org/knowledge/vapour.htm).

Modelling the impact of a switch to H_2 energy sources on chemical composition and climate

Slimane Bekki, Service d'Aeronomie, IPSL/CNRS/UPMC, Universite Paris VI
B.102, 4 Place Jussieu, 75252 Paris Cedex 05, France

The presentation focuses on the uncertainties on the impact of a switch to H_2 energy sources on the chemical composition of the atmosphere, in particular the stratosphere, and on climate. The uncertainties are very large indeed. For example, previous studies based on 2-D model calculations (Tromp et al., 2003; Warwick et al., 2004) reached opposite conclusions concerning the impact of enhanced H_2 emissions on stratospheric ozone. The Tromp et al study did take into account the expected trade-offs associated with a switch to H_2 energy sources (e.g. the concurrent reductions in carbon monoxide, methane and nitrogen emissions from the fossil fuel industry, see the study by Schultz et al., 2003). The impact of a switch to H_2 energy sources is highly dependent upon the magnitude and nature of these trade-offs. If some switch to H_2 energy sources is to occur, more work is required in defining the most probable and realistic emission scenarios in order to assess the environmental impact using models. It is also clear that fully interactive 3-D chemistry-climate models (CCM) are needed for assessing the impact on the stratosphere because the ozone response do not depend only on changes in H_2 levels but also in CH_4, H_2O and CO_2 which, with ozone, determine the radiative balance of the stratospheres. Since the troposphere and stratosphere are strongly coupled, any stratospheric changes will impact the troposphere and, in fine, the climate. There is also the need to check the stratospheric H_2 budget in global models. Isotope measurements would provide useful constraints. Then, models could be used for various tasks such as estimating the fraction of H_2 originating from direct H_2 emissions and the fraction coming from the CH_4 oxidation or also working out which fossil fuel sources replacement would minimise the environmental impact (pollution, climate)

References

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

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

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(5), doi: 10.1029/2003GL019224, 2004.

Changing to a Hydrogen Economy: Study of Atmospheric Impact (CHESAI)

Euan Nisbet[1] and Frode Stordal[2],
[1] University of London, Royal Holloway, Egham, Surrey TW20 0EX, United Kingdom
[2] University of Oslo, Boks 1072 Blindern, 0316 Oslo, Norway.

The CHESAI proposal is being prepared for submission to the EU/NEST program. For the time being, the abstract of this proposal is as follows:

The proposal is for piloting work to assess the atmospheric risks and benefits of the hydrogen economy. Recent research in atmospheric chemistry has shown that increased hydrogen emissions may have profound atmospheric consequences, changing the oxidative, cleansing capacity of the air. Concerns include the effects on tropospheric chemistry, including ozone and air pollution, and the impact on stratospheric water content and ozone decline. Hydrogen is also an indirect greenhouse gas, as a result of its effect on the atmospheric methane burden. Many impacts involve trade-offs with emissions of other species, such as methane, carbon monoxide and nitrogen oxides. These trade-offs need to be understood.

The hydrogen economy will have major atmospheric consequences, some beneficial, some damaging, both for Europe and for Earth as a whole. These consequences are poorly known. The risks have not been considered in decision-making. This debate is new. There is urgent need for better understanding of hydrogen, before committing massive investment. CHESAI seeks to develop Insight into this immediate and important problem.

The project will:

1. study the present-day hydrogen budget of Europe and Russia, prior to the onset of large-scale hydrogen use; and
2. model the likely impacts of the hydrogen economy on European and global atmospheric chemistry and climate.

The work includes:

1. Continuous measurement of hydrogen as well as grab sampling for determining its stable isotope ratio ($^2H/^1H$), to assess the present day hydrogen budget on the regional European and on the global scale, before new large-scale emissions occur.
2. Field campaigns, including diurnal studies, aimed at assessing the soil sink and controls on urban budgets (including vehicle emissions).
3. Modelling studies, including work to understand present-day regional and global H_2 budgets, and also scenario development to model future impacts.

Atmospheric chemistry/climate gas modelling studies at the University of Oslo

Ivar S.A. Isaksen, Department of Geosciences and CICERO, University of Oslo, Boks 1072 Blindern, 0316 Oslo, Norway.

Modeling studies of chemical compounds at the University of Oslo has focused on estimating large scale distribution and changes of chemical compounds which are affected by human activities. More specifically the studies have focused on: Impact on climate through changes in greenhouse gases and particles (CO2,, CH4, O3, N2O, CFCs, particles) (Myhre and Stordal, 1997; Endresen et al., 2003); Impact on regional air quality (O3, particles) and the oxidation capacity (OH) through pollution emission (Gauss et al., 2003; Prather et al., 2003, Isaksen et al., 2005); Stratospheric ozone depletion and recovery caused by the emissions of CFCs and the reduction in their emissions; Effect of emission reductions, globally as well as regionally and in different sectors (Berglen et al., 2004; Endresen et al., 2003).

Modeling tools

Several models have been used to study the impact of changes in atmospheric composition. The main modeling tool is the global scale Oslo CTM2. It has been used in several national and EU funded projects where the focus have been changes in chemical composition, and impact on climate and pollutants. It is a global 3-dimensional (3D) chemical transport model (CTM) for the troposphere and stratosphere. It consists of 40 (60) layers extending from the surface up to 10 (0.1) hPa. Various options for the horizontal resolution are available from T21 (5.7º) to T106 (1.1º). The standard version is T42 (2.8º), but extensive model runs with T63 (1.9º) resolution is also performed. will be used for full chemistry calculations. The model has extensive modules describing stratospheric chemistry (64 chemical compounds) and tropospheric chemistry (51 compounds). The chemistry scheme is integrated by the QSSA method (Berntsen and Isaksen, 1997). A module for the emission, dispersion, and removal of carbonaceous aerosols (soot and organic carbon) has also been included in the CTM, as well as a scheme describing interactions between sulphate and oxidant (Berglen et al., 2004). Dispersion of tracers by advection uses the concept of conservation of Second Order Moments, which is very accurate. Input of meteorology data from ECMWF is available for the period 1996-2001. A simplified climate model, The CICERO SCM (Fuglestvedt et al., 2000) is being used in collaboration with CICERO. This model incorporates a scheme for CO_2 from Joos et al. (1996) and an energy-balance climate/up-welling diffusion ocean model developed. The SCM calculates global concentrations from emissions of 29 GHGs and radiative forcing for 35 components and is well suited scenario studies of development in global mean temperature on a century scale. A Radiative Transfer Model including solar and thermal infrared radiation is used to calculate radiative forcing (RF) from changes in gases and aerosols. For global solar calculations a multi-stream model using the discrete-ordinate method will be used. The radiative transfer model includes Rayleigh scattering, scattering by clouds, gas absorption, and scattering and absorption by aerosols (Myhre et al., 2002). For thermal infrared, a broadband absorptivity/emissivity model is used for absorption by greenhouse gases in the atmosphere (Myhre and Stordal, 1997). A General circulation model, The NCAR Community Atmospheric Model (CAM3) is currently under implementation at the University of Oslo, and is tested out for studies of water vapour distribution and the distribution chemically active climate compounds like O3 and CH4. It will be extensively used in the near future as part of our involvement in national and EU funded projects.

Selected model studies

We will select a few model studies performed with the Oslo CTM2 to illustrate model performance and type of studies that have been done. Figure 1 shows calculated changes in ozone distribution in the troposphere and stratosphere between 1980 and 2000. The numbers are monthly average values for July. In the stratosphere ozone is depleted due to the increase in the ozone depleting substances CFCs, while tropospheric ozone increases due to increases in ozone precursors (CO, NOx, VOC). Maximum ozone depletion (in %) occurs around 40 km. The tropospheric increase is clearly linked to regions where the precursors are emitted. There is also ozone increases in the lower stratosphere at mid- and low-latitudes.

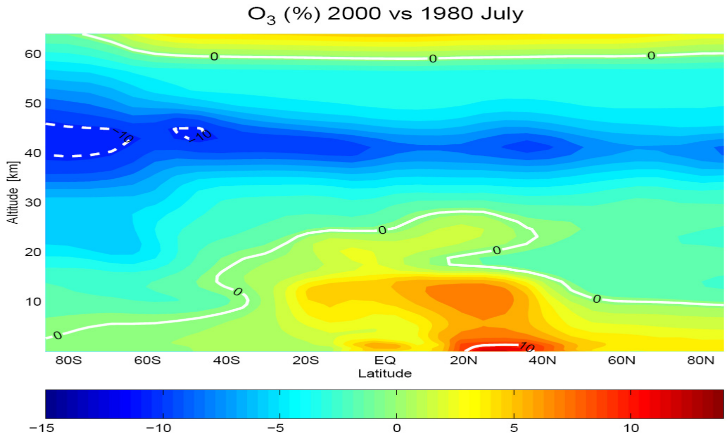


Figure 1: Calculated zonal average ozone change (%) between 1980 and 2000 for the atmosphere up to 64 km. Calculations are done with the Oslo CTM2 with horizontal resolution 5.7°. The ERA40 data are used as meteorological input data.

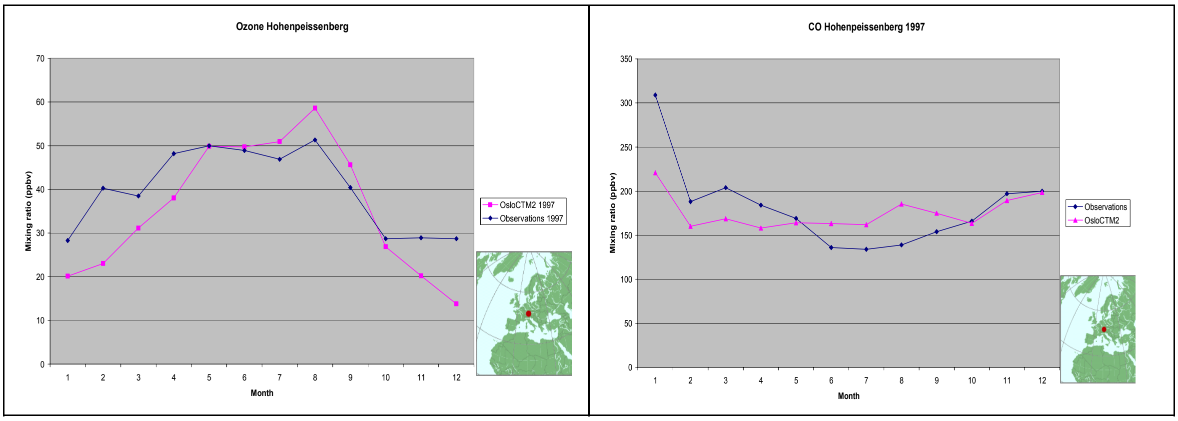


Figure 2: Calculated and observed monthly average surface ozone (left panel) and CO (right panel) mixing ratios (in ppb) at Hohenpeissenberg, in 1996 using the Oslo CTM2 model.

A comparison between model calculated monthly average ozone and CO changes over 1 year, compared with observations at Hohenpeissenberg, Germany is shown in Figure 2 (Isaksen et al., 2005). The calculation is from a study of the sensitivity of ozone and its precursors to changes in UV fluxes. Calculated and observed values are compared at different stations. The study demonstrates that the model is capable of reproducing the yearly variation in ozone and its precursors.

Implementation of control measures to reduce anthropogenic impact on the atmospheric concentration of pollutants has had significant impact during the last decades. This is demonstrated in Figure 3 where calculated changes in sulfate distribution and its radiative impact is given. Reduced emission of sulfur dioxide between 1985 and 1996 in the US and in particular in Europe have led to drastic reduction in sulfate loading, in some areas more than 50 %, at the same time is emission estimated to increase similarly over South-East Asia. This has led to significant impact on radiative forcing. There is an increase over Europe (~1 W/m^2 in region of maximum reduction), while there is a reduction over South-East Asia (~ -2 W/m^2). The strong regional differences in RF reflect the different trends in emissions.

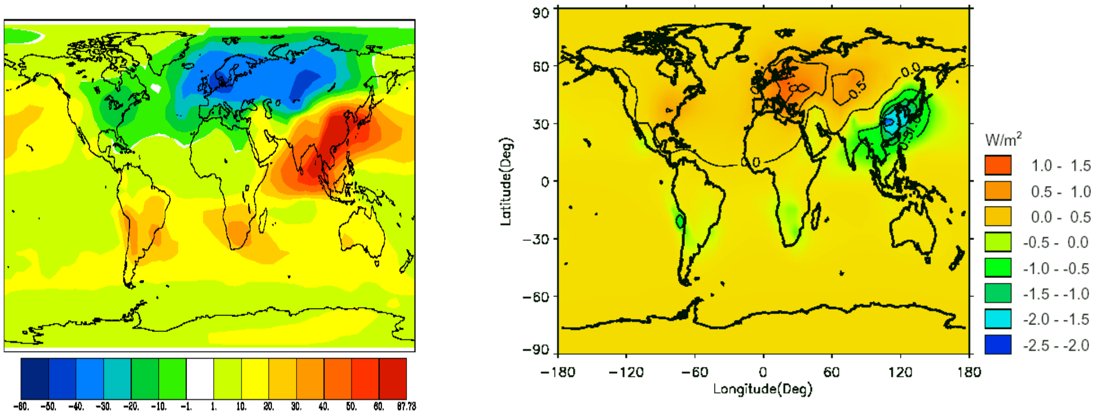


Figure 3: Calculated changes in surface sulfate levels (%) (left panel) and radiative forcing (W/m^2) (right panel) between 1985 and 1996 (calculated in the Oslo CTM2).

Radiative forcing from the transport sector

The estimated impact of the different modes of transportation on RF for current emissions is shown in Figure 4. The figure demonstrates that the contribution from the different forcing agents varies strongly with mode of transportation. For road transport, which has the largest overall emissions, CO_2 is the main contributor, while the estimates for ship emissions give the largest contribution from sulfate (indirect effects). For air traffic, cirrus formation seems to give the largest contributions. It should be noted that other components than CO_2, in particular ship and air traffic, contribute significantly to RF.

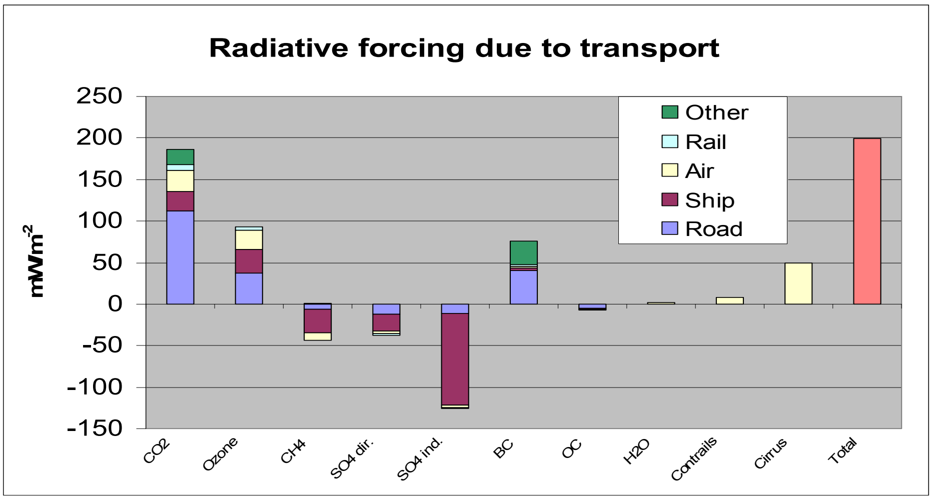


Figure 4: RF from different forcing agents from the different modes of transportation.

The use of hydrogen as fuel

A first study of the use of hydrogen as fuel for aircraft was performed in the EU financed project CRYOPLANE which was completed in 2003, and where the University of Oslo participated with model studies of atmospheric impact (Gauss et al., 2003b). The CRYOPLANE studies showed that there could be noticeable changes in climate compounds like O_3, CH_4, H_2O and contrails, and that there could be clear tradeoffs between the different impacts. Future studies of the transformation to a "hydrogen economy" need to look into the different sectors in detail since the contribution differs strongly as shown in Figure 4. It should, however, be remembered that some of the calculated RFs are connected with large uncertainties.

Further studies on transformation to hydrogen as fuel should focus on modeling studies on: Enhanced hydrogen concentrations and impact on climate and air quality through impact on atmospheric chemistry; Reduced climate impact through reduced emission of fossil fuel in different sectors (CO2, CH4, ozone); Reduced pollution levels (improved air quality) through reduced emission of NOx and particles, future emission scenarios on policy options for transformation to a "hydrogen economy (Schultz, et al., 2003; Prather, 2003).

References

Berglen, T.F, T.K Berntsen, I.S.A Isaksen and J.K. Sundet: A global model of the coupled sulfur/oxidant chemistry in the troposphere: The sulphur cycle, J. Geophys. Res., submitted (2004).

Berntsen, T., and I.S.A. Isaksen. A global 3-D chemical transport model for the troposphere; 1. Model description and CO and ozone results, J. Geophys. Res., 102, 21239-21280, *1997*.

Fuglestvedt, Jan S., Terje Berntsen, Odd Godal and Tora Skodvin, 2000. Climate implications of GWP-based reductions in greenhouse gas emissions. *Geophys Res. Lett.*, 27 (3): pp. 409-412.

Gauss, M. et al.,. Radiative forcing in the 21st century due to ozone changes in the troposphere and the lower stratosphere. J. Geophys. Res., Vol. 108 (D9), 4292, doi:10.1029/2002JD002624, 2003

Gauss, M., I.S.A. Isaksen, S. Wong, and W.-C. Wang: The impact of H_2O emissions from kerosene aircraft and cryoplanes on the atmosphere. J. Geophys. Res., 108(0), doi:10.1029/2002JD002623, 2003b.

Isaksen, I.S.A., C. Zerefos, K. Kourtidis, C. Meleti, S. B. Dalsøren, J.K Sundet, P. Zanis and D. Balis, Tropospheric ozone changes at unpolluted and semi-polluted regions induced by stratospheric ozone changes, J.Geophys. Res., in print (2005)

Joos, F., Bruno, M., Fink, R., Siegenthaler, U., Stocker, T.F., Quéré, C. Le and Sarmiento, J.L., 1996. An efficieny and accurate representation of complex oceanic and biospheric models of anthropogenic carbon uptake. Tellus, 48B: 397-417.

Myhre, G., and F. Stordal, 1997, Role of spatial and temporal variations in the computation of radiative forcing and GWP, J. Geophys. Res., 102, 11,181-11,200.

Myhre, G., J.E. Jonson, J. Bartnicki, F. Stordal, and K.P. Shine, Role of spatial and temporal variations in the computation of radiative forcing due to sulphate aerosols: A regional study, 2002, Q. J. R. Meteorol. Soc., 128, 973-989.

Prather, M., et al., Fresh air in the 21th century?, Geophys. Res. Lett., V30, No2, 1100, doi: 10.1029/2002GL016285, 2003.

Prather, M., An Environmental Experiment with H_2, Science, 302, 581-582, 2003

Schultz, M.G., T. Diehl, G.P. Brasseur and W. Zittel, Air Pollution and Climate-Forcing Impacts of a Global Hydrogen Economy, Science 24, 302, 624-627, 2003

Hydrogen, the energy crisis, and climate change

Martin Schultz, Max-Planck-Institut für Meteorologie, Germany

adapted from chapter 6.1 of the RISO energy report No. 3 (co-authors Frank Markert and Kim Pilegaard, Risø National Laboratory) with additions from Schultz et al., 2003 (Science) and remarks on planned research activities

Introduction

Man has begun to significantly affect the composition of the global atmosphere, and the consequences for the Earths climate and air quality are already being felt. The fundamental problem of humanity is that its economic growth relies heavily on the exploitation of natural resources, in particular the use of fossil fuels. As an example, Figure 1 (from Schultz *et al.*, 2004) shows the steep increase in road traffic over the past 30 years, and this is reflected in rising emissions of air pollutants, in spite of the introduction of pollution control technology.

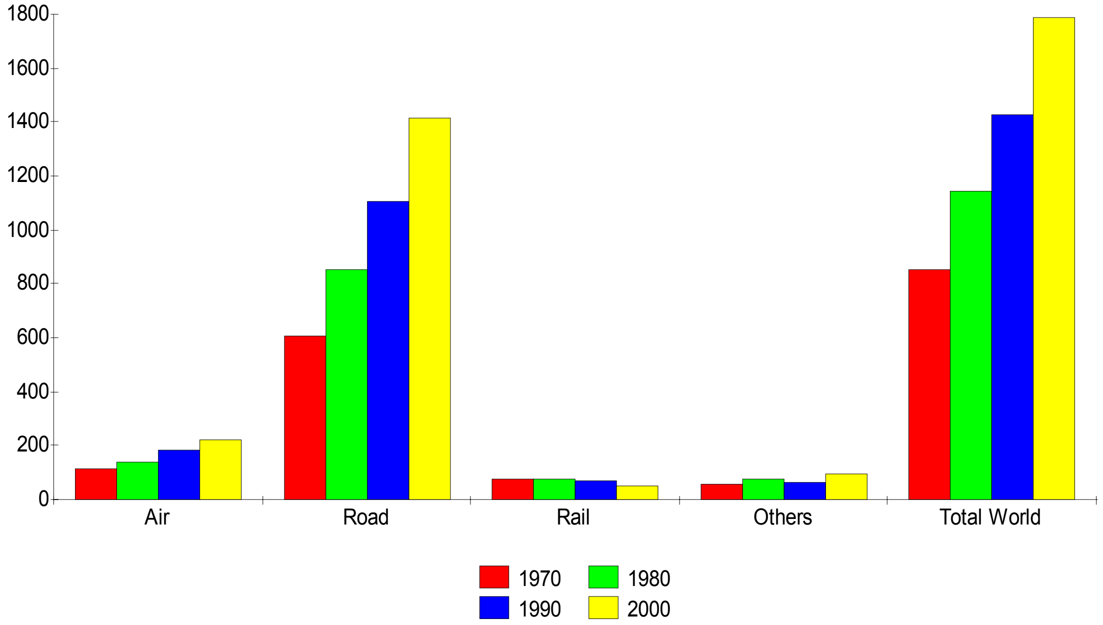


Figure 1: Modal split and total final energy consumption by the transport sector, 1970 to 2000, world, in Million Tons Oil Equivalent (OECD, 2002). « Others » including estimates for pipelines, waterways transports and international marine bunker.

Hydrogen (H_2) is widely regarded as a key component in future energy systems because it is a sustainable, clean, and transportable energy carrier. It can be generated from pure water, and burned to produce nothing but water. Thus if hydrogen generated using clean and sustainable processes replaces fossil fuels as our main energy carrier, we will have significantly lower emissions of greenhouse gases, especially carbon dioxide (CO_2), and air pollutants, notably nitrogen oxides and volatile organic compounds.

This view is somewhat idealistic, however, as the technology for the clean and sustainable production of hydrogen is still in the pioneering phase. A great deal of effort will have to be made to build up sufficient hydrogen production capacity from sustainable energy sources such as wind power and solar cells.

The production and distribution of hydrogen inevitably involves energy losses. If the energy source is a fossil fuel, the energy losses and pollution involved in producing and distributing hydrogen may turn out to be greater than those from direct use of the fuel via conventional technology. When considering the use of hydrogen in any application, it is therefore important to check the overall environmental balance and to compare this with alternatives such as the direct use of electricity from windmills or solar cells.

Initially at least, the production of hydrogen will be based largely on the chemical conversion of fossil fuels such as natural gas and coal. Such processes generate carbon dioxide emissions which may exceed those from the direct use of the fossil fuel in an internal combustion engine. When hydrogen is produced at a large centralised plant, however, it may be possible to capture the carbon dioxide and so end up with a net reduction in greenhouse gas emissions. In terms of other air pollutants, reforming would almost certainly be preferable to the present state of affairs.

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

This chapter gives an overview, based on the scientific literature, of current knowledge of the consequences of hydrogen in the soil and in the atmosphere.

Sources, sinks and concentrations of atmospheric hydrogen

The (incomplete) combustion of fossil fuel and biomass in boilers and internal combustion engines generates hydrogen along with carbon monoxide and carbon dioxide. At present, this source accounts for about 40% of all the hydrogen released into the atmosphere.

Another important source, accounting for an estimated 50% of atmospheric hydrogen emissions, is the atmospheric photochemical oxidation of methane (CH_4) and non-methane hydrocarbons (NMHCs). Emissions from volcanoes, oceans and nitrogen-fixing legumes account for the remaining 10% (Novelli *et al.*, 1999; Hauglustaine and Ehhalt, 2002). These estimates are still very uncertain.

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

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

(R1) $H_2 + OH \rightarrow H + H_2O$

(R2) $H + O_2 + M \rightarrow HO_2 + M$

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

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

(R3) $CO + OH + O_2 \rightarrow HO_2 + CO_2$

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

(R4) $O_3 + h\nu \rightarrow O_2 + O$

(R5) $O + H_2O \rightarrow 2\ OH$

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

(R6) $NO + HO_2 \rightarrow OH + NO_2$

(R7) $NO_2 + h\nu \rightarrow NO + O(^3P)$

(R8) $O(^3P) + O_2 + M \rightarrow O_3 + M$

"hν" denotes a photon of ultraviolet light. Ozone in the troposphere is also an important component of summer smog.

These atmospheric reactions, which are closely linked, are important because they determine the capacity of the atmosphere to neutralise pollutants. The concentration of hydroxyl radicals is particularly important, since it is these radicals that begin the whole oxidative degradation process, and the reactions involved (R1 and R3) are the slowest in the whole sequence. More hydrogen in the atmosphere will tend to lower the concentration of hydroxyl radicals and so inhibit the capacity of the atmosphere to oxidise greenhouse gases and other pollutants. On the other hand, in a hydrogen economy, emissions of other compounds (e.g. CO, NMHC, and NOx), which affect the hydroxyl radical concentration more effectively, will be reduced. The resulting effect is discussed in more detail below (section on oxidizing capacity).

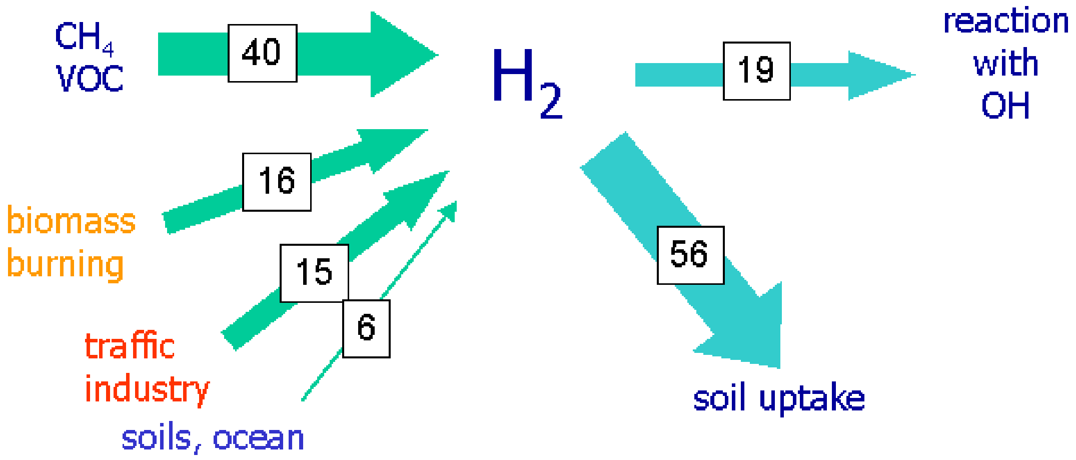


Figure 2: Sources and sinks for hydrogen in the atmosphere (million tonnes/year). The numbers are uncertain, especially for traffic and industry emissions (±10 million tonnes/year) and soil deposition (±15 million tonnes/year).

Measurements from ground stations, balloons and research aircraft typically find about 0.5 ppmv (parts per million by volume) of hydrogen in the troposphere (the part of the atmosphere extending from the earth's surface up to about 10 km), and 0.4–0.5 ppmv in the stratosphere (10–60 km altitude) (Schmidt and Wetter, 2002). No significant trend can be deduced from observations made after 1990, although earlier observations did indicate a positive trend.

The tropospheric hydrogen concentration exhibits a clear yearly cycle. In the northern hemisphere the amplitude of the variation is 0.04–0.08 ppmv, with a maximum in the spring. In the southern hemisphere the amplitude is 0.02–0.04 ppmv, with a maximum during summer in the northern hemisphere. These seasonal variations are caused largely by the build-up of CH_4 and NMHC in the winter, followed by increased oxidation rates in the summer. Seasonal variations in the rate of dry deposition may also contribute to the cycle.

Estimates of future emissions

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

There has been considerable recent controversy in the scientific literature over how much hydrogen a global-scale hydrogen economy would release into the atmosphere. Estimates range from less than 0.1% of hydrogen consumption, for tightly-controlled industrial applications, to 10–20% for evaporation from liquid hydrogen tanks in poorly-designed automobiles. 3% would be a more realistic upper limit, however, simply because higher leakage rates would be neither economic nor safe. Assuming the complete replacement of today's energy system with a hydrogen chain, about 1400-1800 million tons H_2/year would be required[1]. Correcting for the present emissions of 42 – 54 million tons H_2/year and assuming a 3% loss of 42-54 million tons H_2/year the H_2 emissions would increase by 17 - 49 million tons H_2/year (or 22% - 64%), It is worthwhile to note that lower leak rates than 3% could even lead to a net reduction of hydrogen emissions. Of course, a simple 1:1 replacement scenario of the present-day energy demand is overly simplistic, and considerable future efforts are needed to develop more reliable emission scenarios for hydrogen applications.

Our view is that these hydrogen emissions are probably much less important than the overall atmospheric emissions of CO_2, CO, and NO_x from reformers and other hydrogen plants, and the reduction in emissions of these gases as conventional technologies are replaced by their hydrogen equivalents (Schultz *et al.*, 2003). Of particular interest here are emissions of carbon dioxide and NO_x. Carbon dioxide is important because it is the biggest contributor to climate change. NO_x levels drive the oxidising capacity of the atmosphere (essentially the OH concentration), and so regulate the lifetime of the greenhouse gas methane, and they control the amount of photochemical ozone formed in the troposphere. Table lists current estimates of NO_x sources (IPCC, 2001).

Table 1: Global tropospheric NO_x emissions estimates for 2000, after (IPCC, 2001).

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

---

[1] Energy consumption 2001 = $404 \cdot 10^{18}$ J (EIA, 2003), energy density of hydrogen = $1.2 \cdot 10^{8}$ J/kg. Thus, an upper limit for the 1:1 replacement of today's energy demand would be given by 3340 million ton/year. However, one must factor in the efficiency gain when replacing old technology with new one (e.g. factor 2 for fuel cells over internal combustion engines), and conversion efficiency changes (e.g. coal to electricity versus steam reformation for hydrogen production). The value of 1400-1800 million ton/year given in the text is a conservative estimate based on different sources.

As Table 1 makes clear, the burning of fossil fuels is by far the largest present-day source of NO_x. Emissions from fossil fuels are likely to increase in the future, despite successful regulations in Europe, North America and Japan. A large-scale shift to hydrogen would eliminate or at least reduce a significant fraction of traffic-related NO_x emissions. This would improve air quality, or at least help to slow the decline in air quality, over large regions of the world (Schultz *et al.*, 2003; Schultz *et al.*, 2004).

Possible impacts of future hydrogen use

The potential environmental impacts of a global hydrogen economy are:

- Increased hydrogen release would lower the oxidising capacity of the atmosphere, and so increase the lifetime of air pollutants and greenhouse gases such as methane, HCFCs and HFCs.
- Increased hydrogen release would lead to increased water vapour concentrations in the atmosphere, with potential consequences for cloud formation, stratospheric temperatures and stratospheric ozone loss.
- Increased hydrogen release could exceed the uptake capacity of hydrogen by micro-organisms in the soil — currently the main way in which hydrogen is removed from the atmosphere. The result would be that hydrogen concentrations in the atmosphere would increase more quickly, which would reinforce the consequences described above.
- If hydrogen were to be generated using electricity derived from burning coal, NO_x emissions could increase significantly. This would have serious effects on air pollution and the global tropospheric ozone budget.
- Generating hydrogen from fossil fuels could lead to increased emissions of carbon dioxide, which would accelerate global warming, unless the CO_2 is captured and stored.
- Conversely, generating hydrogen from sustainable sources would reduce emissions of carbon monoxide and NO_x, with a consequent fall in tropospheric ozone levels. This would improve air quality in many regions of the world. Furthermore, CO_2 emissions would be reduced, thereby slowing the global warming trend.

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

1. Changes in oxidising capacity

Hydrogen acts as a significant sink for hydroxyl radicals, so increased atmospheric concentrations of hydrogen could lead to a decrease in OH concentration. This in turn could increase the atmospheric lifetime of greenhouse gases and other pollutants, with undesirable consequences for climate change and air quality (Hauglustaine and Ehhalt, 2002).

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

However, significant changes in the oxidising capacity of the atmosphere could well arise from other emissions changes associated with the shift towards hydrogen, most notably emissions of NO_x (Schultz *et al.*, 2003). There is still considerable uncertainty over the global OH budget and its historical trends (IPCC, 2001). Generally, scientists believe that the burning of fossil fuels has produced only small changes in the balance between NO_x (which tends to increase OH) and carbon monoxide (which tends to decrease OH) since pre-industrial times, and that the global average OH concentration has probably remained stable within about 10% over this time.

Significant future changes in either NO_x or carbon monoxide emissions could have a much larger effect on OH levels. Such changes could happen in a hydrogen economy, but equally they could happen in a world of fossil fuels as a result of tightening emissions controls. More research is clearly needed to produce reliable estimates based on probable emission scenarios.

2. Changes in atmospheric water vapour

The oxidation of hydrogen produces water vapour, which could have different consequences depending on where in the atmosphere it is released. One recent article suggests that increasing atmospheric hydrogen concentrations by a factor of four would increase the amount of water vapour in the stratosphere by up to 30% (Tromp *et al.*, 2003). According to these researchers, this could decrease the lower stratospheric temperature at the polar vortex by about 0.2°C, which in turn could trigger additional polar ozone losses of up to 8% (polar ozone depletion is very sensitive to small temperature changes (WMO, 2002)). Another model, however, showed a much weaker effect on stratospheric temperatures and ozone loss (Warwick *et al.*, 2004).

As discussed above, hydrogen levels are more likely to increase by 20% than by 400% in the coming decades. Even when we use the more pessimistic model (Tromp *et al.*, 2003), therefore, the consequences for stratospheric temperatures and ozone concentrations are expected to be negligible (Figure 3).

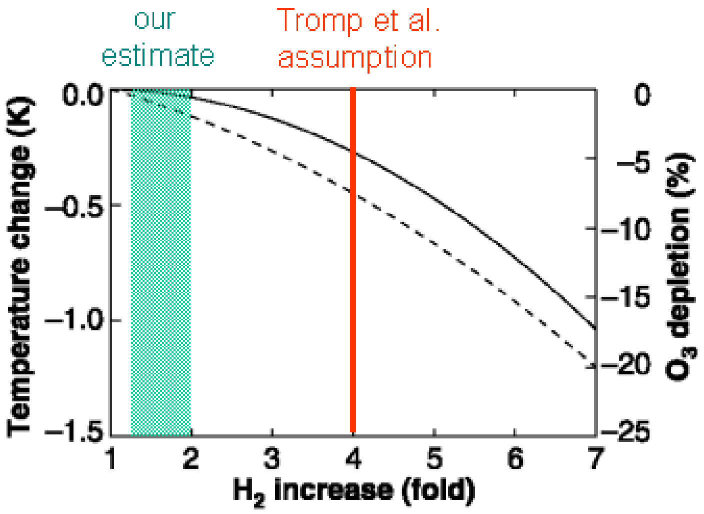


Figure 3: Relative temperature changes in the lower stratosphere at 74°N (solid line) and the resulting maximum ozone depletion in the northern polar vortex (dashed line) as a function of increased atmospheric hydrogen concentrations relative to the today's actual hydrogen concentration of about 0.5 ppmv. The cause of the temperature change is the stratospheric water vapour resulting from the oxidation of hydrogen. The graph is taken from Tromp et al., (2003), with additions.

Increased water vapour concentrations in the upper troposphere can be expected if air traffic increases as projected, especially if aircraft begin to use hydrogen as fuel. At these altitudes, increased water vapour may cause cirrus clouds to form. This would increase or decrease heat radiation, depending on the height and thickness of the cloud, and so could lead to either cooling or warming of the atmosphere.

It is difficult to establish reliable estimates of the potential water vapour release from aircraft, and even harder to model the effects of extra water vapour on this highly-sensitive region of the atmosphere. Emissions depend strongly on engine design, and the effects will be very different depending on the altitude, air temperature, exhaust temperature and background humidity.

If hydrogen combustion engines were used widely in aircraft, another source of concern could be emissions of NO_x. Even under present-day conditions, NO_x emissions are believed to significantly perturb the amount of ozone in the upper troposphere (IPCC, 2001). These processes in the upper troposphere and lower stratosphere region are still the subject of much research, and more measurements and better models are needed to assess them reliably.

3. Soil uptake

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

At the moment there is no sign that the process of hydrogen uptake in the soil is becoming saturated. Increased fossil fuel combustion has presumably increased atmospheric hydrogen concentrations significantly in the last century, but there has been no detectable increase since 1990. If hydrogen uptake in the soil were becoming saturated, we would expect the concentration of hydrogen in the atmosphere to have increased, even if hydroxyl radical concentration were increasing as well.

Since we do not expect the amount of hydrogen released to change very significantly in the next few decades, we currently have no reason to expect serious consequences from changes in the soil uptake rate. This is rather speculative, however, and further research is urgently required.

4. Carbon dioxide emissions

In a recent study, today's surface traffic sector was assumed to be replaced by hydrogen generated from renewable sources leading to a 20% CO_2 emission reduction (Schultz *et al.*, 2004). However, as long as hydrogen is generated from fossil fuels, CO_2 emissions from reforming can easily rival today's emissions from power plants and traffic. From the standpoint of avoiding CO_2 emissions in the short to medium term, centralized facilities appear preferable, because this might allow efficient capturing and storing of the CO_2 produced [2]. In the long term, it is obvious that hydrogen generation has to be based on renewable sources to avoid the environmentally adverse effects of carbon dioxide.

5. Air quality effects

Probably the most immediate implication of a large-scale shift to hydrogen, especially in road transport, would be a significant drop in emissions of air pollutants (NO_x, benzene and other VOCs) and an associated fall in ground-level ozone concentrations (Figure 4).

In most regions of the world, ozone formation is limited by the amount of NO_x in the atmosphere. However, many big cities emit such large amounts of NO_x that ozone formation is limited instead by the availability of VOCs and carbon monoxide, which are produced by plants and soil bacteria as well as vehicles and industrial processes.

As a result, it is well known that lowering emission levels can actually increase ozone concentrations at first; only if the reduction is large enough will ozone concentrations decrease. This effect probably lies behind observations that though emissions of ozone precursors have decreased significantly in Europe over the past decade or so (Volz-Thomas *et al.*, 2003), summertime surface ozone concentrations have remained stable. All this means that the reduction of NO_x and VOC emissions following the introduction of hydrogen vehicles could initially increase ozone levels in some areas. However, the reduced NO_x and VOC concentrations will bring their own health benefits, and ozone levels downwind of the

---

[2] Using electricity from coal fired power plants, for example, could increase CO2 emissions by a factor of 2-4. But, as long as efficient technology is employed we would not expect significant change in CO2 emissions in the coming decades.

city will fall. As a result, the damaging effects of ozone on crops and natural ecosystems will be reduced.

Simulations also show that drastic cuts in NO_x emissions are especially effective in reducing peak ozone concentrations and the number of days on which air quality standards are exceeded (Schultz *et al.*, 2003).

Thus there is little reason to doubt that the widespread use of hydrogen should bring significant improvements of air quality. This would only be untrue if coal-fired power stations with little emission control were used to produce the hydrogen (in particular in developing countries, e.g. China). In this case NO_x emissions might actually increase compared to today, with a further rise in tropospheric ozone concentrations.

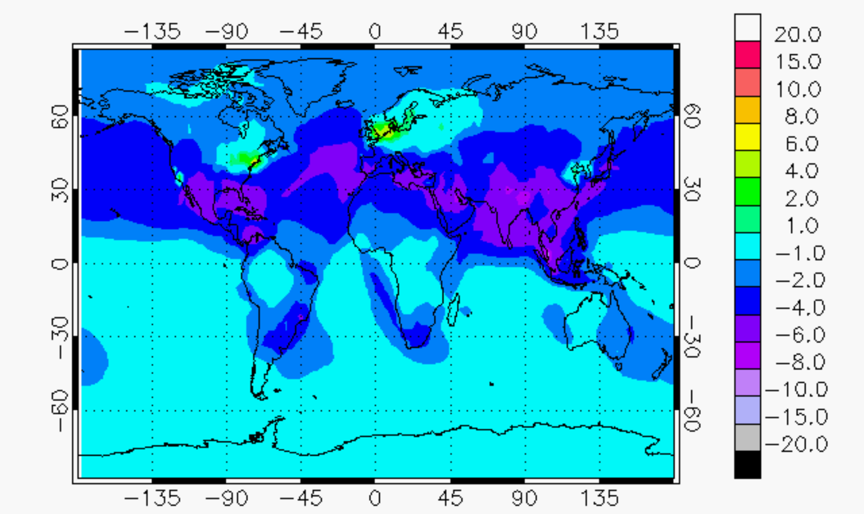


Figure 4: Simulated annual mean surface ozone change (in ppb) in a simple energy replacement scenario. In these simulations, it was assumed that 100% of today's global traffic is replaced by hydrogen vehicles, and that the hydrogen is produced entirely emission-free. A global average leak rate of 3% was assumed for the hydrogen energy chain (from Schultz et al., 2003).

Conclusions

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

- Hydrogen should not be produced using electricity generated by burning fossil fuels. Instead, natural gas or coal reformers should be used at first, and replaced by renewable energy sources as soon as possible. CO_2 capture from reformers should be seriously considered.
- Hydrogen should be used predominantly on the ground rather than in aircraft, and to achieve full benefits, fuel cells would be preferable against internal combustion engines.
- Leakage in the hydrogen energy chain should be limited to 1% wherever feasible, and global average leakage should not exceed 3%.
- Atmospheric hydrogen concentrations should be carefully monitored. Enough research should be carried out to obtain a better understanding of hydrogen sources and sinks, and to provide an early warning system in case we have overlooked something.

Further research related to hydrogen at the MPI-M will make use of the newly developed coupled chemistry climate models. Specific research questions of interest to our laboratory are:

- Analysis of current hydrogen budget and possible cause for insignificant trend (methane increase versus fossil fuel emission decrease)
- Implications of hydrogen economy for global air quality under different climate conditions
- Assess the potential of a future H_2 economy to slow down climate change

References

Hauglustaine, D. A., and D.H. Ehhalt, (2002). A three-dimensional model of molecular hydrogen in the troposphere, J. Geophys. Res. 107, 4330, doi:10.1029/2001JD001156.

IPCC, (2001). Climate Change – The Scientific Basis, Report from the working group I, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, (J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, C.A. Johnson, eds.), Cambridge University Press.

Novelli P. C., P.M. Lang, K.A. Masarie, D.F. Hurst, R. Myers, and J.W. Elkins, (1999). Molecular hydrogen in the troposphere: Global distribution and budget, Journal of Geophysical Research, 104 (D23), 30427-30444.

Schmidt, U., and T. Wetter, (2002). Tropospheric chemistry and composition: H2, in: Encyclopedia of Atmospheric Sciences, (J. Holton, J. Pyle, and J.A. Curry, eds.), Vol. 6, pp. 2397-2402, Academic Press.

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

Schultz, M.G., J. Feichter, and J. Leonardi, (2004). Climate Impact of Surface Traffic, in: R.E. Hester and R.M. Harrison (eds.), Issues in Environmental Science and Technology, Vol. 20, The Royal Society of Chemistry.

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

Volz-Thomas, A., M. Beekmann, D. Derwent, K. Law, A. Lindskog, A. Prevot, M. Roemer, M. Schultz, U. Schurath, S. Solberg, and A. Stohl, (2003). Tropospheric Ozone and its Control, Chapter 3 in: Towards Cleaner Air for Europe – Science, Tools and Applications, Part 1 from the EUROTRAC-2 Synthesis and Integration Project, Margraf Publishers, p. 73-122.

Warwick N. J., S. Bekki, E. G. Nisbet, J. A. Pyle (2004), 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.

WMO, (2003). Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project - report No. 47, Geneva.

Results from the Environmental Consequences from the CRYOPLANE Project

Christos S. Zerefos[1] **and K. Eleftheratos**[2]**,**
[1] **Laboratory of Climatology and Atmospheric Environment, University of Athens**
[2] **Foundation for Biomedical Research of the Academy of Athens**

Abstract

Based on a climate model parameterisation for the contrail global mean radiative forcing it was found that the global climate impact of line-shaped persistent contrails is probably smaller than the best estimate established by IPCC (1999). The best estimate for conventional air traffic is $9.8 \cdot 10^{-3}$ W/m^2 and $19.4 \cdot 10^{-3}$ W/m^2 for a typical 2015 and 2050 scenario, respectively.

A switch from conventional to cryoplane air traffic is likely to reduce the aircraft radiative forcing due to contrails by roughly 20% ($8.0 \cdot 10^{-3}$ W/m^2 and $13.9 \cdot 10^{-3}$ W/m^2 in the 2015 and 2050 simulations, respectively). The reason is the larger mean effective particle size in cryoplane contrails, leading to a reduction in emissivity and optical depth that overcompensates the effect of increasing cloud coverage for cryoplanes. The change of radiative forcing is quite different in different geographical regions.

Estimating the global mean climate impact change resulting from a realistic transition to cryoplane technology between 2015 and 2050 with a linear climate response model a typical value of about 25% reduction in radiative forcing at the 2050 time slice with tendency to increasing reduction thereafter will be shown.

A sensitivity analysis was performed, using a radiative transfer model, for the expected changes in the photolysis rates of ozone and nitrogen dioxide. These changes are perturbations in the radiative transfer, caused by contrails and cirrus clouds generated from the potential use of hydrogen as fuel by the aviation. First the model has been validated and then the results were compared to those, which correspond to contrails from conventional (kerosene-fuelled) aircraft.

For the same amount of total ozone the existence of a cirrus cloud and/or contrail at an altitude of 10-11 km introduces relative to the clear sky case a small increase of photolysis rates below the clouds/contrail and for the case of $J(O^1D)$ a decrease at the Earth's surface.

1. Introduction

The aircraft emissions of importance to the global mean climate impact of kerosene fuelled aircraft and cryoplanes are CO_2, NO_X (influencing ozone and methane in the atmosphere) and water vapour. New simulations with a 3D climate model using higher vertical resolution confirm that the linear dependence between ozone concentration increase and NOx emissions can still be used for estimates of global climate change between 2015 and 2050.
The tropopause radiative forcing estimates for aircraft related ozone and methane changes at the 2015 time horizon amount to 0.054 Wm^{-2} and -0.036 Wm^{-2}, respectively, for conventional air traffic, and to 0.005 Wm^{-2} and -0.004 Wm^{-2} for a minimum estimate of cryoplane air traffic, if it is assumed that the NO_X emissions from LH_2 engines are up to 90% smaller (Dahl 1999).

If the existence of higher climate sensitivity due to atmospheric ozone changes were confirmed, this would mean an even larger decrease of aircraft climate impact as a result of reduced gaseous emissions by a LH_2-fuelled air fleet.

Concerning the climate impact of gaseous water emissions this was found to be negligible in either case and it is unlikely that the enhanced water vapour emissions caused by a switch to the cryoplane technology will induce a substantial contribution to the total climate impact from these aircraft.

2. Effects of contrails on climate

Persistent contrails have been considered to be one of the most important contributors to the net climate impact of air traffic and the effect is quantified to grow by about 50% due to the mean contrail coverage increase in a cryoplane scenario. This would enhance the contrail radiative forcing accordingly. However, the microphysical properties of a cryoplane contrail are different. Microphysical simulations of two extreme cases (very warm, -47°C, and very cold, -62°C) were performed using the 2-D microphysical model MESOSCOP (Sausen 2001). They show that cryoplane contrails are optically thinner under the same ambient conditions, as less but larger particles form during the contrail development. They also show that a substantially reduced persistence of cryoplane contrails due to more efficient sedimentation of ice crystals is unlikely.

Representative numbers for the difference of radiative impact in the conventional and the cryoplane scenario have been obtained from three simulations performed with the 3D global climate model on the basis of an aircraft emission inventory for the 2015 time slice. It has been assumed that all air traffic in 2015 is operated either by kerosene or by LH_2 fuelled aircraft. For the conventional scenario the resulting global mean net radiative forcing is $9.8 \cdot 10^{-3}$ W/m^2. This value increases to $16.5 \cdot 10^{-3}$ W/m^2, if only the increase of contrail formation probability for cryoplanes is taken into account. However, if the changes in optical properties are also considered a radiative forcing of $8.0 \cdot 10^{-3}$ W/m^2, about 15% *smaller* than the reference value, is estimated for the cryoplane case.

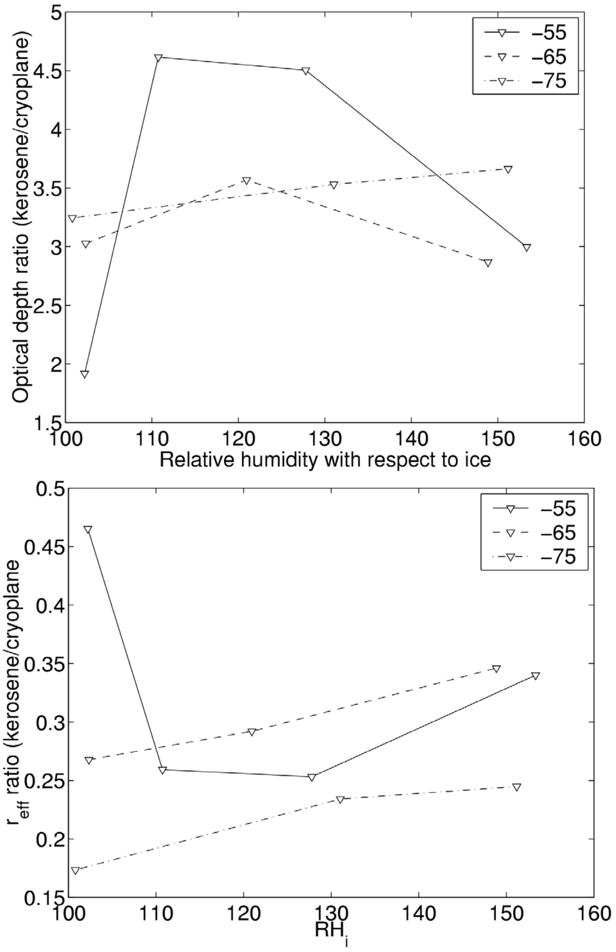


Figure 1: Ratio (kerosene/cryoplane) of optical depth (left) and mean effective crystal radius (right), respectively, calculated for each ambient condition parameter pair of temperature (-55°C; -65°C;-75°C) and humidity (adopted from Sausen and Ponater, 2001).

3. Effects of contrails and clouds upon UV-radiation and photochemistry

A sensitivity analysis was performed, using a radiative transfer model, for the expected changes in the photolysis rates of ozone and nitrogen dioxide. These changes are perturbations in the radiative transfer, caused by contrails and cirrus clouds generated from the potential use of hydrogen fuel by the aviation. First the model has been validated and then the results were compared to those, which correspond to contrails from conventional (kerosene-fuelled) aircraft.

Predicted from CTM models ozone changes for the year 2050 are responsible for the main perturbation (10% decrease) of $J(O^1D)$ but don't affect $J(NO_2)$.

For the same amount of total ozone the existence of a cirrus cloud and/or contrail at an altitude of 10-11km introduces relative to the clear sky case a small increase of photolysis rates below the clouds/contrail and for the case of $J(O^1D)$ a decrease at the Earth's surface.

The additional perturbations induced to the photolysis rates from contrails are larger for the kerosene contrails compared to the ones induced by LH_2 contrails, since they are expected to have smaller optical depths.

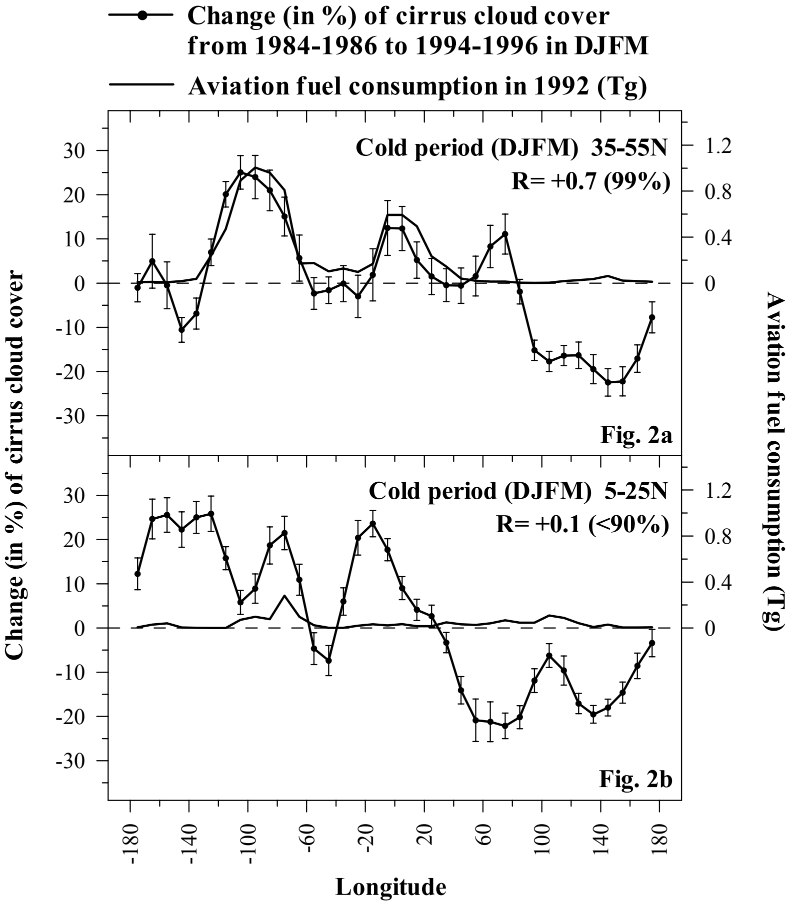


Figure 2: (a) Longitudinal distribution of the percentage changes of cirrus cloud cover and their standard errors from 1984-1986 to 1994-1996 and of the total fuel consumption in 1992 in the wintertime (DJFM), over heavy air traffic locations (35°N-55°N). (b) Same as (a) but for low air traffic locations (5°N-25°N). Values on the abscissa correspond to 36 equal regions of 10 degrees longitude, from west to east, in which cirrus cloud cover and fuel consumption have been averaged for the two latitudinal belts. R is the correlation coefficient between the two lines (adopted from Zerefos et al., 2003).

Cirrus cloud cover data for almost two decades (1984-1998) were analyzed using the ISCCP D2 data set (Zerefos 2003). Isolation of natural fluctuations in global cirrus cloud cover show that the longitudinal distribution of decadal changes in cirrus cloud cover along the latitude belt centered at the North Atlantic air corridor, parallels the spatial distribution of fuel consumption from highflying air traffic, providing an independent test of possible impact of aviation on contrail cirrus formation. The correlation between the fuel consumption and the longitudinal variability of cirrus cloud cover is significant (+0.7) over the middle latitudes (Figure 2a) but not over the tropics (Figure 2b). This could be explained by the fact that over the tropics the variability of cirrus cloud cover is dominated by dynamics while at middle latitudes microphysics explain most of its variability.

4. Simulation of regional effects of aviation

Local perturbations in NO_y. (reactive nitrogen compounds, including nitric acid) and ozone in the tropopause region over Scandinavia have been assessed along with their seasonal variation. For the same region the local effects of H_2O emissions have been assessed. For the perturbation studies the OSLO CTM-2 model (Gauss 2001) has been used, which has been thoroughly validated especially for the tropopause region.

Subsonic aviation in the year 2000 is found to have only little effect upon the stratosphere, but leads to significant increases in zonal-mean NO_y and ozone in the tropopause region of the Northern Hemisphere. The location and magnitude of maximum perturbations exhibit a distinct seasonal variation. Maximum absolute increases in ozone are modelled at about 11km. Over Scandinavia a clear seasonal dependence of the aircraft-induced ozone change is seen with maxima in May-June-July.

The lifetime of methane will decrease as a result of enhanced OH levels. It has been estimated on an annual basis that the lifetime of methane will decrease by 0.7% from the surface up to 300 hPa.

The increase in water vapour due to aircraft and the resulting radiative forcing has been calculated for the year 2015 for different types of aircraft and different assumptions on the tropospheric lifetime of aircraft-emitted water vapour, τH_2O. Due to cryoplanes maximum annual-mean perturbations are in the range 200 – 300 ppbv.

Despite the lower total water vapour emission, the scenario including supersonic (kerosene) aviation leads to a more pronounced effect on lower stratospheric water vapour, while subsonic kerosene aircraft have only a minor impact.

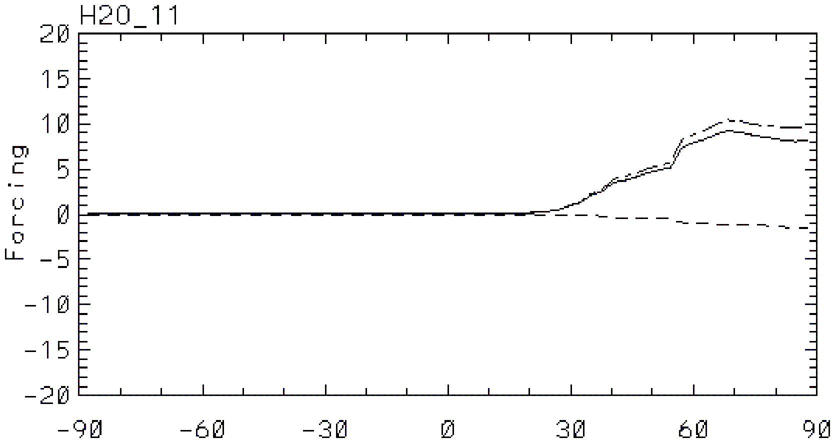


Figure 3: Zonal-mean radiative forcing for a cryoplane scenario in April 2015 [10^{-2} Wm^{-2}] over latitude. The dashed lines depict the short-wave radiative forcing, the dash-dotted lines

the long-wave radiative forcing, and the solid lines the total radiative forcing (adopted from Gauss et al., 2001).

Averaged over the considered seasons the global-mean radiative forcing is calculated to be in the range 0.0043 to 0.0065 Wm^{-2} for the cryoplane scenarios, where the tropospheric τH_2O is calculated from meteorological data. The corresponding value for subsonic kerosene aircraft is relatively small amounting to 0.0026 Wm^{-2}. The case including supersonic aircraft yields much larger radiative forcing near 0.05 Wm^{-2}, because the H_2O perturbation is larger and located at a higher altitude.

The main uncertainty of this study, not unlike other CTM studies of this type, lies in the estimation of the lifetime of aircraft-emitted H_2O in the troposphere, which may not represent the real removal of excess water vapour by the hydrologic cycle. However, even in the short lifetime case, significant water vapour perturbations are calculated.

5. Global effects of gaseous emissions and contrails

Based on a climate model parameterisation for the contrail global mean radiative forcing we have found that the global climate impact of line-shaped persistent contrails is probably smaller than the best estimate established by IPCC (1999). Our own best estimate for conventional air traffic is $9.8 \cdot 10^{-3}$ W/m^2 and $19.4 \cdot 10^{-3}$ W/m^2 for a typical 2015 and 2050 scenario, respectively.

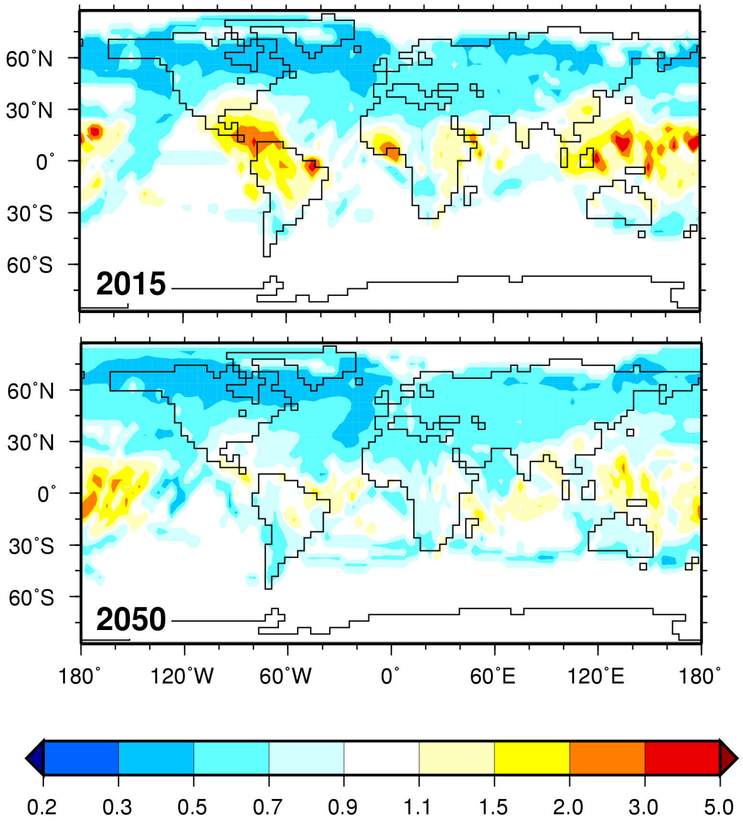


Figure 4: Ratio of the net radiative forcing of cryoplane contrails and the respective value for contrails from conventional aircraft (see Fig. 1). Top panel relates two scenarios for an air traffic density expected for year 2015; bottom panel relates two respective scenarios for 2050 (see text). Red (blue) areas indicate those regions, where cryoplanes cause a larger (smaller) contrail climate impact (adopted from Sausen and Ponater, 2002).

A switch from conventional to cryoplane air traffic is likely to reduce the aircraft climate impact (radiative forcing) due to contrails by roughly 20% ($8.0 \cdot 10^{-3}$ W/m^2 and $13.9 \cdot 10^{-3}$ W/m^2 in the 2015 and 2050 simulations, respectively). The reason is the larger mean effective particle size in cryoplane contrails, leading to a reduction in emissivity and optical depth that overcompensates the effect of increasing cloud coverage for cryoplanes. The change of radiative forcing is quite different in different geographical regions (Figure 4). If the size of ice particles in contrails were substantially lower than hitherto assumed, a qualitatively different assessment of the cryoplane contrail effect cannot be excluded. In the latter case, much will depend on the range of possible ice particle shapes in persistent contrails.

Our studies do not account for possible changes in the background climate up to 2050 (global warming). Also not yet included is the problem of a specific climate sensitivity (different from that of CO_2) for contrails. This possibility has to be studied by much more extensive climate model simulations than have been performed in CRYOPLANE.

Concerning radiative forcing contributions from ozone, methane, and stratospheric water vapour changes due to air traffic, there appears to be no need for a thorough revision of the key numbers documented in IPCC (1999) and in Marquart et al. (2001).

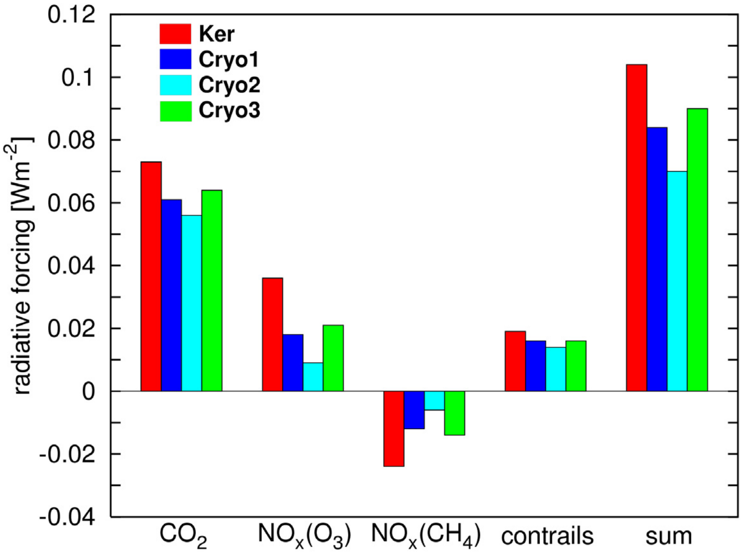


Figure 5: Radiative forcing (in W/m^2) of CO_2, NO_x (either due to ozone or methane changes), and contrails to be expected at year 2050 for a conventional aircraft increase scenario (Ker) and three different transition scenarios to cryoplanes (Cryo1/2/3). The respective best estimates for the various contributions are shown. The columns represent global mean values, as calculated by means of a linear response model. The rightmost panel shows the sum of all displayed components, not including further contributions from soot and sulphur aerosols as well as water vapour increases (adopted from Sausen and Ponater, 2002).

6. Conclusions

Estimating the global mean climate impact change resulting from a realistic transition to cryoplane technology between 2015 and 2050 with a linear climate response model, we determine a typical value of about 25% reduction in radiative forcing at the 2050 time slice with tendency to increasing reduction thereafter.

Depending on the speed of the transition to cryoplanes best estimates range between 16% and 29% climate impact reduction (*Figure 5*). Due to inherent scientific uncertainties with respect to the individual climate impact contributions of the various effects considered here (CO_2 and NO_x emissions, contrails), the respective uncertainty range widens to between 14% and 40% at 2050.

Further sources of potential importance (Contrail cirrus, CO_2 emitted during the production process) could not be quantified here, but can be included in the assessment as soon as the level of scientific understanding has improved.

References

Dahl, G.; Suttrop, F.; Engine control and low- NO_X combustion for hydrogen fuelled aircraft gas turbines, Int. J. Hydrogen Energy, **1999,** 23, 695-704.

Gauss, M.; Isaksen, I.; Wong, S.; Wang, W.-C.; TFR6-5 Simulation of regional effects of aviation, Liquid hydrogen fuelled aircraft – System analysis, 5th Framework program of the European Communities, Contract No. G4RD-CT-2000-00192, **2001**.

Intergovernmental Panel on Climate Change (IPCC), Aviation and the Global Atmosphere. *Cambridge University Press, Cambridge, UK*, **1999**.

Marquart, S.; Sausen, R.; Ponater, M.; Grewe, V.; Estimate of the climate impact of cryoplanes, Aerosp. Sci. Techn., **2001,** 5, 73-84.

Sausen, R.; Ponater, M.; TFR6-3 Effects of contrails on climate, Liquid hydrogen fuelled aircraft – System analysis, 5th Framework program of the European Communities, Contract No. G4RD-CT-2000-00192, **2001**.

Sausen, R.; Ponater, M.; TFR6-6 Global Effects of Gaseous Emissions and Contrails, Liquid hydrogen fuelled aircraft – System analysis, 5th Framework program of the European Communities, Contract No. G4RD-CT-2000-00192, **2002**.

Sausen, R.; Ponater, M.; TFR6-7 Global Mean Climate Response from Transition Scenarios, Liquid hydrogen fuelled aircraft – System analysis, 5th Framework program of the European Communities, Contract No. G4RD-CT-2000-00192, **2002**.

Zerefos, C.S.; Eleftheratos, K.; Balis, D.S.; Zanis, P.; Tselioudis, G.; Meleti, C; Evidence of impact of aviation on cirrus cloud formation, Atmos. Chem. Phys., **2003,** 3, 1633-1644.

Bibliography

2003/2004

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, L05107, doi:10.1029/2003GL019224.

Barnes, D.H., S.C. Wofsy, B.P. Fehlau, E.W. Gottlieb, J.W. Elkins, G.S. Dutton, and P.C. Novelli, (2003). Hydrogen In The Atmosphere: Observations Above A Forest Canopy In A Polluted Environment Journal Of Geophysical Research-Atmospheres, 108/D6.

Barreto, L., A. Makihira, and K. Riahi, (2003): The hydrogen economy in the 21st century: a sustainable development scenario. International Journal of Hydrogen Energy, 28 (3), 267-284.

Dong, Z., L. Wu, B. Kettlewell, C.D. Caldwell, and D.B. Layzell, (2003). Hydrogen Fertilization Of Soils - Is This A Benefit Of Legumes In Rotation?, Plant Cell And Environment, 26/11, 1875-1879.

King, G. M. (2003). Contributions of atmospheric CO and hydrogen uptake to microbial dynamics on recent Hawaiian volcanic deposits. Appl. Environ. Microbiol. 69: 4067-4075.

Prather, M.J., (2003). An Environmental Experiment with H_2?, Science, 302, 624-627.

Röckmann T., T. S. Rhee, A. Engel, (2003). Heavy hydrogen in the stratosphere. Atmospheric Chemistry and Physics, 3, 2015-2023.

Sanderson, M.G., W.J. Collins, R.G. Derwent, and C.E. Johnson, (2003). Simulation Of Global Hydrogen Levels Using A Lagrangian Three-Dimensional Model, Journal Of Atmospheric Chemistry, 46/1, 15-28.

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

Sonnemann, G.R., and U. Korner, (2003). Total Hydrogen Mixing Ratio Anomaly Around The Mesopause Region, Journal Of Geophysical Research-Atmospheres, 108/D22.

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

Venetsanos A.G., T. Huld, P. Adams, and J.G. Bartzis, (2003). Source, dispersion and combustion modeling of an accidental release of hydrogen in an urban environment, Journal of Hazardous Materials, A105, 1-25.

2002

Schmidt, U., and T. Wetter, (2002). Tropospheric chemistry and composition: H_2, in: Encyclopedia of Atmospheric Sciences, (J. Holton, J. Pyle, and J.A. Curry, eds.), Vol. 6, pp. 2397-2402, Academic Press.

Hauglustaine D. A., and D.H. Ehhalt, (2002). A three-dimensional model of molecular hydrogen in the troposphere, J. Geophys. Res. 107, 4330, doi:10.1029/2001JD001156.

2001

Gerst, S., and P. Quay, (2001). Deuterium Component Of The Global Molecular Hydrogen Cycle, Journal Of Geophysical Research-Atmospheres, 106/D5, 5021-5031.

Marquart, S., R. Sausen, M. Ponater, and V. Grewe, (2001). Estimate Of The Climate Impact Of Cryoplanes, Aerospace Science And Technology, 5/1, 73-84.

2000

Gödde, R., K. Meuser, and R. Conrad, (2000). Hydrogen Consumption And Carbon Monoxide Production In Soils With Different Properties, Biology And Fertility Of Soils, 32/2, 129-134.

Madamwar, D., N. Garg, and V. Shah, (2000). Cyanobacterial Hydrogen Production, World Journal Of Microbiology & Biotechnology, 16/8-9, 757-767.

Momoshima, N., H. Kakiuchi, T. Okai, S. Hisamatsu, and Y. Maeda, (2000). Tritium In A Pine Forest Ecosystem: Relation Between Fresh Pine Needles, Organic Materials On A Forest Floor And Atmosphere, Journal Of Radioanalytical And Nuclear Chemistry, 243/2, 479-482.

Gerst, S., and P. Quay, (2000). The Deuterium Content Of Atmospheric Molecular Hydrogen: Method And Initial Measurements, Journal Of Geophysical Research-Atmospheres, 105/D21, 26433-26445.

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, and L.E. Hudson, (2000). Continuous High-Frequency Observations Of Hydrogen At The Mace Head Baseline Atmospheric Monitoring Station Over The 1994-1998 Period, Journal Of Geophysical Research-Atmospheres, 105/D10, 12105-12121.

Yonemura, S., S. Kawashima, and H. Tsuruta, (2000a). Carbon monoxide, hydrogen, and methane uptake by soils in a temperate arable field and a forest, J. Geophys. Res. 105: 14347-14362.

Yonemura, S., M. Yokozawa, S. Kawashima, and H. Tsuruta, (2000b). Model analysis of the influence of gas diffusivity in soil on CO and H_2 uptake, Tellus 52B: 919-933.

1995-1999

Ehhalt, D.H., (1999). Gas phase chemistry of the troposphere. In: Baumgärtl, H., W. Grünbein, and F. Hensel (eds.): Global Aspects of Atmospheric Chemistry, Dr. Dietrich Steinkopf Verlag, Darmstadt, Germany, pp. 21-110.

Conrad, R., (1999). Soil microorganisms oxidizing atmospheric trace gases (CH_4, CO, H_2, NO), Ind. J. Microbiol., 39, 193-203.

Novelli P. C., P.M. Lang, K.A. Masarie, D.F. Hurst, R. Myers, and J.W. Elkins, (1999). Molecular hydrogen in the troposphere: Global distribution and budget, Journal of Geophysical Research, 104 (D23), 30427-30444.

Yonemura, S., S. Kawashima, and H. Tsuruta, (1999). Continuous measurement of CO and H_2 deposition velocities onto an andisol: uptake control by soil moisture. Tellus 51B, 688-700.

Francey, R.J., L.P. Steele, R.L. Langenfelds, C.E. Allison, L.N. Cooper, B.L. Dunse, B.G. Bell, T.D. Murray, H.S. Tait, L. Thompson, and K.A. Masarie, (1998). Atmospheric Carbon Dioxide and its Stable Isotope Ratios, Methane, Carbon Monoxide, Nitrous Oxide And Hydrogen from Shetland Isles, Atmospheric Environment, 32/19, 3331-3338.

Yokelson, R.J., R. Susott, D.E. Ward, J. Reardon, and D.W.T. Griffith, (1997). Emissions from Smoldering Combustion of Biomass Measured by Open-Path Fourier Transform Infrared Spectroscopy, Journal Of Geophysical Research-Atmospheres, 102/D15, 18865-18877.

Conrad, R., (1996). Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O, and NO), Microbiol. Rev., 60, 609-640.

Zittel, W., and M. Altmann, (1996). Molecular Hydrogen and Water Vapour Emissions in a Global Hydrogen Energy Economy, Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, June 1996. (Schön & Wetzel, Frankfurt am Main, Germany, 1996), pp. 71-82.

Conrad, R., (1995) Soil microbial processes involved in production and consumption of atmospheric trace gases, Adv. Microb. Ecol., 14, 207-250.

Conrad, R., (1995). Soil Microbial Processes And The Cycling Of Atmospheric Trace Gases, Mathematical Physical And Engineering Sciences, 351/1696, 219-230.

1990-1994

Conrad, R., (1994). Compensation concentration as critical variable for regulating the flux of trace gases between soil and atmosphere, Biogeochem., 27, 155-170.

Corazza, E., M. Montagnoli, and G. Tesi, (1994). Hydrogen and Carbon-Monoxide at Terra-Nova Bay (Antarctica), International Journal Of Environmental Analytical Chemistry, 55/1-4, 297-310.

Häring, V., and Conrad, R., (1994). Demonstration of 2 different H_2-oxidizing activities in soil using an H_2 consumption and a tritium exchange assay. Biol. Fertil. Soils, 17, 125-128.

Häring, V., H.D. Klüber, and R. Conrad, (1994). Localization of atmospheric H_2-oxidizing soil hydrogenases in different particle fractions of soil, Biol. Fertil. Soils, 18, 109-114.

W. Zittel, and M. Altmann, (1994). Der Einfluß von Wasserdampf auf das Klima, Energie 1994, 25-29.

Corazza, E., and G. Tesi, (1991). Carbon Oxides and Hydrogen in Antarctic Atmosphere, Annali di Chimica, 81/7-8, 439-451.

Schuler, S., and R. Conrad, (1991). Hydrogen Oxidation in Soil Following Rhizobial H_2 Production due to N_2 Fixation by a Vicia-Faba-Rhizobium-Leguminosarum Symbiosis, Biology and Fertility of Soils, 11/3, 190-195.

Schuler, S., and R. Conrad, (1991). Hydrogen oxidation activities in soil as influenced by pH, temperature, moisture, and season, Biol. Fertil. Soils, 12, 127-130.

Häring, V., and R. Conrad, (1991). Kinetics of H_2-Oxidation in Respiring and Denitrifying Paracoccus-Denitrificans, Fems Microbiology Letters, 78/2-3, 259-264.

Khalil, M.A.K., and R.A. Rasmussen, (1990). Global Increase of Atmospheric Molecular-Hydrogen, Nature, 347/6295, 743-745.

Schuler, S., and R. Conrad, (1990). Soils contain two different activities for oxidation of hydrogen, FEMS Microbiol. Ecol., 73, 77-84.

1985-1989

Conrad, R., (1988). Biogeochemistry and Ecophysiology of atmospheric CO and H_2, Adv. Microb. Ecol., 10, 231-283.

Schütz, H., R. Conrad, S. Goodwin, and W. Seiler, (1988). Emission of hydrogen from deep and shallow freshwater environments, Biogeochem., 5, 295-311.

Seiler, W., and R. Conrad, (1987). Contribution of tropical ecosystems to the global budget of trace gases, especially CH_4, H_2, CO, and N_2O. In: The Geophysiology of Amazonia: Vegetation and Climate Interactions, ed. by R.E. Dickerson, John Wiley, New York, pp. 33-62.

Conrad, R., and W. Seiler, (1985). Influence of temperature, moisture and organic carbon on the flux of H_2 and CO between soil and atmosphere. Field studies in subtropical regions, J. Geophys. Res., 90, 5699-5709.

1980-1984

Nass, H.U., and H.J. Fahr, (1984). Plasma-Gas Interactions in Planetary-Atmospheres and their Relevance for the Terrestrial Hydrogen Budget, Journal Of Geophysics-Zeitschrift für Geophysik, 56/1, 34-46.

Conrad, R., M. Aragno, and W. Seiler, (1983). The Inability of Hydrogen Bacteria to Utilize Atmospheric Hydrogen is due to Threshold and Affinity for Hydrogen, Fems Microbiology Letters, 18/3, 207-210.

Conrad, R., M. Weber, and W. Seiler, (1983). Kinetics and Electron-Transport of Soil Hydrogenases Catalyzing the Oxidation of Atmospheric Hydrogen, Soil Biology & Biochemistry, 15/2, 167-173.

Fallon, R. D., (1982). Molecular tritium uptake in Southeastern U.S. soils, Soil Biol. Biochem., 14, 553-556.

Zimmerman, P.R., J.P. Greenberg, S.O. Wandiga, and P.J. Crutzen, (1982). Termites - A Potentially Large Source of Atmospheric Methane, Carbon-Dioxide, and Molecular-Hydrogen, Science, 218/4572, 563-565.

Conrad, R., and W. Seiler, (1981). Decomposition of Atmospheric Hydrogen by Soil-Microorganisms and Soil Enzymes, Soil Biology & Biochemistry, 13/1, 43-49.

Conrad, R., and W. Seiler, (1980). Contribution of hydrogen production by biological nitrogen fixation to the global hydrogen budget, J. Geophys. Res., 85, 5493-5498.

Schmidt, U., and W. Seiler, (1980). Comments on Molecular-Hydrogen in the Near-Surface Atmosphere and Dissolved in Waters of the Tropical North-Atlantic, by Herr, F.L. and Barger, W.R., Journal of Geophysical Research-Oceans and Atmospheres, 85/NC4, 1959-1960.

Herr, F.L., W.R. Barger, and M.I. Scranton, (1980). Comments on Molecular-Hydrogen in the Near-Surface Atmosphere and Dissolved in Waters of the Tropical North-Atlantic, by Herr,F.L. and Barger, W.R. - Reply, Journal of Geophysical Research-Oceans and Atmospheres, 85/NC4, 1961-1962.

Scranton, M. I., W. R. Barger, and F. L. Herr, (1980). Molecular Hydrogen in the Urban Troposphere – Measurement of Seasonal Variability, Journal of Geophysical Research, 85, 5575-5580.

1975-1979

Schmidt, U., (1979). Solubility of Carbon-Monoxide and Hydrogen in Water and Sea-Water at Partial Pressures of about 10^{-5} Atmospheres, Tellus, 31/1, 68-74.

McFarlane, J. C., R.D. Rogers, and J. Bradley, (1978). Environmental Tritium Oxidation in Surface Soil, Environ. Sci. Technol., 12, 590-593.

Seiler, W., (1978). The influence of the biosphere on the atmospheric CO and H_2 cycles. In: Environmental Biogeochemistry and Geomicrobiology. Volume 3: Methods, Metals and Assessment, Krumbein, W. (ed.), Ann Arbor Science Publ., Ann Arbor, MI, 773-810.

Seiler, W., K.H. Liebl, W.T. Stöhr, and H. Zakosek, (1977). CO- und H_2-Abbau in Böden, Z. Pflanzenernähr. Bodenkd., 140, 257-272.

Liebl, K.H., and W. Seiler, (1976). CO and H_2 destruction at the soil surface, In Microbial Production and Utilization of Gases, Schlegel, H. G., Gottschalk, G., and Pfennig, N. (eds.), E. Goltze, Göttingen, 215-229.

Decker, P., (1975). Inverse Assimilation - Was Hydrogen Escape from Earths Primary Atmosphere Enhanced by H_2-Evolution Coupled with Biophotooxidation of Methane, Transactions-American Geophysical Union, 56/3, 176-176.

1970-1974

Liu, S.C., and T.M. Donahue, (1974). Realistic Model of Hydrogen Constituents in Lower Atmosphere and Escape Flux from Upper-Atmosphere, Journal of the Atmospheric Sciences, 31/8, 2238-2242.

Martin, J.D., and J.P. Hackett, (1974). Tritium in Atmospheric Hydrogen, Tellus, 26/5, 603-608.

Schmidt, U., (1974). Molecular-Hydrogen in Atmosphere, Tellus, 26/1-2, 78-90.

Liu, S.C. and T.M. Donahue, (1974). Aeronomy of Hydrogen in Atmosphere of Earth, Journal of the Atmospheric Sciences, 31/4, 1118-1136.

Friedman, I., and T.G. Scholz, (1974). Isotopic Composition of Atmospheric Hydrogen, 1967-1969, Journal Of Geophysical Research, 79/6, 785-788.

Martin, J.D., and J.P. Hackett, (1972). Tritium in Atmospheric Hydrogen, Transactions-American Geophysical Union, 53/11, 995ff.

Calvert, J.G., K.L. Demerjian, R.D. Mcquigg, and J.A. Kerr, (1972). Photolysis of Formaldehyde as a Hydrogen-Atom Source in Lower Atmosphere, Science, 175/4023, 751ff.

Venkates, S.V. , (1971). Escape of Hydrogen and Helium from Earths Atmosphere, Planetary and Space Science, 19/2, 275ff.

King, W.H., (1970). Monitoring of Hydrogen, Methane, and Hydrocarbons in Atmosphere, Environmental Science & Technology, 4/12, 1136ff.

Metzger, P.H., and M.A. Clark, (1970). Resonance Filter Spectroscopy of Earths Hydrogen Atmosphere, Transactions-American Geophysical Union, 51/11, 795ff.

Jones, R.A., E.C. Bruner, and W.A. Rense, (1970). Absorption Measurements of Earths Hydrogen Atmosphere from Solar Hydrogen Lyman Alpha Rocket Data, Journal of Geophysical Research, 75/10, 1849ff.

Schmidt, U., and W. Seiler, (1970). A New Method for Recording Molecular Hydrogen in Atmospheric Air, Journal of Geophysical Research, 75/9, 1713ff.

1965-1969

Fahr, H.J., (1969). Influence of Interstellar Matter on Density of Atmospheric Hydrogen, Annales de Geophysique, 25/2, 475ff.

King, W.H., (1969). Continuous Measurement of Hydrogen, Methane, and Hydrocarbons in Atmosphere, Abstracts of Papers of the American Chemical Society, SEP, WA47ff.

Begemann, F., and I. Friedman, (1968). Isotopic Composition of Atmospheric Hydrogen, Journal of Geophysical Research, 73/4, 1139ff.

Liwshitz, M., S.K. Lew, and S.V. Venkates, (1966). Comments on a Study of Hydrogen Diffusion in Earths Upper Atmosphere Near Critical Level, Journal of the Atmospheric Sciences, 23/6, 816ff.

Ehhalt, D.H., (1966). Tritium and Deuterium in Atmospheric Hydrogen, Tellus, 18/2-3, 249ff.

Gonsior, B., I. Friedman, and G. Lindenma, (1966). New Tritium and Deuterium Measurements in Atmospheric Hydrogen, Tellus, 18/2-3, 256ff.

Ehhalt, D.H., and A.E. Bainbrid, (1966). A Peak in Tritium Content of Atmospheric Hydrogen Following Accident at Windscale, Nature, 209/5026, 903ff.

Lew, S.K., and S.V. Venkates, (1965). A Study of Hydrogen Diffusion in Earths Upper Atmosphere Near Critical Level, Journal of the Atmospheric Sciences, 22/6, 623ff.

Bates, D.R., and M. Nicolet, (1965). Atmospheric Hydrogen, Planetary and Space Science, 13/9, 905ff.

before 1965

Bauer, S.J., (1964). Some Implications of Direct Measurement of Hydrogen and Helium Ion Distribution in Upper Atmosphere, Journal of Geophysical Research, 69/3, 553ff.

Begemann, F., (1963). Tritium Content of Atmospheric Hydrogen and Atmospheric Methane, Journal of Geophysical Research, 68/13, 3757ff.

Ehhalt, D., G. Israel, W. Stich, and W. Roether, (1963). Tritium and Deuterium Content of Atmospheric Hydrogen, Journal of Geophysical Research, 68/13, 3747ff.

Gonsior, B., I. Friedman, and D. Ehhalt, (1963). Measurements of Tritium and Deuterium Concentration in Atmospheric Hydrogen, Journal of Geophysical Research, 68/13, 3753ff.

Koyama, T., (1963). Gaseous Metabolism in Lake Sediments and Paddy Soils and Production of Atmospheric Methane and Hydrogen, Journal of Geophysical Research, 68/13, 3971ff.

Donahue, T.M., and G. Thomas, (1963). Distribution of Hydrogen in the Outer Atmosphere, Planetary and Space Science, 10, 65-72.

Bainbridge, A., I. Friedman, and H.E. Suess, (1961). Isotopic Composition of Atmospheric Hydrogen and Methane, Nature, 192/480, 648ff.

Bishop, K.F., B.T. Taylor, and A.E. Eggleton, (1961). Isotopic Composition of Atmospheric Hydrogen and Methane – Reply, Nature, 192/480, 649ff.

Wolfgang, R., (1961). Origin of High Tritum Content of Atmospheric Methane, Hydrogen and Stratospheric Water, Nature, 192/480, 1279ff.

Fireman, E.L., and F.S. Rowland, (1961). Additional Measurement of Tritium Content of Atmospheric Hydrogen of 1949, Journal of Geophysical Research, 66/12, 4321ff.

Bishop, K.F., and B.T. Taylor, (1960). Growth of the Tritium Content of Atmospheric Molecular Hydrogen, Nature, 185/4705, 26-27.

Begemann, F., and I. Friedman, (1959). Tritium and Deuterium Content of Atmospheric Hydrogen, Physikalische Chemie, 14/12, 1024-1031.

Butner, E.K., (1959). Dissipation of Hydrogen from the Atmospheres of Planets, Doklady Akademii Nauk SSSR, 124/1, 53-56.

Paneth, F. A., (1937). The Chemical Composition of the Atmosphere, Quart. J. Roy. Meteorol. Soc., 63, 433-438.

Annex A: Meeting Agenda

Strategic Discussion Meeting on Research Needs Concerning Environmental Impacts of a Hydrogen Economy

Max Planck Institute for Meteorology, Bundesstr. 53, Hamburg
Thursday, Dec. 16 – Friday, Dec. 17, 2004

Thursday, Dec. 16, 2004

12:00	Arrival (Sandwiches)
12:30	Welcome (J. Marotzke, MPI-M managing director)
12:40	Welcome address from a representative of the city of Hamburg (Staatsrat Dr. Salchow)
12:50	Welcome address from the German Hydrogen Society (O. Weinmann)
13:10	Introduction to HyCARE and review of meeting objectives (M. Schultz)
13:30	The European Hydrogen and Fuel Cell Platform (M. Altmann/W. Zittel)
13:50	Key results from the CONCAWE-EUCAR well-to-wheels analysis (H. Hass)
14:10	*Coffee Break*
14:40	**Session 1: Hydrogen in the Environment – Results and Research Needs Regarding Measurements and Modelling of the Present-Day Budget of Hydrogen** (10 minute overview presentations by) A. Engel, Uni Frankfurt M. Steinbacher, EMPA, Dübendorf T. Röckmann, MPI-K, Heidelberg W. Sturges, UEA, Norwich R. Conrad, MPI-MB, Marburg P. Ambus, Risø, Kopenhagen H. Schlünzen, Uni Hamburg H. Keller, PSI M. Kaufmann, FZ Jülich H. Schmidt, MPI-M, Hamburg T. Laurila, FMI, Helsinki F. Coutelieris, DEMOKRITOS
18:00	*Break – Preparation of a Summary*
18:30	Summary of Measurement Needs and Discussion
19:00	Summary of Modelling Needs and Discussion
19:30	Adjourn – bus transfer to the restaurant (Fischereihafen, Große Elbstr. 143)
20:15	*Dinner*

Friday, Dec. 17, 2004

08:30 **Session 2: Future Hydrogen Emissions (and Hydrogen-related Emission Changes), Scenario Development and Implications**
(10 minute overview presentations by)
W. Zittel, LBST, Munich
S. Berger, Adam Opel AG
M. Schwoon, Uni Hamburg
T. Pulles, TNO, Apeldoorn
N. Warwick, Uni Cambridge (presentation given by S. Bekki)
S. Bekki, Univ. Pierre et Marie Curie, Paris
F. Stordal, Uni Oslo
I. Isaksen, Uni Oslo
M. Schultz, MPI-M, Hamburg
(C. Zerefos, NKUA, Athens)

10:30 *Coffee Break – Preparation of a Summary*

11:00 Discussion on Scenario Needs and Modelling Strategy
11:30 Attempt to Summarize and Structure Research Needs, Identification of Funding Opportunities

12:30 *Lunch (Sandwiches)*

13:30 Adjourn

Annex B: List of Participants

Dr. Per Ambus
Plant Research Department
Risø National Laboratory
Frederiksborgvej 399, PO Box 49
DK-4000

Dr. Spiros Andronopolous
Environmental Research Lab.
Inst. of Nucelar Techn. and Radiation Protection
Nat. Center for Scientific Research Demokritos
GR-15310 Aghia Paraskevi Attikis

Dr. Slimane Bekki
Service d'Aéronomie du CNRS
Institut Pierre-Simon Laplace
Université Paris VI, B. 102, 4
Place Jussieu
F-75252 Paris, CEDEX 05

Dr. Stefan Berger
Hydrogen Storage and Technology
Fuel Cell Activities
IPC MK-01
Adam Opel AG
D-65423 Rüsselsheim

Prof. Dr. Ralf Conrad
Max Planck Institute for Terrestrial Microbiology
Karl-von-Frisch-Str.
D-35043 Marburg

Dr. Andreas Engel
Institut für Meteorologie und Geophysik
J.W. Goethe Universität Frankfurt
Georg-Voigt-Str. 14
D-60325 Frankfurt

Thomas Feck
Projekt Brennstoffzelle
Forschungszentrum Jülich
D-52425 Jülich

Samuel Hammer
Institut für Umweltphysik
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 229
D-69120 Heidelberg

Dr. Heinz Hass
Ford Forschungszentrum
Süsterfeldstr. 200
D-52072 Aachen

Prof. Dr. Ivar Isaksen
Department of Geophysics
University of Oslo
PO Box 1002
N-0315 Blindern, Oslo

Dr. Martin Kaufmann
Inst. für Chemie und Dynamik der Geosphäre I
Forschungszentrum Jülich
D-52425 Jülich

Dr. Johannes Keller
Laboratory for Atmospheric Chemistry
Paul Scherrer Institut, Building OFLA/012
CH-5232 Viligen

Dr. Gerhard Lammel
Institut für Chemie
Universität Hamburg
Bundesstr. 57
D-20146 Hamburg

Dr. Tuomas Laurila
Climate and Global Change Research
Finnish Meteorological Institute
Sahaajankatu 20E
FI-00880 Helsinki

Elke Meyer
Meteorologisches Institut, ZMK
Universität Hamburg
Bundesstr. 55
D-20146 Hamburg

Dr. Rolf Müller
Inst. für Chemie und Dynamik der Geosphäre I
Forschungszentrum Jülich
D-52425 Jülich

Dr. Tinus Pulles
MEP-TNO
Laan van Westenenk 501, PO Box 342
NL-7300 Apeldoorn

Dr. Martin Riese
Inst. für Chemie und Dynamik der Geosphäre I
Forschungszentrum Jülich
D-52425 Jülich

Dr. Thomas Röckmann
MPI für Kernphysik, Bereich Atmosphärenphysik
Saupfercheckweg 1
D-69117 Heidelberg

Prof. Dr. Heinke Schlünzen
Meteorologisches Institut, ZMK
Universität Hamburg
Bundesstr. 55
D-20146 Hamburg

Dr. Hauke Schmidt
Max Planck Institute for Meteorology
Bundesstr. 53
D-20146 Hamburg

Dr. Martin Schultz
Max Planck Institute for Meteorology
Bundesstr. 53
D-20146 Hamburg

Malte Schwoon
Research Unit Sustainability and Global Change
Centre for Marine and Atmospheric Sciences
Bundesstr. 55
D-20146 Hamburg

Dr. Martin Steinbacher
Air Pollution/Environmental Techn. Lab., LA027
Swiss Federal Institute for Materials Science
and Technology
Überlandstr. 129
CH-8600 Dübendorf

Dr. Frode Stordal
Department of Geophysics
University of Oslo
PO Box 1002
N-0315 Blindern, Oslo

Dr. William Sturges
Climate Research Unit
School of Environmental Sciences
University of East Anglia
Norwich Norfolk UK NR4 7TJ, UK

Dr. Oliver Weinmann
Vattenfall Europe AG
Chausseestr. 23
D-10115 Berlin

Prof. Dr. Christos Zerefos
Laboratory of Climatology and Atmospheric
Environment
Faculty of Geology
University of Athens
GR-15784 Athens

Dr. Werner Zittel
Ludwig-Bölkow Systemtechnik GmbH
Daimlerstrasse 15
85521 Ottobrunn

ISSN 1614-1199