Global Environmental Impacts of the Hydrogen Economy

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ABSTRACT
Hydrogen-based energy systems appear to be an attractive proposition in providing a future replacement for the current fossil-fuel based energy systems. Hydrogen appears attractive because it is a clean fuel and because it offers efficiency improvements when it is utilised. The transport sector may provide some of the first applications of the novel hydrogen technologies.
Hydrogen is an important, though little studied, trace component of the atmosphere. It is present at the mixing ratio of about 510 ppb currently and has important man-made and natural sources. It atmospheric lifetime is about 2.5 years and there is a global burden of about 180 Tg in the atmosphere.
Because hydrogen reacts with tropospheric hydroxyl radicals, emissions of hydrogen to the atmosphere perturb the distributions of methane and ozone, the second and third most important greenhouse gases after carbon dioxide. Hydrogen is therefore an indirect greenhouse gas with a global warming potential GWP of 5.8 over a 100-year time horizon. A future hydrogen economy would therefore have greenhouse consequences and would not be free from climate perturbations.
If a global hydrogen economy replaced the current fossil fuel-based energy system and exhibited a leakage rate of 1% then it would produce a climate impact of 0.6% of the current fossil fuel based system. If the leakage rate were 10%, then the climate impact would be 6% of the current system.
Careful attention must be given to reduce to a minimum the leakage of hydrogen from the synthesis, storage and utilisation of hydrogen in a future global hydrogen economy if the full climate benefits are to be realised in comparison to fossil fuel-based energy systems.

Keywords: hydrogen, greenhouse effect

1. INTRODUCTION

There is much current interest from scientists, engineers, industry and policy-makers in the role that hydrogen H_2 may play as a synthetic fuel and energy carrier in the future. Hydrogen is seen as having a particularly important future role in the transport sector. Basically, there are two ways to make a vehicle run on hydrogen: by using the hydrogen in an internal combustion engine or by using the hydrogen in a fuel cell. In the latter method, hydrogen is 'burnt' electrochemically in a fuel cell producing electricity which is then used to drive an electric motor generating the traction. The efficiency of the

conversion of chemical energy into mechanical energy is potentially far greater for the fuel cell vehicle compared with the modern internal combustion engined vehicle running on petrol. The combination of an overall efficiency improvement together with a dramatic reduction in pollutant emissions explains the attraction of hydrogen as a future vehicle technology.

Any future hydrogen economy will need to solve the challenging problems involved with the synthesis of hydrogen, its storage and distribution and utilisation in all of the sectors of the energy economy, transport included. Careful environmental assessments will be needed for all of the technologies that are to be employed at each step from synthesis through to utilisation to ensure that overall environmental pollution is minimised and that the full potential of hydrogen as a clean fuel is being realised.

Here we review current understanding of the fate and behaviour of hydrogen in the atmosphere and characterise its major sources and sinks. We show that hydrogen itself, in contrast to most expectations, is a greenhouse gas and we quantify its global warming potential relative to carbon dioxide. Then we go on to quantify the global warming consequences of replacing the current fossil-fuel based energy economy with one based on hydrogen. The conclusion reached is that unless the leakage of hydrogen from any future hydrogen economy is carefully controlled, there may be little improvement in global warming from the replacement of fossil fuel based energy systems.

2. OBSERVATIONS OF HYDROGEN IN THE ATMOSPHERE

Hydrogen H_2 is one of the major trace gases in the lower atmosphere or troposphere. The mean global mixing ratio of hydrogen is currently about 510 ppb, 500 ppb in the northern hemisphere and 520 ppb in the southern hemisphere (Simmonds et al. 2000). Hydrogen is somewhat unusual among trace gases in that, although its life cycle has been heavily influenced by human activities, its mixing ratios in the northern hemisphere are lower than those in the southern hemisphere. This phenomenon is caused by the main sink for hydrogen, surface uptake by soils, which accounts for 80% of the total loss of hydrogen from the atmosphere. The majority of the sink is therefore occurring over the continental land masses in the northern hemisphere.

Recent analyses of long-term observations of hydrogen in the troposphere indicate that mixing ratios have remained fairly constant during the last decade or so. For the northern hemisphere, a downwards trend of -2.7 ± 0.2 ppb per year has been reported between 1991 and 1996 (Novelli et al. 1999), a slight upwards trend of $+1.2 \pm 0.8$ ppb per year has been reported based on the continuous observations performed at the Mace Head, Ireland baseline station during 1994-1998, as part of the AGAGE programme (Simmonds et al. 2000). Hydrogen mixing ratios over the entire 1995-2004 period at Mace Head, Ireland have remained steady at close to 500 ppb and have kept within the range from 494 to 508 ppb, on an annual mean basis.

3. GLOBAL MODELLING OF HYDROGEN IN THE TROPOSPHERE

There have been several previous estimates of the global hydrogen budget. The first analysis (Schmidt 1974) estimated a global production rate of 23.9 Tg yr^{-1}, largely from human activities and a global sink strength of 17.5 Tg yr^{-1}, largely from:

$$OH + H_2 = H + H_2O \qquad\qquad (1).$$

Table 1. Globally-integrated sources and sinks for hydrogen.

	Seiler&Conrad	Warneck	Novelli et al	Sanderson et al

Sources and sinks in Tg yr^{-1}

Sources				
Man-made[a]	20	17	15	20
Biomass burning	20	19	16	20
Methane oxidation	15	20	26	15
Oxidation of organic compounds[b]	25	18	14	15
Oceans	4	4	3	4
N_2 fixation	3	3	3	4
Total sources	87	81	77	78
Sinks				
OH-oxidation	8	16	19	17
Soil uptake	90	70	56	58
Total sinks	98	86	75	74

Notes:
   a. hydrogen produced by fuel combustion.
   b. 1 Tg = 10^{12} g

A global box model has been used (Crutzen and Fishman 1977) to estimate the production of hydrogen from methane CH_4 oxidation, through the photolysis of formaldehyde HCHO:

$$OH + CH_4 = CH_3 + H_2O \qquad (2)$$
$$CH_3 + O_2 + M = CH_3O_2 + M \qquad (3)$$
$$CH_3O_2 + NO = CH_3O + NO_2 \qquad (4)$$
$$CH_3O + O_2 = HO_2 + HCHO \qquad (5)$$
$$HCHO + radiation = H_2 + CO \qquad (6)$$
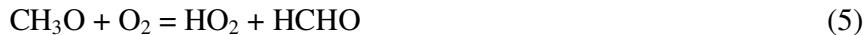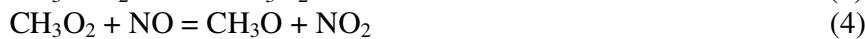
An additional sink for hydrogen was required to balance these early budgets and this is now known to be the uptake of hydrogen by soils (Schmidt 1974). Subsequently, global hydrogen budgets have been based on the oxidation rates of the primary emitted hydrocarbons and removal by OH-oxidation and uptake by soils (Novelli et al. 1999; Seiler and Conrad 1987; Warneck 1995).
A global Lagrangian three-dimensional chemistry transport model STOCHEM has been employed to represent the various sources and sinks of hydrogen in the current atmosphere (Sanderson et al. 2003). Global budgets are shown in Table 1. Hydrogen

therefore has both natural and man-made sources. Man-made sources include fossil fuel combustion, mainly from petrol-engined motor vehicles through the water gas reaction:

$$CO + H_2O = H_2 + CO_2 \qquad\qquad\qquad (7)$$

Biomass burning is another important source as a by-product of incomplete combustion. The surface ocean waters are generally supersaturated with hydrogen and so act as a small source (Schmidt 1974). Hydrogen is also formed as a by-product of nitrogen fixation in leguminous plants (Conrad and Seiler 1980), see Table 1.

Significant production of hydrogen also occurs from the oxidation of organic compounds together with methane, by hydroxyl radicals. All these compounds are degraded by OH-oxidation through to formaldehyde (Atkinson 2000) which undergoes photolysis to produce hydrogen (Calvert and Pitts 1967). The global Lagrangian modelling study using STOCHEM shows that the OH-oxidation of methane produces 15.2 Tg yr^{-1} of hydrogen and that of isoprene, 11.0 Tg yr^{-1} and other organic compounds account for a further 4.1 Tg yr^{-1}.

The main chemical sink for hydrogen in the troposphere in the global Lagrangian modelling study is the reaction with hydroxyl radicals in reaction 1 above. The largest source of hydroxyl radicals is the reaction of electronically excited oxygen atoms O^1D from the photolysis of ozone O_3, with water vapour H_2O:

$$O_3 + radiation = O^1D + O_2 \qquad\qquad\qquad (8)$$
$$O^1D + H_2O = OH + OH \qquad\qquad\qquad (9)$$
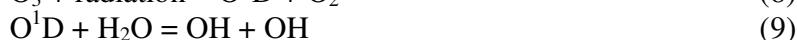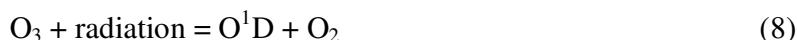
The main sink for hydroxyl radicals is its reaction with carbon monoxide CO:

$$OH + CO = H + CO_2 \qquad\qquad\qquad (10)$$

The other major sink for hydrogen is uptake by soils at the earth's surface. Soil uptake rates depend on the nature of the soils, the properties of each trace gas and the rate of transport of the trace gas through the atmospheric boundary layer by turbulence to the earth's surface. Field studies have indicated a dependence of the soil uptake of hydrogen on soil moisture content and on the ecosystem type growing on the soil (Conrad and Seiler 1985; Yonemura et al. 1999; Yonemura et al. 2000). Measured soil uptake rates, expressed as dry deposition velocities, range from 1.3 mm s^{-1} for savannah systems to 0.1 mm s^{-1} for semi-desert systems. Hydrogen is not removed by uptake on snow, ice, desert or water surfaces. Altogether, soil uptake provides a global sink strength of 58 Tg yr^{-1}, dominating over OH-oxidation by nearly a factor of four.

For an observed (Simmonds et al. 2000) global hydrogen burden of 182 Tg, the global sink strength of 74.4 Tg yr^{-1} from Table 1, implies an atmospheric lifetime of 2.5 years or thereabouts for hydrogen.

4. HYDROGEN AS A GREENHOUSE GAS

Any trace gas can be classified as a greenhouse gas if, when present in the atmosphere, it interacts with the incoming solar radiation or with the outgoing terrestrial radiation. Such trace gases are termed direct greenhouse gases or direct radiatively active gases. There is

an additional class of trace gases that are not themselves directly radiatively active but they act like radiatively active gases because their presence in the atmosphere perturbs the global distribution of the greenhouse gases. These additional classes of trace gases are termed indirect greenhouse gases or indirect radiatively active trace gases.

It is well recognised that the emissions of a number of short-lived tropospheric ozone precursor species exert a profound influence on the urban, regional and global distributions of ozone in the troposphere (Leighton 1961). These tropospheric ozone precursor species include nitrogen oxides (NO_x), methane (CH_4), organic compounds, hydrogen and carbon monoxide (CO). Each of these trace gases has important emission sources from human activities and from natural biospheric processes (Olivier et al. 1996). Since tropospheric ozone is the third most important greenhouse gas (IPCC 2001), it follows that an indirect greenhouse effect may be, in principle, associated with the emissions of each of these ozone precursor species because of their potential impact on the tropospheric ozone distribution (Derwent 1990). Hydrogen, like all of the ozone precursors, may potentially be an indirect greenhouse gas because its emissions may influence the tropospheric distribution of ozone.

In addition to controlling tropospheric ozone production and destruction, the ozone precursor species also control the tropospheric distribution of hydroxyl radicals (Levy 1971) and hence the oxidising capacity of the troposphere. The tropospheric distribution of hydroxyl radicals in turn controls the lifetime and hence global scale build-up of methane (Ehhalt 1974), the second most important greenhouse gas after carbon dioxide (IPCC 2001). There is therefore the potential for the emissions of the ozone precursor gases to alter the tropospheric distribution of hydroxyl radicals and perturb the global scale build-up of methane (Isaksen and Hov 1987). Again, hydrogen, like all of the ozone precursors, may potentially be an indirect greenhouse gas because its emissions may influence the tropospheric distribution of methane.

The importance of hydrogen as a greenhouse gas was quantified (Derwent et al. 2001) using the global Lagrangian chemistry transport model STOCHEM. The model was started from an initial set of trace gas concentrations in October 1994 and using analysed wind fields to run the model through to 1st January 1995. At that point, two model experiments were initiated. The first model experiment continued on without change until 31st December 1998 and this formed the base case. In the second model experiment, the transient case, the hydrogen emission source strength was increased so that a pulse containing an additional 40 Tg of hydrogen was emitted into the model by the 31st January 1995. At this point, the hydrogen emission was reset to the base case value and the model experiment was continued until 31st December 1998. The impacts of the additional hydrogen on the composition of the model troposphere were followed by taking differences between the base and transient cases. These differences in composition between the two experiments were termed 'excess' concentrations. There was no particular significance to the size chosen for the emission pulse and it was given the same spatial distribution as that given to the man-made sources.

A diagrammatic representation of the base and transient case experiments is given in Figure 1 which follows the impact of an emission pulse of hydrogen on the composition of the model troposphere. Figure 1a presents the globally-integrated hydrogen emissions over the four year's experiment, showing the emission pulse of hydrogen during January 1995. The effect of the additional hydrogen emissions is to raise the hydrogen burden in
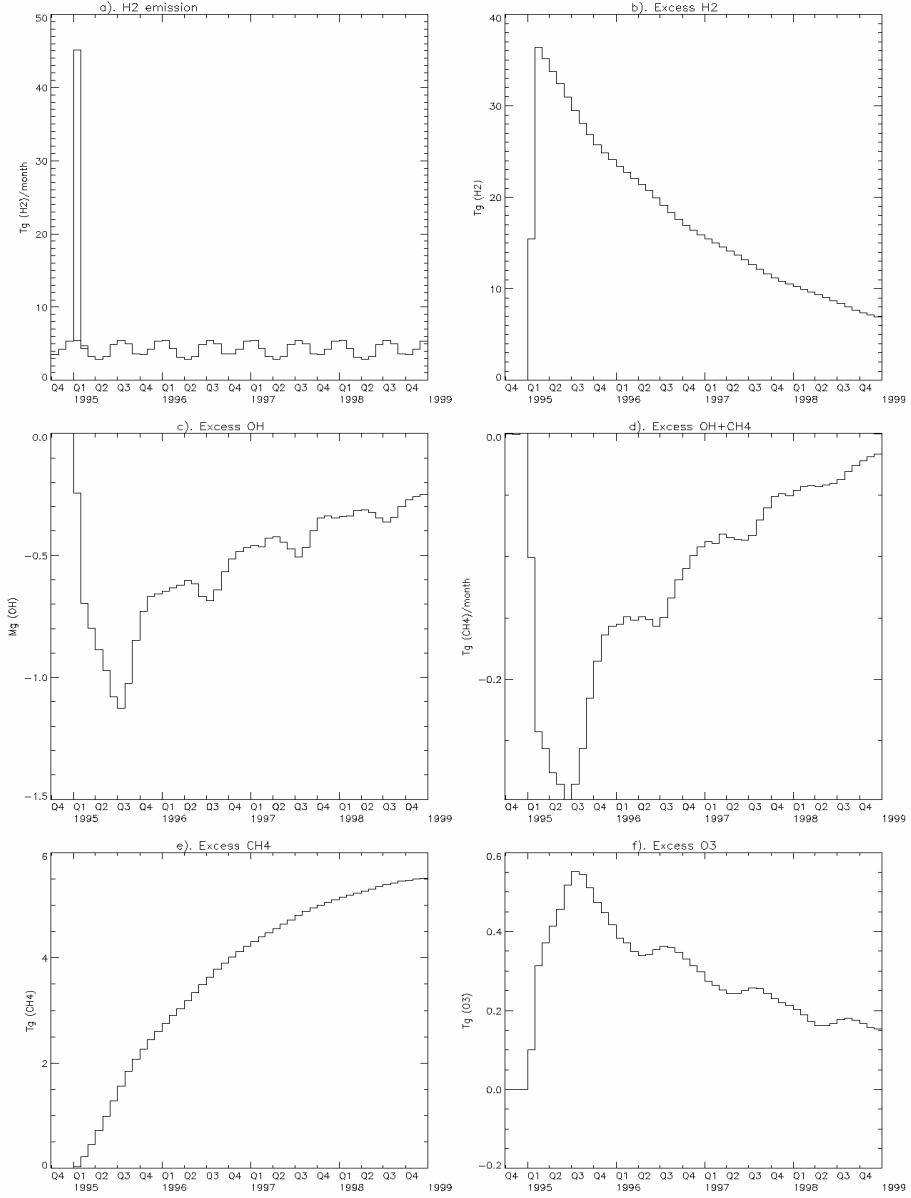
Figure 1. The time development in the composition of the global Lagrangian model troposphere following the emission of a 40 Tg pulse of hydrogen, showing in a). the global hydrogen emissions, b). 'excess' H_2 burden, c). 'excess' OH burden, d). 'excess' OH + CH_4 reaction flux, e). 'excess' CH_4 burden, and f). 'excess' O_3 burden.

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the transient experiment relative to the base case, generating an 'excess' hydrogen burden which is plotted out in Figure 1b. This 'excess' hydrogen decays away with an e-folding time of about 2 years which is close to the atmospheric lifetime of hydrogen.

Because of the increased hydrogen burden in the transient experiment, a decrease is created in the OH burden which appears as a negative 'excess' in the OH burden, see Figure 1c, through the OH + H_2 reaction. Again, the 'excess' OH burden decays away with the same e-folding time constant as the 'excess' hydrogen, close to 2 years. The reduced OH burden in the transient experiment, in turn, leads to a decrease in the OH + CH_4 reaction flux, see Figure 1d and the development of a small systematic difference in the globally-integrated methane loss rate from the base case. The time development of the 'excess' OH + CH_4 reaction flux follows that shown by the 'excess' OH, decaying away with an e-folding time of just under 2 years. Since the OH + CH_4 reaction is the major loss process for methane, the hydrogen emission pulse leads to slightly different methane loss rates in the two model experiments and the methane burdens begin to diverge with time. The time development of the 'excess' methane burden resulting from the emission pulse of hydrogen is shown in Figure 1e. The 'excess' methane burden took about 4 years to reach its maximum before decaying away with the time constant associated with the methane adjustment time of about 12 years.

As a result of the increase in the atmospheric burden of hydrogen following the emission pulse, adjustments followed on in the concentrations of all the major tropospheric free radical species and ultimately in tropospheric ozone. Figure 1f shows that ozone production was stimulated in the transient case and that an 'excess' ozone burden quickly developed following the emission pulse. The 'excess' ozone burden decayed away with an e-folding time of about 2.5 years, close to the atmospheric lifetime of hydrogen.

Using the literature radiative forcing formulae (IPCC 1990), the time-integrated 'excess' methane burdens in Figure 1e were converted into time-integrated radiative forcing, over a 100-year time horizon. The 1 Tg hydrogen emission pulse produced a time-integrated methane radiative forcing of 0.35 mW m^{-2} year over a 100-year time horizon. The radiative forcing consequences of the tropospheric ozone burden changes were evaluated using an appropriate radiation code (Edwards and Slingo 1996). The 1 Tg emission pulse produced a time-integrated ozone radiative forcing of 0.25 mW m^{-2} year over a 100-year time horizon.

These time-integrated radiative forcings were converted into Global Warming Potentials GWPs by comparison with the time-integrated radiative forcing of a reference gas, usually taken to be carbon dioxide, CO_2. Here we define the Global Warming Potential of hydrogen as the ratio of the time-integrated radiative forcing for a particular radiative forcing mechanism (whether through methane or ozone changes) resulting from the emission of 1 Tg of hydrogen compared with that from the emission of 1 Tg of CO_2 over a 100-year time horizon. The fate of a 1 Tg emission pulse of CO_2 was described using the CO_2 response function of the Bern carbon cycle model (IPCC 1996). On this basis, the GWP^{CH_4} and GWP^{O_3} for hydrogen were found to be 3.4 and 2.4, respectively, over a 100 year time horizon. The overall GWP for hydrogen is therefore 5.8 over a 100-year time horizon.

As a consequence of the emission of hydrogen to the troposphere, changes occur in the global distributions of methane and ozone (Derwent et al. 2001), the second and third most important greenhouse gases. Emissions of hydrogen lead to increased burdens of

methane and ozone and hence to an increase in global radiative forcing. Hydrogen is accordingly an indirect radiatively active trace gas with a global warming potential of 5.8 over a 100-year time horizon.

5. GREENHOUSE GAS CONSEQUENCES OF A GLOBAL HYDROGEN ECONOMY

The emission of hydrogen to the troposphere leads to changes in the global distributions of methane and ozone, leading to increased radiative forcing. This prompts the questions whether a global hydrogen economy would have consequences for global warming and ultimately whether a hydrogen economy would be better or worse than the fossil-fuel economy that it replaces.

It is estimated that the global hydrogen production capacity required to replace the entire current fossil-fuel based energy system would need to be of the order of about 2500 Tg H_2 yr^{-1}. If there was a leakage rate of the order of say 1%, then the global hydrogen economy would emit about 25 Tg H_2 yr^{-1}. Using the GWP of 5.8 described in Chapter 3 above, the global hydrogen economy would have the radiative forcing equivalent to 25 * 5.8 Tg CO_2 yr^{-1}, that is to say about 150 Tg CO_2 yr^{-1}. The fossil fuel system it would replace has a CO_2 emission of 23,000 Tg CO_2 yr^{-1}. On this basis, the global hydrogen economy with a leakage rate of 1% has a climate impact of 0.6% of the fossil fuel system it replaces. If the leakage rate was 10%, then the climate impact would be 6% of that of the fossil fuel system.

6. CONCLUSIONS

Hydrogen-based energy systems appear to be an attractive proposition in providing a future replacement for the current fossil-fuel based energy systems. Hydrogen appears attractive because it is a clean fuel and because it offers efficiency improvements when it is utilised. The transport sector may provide some of the first applications of the novel hydrogen technologies.

Because hydrogen reacts with tropospheric hydroxyl radicals, emissions of hydrogen to the atmosphere perturb the distributions of methane and ozone, the second and third most important greenhouse gases after carbon dioxide. Hydrogen is therefore an indirect greenhouse gas with a global warming potential GWP of 5.8 over a 100-year time horizon. A future hydrogen economy would therefore have greenhouse consequences and would not the free from climate perturbations. If a global hydrogen economy replaced the current fossil fuel-based energy system and exhibited a leakage rate of 1% then it would produce a climate impact of 0.6% of the current fossil fuel based system. If the leakage rate were 10%, then the climate impact would be 6% of the current system. Careful attention must be given to reduce to a minimum the leakage of hydrogen from the synthesis, storage and utilisation of hydrogen in a future global hydrogen economy if the full climate benefits are to be realised in comparison to fossil fuel-based energy systems.

7. ACKNOWLEDGEMENTS

References

Atkinson, R.,: Atmospheric chemistry of VOCs and NO_x, Atmos. Environ., **34**, (2000), 2063-2101.

Calvert, J.G., Pitts, J.N.,: in "Photochemistry, Wiley, New York, (1967).

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

Conrad, R., Seiler, W., : 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**, (1985), 5699-5709.

Crutzen, P.J., Fishman, J.,: Average concentrations of OH in the troposphere, and the budgets of CH_4, CO, H_2 and CH_3CCl_3, Geophys. Res. Letters, **4**, (1977), 321-324.

Derwent, R.G.,: Trace gases and their relative contribution to the greenhouse effect, AERE Report R-13716. H.M. Stationery Office, London, (1990).

Derwent, R.G., Collins, W.J., Johnson, C.E., Stevenson, D.S.,: Transient behaviour of tropospheric ozone precursors in a global 3-D CTM and their indirect greenhouse effects, Climatic Change, **49**, (2001), 463-487.

Edwards, J.M., Slingo, A..,:Studies with a flexible new radiation code: I. Choosing a configuration for a large-scale model, Q. J. R. Meteorol. Soc., **122**, (1996), 689-719.

Ehhalt, D.H.,: The atmospheric cycle of methane, Tellus, **26**, (1974), 58-70.

IPCC.,: Climate Change : The IPCC Scientific Assessment, Eds. J.T. Houghton et al., Cambridge University Press, Cambridge, (1990).

IPCC,:Climate Change 1995: The IPCC Scientific Assessment, Eds. J.T. Houghton et al., Cambridge University Press, Cambridge, (1996).

IPCC.,: Climate Change 2001: The Scientific Basis, Eds. J.T. Houghton et al., Cambridge University Press, Cambridge, (2001).

Isaksen, I.S.A., Hov, O.,: Calculation of trends in the tropospheric concentrations of O3, OH, CO, CH_4 and NO_x, Tellus, **33B**, (1987), 271-283.

Leighton, P.A.,: in "Photochemistry of Air Pollution", Academic Press, New York, (1961).

Levy, H.,: Normal atmosphere: Large radical and formaldehyde concentrations predicted, Science, **173**, (1971), 141-143.

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

Olivier, J.G.J., Bouwman, A.F., van der Maas, C.W.M., Berdowski, J.J.M., Veldt, C., J.P.J., Bloos, Visschedijk, A.J.H., Zandveld, P.Y.J., Haverlag, J.L.,: Description of EDGAR version 2.0, RIVM Report nr. 771060 002, Bilthoven, Netherlands, (1996).

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

Schmidt, U.,: Molecular hydrogen in the atmosphere, Tellus, **26**, (1974), 78-90.

Seiler, W., Conrad, R.,: Contribution of tropical ecosystems to the global budgets of trace gases, especially CH_4, H_2, CO and N_2O. in "The Geophysiology of Amazonia", ed. R.E. Dickinson, John Wiley and Sons, New York, (1987).

Simmonds, P.G., Derwent, R.G., O'Doherty, S., Ryall, D.B., Steele, L.P., Langenfelds, R.L., Salameh, P., Wang, H.J., Dimmer, C.H., Hudson, L.E.,: Continuous high-frequency observations of hydrogen at the Mace Head baseline atmospheric monitoring station over the 1994-1998 period, J. Geophys. Res., **105**, (2000), 12,105-12,121.

Warneck, P.,: in "Chemistry of the Natural Atmosphere", International Geophysics Series, **71**, Academic Press, New York, (1995).

Yonemura, S., Kawashima, S., Tsuruta, H.,: Continuous measurement of CO and H2 deposition velocities onto an andisol: Uptake control by soil moisture, Tellus, **51B**, (1999), 688-700.

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