



Simulation of Global Hydrogen Levels Using a Lagrangian Three-Dimensional Model

M. G. SANDERSON, W. J. COLLINS, R. G. DERWENT and C. E. JOHNSON

*Climate Research, Met Office, London road, Bracknell, Berkshire, RG12 2SZ, U.K.,
e-mail: michael.sanderson@metoffice.com*

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Abstract. Many previous assessments of the global hydrogen budget have used assumed global averages of temperatures and levels of key reactants to calculate the magnitudes of the various sinks. Dry deposition is by far the largest hydrogen sink but has not been considered in detail in previous estimates of the hydrogen budget. Simulations of hydrogen using a global three-dimensional Lagrangian chemistry-transport model and two different dry deposition schemes were compared with surface measurements. An improved dry deposition scheme which included the effects of soil moisture gave better agreement between the modelled hydrogen levels and surface measurements. The seasonal variation in the hydrogen levels was also simulated much more accurately with the new dry deposition scheme. The model results at high southern latitudes were insensitive to the relative partitioning of the sources between fossil fuel combustion and biomass burning. The results indicate a global mean hydrogen dry deposition velocity of $5.3 \times 10^{-4} \text{ m s}^{-1}$ which is lower than the previously used $7 \times 10^{-4} \text{ m s}^{-1}$.

Key words: biomass burning, chemistry-transport model, dry deposition, hydrogen, soil moisture.

1. Introduction

Hydrogen (H_2) is one of the major tropospheric trace gases, but has received relatively little attention in recent years. It has a minor effect on the levels of the hydroxyl radical (OH) and hence on methane (Derwent *et al.*, 2001), but in the stratosphere it controls the water budget along with methane and transport of water vapour from the troposphere. The mean concentration of hydrogen in the troposphere is about 520 ppbv (Simmonds *et al.*, 2000). Hydrogen is relatively unusual among atmospheric trace gases in that although its life cycle has been heavily influenced by human activities, its concentrations in the northern hemisphere are lower than those in the southern hemisphere. This phenomenon is due to the fact that the main sink for hydrogen is uptake by soils, which accounts for about 80% of the total loss. Recent analyses of long-term measurements of hydrogen indicate that the levels have remained fairly constant during the middle of the 1990s. For the northern hemisphere, Novelli *et al.* (1999) obtained a downward trend of -2.7 ± 0.2 ppbv yr^{-1} between 1991 and 1996 using data from the NOAA/CMDL co-operative air sampling network, whereas Simmonds *et al.* (2000) inferred a slight upward

trend of 1.2 ± 0.8 ppbv yr^{-1} from measurements performed under the AGAGE experiment at Mace Head for the period 1994–1998.

There have been several previous estimates of the global hydrogen budget. Using various measurements of hydrogen concentrations and loss rates, Schmidt (1974) estimated a global production rate of 23.9 Tg yr^{-1} , and a global sink of 17.5 Tg yr^{-1} . Crutzen and Fishman (1977) performed the first modelling study on tropospheric hydrogen levels. They used a simple box model and considered the photochemistry of methane and formaldehyde to estimate the production and loss rates of hydrogen. An additional sink of hydrogen was required to balance their budget, which is now known to be the uptake of hydrogen by soils identified by Schmidt (1974). Seiler and Conrad (1987), Novelli *et al.* (1999) and Warneck (1999) have estimated the global hydrogen budget using simple calculations based on the oxidation rates of the primary hydrocarbons and assumed yields of formaldehyde and in turn hydrogen. However, none of these authors have considered the dry deposition term in detail. The hydrogen dry deposition velocity has been shown to be strongly dependent on soil moisture (Conrad and Seiler, 1985; Yonemura *et al.*, 1999, 2000). In this paper, we employ a global three-dimensional chemistry-transport model to represent the various sources and sinks of hydrogen. Two different dry deposition schemes are employed. The original approach uses a fixed value over all land surfaces. The second considers various ecosystems and the effects of soil moisture on the dry deposition velocity. Given that soil uptake represents about 80% of the total hydrogen sink, it is important to represent this process as accurately as possible. The main focus of this paper is therefore on dry deposition of hydrogen, and the effect of the new scheme on the modelled seasonal variation in the hydrogen concentrations. The model predictions are compared with surface measurements, and the magnitude of the hydrogen sources and sinks are calculated. The production of hydrogen from the tropospheric oxidation of each primary emitted hydrocarbon is also given.

2. Model Description

The model used for this work is the Met Office chemistry-transport model STOCHEM which has been described in detail elsewhere (Collins *et al.*, 2000, and references therein), so only a brief description is given here. In STOCHEM a Lagrangian approach is used where the atmosphere between the surface and a pressure of 100 hPa is divided into 50,000 air parcels which are advected with a three hour timestep. STOCHEM itself uses a horizontal resolution of $5^\circ \times 5^\circ$ with nine levels in the vertical. STOCHEM is fully coupled to the Hadley Centre climate model HadCM3 (Gordon *et al.*, 2000) which has a resolution of $3.75^\circ \times 2.5^\circ$ and 19 vertical levels. At each coupling step, fields of winds, temperature, specific humidity, surface data and many other data are passed to STOCHEM. The initial meteorological conditions were taken from a general climatology suitable for the 1990s, generated as part of a long integration of HadCM3.

STOCHEM uses an explicit description of the fast photochemistry in the troposphere and the reactions of free radicals which initiate the removal of the tropospheric source gases. The chemical scheme used in the present work incorporates the chemistry of nitrogen oxides, ozone, methane, isoprene, other hydrocarbons and a number of organic hydroperoxides. It was reduced to 50 chemical species by removing the sulphur compounds and the aromatic hydrocarbon chemistry to reduce the execution time. A complete listing of rate coefficient, absorption cross-section and quantum yield data is given elsewhere (Collins *et al.*, 2000). Anthropogenic emission estimates were in accordance with the A2 scenario from the IPCC Special Report on Emission Scenarios (IPCC, 2000) for the years 1994–1995.

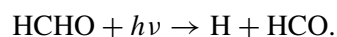
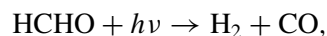
The surface energy balance in HadCM3 is calculated by the Met Office Surface Exchange Scheme, MOSES (Cox *et al.*, 1999). In the current version of MOSES, the subgrid land surface heterogeneity is treated explicitly by dividing the surface of the bottom model grid boxes into a maximum of nine different types of which five are covered with vegetation (Essery *et al.*, 2001). The nine surface types are broadleaf trees, needleleaf trees, C₃ grass, C₄ grass, shrubs, urban, bare soil, water and ice. C₃ and C₄ grasses generally occur in temperate and tropical regions, respectively. Shrubs occur mostly in semi-desert, steppe and tundra regions. Separate surface temperatures and fluxes of radiation, moisture, snow cover etc. are calculated for each surface type within a model grid box at every model timestep. Appropriate data are passed to STOCHEM every 3 hours for use in calculating dry deposition velocities (see Section 4).

3. Sources of Hydrogen

Hydrogen has both anthropogenic and natural sources. Anthropogenic sources include combustion of fossil fuels (Novelli *et al.*, 1999; Simmonds *et al.*, 2000) and biomass burning, where a small amount of hydrogen is produced directly as a by-product of incomplete combustion. These two sources were assumed to have magnitudes of 20 Tg yr⁻¹ each (Seiler and Conrad, 1987). The surface ocean waters are generally supersaturated with hydrogen (Schmidt, 1974), and so represent a small source. Hydrogen is also formed as a by-product from the fixation of nitrogen in leguminous plants (Conrad and Seiler, 1980). Each of these sources produces 4 Tg yr⁻¹. The anthropogenic emissions are input at a constant rate, and all the others vary seasonally. Biomass burning emissions are distributed using monthly fields from Cooke and Wilson (1996). Emissions from nitrogen fixation and the oceans vary according to monthly fields of non-methane VOC emissions from Guenther *et al.* (1995). Hydrogen in the surface ocean waters most likely comes from bacteria, and emission from this source will vary with season and nutrient concentration (Schmidt, 1974).

Hydrogen is emitted directly by the sources described above. Significant production of hydrogen also occurs from the oxidation of volatile organic compounds

(VOCs). As these compounds are degraded, they produce formaldehyde (Atkinson, 2000), which in turn undergoes photolysis. There are two photolysis routes, one of which gives molecular hydrogen (Ravishankara, 1988)



Previous studies indicate that oxidation of methane and isoprene will make the biggest contributions (Seiler and Conrad, 1987; Novelli *et al.*, 1999; Warneck, 1999). A small amount of hydrogen is formed directly from the reaction of ozone with certain alkenes (Horie and Moortgat, 1991). Volcanoes emit hydrogen but the amount is small; Warneck (1999) estimates 0.2 Tg yr^{-1} . The volcanic source has not been included in the present study.

Measurements of hydrogen in the free troposphere and lower stratosphere indicate that there is no vertical gradient in the hydrogen concentrations (Schmidt, 1974; Zöger *et al.*, 1999; Warneck, 1999; and references therein), demonstrating that any flux of hydrogen between the stratosphere and the troposphere must be negligible (Warneck, 1999). Other measurements of hydrogen concentrations in the lower stratosphere indicate that they are essentially the same as those in the troposphere (Elkins *et al.*, 1996).

4. Sinks of Hydrogen

The only known chemical sink of hydrogen in the troposphere is the slow reaction with hydroxyl radicals: $\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$, $k = 6.7 \times 10^{-15} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson *et al.*, 2000). Hydroxyl radical concentrations are calculated directly by STOCHEM. The largest source is the reaction of excited-state oxygen atoms with water vapour, the former being produced from the photolysis of ozone. Globally, the main sink for hydroxyl radicals is their reaction with methane and carbon monoxide, but reactions with other gases such as isoprene are also important. In another simulation over the time period 1997–1998, the decline in methyl chloroform was followed. This compound provides an accurate test of a model's OH levels, and measured concentrations from the AGAGE network are used to infer global and hemispheric OH levels (Prinn *et al.*, 2000). The methyl chloroform concentrations modelled by STOCHEM matched the measurements closely, although the levels in the northern hemisphere tended to be slightly larger than the measurements. The average turnover time (burden divided by loss rate) was 5.2 years, in good agreement with the observed lifetime of 5.0 years (Prinn *et al.*, 2000). On this basis, we consider that the global tropospheric distribution of OH radicals simulated in STOCHEM is reasonable.

The main sink for tropospheric hydrogen is dry deposition. The lifetime of hydrogen with respect to oxidation by the OH radical in the model is 10 years, but only 2.9 years for dry deposition. The dry deposition rate of a species is controlled

by the stability of the boundary layer, the chemical nature of the species, and the type of surface. It is assumed that the dry deposition flux is directly proportional to the concentration of the depositing species at a reference height above the surface; in the present work, a height of 50 m has been used (Hov *et al.*, 1994). Dry deposition processes can be considered either as resistances, or as velocities. A dry deposition velocity v is the reciprocal of the resistance R , i.e., $v = 1/R$.

In the previous scheme used in STOCHEM (Collins *et al.*, 2000), the dry deposition velocity was calculated from the aerodynamic resistance and a fixed species dependent surface deposition velocity using a similar approach to Hov *et al.* (1994). In this work, a new dry deposition scheme for hydrogen has been added to the model which includes terms for the thin stagnant layer of air immediately above the surface (quasi-laminar resistance), and the bulk resistance of the vegetative canopy to the movement of air through the canopy to reach the surface (Seinfeld and Pandis, 1998). Hydrogen does not undergo dry deposition to vegetation, and is removed by bacteria in soils (Yonemura *et al.*, 2000) and in some circumstances extracellular enzymes (Conrad *et al.*, 1983; Förstel and Jansen, 1991). A model of dry deposition for hydrogen is therefore relatively simple. The scheme is fully coupled so that every 3 hours, all key parameters such as soil moisture and leaf area index are updated by MOSES and passed to STOCHEM. The resistance terms needed to calculate the overall dry deposition velocity (see below) are then calculated at each model time step. Hence, all dry deposition velocities are consistent with local conditions and will vary both diurnally as the stability of the boundary layer changes, and in the longer term as, for example, the leaf area index of the plants and soil moisture contents change.

The total resistance to deposition, R_t , is the sum of the aerodynamic resistance R_a , the quasi-laminar resistance R_b , the in-canopy resistance R_i , and the surface resistance R_s . The in-canopy resistance term is, of course, neglected over bare soils. By definition, the overall dry deposition velocity is the inverse of the sum of the resistance terms, i.e., $v_d = 1/R_t = 1/(R_a + R_b + R_i + R_s)$. Detailed descriptions of these terms are given elsewhere (van Pul and Jacobs, 1994; Ganzeveld and Lelieveld, 1995; Seinfeld and Pandis, 1998) and so only a brief explanation is given here.

The aerodynamic resistance term controls the transport of a trace gas from the well-mixed boundary layer to the surface, and depends on the stability of the surface layer of air. This term was calculated from dimensionless profiles of heat recommended in a review by Dyer (1974). Heat transport is more similar to trace gas transport than momentum transfer. For example, Pasquill and Smith (1983) show measured dimensionless profiles of momentum, heat and moisture. The profiles of heat and moisture are the same, whereas the momentum profile is significantly different.

The quasi-laminar resistance term describes the diffusion of the trace gas through a thin stagnant layer of air immediately above the absorbing surface, and was calculated using an equation which utilises the diffusivities of air and the

trace gas in question (Ganzeveld and Lelieveld, 1995). The in-canopy resistance is a measure of the rate that air can penetrate the vegetative canopy (owing to gusts and eddies) and reach the surface (van Pul and Jacobs, 1994). The surface resistance term is an overall parameter which incorporates diffusion of the air into the soil, and the subsequent oxidation of the hydrogen by enzymes and bacteria in the soil. An early laboratory study indicated a dependence of the surface resistance for hydrogen deposition on temperature, but this dependence was not seen in field measurements (Liebl and Seiler, 1976). Later field studies indicate a dependence of the hydrogen dry deposition velocity on soil moisture content and ecosystem type only (Conrad and Seiler, 1985; Yonemura *et al.*, 1999, 2000). The small number of hydrogen dry deposition measurements mean that no data exist for some ecosystems. Therefore, the deposition velocity measured by Yonemura *et al.* (2000) in a deciduous forest was assumed to be representative of all forests; similarly, the deposition velocity for grasslands measured by Conrad and Seiler (1980) was used for all grasslands and prairies. The deposition velocity calculated by Simmonds *et al.* (2000) was used for wetland regions and tundra. Hydrogen is not removed by dry deposition over snow, ice, desert or water surfaces. See Table I for the list of deposition velocities. In the original scheme, all land areas not covered by snow and ice were assigned a fixed value of $2,200 \text{ s m}^{-1}$ (equivalent to a surface velocity of $4.5 \times 10^{-4} \text{ m s}^{-1}$). Results from these simulations indicated that this value was too small.

The surface exchange scheme in HadCM3, MOSES (Section 2) does not explicitly represent many of the ecosystems where hydrogen dry deposition has been measured. Hydrogen dry deposition velocities to the MOSES surface types C₃ and C₄ grasses, shrubs and bare soil, were assigned by comparing maps of each of these surface types with maps of natural ecosystems and agricultural regions in the Times World Atlas (Bartholomew, 1994). For example, many regions classed as C₃ grass in MOSES are used for growing wheat and other cereals, and the appropriate dry deposition velocity was assigned to this surface type. Dry deposition velocities were then calculated at each model timestep using the appropriate equations for each ecosystem. The deposition velocities and their dependencies on soil moisture for each ecosystem are listed in Table I.

5. Comparison of Surface Observations with Model Results

Initial concentrations of most species such as methane, carbon monoxide and ozone were based on measurements and previous model integrations, except those for hydrogen and methane which used a two-dimensional interpolation of surface measurements. The concentrations of the more reactive species will adjust to equilibrium values quickly, so their initial values are not too critical. STOCHEM was set up with the source magnitudes of Seiler and Conrad (1987), which lie within the ranges calculated by Novelli *et al.* (1999). The model was spun up for 3 months and then integrated for another 12 months using the original simple dry deposition

Table I. Summary of measured hydrogen dry deposition velocities used in the model. The surface resistance R_S is the reciprocal of the deposition velocity

Ecosystem	Measured deposition velocity/ 10^{-4} m s $^{-1}$	Variation with soil moisture	Reference
Savannah	13.1	Yes	Conrad and Seiler (1985)
Agricultural	4.3	Yes	Yonemura <i>et al.</i> (2000)
Forest	6.3 ^a	Yes	Yonemura <i>et al.</i> (2000)
Grasslands, prairies	5.2 ^b	Yes	Conrad and Seiler (1980)
Peat/tundra	2.6	No	Simmonds <i>et al.</i> (2000)
Semi-desert	1.0	No	Conrad and Seiler (1985)
Desert	0.0	No	Yonemura <i>et al.</i> (2000)

Soil moisture dependencies: v = dry deposition velocity (10^{-4} m s $^{-1}$), x = soil moisture content (as volume ratio, i.e., volume of water per unit volume of soil), $z = \log_e$ (soil moisture content). Savannah: $v = az^2 + bz + c$, $a = 0.270$, $b = -0.472$, $c = 1.235$. Agricultural land: $v = bx + c$, $b = -41.39$, $c = 16.85$. Forest: $v = bx + c$, $b = -41.9$, $c = 19.7$. Grasslands: $v = bx + c$, $b = -41.39$, $c = 17.7$.

^a Yonemura *et al.* (2000) quote two different dependencies; the fitted straight line with the larger correlation coefficient was used.

^b Mean value estimated using an average hydrogen decomposition rate of 3×10^{-8} cm 3 cm $^{-2}$ s $^{-1}$ and a given relationship between the decomposition rate and deposition velocity. Dependence on soil moisture assumed the same as agricultural soils but scaled to give a deposition velocity of 5.2×10^{-4} m s $^{-1}$ for a soil moisture content of 0.30.

scheme. The simulation was then repeated using the soil moisture dependent dry deposition scheme described above. Further simulations were performed to examine the model sensitivity to changes in emissions and dry deposition rates. The model was initialised at the beginning of January, and so the last 12 months used for comparison with measurements run from April to March.

The modelled hydrogen concentrations from the last 12 months of the integrations with the old dry deposition scheme (which just used the aerodynamic resistance and a fixed surface resistance for all land surfaces) and the new dry deposition scheme (which uses a map of various ecosystems and also takes into account the effects of soil moisture; see Section 3 and Table I) were compared with surface measurements from the NOAA/CMDL Co-operative Air Sampling Network (a detailed explanation of the sampling, analysis and data selection processes is given by Novelli *et al.*, 1999). Some of these comparisons are shown in Figure 1. The sites were chosen to give a good latitudinal cross-section of the hydrogen levels, but with a bias toward the northern hemisphere, as most of the deposition occurs here. These sites include both oceanic and continental locations. Note that the model predictions using the simple dry deposition scheme (dashed line) have been detrended for easier comparison of the seasonal cycles. This was necessary because in the simple scheme the source and sink terms were out of balance. To do this, a straight line was fitted through the model predictions for April and March

(i.e., the first and last months of the comparison). An offset in the hydrogen levels between each month from May to March, and the level for April, was evaluated from this line, and subtracted from the model prediction for the particular month. In this way, the model predictions for April and March are made the same. The key feature is the seasonal variation in the hydrogen levels rather than their absolute values. Model predictions using the improved dry deposition scheme have not been modified in any way. Average measured monthly mean concentrations were calculated for each location using measurement data from 1994–1996.

A better agreement between the model predictions and the measurements can be seen when the improved dry deposition scheme is used (Figure 1), except at remote locations in the southern hemisphere (Cape Grim) where no real change has occurred. The model captures the seasonal cycle at each location quite well, except for high southern latitudes (South Pole). The hydrogen levels in the simulation rise by an average of 7 ppbv yr^{-1} which is larger than the estimate of Simmonds *et al.* (2000), 1.2 ppbv yr^{-1} . The increase of 7 ppbv yr^{-1} is equivalent to a source-sink imbalance of just 3.8 Tg yr^{-1} . Given the lack of measurements of deposition values and the uncertainties in the emissions, the small source-sink imbalance in the simulation is reasonable. Using best estimates of emissions and dry deposition velocities it has been possible to achieve a good balance without any deliberate changes to make the hydrogen sources and sinks balance exactly. The global mean hydrogen deposition velocity is $5.3 \times 10^{-4} \text{ m s}^{-1}$, which lies between the values of $3.5 \times 10^{-4} \text{ m s}^{-1}$ and $7 \times 10^{-4} \text{ m s}^{-1}$ estimated by Schmidt *et al.* (1980) and Liebl and Seiler (1976) respectively. By decreasing the emissions or increasing the dry deposition velocities, it will be possible to make the sources and sinks exactly balance out, a result which would lie between the slight decrease inferred by Novelli *et al.* (1999) from the NOAA/CMDL measurements, and the small increase obtained by Simmonds *et al.* (2000) from AGAGE data. It is possible that a number of different scenarios could achieve an exact balance and the same level of agreement with the measurements, however, they may not be physically realistic.

Another model integration was performed with no isoprene emissions, to see if transport of hydrogen produced by isoprene oxidation in the tropics was the cause of the lack of seasonal variation at the South Pole. The results from this last simulation were inconclusive. The hydrogen levels in the southern hemisphere fell at a fairly constant rate throughout the simulation, and no seasonal cycle could be seen in the predictions. This result is puzzling; the predicted methane and carbon monoxide concentrations at the South Pole and other high southern latitudes exhibit a clear seasonal cycle in good agreement with the measurements, although the magnitude is slightly smaller (data not shown). Currently, we cannot explain the lack of seasonality in the hydrogen levels at high southern latitudes. It should be noted that measurements show that the hydrogen seasonal cycle is out of phase with the seasonal cycle of methane at the South Pole by several months, indicating different controlling factors. One possibility is that the southern ocean acts as a sink

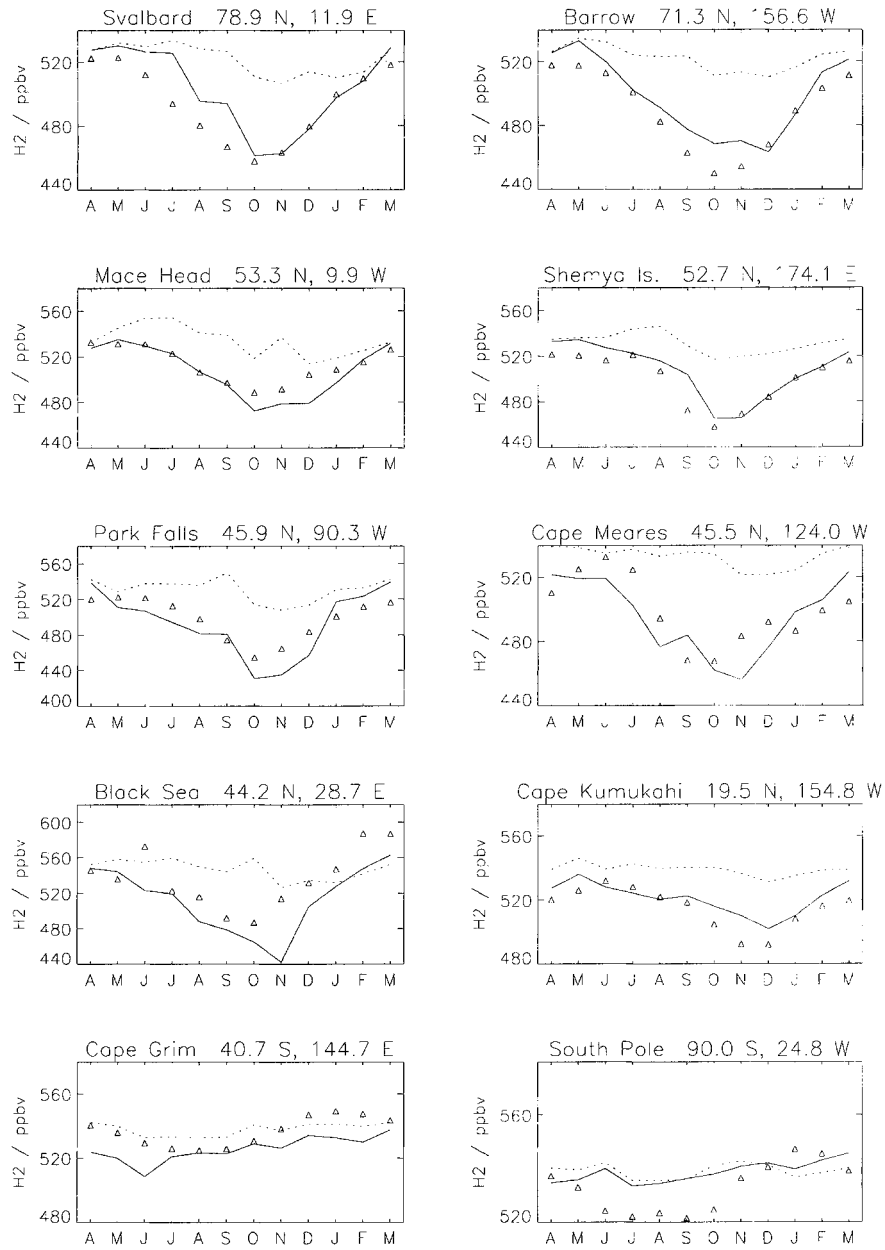


Figure 1. Comparison of the modelled hydrogen levels from the lowest model layer (950 mbar, 500 m) with surface measurements from the NOAA/CMDL monitoring network (Novelli *et al.* (1999) and references therein). Triangles represent measured monthly mean hydrogen levels. The solid line denotes the model predictions using the improved dry deposition scheme, and the dashed line the model predictions using the old dry deposition scheme. The latter data were detrended for easier comparison; see text for details. The other model data have not been modified in any way. Note that the vertical scales on each panel are different.

for hydrogen at certain times. Uptake of hydrogen by the oceans has been observed on a few occasions (Schmidt, 1979; Conrad and Seiler, 1988).

Novelli *et al.* (1999) have suggested that the seasonal variation in the hydrogen levels in the southern hemisphere are controlled by biomass burning emissions. The simulation with the new dry deposition scheme was repeated by halving the biomass burning source and increasing the fossil fuel source to keep the total emissions the same. However, the model predictions using these revised values were very similar in equatorial regions compared to the original simulation, and no significant change was predicted at high latitudes. While this result does not disprove the proposal of Novelli *et al.* (1999), it suggests that long-range transport is the dominant controlling factor at high latitudes in the southern hemisphere, and mixing of air masses has removed any biomass burning signal.

Finally, the model was set up with the sources and sinks set to the values recommended by Warneck (1999; see Table III). The source magnitudes are similar to the previous simulation. The dry deposition scheme was modified so that the surface resistance term (R_s) over all land surfaces where hydrogen dry deposits was equivalent to the global mean velocity of $7 \times 10^{-4} \text{ m s}^{-1}$ suggested by Warneck (1999). In the previous simulations, the rate at which the hydrogen levels rose was slightly too high, and one reason may be that the dry deposition velocities are, on average, too low. However, the simulated hydrogen levels using the mean velocity of $7 \times 10^{-4} \text{ m s}^{-1}$ decreased fairly quickly over the entire globe, indicating a significant source-sink imbalance. The last model simulation suggests this mean value is too large. Measurements of the surface hydrogen dry deposition velocities (Table I) are generally smaller than $7 \times 10^{-4} \text{ m s}^{-1}$.

6. The Hydrogen Budget for the STOCHEM Model

The yields of hydrogen from each primary VOC in the model using the last 12 months of the simulation with the improved dry deposition scheme are listed in Table II. The largest amounts come from methane and isoprene, in agreement with previous assessments (Novelli *et al.*, 1999; Warneck, 1999). The yields from the remaining VOCs are much smaller, but the sum is significant.

A global hydrogen budget from the same simulation is given in Table III. The overall production of hydrogen from the oxidation of methane and other VOCs agrees well with the estimates of Warneck (1999) and is within the range of values calculated by Seiler and Conrad (1987) but lower than the estimate of Novelli *et al.* (1999). For the NMHC source, Warneck (1999) only considered isoprene oxidation and estimated 18 Tg yr^{-1} . In our simulation, isoprene oxidation produces a lower value of 11.0 Tg yr^{-1} (Table II). One possible reason is that the yield of formaldehyde from the degradation of isoprene is smaller than that assumed by Warneck (1999). However, Seiler and Conrad (1987) calculated a larger source of hydrogen from NMHC oxidation and a lower source from methane oxidation, whereas Novelli *et al.* (1999) calculated the reverse. The hydrogen sink due to

Table II. Globally-integrated annual hydrogen source terms for the VOCs considered in the STOCHEM model. The sum of the sources from the non-methane VOCs may not add up to the total in Table III owing to rounding of the source values

Species	Globally annually integrated hydrogen source term (Tg yr ⁻¹)
Methane	15.2
Ethane	0.2
Propane	0.3
Butane	1.2
Ethene	0.8
Propene	0.6
Isoprene	11.0
Methanol ^a	0.3
Formaldehyde ^b	0.1
Acetaldehyde ^b	0.1
Acetone ^b	0.5

^a Includes emission and production from CH₃O₂ self reaction.

^b From direct emission only.

Table III. Hydrogen budget. All values quoted in Tg yr¹ (1 Tg = 1,012 g)

	Seiler and Conrad (1987)	Warneck (1999)	Novelli <i>et al.</i> (1999)	This work
<i>SOURCES</i>				
Anthropogenic ^a	20 ± 10	17	15 ± 10	20.0
Biomass burning	20 ± 10	19	16 ± 11	20.0
Methane oxidation	15 ± 5	20	26 ± 9	15.2
NMHC oxidation ^b	25 ± 10	18 ^c	14 ± 7	15.0
Oceans	4 ± 2	4	3 ± 2	4.0 ^d
N ₂ fixation	3 ± 2	3	3 ± 1	4.0 ^e
Total	87	81	77	78.2
<i>SINKS</i>				
Oxidation by OH	8 ± 3	16	19 ± 5	17.1
Dry deposition	90 ± 20	70	56 ± 41	58.3
Total	98	86	75	74.4

^a H₂ produced directly by combustion of fossil fuels.

^b NMHC = Non-methane hydrocarbon (refer to Table II).

^c Estimate only considers oxidation of isoprene; see text.

^d From Schmidt (1974).

^e From Conrad and Seiler (1980).

reaction with hydroxyl radicals agrees well with previous estimates except the low value of Seiler and Conrad (1987). The loss due to dry deposition in the present work agrees well with the estimate of Novelli *et al.* (1999), but is lower than the estimates of Seiler and Conrad (1987) and Warneck (1999). These two latter studies assumed a global average hydrogen dry deposition velocity of 7×10^{-4} in s^{-1} . As described previously, hydrogen levels in a model simulation using this value over all land types decreased throughout the simulation. Hence, it is suggested that the dry deposition losses calculated by Seiler and Conrad (1987) and Warneck (1999) are too large. The atmospheric burden of 172 Tg lies between the values of 155 Tg and 182 Tg calculated by Novelli *et al.* (1999) and Simmonds *et al.* (2000) respectively from surface measurements. The turnover time of 2.2 years is slightly larger than the estimates of 1.9 and 2.0 years calculated by Warneck (1999) and Novelli *et al.* (1999) respectively.

7. Summary

An improved hydrogen dry deposition scheme has been added to the STOCHEM model and shown to greatly improve the simulation of the seasonal cycles in hydrogen levels at many locations. These results demonstrate the importance of soil moisture variation as a controlling factor of hydrogen uptake by soils, and models should include a parameterisation for this. It is likely that soil moisture variation will also affect the uptake of carbon monoxide and methane as well, as these two trace gases are also removed by microbes and bacteria in soils. The magnitude of the sink terms agree well with other estimates. An often quoted global mean hydrogen dry deposition velocity of $7 \times 10^{-4} \text{ m s}^{-1}$ has been shown to be too large. The results presented here indicate a better value is $5.3 \times 10^{-4} \text{ m s}^{-1}$. Novelli *et al.* (1999) have proposed that the seasonal cycle in the southern hemisphere hydrogen levels is dominated by emissions from biomass burning. Results from another simulation with reduced emissions from biomass burning and increased anthropogenic emissions did not differ from the standard simulation in the middle and high southern latitudes. These results suggest that sufficient mixing of the air masses has occurred so that any such signal has been removed. However, more simulations using different biomass burning emission magnitudes and different seasonal cycles would be needed to investigate this proposal fully. Another simulation without isoprene emissions did not change the modelled seasonal cycle in the southern hemisphere.

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