Global budget of molecular hydrogen and its deuterium content:
Constraints from ground station, cruise, and aircraft observations

Heather Price,1 Lyatt Jaeglé,1 Andrew Rice,2,3 Paul Quay,4 Paul C. Novelli,5 and Richard Gammon4

Received 15 October 2006; revised 21 June 2007; accepted 7 August 2007; published 30 November 2007.

[1] The distribution and atmospheric budgets for molecular hydrogen and its deuterium component δD are simulated with the GEOS-Chem global chemical transport model and constrained by observations of H2 from the NOAA Climate Monitoring and Diagnostics Laboratory network and δD observations from ship and ground stations. Our simulation includes a primary H2 source of 38.8 Tg a−1 (22.7 Tg a−1 from fossil and biofuels, 10.1 Tg a−1 from biomass burning, 6.0 Tg a−1 from the ocean) (where a is years) and a secondary photochemical source from photolysis of formaldehyde of 34.3 Tg a−1. The simulated global tropospheric mean H2 is 525 ppbv, with a tropospheric burden of 141 Tg and tropospheric lifetime of 1.9 a. Uptake by enzymes in soils accounts for 75% of the H2 sink, with the remainder due to reaction with OH. The model captures the observed latitudinal, vertical, and seasonal variations of H2. For δD we find that a photochemical source signature from methane and biogenic volatile organic compound oxidation of 162% yields a global mean atmospheric δD of 130‰, consistent with atmospheric observations. The model captures the observed latitudinal gradient in δD, simulating a 21‰ greater enrichment in the Southern Hemisphere because of the predominance of isotopically depleted fossil fuel emissions in the Northern Hemisphere. We find that stratospheric-tropospheric exchange results in 37‰ enrichment of tropospheric δD. Our simulation provides new simultaneous constraints on the H2 soil sink (55 ± 8 Tg a−1), the ocean source (6 ± 3 Tg a−1), and the isotopic signature for photochemical production (162 ± 57‰).


1. Introduction

[2] Hydrogen could be a promising alternative to fossil fuels. A traffic fleet powered by hydrogen could improve air quality, as such a fleet does not emit ozone precursors (for example, carbon monoxide and nitrogen oxides). However, leakage of hydrogen would reduce global levels of the hydroxyl radical OH and hence increase the lifetime and forcing of methane [Schultz et al., 2003; Warwick et al., 2004]. In addition, switching to a hydrogen-based energy system might result in an increase in stratospheric H2O affecting stratospheric temperatures and ozone depletion.

[3] Human activities have significantly influenced atmospheric H2, with anthropogenic emissions resulting in a presumed doubling of H2 levels since preindustrial times [Khalil and Rasmussen, 1990]. Today hydrogen is the second most abundant reactive gas in the troposphere after CH4, with a mean tropospheric mixing ratio of ~350 parts per billion by volume (ppbv) [Novelli et al., 1999]. Despite the predominance of Northern Hemisphere (NH) sources from fuel combustion, the H2 distribution is opposite from most anthropogenically influenced gases. Hydrogen is 3% more abundant in the Southern Hemisphere (SH) than in the NH [Khalil and Rasmussen, 1989; Novelli et al., 1999].

[4] Table 1 summarizes the principal sources and sinks of H2 as reported in a number of studies published over the past 20 years (a). The primary sources for H2 include fossil fuel combustion, biofuel combustion, and biomass burning, with additional sources from terrestrial and oceanic nitrogen fixation. Another significant source of H2 is photochemical production, occurring through the photolysis of formaldehyde (HCHO). The main source for HCHO in much of the

1 Department of Atmospheric Sciences, University of Washington, Seattle, Washington, USA.
2 Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, Seattle, Washington, USA.
3 Now at Department of Physics, Portland State University, Portland, Oregon, USA.
4 School of Oceanography, University of Washington, Seattle, Washington, USA.
5 National Oceanic and Atmospheric Administration, Climate Diagnostics Center, Boulder, Colorado, USA.

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0148-0227/07/2006JD008152$09.00
Table 1. Global Tropospheric Sources and Sinks of H$_2$ (Tg H$_2$ a$^{-1}$) and Their Isotopic Signatures$^a$

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel</td>
<td>20 ± 10</td>
<td>17</td>
<td>20</td>
<td>15 ± 16</td>
<td>20.0</td>
<td>15 ± 6</td>
<td>-196$^d$, -49</td>
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<tr>
<td>Biomass</td>
<td>20 ± 10</td>
<td>15</td>
<td>10</td>
<td>16 ± 5</td>
<td>20.0</td>
<td>16 ± 3</td>
<td>-290$^c$, -40</td>
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<tr>
<td>Biofuel$^b$</td>
<td>4 ± 2</td>
<td>4</td>
<td>3</td>
<td>3 ± 2</td>
<td>5</td>
<td>4 ± 6</td>
<td>6.0, -628$^c$, -52</td>
</tr>
<tr>
<td>Ocean N$_2$</td>
<td>2 ± 2</td>
<td>2</td>
<td>3</td>
<td>3 ± 1</td>
<td>5</td>
<td>4 ± 6</td>
<td>0, 0</td>
</tr>
<tr>
<td>Land N$_2$</td>
<td>2 ± 2</td>
<td>3</td>
<td>3</td>
<td>3 ± 1</td>
<td>5</td>
<td>4 ± 6</td>
<td>0, 0</td>
</tr>
<tr>
<td>Photochemical production</td>
<td>Methane</td>
<td>15 ± 5</td>
<td>29</td>
<td>26 ± 9</td>
<td>15.2</td>
<td>24.5</td>
<td>162$^f$</td>
</tr>
<tr>
<td></td>
<td>VOCs</td>
<td>25 ± 10</td>
<td>21</td>
<td>14 ± 7</td>
<td>9.8</td>
<td>16</td>
<td>162$^f$</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>40</td>
<td>50</td>
<td>35</td>
<td>40</td>
<td>31</td>
<td>30.2</td>
</tr>
<tr>
<td>Sources total</td>
<td>87 ± 39</td>
<td>89</td>
<td>77</td>
<td>71</td>
<td>17 ± 6</td>
<td>70</td>
<td>78.2</td>
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<tr>
<td>OH</td>
<td>8 ± 3</td>
<td>11</td>
<td>25</td>
<td>19 ± 5</td>
<td>15</td>
<td>17.1</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>Soils</td>
<td>90 ± 20</td>
<td>78</td>
<td>40</td>
<td>56 ± 41</td>
<td>55</td>
<td>58.3</td>
<td>88 ± 11</td>
</tr>
<tr>
<td>Sinks total</td>
<td>98 ± 23</td>
<td>89</td>
<td>65</td>
<td>75 ± 41</td>
<td>70</td>
<td>75.4</td>
<td>107 ± 11</td>
</tr>
<tr>
<td>Burden, Tg H$_2$</td>
<td>163</td>
<td>150</td>
<td>155</td>
<td>136</td>
<td>172</td>
<td>76</td>
<td>141</td>
</tr>
<tr>
<td>Lifetime, a</td>
<td>1.8</td>
<td>2.3</td>
<td>2.1</td>
<td>1.9</td>
<td>2.3</td>
<td>0.71</td>
<td>1.9</td>
</tr>
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</table>

$^a$Isotopic signatures for sources are listed as δD in per million (%), isotopic signatures of sinks are listed as $\alpha$, and the ratio of the rate constants are listed as H$_2$/HD.

$^b$Individual contributions of sources to δD. δD$_{source}(i)$ = δD$_{i}$ with δD$_{i}$ the isotopic signature of the source weighted by $f_i$, the relative source strength. Similarly, $\alpha_{sink}(i)$ = $\alpha_i$, where $f_i$ is the relative sink strength.

$^c$Gerst and Quay [2001].

$^d$We list separate biofuel emissions for this work. No separate biofuel combustion emissions are reported for the other estimates, which include biofuels as part of biomass burning or fossil fuel combustion.

$^e$Rice and Quay [2006].

$^f$Values are from this work.

$^g$Tropical mean $\alpha$, weighted by H$_2$ concentrations.

$^h$In calculating the relative δD$_{sink}$ we use the globally averaged tropospheric $\alpha$ = 0.926.

Troposphere is the oxidation of CH$_4$, while dominant continental sources include oxidation of volatile organic compounds (VOCs).

[5] The major tropospheric H$_2$ sink is removal by bacteria in soils [Yonemura et al., 2000] as well as by extracellular enzymatic activity of soil hydrogenases [Conrad and Seiler, 1980], which account for 60–90% of the total sink and explain the lower abundance of H$_2$ in the NH [Seiler and Conrad, 1987; Warneck, 1988; Ehalt, 1999; Novelli et al., 1999; Hauglustaine and Ehalt, 2002; Sanderson et al., 2003; Rahn et al., 2003; Rhee et al., 2006]. Large uncertainties are associated with the magnitude of this soil sink and its mechanisms are not completely understood. Oxidation of H$_2$ by OH accounts for the remaining loss. In the stratosphere the main sinks for H$_2$ are reactions with OH and O(D) radicals, while reaction with chlorine radicals is a minor sink.

[6] Observation of the deuterium component can be used to constrain aspects of the hydrogen budget. In the troposphere the deuterium enrichment of H$_2$ (δD of H$_2$) averages +130 ± 4% [Gerst and Quay, 2000]. Note by convention δD is expressed as a ratio of deuterium to hydrogen, where δD = 1000 × [(D/H)$_i$]/[(D/H)$_{VSMOW}$ – 1], $x$ represents an observation, and Vienna standard mean ocean water (VSMOW = 1.5575 × 10$^{-4}$) is an internationally recognized standard [Gonfiantini et al., 1995].

[7] The isotopic signatures for fossil fuel, biofuel, biomass burning, and ocean sources are all depleted in δD relative to the atmosphere (Table 1). The isotopic signature of the photochemical source (δD$_{photo}$) from the oxidation of CH$_4$ and VOCs has not yet been determined but to explain the atmospheric observed enrichment δD$_{obs}$ must have a large positive value [Gerst and Quay, 2001]. The recent observations of enriched δD in atmospheric formaldehyde are supportive of this estimation [Rice and Quay, 2006]. There is also a strong gradient in δD of H$_2$ with altitude, with enhancements up to 440% observed in the stratosphere because of the strongly enriched photochemical source from CH$_4$ oxidation [Rahn et al., 2003; Röckmann et al., 2003]. Transport of elevated stratospheric δD to the troposphere may thus be a significant source for tropospheric δD [Rahn et al., 2003].

[8] There is a significant difference between the fractionation effects for the soil and OH sinks. The soil sink has a weak fractionation effect. The OH sink fractionates more strongly, as the rate of reaction for OH + H$_2$ proceeds almost twice as fast as the OH + HD reaction [Talukdar et al., 1996].

[9] The unique distribution of atmospheric H$_2$ and large uncertainties in the budget terms, compared to other anthropogenically influenced gases, underscores the importance of understanding the H$_2$ budget. A valuable way to draw information on the cycling and budget for H$_2$ is through global modeling of H$_2$ and δD constrained by observations. Additionally, better constraint of the hydrogen budget will also provide constraints on atmospheric budgets of CH$_4$, VOCs, and CO.

[10] While previous modeling studies [Hauglustaine and Ehalt, 2002; Sanderson et al., 2003] focused exclusively on molecular hydrogen, in this paper we present a first coupled global simulation of H$_2$ and δD. We use the GEOS-Chem model of tropospheric chemistry [Bey et al., 2001a]. Our goals are to assess the consistency of H$_2$ and δD budgets using constraints from H$_2$ and δD measurements from a suite of ground stations, cruises, and aircraft. In particular, we examine the magnitude of the soil sink, the photochemical oxidation source and its enrichment, the
effect of the ocean source on H$_2$ and $\delta$D, and the role of stratosphere-troposphere exchange in enriching tropospheric $\delta$D.

2. Model Description

2.1. General

[11] The GEOS-Chem model of tropospheric chemistry is driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the Global Modeling Assimilation Office (GMAO). We conduct a simulation for 2001 using GEOS-Chem v.5-05 (http://www.as.harvard.edu/chemistry/trop/geos) and GEOS-3 meteorological fields with a horizontal resolution of 1° latitude by 1° longitude and 48 vertical layers. For computational expediency we degrade the resolution of the meteorological fields to 4 × 5° and 30 vertical levels. Surface and upper level fields are updated every 3 and 6 h, respectively. Evaluations of the GEOS-Chem O$_3$-NO simulation have been presented by Bey et al. [2001a, 2001b], Palmer et al. [2001], Martin et al. [2002], Liu et al. [2002], Fiore et al. [2002], Heald et al. [2003, 2004], Liang et al. [2004], and Liu et al. [2006].

2.2. Molecular Hydrogen

[12] Hydrogen and CO have similar surface sources including biomass burning, the combustion of biofuels and fossil fuels, and photochemical production through the oxidation of CH$_4$ and VOCs. Thus we use the GEOS-Chem CO emission inventory to determine the H$_2$ emissions using measured ratios of H$_2$/CO, a method also followed by Hauglustaine and Ehhalt [2002]. Duncan et al. [2007] present a detailed description and evaluation of the GEOS-Chem CO simulation. Fossil and biofuel emissions are from Duncan et al. [2007] and Yevich and Logan [2003], respectively. Monthly varying climatological biomass burning emissions are from Duncan et al. [2003]. The H$_2$/CO molar emission ratios used in the model are 0.588 mol/mol for fossil fuels [Olivier et al., 1996] and 0.32 mol/mol for biofuels [Andreae and Merlet, 2001]. For biomass burning we calculate a mean emission ratio for all vegetation, weighted by the respective emissions, resulting in a molar ratio of 0.29 mol/mol based on vegetation specific emission ratios of Andreae and Merlet [2001]. The resulting H$_2$ sources are 18.5 Tg a$^{-1}$ for fossil fuels, 4.5 Tg a$^{-1}$ for biofuels, and 10.4 Tg a$^{-1}$ for biomass burning (Table 1).

[13] The ocean H$_2$ source from biological nitrogen fixation is poorly understood and is estimated to range from 3 [Novelli et al., 1999; Ehhalt, 1999] to 6 Tg a$^{-1}$ [Seiler and Conrad, 1987]. These estimates are based on a few observations of H$_2$ supersaturation in ocean water by Schmidt [1974] and Seiler and Schmidt [1974]. In our study we assume a total H$_2$ ocean source of 6 Tg a$^{-1}$, which is at the higher end of the range of previous estimates. We distribute ocean emissions following the global spatial distribution of biological ocean nitrogen fixation estimated by Deutsch et al. [2007] on the basis of the oceanic distribution of nutrients.

[14] The soil source for H$_2$ comes from biological nitrogen fixation in the root nodules of leguminous plants [Conrad and Seiler, 1980, 1985; Dong and Layzell, 2001]. We neglect this land source, assuming that most of the H$_2$ microbially produced in soils is consumed before it can escape to the atmosphere [McLearn and Dong, 2002]. Observations show that soils planted with legumes emit H$_2$ into the atmosphere for only 2 months of the year, while during the rest of the year the net flux is from atmosphere to soil [Conrad and Seiler, 1980].

[15] The photochemical source of hydrogen is calculated from the CO produced from the oxidation of methane and biogenic VOCs (BVOCs), which refers to isoprene, monoterpenes, acetone, and methanol in the present work. The production of CO from the photooxidation of BVOCs is discussed by Duncan et al. [2007]. Using a full chemistry simulation, we archived monthly mean H$_2$/CO production ratios from the oxidation of methane and BVOCs. The resulting H$_2$ source from CH$_4$ oxidation is 24.5 Tg a$^{-1}$. For BVOC oxidation we calculate a total source of 9.8 Tg a$^{-1}$ (isoprene 5.6 Tg a$^{-1}$, methanol 2.0 Tg a$^{-1}$, monoterpenes 1.5 Tg a$^{-1}$, acetone 0.7 Tg a$^{-1}$).

[16] The soil uptake of H$_2$ is poorly characterized and according to the few studies conducted depends on soil moisture, temperature, texture, and microbial activity [Conrad and Seiler, 1985; Yonemura et al., 1999, 2000; Chidthaisong et al., 2002; Smith-Downey et al., 2006; A. Dayalu et al., unpublished data, 2006]. Because of the lack of specific information on these dependencies we use a simple approach, assuming a uniform soil deposition velocity of 3.94 × 10$^{-2}$ cm s$^{-1}$. This value was selected to obtain the best agreement with mean surface observations of H$_2$ (section 4) and is evaluated by comparing the model to observed latitudinal, seasonal, and vertical trends. Liebl and Seiler [1976] and Conrad and Seiler [1980, 1985] reported average H$_2$ uptake rates of 7 × 10$^{-2}$ cm s$^{-1}$ over German grassland sites. Yonemura et al. [2000] measured deposition velocities in temperate Japan, observing 0–9 × 10$^{-2}$ cm s$^{-1}$ in an arable field and 6.3 × 10$^{-2}$ cm s$^{-1}$ in a forest. More recently, A. Dayalu et al. (unpublished data, 2006) measured deposition velocities ranging from 2 × 10$^{-2}$ cm s$^{-1}$ to 6 × 10$^{-2}$ cm s$^{-1}$ in Washington state forest sites.

[17] In our model a uniform deposition velocity of 3.94 × 10$^{-2}$ cm s$^{-1}$ is applied over nonsnow-covered land with surface temperatures above 0°C. This is reduced by half where temperatures are below freezing and by an additional half where temperatures are below −15°C [Smith-Downey et al., 2006]. When snow is present (as diagnosed in the GEOS meteorological fields) we set the dry deposition velocity to zero over the snow-covered part of the model grid box. For consistency with field measurements we also set the soil deposition velocity to zero over deserts. Conrad and Seiler [1985] measured the H$_2$ deposition velocity in semidesert soil at 1 × 10$^{-2}$ cm s$^{-1}$. Prolonged dryness and elevated temperatures (>40°C) appear to deactivate soil hydrogenase [Conrad and Seiler, 1985; Liebl and Seiler, 1976).

[18] For the loss of H$_2$ by OH oxidation we use archived monthly global OH fields from a full chemistry simulation with $k_{\text{OH-H}_2} = 5.5 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ [Talukdar et al., 1996]. We also include simple stratospheric chemistry of H$_2$ with a source from methane oxidation and sinks from the reactions with OH and O(1D) radicals. The
monthly fields for O(1D) are archived from a stratospheric chemistry simulation (G. Curci, personal communication, 2005).

2.3. Deuterium Component

We incorporate HD as an additional tracer in the model to determine the $\delta D$ of $H_2$ in the atmosphere. We use source signatures for biomass burning (~290%) and fossil fuels (~196%) from Gerst and Quay [2001]. We assume that biofuel combustion has the same isotopic signature as biomass burning. The $H_2$ emitted from oceans is highly depleted, and we use a measured value of $\delta D_{\text{ocean}} = -628\%$ [Rice and Quay, 2006]. The high-ocean depletion results from the theoretical equilibrium constant between ocean water and $H_2$, of the order of ~750% at 20°C.

As noted in section 1, the isotopic effect that occurs with the photolysis of formaldehyde has not been measured directly. A parameterized value for $\delta D_{\text{hv}} = +162\%$ gives us the best agreement with surface and free tropospheric observations of atmospheric $\delta D$ (section 3.4).

Stratosphere-troposphere exchange has been suggested as an important source for enriching tropospheric $\delta D$ [Rahn et al., 2003; Röckmann et al., 2003]. The magnitude of cross-tropopause fluxes in the GEOS meteorological fields are too large a factor of 3–4 [Bey et al., 2001b; Liu et al., 2001, 2003]. As a result, GEOS-Chem simulations of ozone have been using the Synoz (synthetic ozone) flux boundary condition of McLinden et al. [2000]. In this method, stratospheric ozone is represented by a passive tracer released in the lower tropical stratosphere at a rate constrained to match a prescribed global mean cross-tropopause ozone flux. We have adopted the same method for simulating HD in the stratosphere. This results in a mean troposphere-stratosphere HD flux of 0.15 Gg a$^{-1}$, which yields reasonable agreement with $\delta D$ observations in the lower stratosphere (section 3.4). Because $H_2$ mixing ratios remain nearly invariant vertically in the troposphere and stratosphere, excessive cross-tropopause flux is not an issue for $H_2$.

Isotopic fractionations for the OH and soil sinks are based on the rate of removal of HD versus $H_2$. Specifically, $\alpha$ is the ratio of the rate constants for removal of HD versus $H_2$. For the soil isotopic signature we use the measured soil fractionation ($\alpha_{\text{soil}} = 0.943 \pm 0.024$) from Gerst and Quay [2001], which agrees with more recent measurements of the soil fractionation by Rahn et al. [2003] of 0.94 ± 0.01 and A. Dayalu et al. (unpublished data, 2006) of $\alpha_{\text{soil}} = 0.941 \pm 0.018$. We calculate the OH fractionation on the basis of measured laboratory rates constants for $H_2 + OH$ [Talukdar et al., 1996] and HD + OH [Heizswolf et al., 1996].

Figure 1. Global annual sources of $H_2$: (a) fossil fuel and biofuel combustion, (b) biomass burning, (c) ocean production, and (d) photochemical production.
resulting $\alpha_{\text{OH}}$ has a global average of 0.568 (Table 1) thus enriching atmospheric $\delta D$.

3. Results and Discussion

3.1. Hydrogen

[23] The global budget for $H_2$ calculated from GEOS-Chem is shown in Table 1. In our simulation the total sources are 73 Tg a$^{-1}$, and the tropospheric burden for $H_2$ is 141 Tg. The global mean atmospheric lifetime is 1.9 a, while the lifetime with respect to OH oxidation alone is 9 a. Our total source estimate agrees well with the previous studies, which range from 70–89 Tg a$^{-1}$ (Table 1). Our annual mean lifetime also compares well with previous estimates of 0.7–2.3 a. Recent work by Rhee et al. [2006] suggests higher sources (107 Tg a$^{-1}$) and a shorter lifetime (0.7 a).

[24] Our photochemical source (34.3 Tg a$^{-1}$) is in good agreement with the range of previous estimates (31–64 Tg a$^{-1}$) in Table 1. The range of previously estimated fossil fuel emissions (15–20 Tg a$^{-1}$) is also consistent with our budget (18.3 Tg a$^{-1}$). Our biomass burning source (10.1 Tg a$^{-1}$) is at the lower end of the range of previous estimates (10–20 Tg a$^{-1}$).

[25] Soil uptake, at 55 Tg a$^{-1}$ globally, accounts for 75% of the total $H_2$ loss in our simulation. This is in good agreement with the 75% estimate of Novelli et al. [1999], 79% of Hauglustaine and Ehhalt [2002], 76% from Sanderson et al. [2003], 77% from Rahn et al. [2003], but lower than the 82% estimate of Rhee et al. [2006], and the earlier estimates from Seiler and Conrad [1987] (92%) and Warneck [1988] (87%).

[26] The spatial distribution of the total annual emissions for $H_2$ is shown in Figure 1, while the latitudinal and seasonal distributions are shown in Figures 2a and 3. Fossil fuel emissions, apparent over Europe, North America, and Asia, are dominant in the NH. Biomass burning emissions are concentrated in the tropics (Figures 2a and 3), where they exhibit a pronounced seasonality, with two broad maxima occurring during the NH dry season in January–April and the SH dry season during August–October (Figure 3) [Duncan et al., 2003].

[27] Methane oxidation accounts for a majority of the global annual photochemical source (24.5 Tg a$^{-1}$), while BVOC oxidation accounts for another 10.1 Tg a$^{-1}$. These photochemical sources reach a maximum during summer (Figure 3), concurrent with the maximum in BVOC emissions and OH concentrations.

[28] For our ocean $H_2$ source, emissions are concentrated between 40$^\circ$N and 40$^\circ$S. Peak ocean emissions occur over the central Pacific near 20$^\circ$N and 20$^\circ$S, where nitrogen fixation is expected to be at a maximum in the oligotrophic (nutrient poor) waters of subtropical gyres [Deutsch et al., 2007]. Deutsch et al. [2007] estimate a global ocean nitrogen fixation rate of 150 ± 50 TgN a$^{-1}$. Assuming a 1:1 stoichiometry for the number of $H_2$ molecules produced per $N_2$ fixed [Brock and Madigan, 1991], yields an 11 ± 4 Tg$H_2$ a$^{-1}$ ocean source. This is an upper estimate, as reuptake of $H_2$ by ocean microbe hydrogenases likely reduces this total [Brock and Madigan, 1991]. Our assumed ocean source of 6 Tg a$^{-1}$ implies a 45% recycling rate.

[29] The temperature dependence in our formulation for soil deposition velocity (section 2) results in a strong seasonal cycle in the NH soil sink, which increases by nearly a factor of 2, from winter to summer (Figure 3). Similar seasonality would be expected from the incorporation of soil moisture, whereby diffusion could be reduced during NH winters because of a combination of increased moisture and ice and snow cover [Yonemura et al., 2000; Conrad and Seiler, 1980, 1985]. In contrast, there is no
seasonality in the tropical soil sink (Figure 3), because the majority of the land area remains above freezing year-round.

The simulated surface mixing ratios of H$_2$ vary between 400 and 700 ppbv (Figure 4) with some seasonal and geographical variations, with a global surface mean of 521 ppbv and a tropospheric mean of 525 ppbv. High-H$_2$ levels (525–700 ppbv) are predicted over the main anthropogenic source regions in the NH (East Asia, Europe, the eastern United States) as well as over biomass burning regions (southeast Asia in MAM, northern equatorial Africa in DJF, southern Africa and South America during JJA and SON, Indonesia in SON). The effect of the ocean source can be seen over the tropical Pacific in JJA and SON (Figure 4). The lowest levels (less than 475 ppbv) (Figure 4) are predicted over the NH high latitudes during fall and winter months (September–February), where the soil sink dominates but sources such as photochemical oxidation of VOCs and CH$_4$ are lacking, and a stable boundary layer impedes vertical mixing. Values are particularly low over Siberia because of the long continental fetch.

The SH mid to high latitudes (south of 24$^\circ$S) have surface H$_2$ mixing ratios that are 42 ppbv higher than the NH mid to high latitudes (north of 24$^\circ$N) because of the asymmetry of soil uptake. This is because 2/3 of Earth’s land area is in the NH, resulting in 69% of the H$_2$ soil sink occurring in the NH.

3.2. Comparison With Hydrogen Observations

We compare our global H$_2$ simulation with surface observations from the CMDL network of ground sites and ship cruises [Novelli et al., 1999]. We use mean climatological observations for the 10-a period 1994–2003 (49 sites). Novelli et al. [1999] found little to no secular trend in the CMDL surface observations for 1989 to 1997. The simulation captures the low observed values at the high-latitude NH sites throughout the year, with particularly low values during SON (Figure 4). The high-H$_2$ mixing ratios in regions near large fuel combustion sources can also be seen in both the observations and model. The model tends to overestimate H$_2$ by 10–30 ppbv at continental sites that are influenced by urban emissions in East Asia (Tae-ahn, South Korea, 36.7$^\circ$N, 126.1$^\circ$E) and North America (Wendover, Utah, 39.9$^\circ$N, 113.7$^\circ$W).

A comparison of the seasonally averaged CMDL observations and simulation (Figure 5) shows good correlation ($r^2 = 0.75$) and essentially no model bias, where the bias in ppbv (model–observations) is 0.9, or 0.2 as a percentage [(model–observations)/observations $\times$ 100%].

A comparison of mean annual surface H$_2$ observed and modeled mixing ratios as a function of latitude is shown in Figure 6. In the NH and SH the model and observations show good agreement with no model bias in the NH (0.1 ppbv) and SH ($-$0.8 ppbv). Seasonally, the greatest model bias occurs in the NH during SON (5 ppbv) and in the SH during JJA (4 ppbv). There is no bias during JJA in the NH ($-$0.4 ppbv) or DJF in the NH ($+$0.4 ppbv). We define the interhemispheric gradient as the difference between the average mixing ratio north of 24$^\circ$N and south of 24$^\circ$S, sampled at the CMDL sites binned by latitude on Figure 6. The simulated gradient corresponding directly with observational grid points is 28 ppbv, which is in very good agreement with the observed gradient of 27 ppbv by season the largest gradient occurs in the observations (44 ppbv) and simulation (40 ppbv) during SON (Figure 4) because of the NH soil sink reducing H$_2$ levels in the NH, while photochemical sources increase H$_2$ in the SH.
weakest gradient occurs during JJA in the observations (12 ppbv) and simulation (16 ppbv), reflecting the increase in \( \text{H}_2 \) from photochemical sources in the NH, and reduced SH source. We note that the modeled interhemispheric gradient sampled at CMDL sites is weighted toward ocean sites and is thus lower than the gradient for the entire model domain (42 ppbv).

[36] Both observations and model display a local maximum over the equatorial Pacific (Figures 4 and 6). In the model this is due to the ocean source.

[37] The greatest variability in both measurements and simulation occurs between 35 and 50°N (Figures 5 and 6) at land sites that are close to source regions. These include continental sites in Asia and North America, such as Ulaan, Mongolia, Tae-ahn, Korea, and Wendover, Utah. At higher latitudes (north of 50°N) the model captures well the decrease in \( \text{H}_2 \) levels, which is due to a combination of the maximum in soil sink and lack of surface emission sources.

[38] In Figure 7 we compare the observed and modeled seasonal variations of \( \text{H}_2 \), for 12 CMDL sites. Observations at the NH sites north of 50°N (Alert, Barrow, Cold Bay, and Mace Head) reach a maximum during April–May and a minimum in September–October. The model captures the timing of this maximum but shows a 1–2 month delay in the minimum at Alert, Barrow, and Mace Head. At NH continental sites, Park Falls and Ulaan, the model predicts a broader maximum with a 2 month delay compared with observations. At NH sites south of 35°N (Bermuda and Sand Island) the seasonal maximum is shifted to June–July. At high-SH latitudes (north of 55°S) the simulation captures the minimum between July and September but underestimates the maximum in January–February. According to Novelli et al. [1999], the SH seasonal cycle is controlled by biomass burning, while Sanderson et al. [2003] suggested that long-range transport is the dominant controlling factor.

[39] The amplitude of the seasonal cycle decreases from the NH to the SH. The northern most continental sites at Barrow (71.3°N) and Alert (82.4°N) show the strongest seasonal cycle in both the model and measurements (Figure 7), with a seasonal amplitude in the simulation and observations of 74 and 62 ppbv at Barrow and 58 and 71 ppbv at Alert, respectively. The amplitude of the observed and simulated seasonal cycle is smaller (~30 ppbv) at NH island sites at Bermuda and Sand Island. In the SH the amplitude of the seasonal cycle decreases to 19 ppbv.

Figure 4. Seasonal maps of modeled surface \( \text{H}_2 \) mixing ratios (ppbv) averaged by season: December–February (DJF), March–May (MAM), June–August (JJA), and September–November (SON). CMDL observations, shown as circles color coded by the observed values, are climatological averages between 1994 and 2003. The color bar is saturated at 600 ppbv but maximum values over Asia during DJF and MAM are up to 700 ppbv.
The model underestimates the observations at Barrow during all months, with maximum differences during May (48 ppbv) and November (54 ppbv). This underestimation is due to a combination of the coarse resolution of the model and an overestimate of the soil sink from continental influence.

The equatorial site at Mahe Island (4.7°S) has two seasonal maxima in March and November and two minima in January and June. This seasonality is due to a combination of the biomass burning and photochemical sources in the tropics (Figure 3), which peak in March and September and October, respectively. The simulation captures the seasonal minima but underestimates the maxima by 8–9 ppbv, possibly because of an underestimate of regional biomass burning or photochemical sources in the model.

![Figure 5](image1.png)

**Figure 5.** Comparison between seasonally averaged CMDL observations and model results. The CMDL observations are climatological averages between 1994 and 2003. Seasons include DJF (crosses), MAM (circles), JJA (squares), and SON (triangles). The seasonal and annual biases are given, along with the correlation coefficient and reduced major axis slope and intercept.

![Figure 6](image2.png)

**Figure 6.** Latitudinal distribution of annual mean H₂ (ppbv) at the surface. The CMDL observations are the climatological mean for all sites with data spanning 1994–2003 (open circles with 1 standard deviation bars). Solid circles represent the GEOS-Chem simulation, sampled at the CMDL station locations.
Schmidt [1974] first reported a strong vertical gradient in H₂ at high latitudes over Canada during summer, reflecting a strong surface soil sink. In their model simulation, Hauglustaine and Ehhalt [2002] predicted strong vertical gradients during summer. We examine this issue by analyzing CMDL aircraft observations collected between November 2002 and August 2004 at three sites (Figure 8) (P. Novelli, unpublished data, 2005). These include two NH continental sites at Poker Flat, Alaska (65°N, 147.3°W), and Park Falls, Wisconsin (45.9°N, 90.3°W), and a SH island site at the Cook Islands (21.4°S, 160.4°W). Vertical profiles were obtained 2–4 times each month at altitudes up to 7 km.

Figure 7. Seasonal variation in H₂ at 12 CMDL ground sites. The CMDL data include monthly averages for the 1994–2003 observational records (dashed line) with standard deviation. The model is shown with the solid line, and the shaded area encompasses the minimum and maximum values in surrounding grid boxes.
above sea level at Poker Flat, 4 km at Park Falls, and 6 km at the Cook Islands.

In both the observations and simulation, H$_2$ levels decrease near the surface over two continental sites at Park Falls and Poker Flat. This decrease is most pronounced during fall and winter, when shallow boundary layer depths coincide with a decreased photochemical source and continued soil sink. The soil sink controls much of the seasonal cycle at the surface, and thus the amplitude of the seasonal cycles dampens with increasing altitude (Figure 8). By contrast the Cook Islands observed and modeled profiles are relatively uniform with altitude, reflecting the lack of a soil sink.

3.3. Deuterium

The simulated seasonal global distribution of $\delta$D of atmospheric H$_2$ ($\delta$D$_{atmos}$) at the surface, with a global mean of 130‰, is shown in Figure 9. The model simulates a global surface interhemispheric gradient of 27‰, with average global surface levels of 117‰ in the NH (north of 10°N), 130‰ in the tropics (10°N to 10°S), and 144‰ in the SH (south of 10°S). The lowest values (20–40‰) are predicted over industrialized regions of Asia, Europe, and the eastern United States because of fossil fuel emissions that are depleted in deuterium.

The modeled interhemispheric $\delta$D$_{atmos}$ gradient is strongest during MAM when the SH values exceed those of the NH by 36‰ (Figure 9). The enriching photochemical source and OH sink are at a maximum during summer in the SH, while the NH is dominated by depleted emissions and concurrent minimum in the enriching photochemical contribution to $\delta$D$_{atmos}$. The 3-month delay is due to the long lifetimes of H$_2$ and HD. The same processes result in a minimum gradient during September–November (12‰), where the NH maximum in the photochemical source

![Figure 8](image-url). Seasonally averaged CMDL H$_2$ profiles from aircraft observations at Poker Flat (2002–2004), Park Falls (2002–2004), and Cook Islands (2003–2004) are represented by circles with 1σ standard deviation. Observations are averaged every 500 m, and the number of observations in each bin is indicated on the right. The corresponding model mean, shown by the solid line, matches the observational grid box. Dashed lines represent the simulated minimum and maximum H$_2$ levels in horizontally adjacent model grid boxes.
partially offsets the depleted emission sources, while the SH photochemical sources and sinks are at a minimum. The industrialized region of east Asia shows lower $d^D$ than those over the United States and Europe, which is due to the large Asian anthropogenic H$_2$ source from fossil (7.1 Tg a$^{-1}$) and biofuel (2.3 Tg a$^{-1}$) combustion. The depleted signature over Asia is further enhanced during spring, when biomass burning emissions from southeast Asia are at a maximum.

We examine the relative contributions of the isotopic signatures of the sources by defining $d^D$$_{sources}$ as the sum of individual isotopic signatures $d^D_i$ weighted by relative source strengths $f_i$:  

$$d^D_{sources} = d^D_{ff}f_{ff} + d^D_{bf}f_{bf} + d^D_{bb}f_{bb} + d^D_{hv}f_{hv} + d^D_{ocean}f_{ocean}.$$  

The global values for the source-weighted isotopic signatures $d^D_{sources}$ are listed in Table 1. While ocean emissions are a minor source of H$_2$, they contribute heavily to the $d^D$ budget because of their large negative isotopic signature. Their contribution to the $d^D$ budget ($d^D_{ocean}/ocean = -52\%$) is similar to the contribution from fossil fuel combustion ($d^D_{ff}/ff = -48\%$). Biomass burning adds another $-40\%$, and biofuel adds another $-17\%$. Photochemical oxidation has a positive isotopic signature ($d^D_{hv}/hv = +77\%$). Overall, we find $d^D_{sources} = -82\%$.

We define the isotopic signature of sinks $a_{sinks}$ as the sum of OH and soil globally averaged $a_i$ multiplied by the relative strength of these H$_2$ sinks $f_i$:  

$$a_{sinks} = a_{OH} f_{OH} + a_{soil} f_{soil}.$$  

Overall, $a_{sinks} = 0.84$ with OH accounting for $a_{OH} f_{OH} = 0.14$ and $a_{soil} f_{soil} = 0.70$ (Table 1).

The latitudinal distribution of $d^D_{sources}$ and $a_{sinks}$ is displayed on Figure 2b. There is a broad minimum in $d^D_{sources}$ at 10–50$^\circ$N from the combined effects of ocean emissions (10–20$^\circ$N) and fossil fuel/biofuel combustion (30–50$^\circ$N). Near the equator, $d^D_{sources}$ reaches a local maximum as all the negative sources are counterbalanced by the strong positive photochemical source. Integrating over the SH, we find that $d^D_{sources}$ are less negative ($-13\%$) than in the NH ($-67\%$). The isotopic fractionation of the sinks $a_{sinks}$ is shifted toward higher values in the NH because of the influence of the soil sink. As a direct result, there is an asymmetry between the enrichment of the sink processes between the two hemispheres, with NH sinks ($a_{sinks} = 0.56$) less enriching than the SH ($a_{sinks} = 0.28$).
Thus the interhemispheric difference in sources is partially offset by that of the sinks.

[48] From the mass balance equation for (D/H)_{atmos}, and assuming steady state, $\alpha_{sinks}$ and $\delta D_{sources}$ are related to $\delta D_{atmos}$ through the following equation (see derivation in Gerst and Quay [2001]):

$$\left(\frac{\delta D_{source}}{1000} + 1\right) = \alpha_{sink} \left(\frac{\delta D_{atmos}}{1000} + 1\right)$$

(3)

If we use equation (3) to infer $\delta D_{atmos}$ based on $\alpha_{sinks} = 0.84$ and $\delta D_{sources} = -82\%$, we find a value of +93\%. The +37\% difference between this value and the modeled (and observed) $\delta D_{atmos}$ of 130\% comes from the stratospheric enrichment. This value is consistent with our sensitivity study to determine the stratospheric contribution to $\delta D_{atmos}$ (section 3.4).

3.4. Comparison With Deuterium Observations

[49] For comparison with our $\delta D$ simulation we use mean observations from Pacific Ocean ship cruises (38°N to 77°S) during November–December 2001, December 2003, September–October 2004, April 2005, and August 2005 [Rice and Quay, 2006], as well as ground station observations from Cheeka Peak Observatory (CPO), Washington (48°N, 124°W), during 2002–2005 [Rice and Quay, 2006] and Barrow, Alaska (71°N, 156°W), during 1996–1997 [Gerst and Quay, 2000]. These observations are shown as colored circles in Figure 9 and displayed as a function of latitude on Figure 10. For comparison with observations we use results from the model grid cell in which the observations were made.

[50] Model and observed $\delta D_{atmos}$ agree well in their distribution with latitude (Figure 10). In the NH (north of 10°N), modeled and ship cruise observed surface $\delta D_{atmos}$ are both 120\%. In the SH (south of 10°S) these values are both 141\%. The resulting interhemispheric gradient is 21\% for both model and observations. The exception to this apparent agreement between model and measured $\delta D$ is at high latitudes where Gerst and Quay [2000] reported observations of $\delta D$ from Barrow averaging 92 ± 10\%. This suggests that $\delta D$ decreases with increasing latitude in the NH. The model predicts considerably higher values at this latitude (123\%). The reason for this gradient in $\delta D$ is not understood and more observations at high latitudes are necessary to evaluate the robustness of the observed gradient. By season the largest gradient occurs in the model (36\%) and observations (35\%) during MAM. The weakest

Figure 10. Latitudinal distribution of atmospheric $\delta D$ (\%) at the surface. Observations are binned by latitude, as discussed in section 3.4. The bars represent 1 standard deviation. The GEOS-Chem simulation sampled along the cruise tracks is shown by the solid line.

Figure 11. Seasonal variation in $\delta D$ at CPO, including monthly averages for 2002 to 2005 observational record (dashed line) with standard deviation. The model is shown with the solid line, and the shaded area encompasses the minimum and maximum values in surrounding grid boxes.
gradient occurs during SON in the model (12%) and observations (6%) (Figure 9).

Figure 11 shows the seasonal comparison of $d_{\text{Datmos}}$ at CPO. Model and observed $d_{\text{Datmos}}$ show good agreement in mean values (110 and 118%, respectively) and in amplitude and phase of the seasonal cycle. Both modeled and observed $d_{\text{D}}$ peak during fall (123 and 132%, respectively). The simulated seasonal minimum occurs in February (91%), 2 months earlier than observed (April, 94%). This difference may be due to a combination of model resolution and resulting overestimate of the continental influence.

Figure 12 shows the vertical distribution of $d_{\text{Datmos}}$ for latitudes north of 10°N. There is little vertical gradient in the troposphere between the surface observations from Rice and Quay [2001] and Rice and Quay [2006] (128.5%) by Rhee et al. [2006]. We constrain our stratospheric HD values to capture the vertical gradient in the upper troposphere and lower stratosphere observed by Rahn et al. [2003] and Röckmann et al. [2003] (see section 2.3). There is rapid enrichment in modeled $d_{\text{Datmos}}$ from 130% at 10 km to 190% at 20 km. The observations show wide variations that increase with altitude but are within the minimum and maximum range (shaded area) of the simulation. The observations of Rahn et al. [2003] were obtained in the polar vortex and represent air masses that had experienced considerable descent. To obtain values representative of the lower stratosphere, we only used observations where the methane level was 1400 ppbv or higher (Figure 12).

We assessed the role of stratosphere-troposphere exchange by conducting a sensitivity simulation with no stratospheric enrichment in $d_{\text{D}}$. This results in an essentially uniform vertical profile for $d_{\text{D}}$ at 85–100% (Figure 12). The difference between the two simulated profiles represents the stratospheric contribution. Globally, we find a 37% contribution, identical to the number we found in section 3.3 on the basis of budget considerations.

4. Model Sensitivity

Our results (section 3) are consistent with the dominant role of soils as the main $H_2$ sink thus affecting its interhemispheric gradient, vertical distribution, and seasonal cycle. In an attempt to assess a reasonable range for the soil sink we conducted two sensitivity tests, increasing and decreasing the $H_2$ deposition velocity by 15%. We maintained a global $H_2$ burden of 141 Tg by balancing changes in the soil sink with uniform changes in the sources. Thus a change in the soil sink of ±15% required a concurrent ±11.3% change in all sources. For comparison with observations, in section 5 we report the simulated gradients that correspond to the $d_{\text{D}}$ and $H_2$ observations (Figures 6 and 10).

In the +15% soil case the total $H_2$ sources and sinks decrease to 73 Tg a$^{-1}$ to 81 Tg a$^{-1}$ with a corresponding reduction in the $H_2$ lifetime from 1.9 to 1.7 a, well within the range of previous estimates (Table 1). Overall, the $H_2$ simulation compares well with CMDL observations, with a very small model bias of -0.63 ppbv. The interhemispheric gradient increases from 28 ppbv to 34 ppbv, which is in good agreement with the observed CMDL gradient of 27 ppbv. For $d_{\text{Datmos}}$ the global surface mean is reduced by 16%, but the gradient is unchanged. In order to match $d_{\text{Datmos}}$ observations we need to increase the assumed $d_{\text{Dhv}}$ from 162 to 183%.

In the -15% soil case the total $H_2$ sources and sinks decrease to 65 Tg a$^{-1}$ and the $H_2$ lifetime decreases from 1.9 to 2.2 a. The latitudinal gradient decreases to 22 ppbv. There is relatively good agreement with CMDL observations, with a model bias of -3.16 ppbv. Most notably, the $H_2$ simula-
tion underestimates the observations at SH sites during DJF by 10 ppbv. In this simulation the global surface mean $\delta_{\text{atmos}}$ is increased by 21%, while the gradient remains unchanged. Using $\delta_{\text{atmos}} = 136 \pm 50$ results in good agreement with observed $\delta_{\text{atmos}}$. Changes in the deposition velocity beyond ±15% lead to a significant degradation in the agreement between observed and modeled $H_2$.

[57] We compare the sensitivity of our results to assumptions about the ocean source. As we vary the magnitude of the ocean source between 0 and 12 Tg a$^{-1}$ we maintain the same H$_2$ burden by adjusting the soil deposition velocity. While on average the simulations match the mean observed H$_2$ mixing ratios, the interhemispheric H$_2$ and H$_2$/tropospheric means for H$_2$ are 521 and 525 ppbv, respectively. In this simulation the global surface mean $H_2$ underestimates the observations at SH sites during DJF by 10 ppbv. The simulated global surface and upslope gradients also yield reasonable results. For these two cases we reproduce observed $\delta_{\text{atmos}}$ by assuming $\delta_{\text{atmos}} = 107\%$ and $\delta_{\text{atmos}} = 219\%$, respectively.

[58] These sensitivity studies thus provide uncertainty estimates for the soil sink (55 ± 8 Tg a$^{-1}$), ocean source (6 ± 3 Tg a$^{-1}$), and photochemical isotopic source signature ($\delta_{\text{atmos}} = 162 \pm 57\%$). Using stratospheric observations, Röckmann et al. [2003] estimates a range from 150 to 230% for $\delta_{\text{atmos}}$, with a value of 180 ± 50% at the tropopause, while Gerst and Quay [2000] find $\delta_{\text{atmos}} = 130 \pm 70\%$. Thus our estimate for $\delta_{\text{atmos}}$ is between these previous estimates.

[59] The value of our coupled H$_2$ and H$_2$/tropospheric simulation is currently limited by the small number of $\delta_{\text{atmos}}$ observations and by a lack of direct measurements of $\delta_{\text{atmos}}$. Our sensitivity simulation shows that the spatial distribution of both H$_2$ and $\delta D$ is affected by changes in the sources and sinks of H$_2$. In the future, additional $\delta_{\text{atmos}}$ observations over a wider geographical range would allow us to place stricter constraints on the budget of H$_2$ through a coupled H$_2$/$\delta D$ inverse modeling study.

5. Conclusions

[60] To simulate the budget and distributions for hydrogen and deuterium in the atmosphere, we use a global three-dimensional chemical transport model. Sources of H$_2$ are based on the spatial and temporal distributions of CO and include fossil fuel, biofuel, and biomass burning emissions and photochemical sources from oxidation of methane and BVOCs. Our ocean source is based on the spatial distribution of oceanic N$_2$ fixation. For the main H$_2$ sink, soil uptake, we use a uniform dry deposition over land, excluding desert and snow-covered areas, with reductions when temperatures are below freezing. The other main sink is oxidation of H$_2$ by OH. The simulated global surface and tropospheric means for H$_2$ are 521 and 525 ppbv, respectively. The tropospheric burden is 141 Tg, and the overall lifetime in the troposphere is 1.9 a.

[61] Comparison of model results with CMDL observations shows good agreement, with essentially no model bias in the NH (0.1 ppbv) and SH (–0.8 ppbv). The interhemispheric gradient in the observations (27 ppbv) and simulation (28 ppbv) shows good agreement. The model reproduces the seasonal cycle in the observations, with the best fit in the NH during summer (JJA) (bias = 0.4 ppbv) and winter (DJF) (bias = –0.8 ppbv). The greatest deviation is in the NH during SON and the SH during JJA, with model biases of 5 and 4 ppbv, respectively. Seasonally, H$_2$ in the NH reaches a minimum during NH autumn and a maximum during NH spring. In the SH the minimum is during SH winter and the maximum during SH summer. The seasonality in the NH is due to the combination of the soil sink and photochemical source.

[62] Comparison with vertical profiles of H$_2$ in the NH (Poker Flat and Park Falls) and SH (Cook Islands) also show good agreement. Both model and observations capture the low-surface H$_2$ at the continental NH sites because of the strong soil sink, and they also capture the uniform vertical profile over the Cook Islands. For $\delta D_{\text{atmos}}$ we calculate a photochemical source signature of 162% in order to reproduce observations of $\delta D_{\text{atmos}}$. The simulated $\delta D$ in the atmosphere shows a global surface latitudinal gradient with 27% greater enrichment in the SH. When compared directly with observations from several recent Pacific Ocean transects [Rice and Quay, 2006], the model gradient (21%) is in very good agreement with observations (21%). This gradient is due to the predominance of depleted emission sources from fossil fuel combustion in the NH and enriched photochemical sources in the SH.

[63] We use sensitivity studies for soil deposition velocity ±15% and ocean source (0–12 Tg a$^{-1}$) to assess uncertainties in our estimates for the soil sink (55 ± 8 Tg a$^{-1}$), ocean source (6 ± 3 Tg a$^{-1}$), and photochemical isotopic enrichment ($\delta_{\text{atmos}} = 162 \pm 57\%$) in the ranges of previous estimates. By constraining modeled stratospheric $\delta_{\text{atmos}}$ with $\delta D$ observations in the lower stratosphere we estimate that stratosphere-troposphere exchange accounts for a 37% enrichment in the troposphere.

[64] Our $\delta D$ simulation is a successful first attempt at modeling the $\delta D$ of H$_2$. Our simulation is limited by the small number and range of $\delta D$ observations, stressing the need for more atmospheric $\delta D$ measurements to further constrain the budgets of H$_2$ and $\delta D$. Regions of specific interest include high-northern latitudes, such as including northwest Pacific (downwind of Asia), northeast Atlantic (downwind of the United States), and biomass burning regions (tropical Atlantic).

[65] Acknowledgments. Funding from the University of Washing-
one’s Program on Climate Change and National Science Foundation (ATM 0238530 and ATM 0091878) supported this work. This work is also partially funded by the Joint Institute for the Study of the Atmosphere and Ocean (JISAO) under NOAA Cooperative agreement NA17J1232. We thank Curtis Deutsch for providing us with the ocean N$_2$ fixation fields and Gabrielle Curci for providing us with the O(1D) fields.

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R. Gammon and P. Quay, School of Oceanography, Box 357940, University of Washington, Seattle, WA 98195, USA. (gammon@u.washington.edu; quay@ocean.washington.edu)

L. Jaegle and H. Price, Department of Atmospheric Sciences, Box 351640, University of Washington, Seattle, WA 98195, USA. (hprice@u.washington.edu; jaegle@atmos.washington.edu)

P. C. Novelli, National Oceanic and Atmospheric Administration, Climate Diagnostics Center, 325 Broadway Street, Boulder, CO 80303, USA. (pnovelli@cmdl.noaa.gov)

A. Rice, Department of Physics, Portland State University, Portland, OR 97207, USA. (arice@pdx.edu)