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Molecular hydrogen uptake by soils in forest, desert, and marsh ecosystems in California

Nicole V. Smith-Downey, James T. Randerson, and John M. Eiler

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The mechanism and environmental controls on soil hydrogen (H\(_2\)) uptake are not well understood but are essential for understanding the atmospheric H\(_2\) budget. Field observations of soil H\(_2\) uptake are limited, and here we present the results from a series of measurements in forest, desert, and marsh ecosystems in southern California. We measured soil H\(_2\) fluxes using flux chambers from September 2004 to July 2005. Mean H\(_2\) flux rates and standard deviations were -7.9 ± 4.2, -7.6 ± 5.3 and -7.5 ± 3.4 nmol m\(^{-2}\) s\(^{-1}\) for the forest, desert, and marsh, respectively (corresponding to deposition velocities of 0.063 ± 0.029, 0.051 ± 0.036, 0.035 ± 0.013 cm s\(^{-1}\)). Soil profile measurements showed that H\(_2\) mixing ratios were between 3% and 51% of atmospheric levels at 10 cm and that the penetration of H\(_2\) into deeper soil layers increased with soil drying. Soil removal experiments in the forest demonstrated that the litter layer did not actively consume H\(_2\), the removal of this layer increased uptake by deeper soil layers, and the exposure of subsurface soil layers to ambient atmospheric H\(_2\) levels substantially increased their rate of uptake. Similar soil removal experiments at the desert site showed that extremely dry surface soils did not consume H\(_2\) and that fluxes at the surface increased when these inactive layers were removed. We present a model of soil H\(_2\) fluxes and show that the diffusivity of soils, along with the vertical distribution of layers that actively consume H\(_2\) regulate surface fluxes. We found that soil organic matter, CO\(_2\) fluxes, and ecosystem type were not strong controllers of H\(_2\) uptake. Our experiments highlight H\(_2\) diffusion into soils as an important limit on fluxes and that minimum moisture level is needed to initiate microbial uptake.


1. Introduction

The uptake of molecular hydrogen (H\(_2\)) by soils accounts for 62% to 92% of the total atmospheric H\(_2\) sink [Novelli et al., 1999; Gerst and Quay, 2001; Hauglustaine and Ehhalt, 2002; Rahn et al., 2003; Rhee et al., 2006; Price et al., 2007; Xiao et al., 2007]. Relatively few field measurements of soil H\(_2\) uptake are available to improve these estimates. Recently, the atmospheric H\(_2\) budget has received substantial attention because of the possibility of increased tropospheric H\(_2\) emissions and subsequent decreases in stratospheric ozone in a hydrogen economy [Schulz et al., 2003; Tromp et al., 2003; Warwick et al., 2004]. Current understanding of the mechanisms regulating the H\(_2\) soil flux is limited, making it difficult to predict how the soil sink will respond to future increases in emissions or changes in climate.

The uptake of H\(_2\) by soils is a biological process that is inhibited at very low soil moisture levels [Fallon, 1982; Conrad and Seiler, 1985; Smith-Downey et al., 2006] and decreases at high soil moisture levels because of limitation of H\(_2\) diffusion into soils [Yonemura et al., 1999, 2000b]. The temperature dependence of the surface flux of H\(_2\) into soils is not consistent between field studies, and in many cases there is no observable relationship between soil temperature and H\(_2\) flux. Laboratory measurements suggest that H\(_2\) uptake is sensitive to changes in temperature from -4°C to 15°C, after which a broad temperature optimum is observed [Smith-Downey et al., 2006]. Field measurements of soil H\(_2\) uptake have been conducted in boreal forest ecosystems in Alaska [Rahn et al., 2002] and Finland [Lallo et al., 2008], savanna ecosystems in South Africa [Conrad and Seiler, 1985], temperate urban ecosystems in Europe [Conrad and Seiler, 1985], and temperate forest and agricultural ecosystems in Japan [Yonemura et al., 1999, 2000a]. Additional field observations of H\(_2\) uptake by soils are needed to more fully describe the response of soil H\(_2\) uptake to changing environmental conditions.

Here we describe a series of field experiments conducted in three different California ecosystems between September 2004 and July 2005. We measured H\(_2\) fluxes...
and vertical profiles of H₂ mixing ratio in soils at forest, desert and marsh field sites. We performed a series of soil removal experiments to determine the uptake capacity of soil layers at different depths. CO₂ fluxes were also measured at the forest and desert sites and continuous measurements of soil temperature and soil moisture were recorded after February 2005. We found that H₂ fluxes did not depend strongly on ecosystem type and that diffusion of H₂ through dry, inactive surface soil layers limited flux rates.

2. Methods

2.1. Site Descriptions

We measured hydrogen uptake by soils at three sites in Southern California (Table 1) from September 2004 to July 2005. These sites were a mixed conifer and hardwood forest ecosystem in the University of California (UC) James San Jacinto Mountain Reserve (33.81°N, 116.79°W), a desert shrub ecosystem in the UC Burns Piñon Ridge Reserve (34.15°N, 116.45°W), and a freshwater marsh in the UC San Joaquin Freshwater Marsh Reserve (33.66°N, 117.85°W), hereafter referred to as the forest, desert and marsh sites respectively. The overstory canopy at the forest site was dominated by ponderosa pine (Pinus ponderosa), California black oak (Quercus kelloggii), interior live oak (Quercus wislizeni) and incense cedar (Calocedrus decurrens). The sparse desert vegetation was largely composed of piñon pine (Pinus monophylla), junipers (Juniperus californica), Muller’s oak (Quercus cornelius), and cholla (Cylindropuntia echinocarpa). The two marsh sites we first sampled were dominated by cattail (Typha latifolia), and the third marsh site we sampled near the edge of a seasonal pond had both cattail and willow (Salix) species. The mineral soil component of the forest and desert soils were primarily sand and coarse sand, whereas the marsh soil was clay with a surface organic layer that was approximately 20 cm deep.

At the forest site, three replicate soil collars and soil gas samplers were installed near a streambed and on a south-facing hillside. At the desert site, two replicate soil collars and soil gas samplers were installed at three locations along a gradient from high to low soil organic matter (SOM) content (Table 2). The collars with the highest SOM were located directly under an oak (Quercus cornelius-mulleri), the intermediate SOM collar were located ~2m from the oak center, and the low SOM collars were located in bare sand, ~5m from the oak center. At the marsh site, three replicate soil collars and soil gas samplers were installed first near a seasonal pond and in a reed dominated marsh. Depth to the water table was approximately 40 cm at site 1 at the marsh in October 2004. In February 2005, both of the marsh sites flooded, so a third site was established near the edge of a seasonal pond in April 2005.

2.2. Flux Measurements

Soil flux collars were constructed from 20 cm diameter polyvinyl chloride (PVC) pipe cut into 10 cm deep sections and fitted with an acrylic collar (Figure 1a). These collars were permanently installed at each site and remained in place throughout the duration of our field measurements. A flux chamber was constructed from acrylic and included a syringe port for removal of gas samples. A 1/4” thick Viton O-ring was placed between the soil collar and the flux chamber and the chamber was clamped to the soil collar during flux experiments to ensure a tight seal. Once the collars were cuffed with the flux chamber, 10 mL gas samples were withdrawn immediately (after flushing the syringe twice), and at 1, 2, 4, and 8 min intervals using plastic syringes fitted with three way nylon stopcock valves with a high-density polyethylene (HDPE) plug (Kimble-Kontes, Vineland, New Jersey).

The syringes were stored on a layer of bubble wrap in a cooler filled with dry ice. Storing the samples at subzero temperatures preserved the hydrogen mixing ratio for several hours, and laboratory tests showed a leak rate of approximately 2 ppb/h for syringes filled with hydrogen free air. All samples were immediately returned to the lab and measured on the same night of sample collection. All measurements were subsequently corrected for this leak rate using the time interval between sample collection and measurement. Samples were injected into a TA3000R Reducing Gas Analyzer (Ametek Process Instruments, Newark, DE) through a 5 mL sample loop connected to a six port valve (Valco Instruments, Houston, Texas). The TA3000R RGA is a continuous flow instrument with a

<table>
<thead>
<tr>
<th>Table 1. Field Site Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latitude</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Forest</td>
</tr>
<tr>
<td>Desert</td>
</tr>
<tr>
<td>Marsh</td>
</tr>
</tbody>
</table>

*From the Western Regional Climate Center station observations from Idyllwild, California (forest), Twentynine Palms, California (desert), and Newport Beach, California (marsh) (Western Regional Climate Center, 2007). Data were averaged over the period July 1948 to June 2007 for Idyllwild and Twentynine Palms and from November 1934 to June 2007 for Newport Beach.

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil Layer</th>
<th>Ca (%)</th>
<th>Na (%)</th>
<th>C/N*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest streamed</td>
<td>litter</td>
<td>47.5</td>
<td>0.81</td>
<td>59</td>
</tr>
<tr>
<td>Forest streamed</td>
<td>soil (0–5 cm)</td>
<td>19.4 ± 24.2</td>
<td>0.49 ± 0.58</td>
<td>39</td>
</tr>
<tr>
<td>Forest hillside</td>
<td>litter</td>
<td>50.4</td>
<td>1.03</td>
<td>49</td>
</tr>
<tr>
<td>Forest hillside</td>
<td>soil (0–5 cm)</td>
<td>1.1 ± 0.6</td>
<td>0.05 ± 0.02</td>
<td>23</td>
</tr>
<tr>
<td>Desert high SOM</td>
<td>litter</td>
<td>28.4 ± 8.2</td>
<td>0.09 ± 0.32</td>
<td>32</td>
</tr>
<tr>
<td>Desert high SOM</td>
<td>soil (0–5 cm)</td>
<td>1.2 ± 0.2</td>
<td>0.10 ± 0.01</td>
<td>13</td>
</tr>
<tr>
<td>Desert medium SOM</td>
<td>litter</td>
<td>12.3 ± 1.9</td>
<td>0.57 ± 0.12</td>
<td>22</td>
</tr>
<tr>
<td>Desert medium SOM</td>
<td>soil (0–5 cm)</td>
<td>4.2 ± 3.8</td>
<td>0.25 ± 0.21</td>
<td>17</td>
</tr>
<tr>
<td>Desert low SOM</td>
<td>litter</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Desert low SOM</td>
<td>soil (0–5 cm)</td>
<td>0.1 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>13</td>
</tr>
<tr>
<td>Marsh site 3</td>
<td>soil (0–5 cm)</td>
<td>9.2 ± 0.5</td>
<td>0.66 ± 0.01</td>
<td>14</td>
</tr>
</tbody>
</table>

*Soil carbon (C) and nitrogen (N) contents measured with an elemental analyzer, Carlo Erba, Lakewood, New Jersey.

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Unibead 1S and an MS 13X column for separation of H₂ and CO. Exponential curves were fit to the H₂ mixing ratio time series obtained for each chamber flux measurement (e.g., Figure 2)

\[
H_2(t) = H_2(0)e^{-bt},
\]

where \( t \) is time, and the flux of hydrogen into the soil (nmol m\(^{-2}\) s\(^{-1}\)) was calculated as

\[
F_{H_2} = H_2(0)(-b)\frac{P}{RT} \frac{V}{A},
\]

where \( H_2(0) \) is the mixing ratio of H₂ at \( t = 0 \) s, \( P \) is atmospheric pressure (Pa) at each site, \( V \) is the volume of the flux chamber including the space between the collar edge and the soil surface, \( R \) is the gas constant, \( T \) is temperature (K), \( A \) is the area inside the soil collar (0.0324 m\(^2\)), and \( b \) is the constant from equation (1). To normalize for the effect of the initial concentration of H₂ on the relative flux rates, we also calculated deposition velocities (cm s\(^{-1}\)), which are independent of surface concentration as

\[
V_d = (-b)\frac{V}{A}.
\]

For soil CO₂ flux measurements, the same soil collars were used but the syringe port was removed from the flux chamber and replaced with a 1/4” tube fitting that allowed continuous circulation of air through the chamber. A 0.5 L/min pneumatic pump (KNF Neuberger, Trenton, New Jersey) pulled air from the flux chamber through a filter, a LI-800 Gas Hound CO₂ analyzer (LICOR, Lincoln, Nebraska) and finally pushed air back into the flux chamber through a tube fitting at the top of the chamber. The CO₂ efflux was measured for approximately 3 min and the mixing ratio of CO₂ increased linearly with respect to time. The CO₂ flux rate was calculated as

\[
F_{CO_2} = m\frac{PV}{RT} \frac{1}{A},
\]

where \( P, V, R, T, \) and \( A \) are defined as noted above, and \( m \) is the slope of the CO₂ mixing ratio time series from the chamber.

2.3. Soil Profiles

Soil profiles of H₂ concentration with depth were measured using soil gas samplers that were buried and left in place over the entire course of our field study (Figure 1b). The gas samplers were constructed from 25 mL disposable plastic pipets with 1/8” holes drilled in three sides and 1/32” inner diameter Tygon tubing leading to the surface. We dug soil pits to ~50 cm depth, and used a soil corer to remove horizontal plugs of soil at 2.5, 5, 10, 20 and 40 cm depth along the open face of the pit. The soil gas samplers were placed horizontally into the holes (into undisturbed soils).
and the pit was back filled with tubes leading to the surface. Soil gas samples were extracted with 10 mL plastic syringes fitted with a three-way valve and a luer stub adaptor (BD, Franklin Lakes, New Jersey). First, 5 mL of air was removed from the gas samplers and was flushed out of the syringe and valve, then a full 10 mL was withdrawn, the valve was closed, and the syringes were placed on bubble wrap in a dry ice filled cooler.

2.4. Soil Removal Experiments

[12] We conducted a series of soil removal experiments at the forest and desert sites in April of 2005. A 30 cm deep soil collar was inserted into the soil near the hillside site (forest) and in a low SOM area (desert) and the H$_2$ flux was measured as described in section 2.2. Next, the vegetation contained in the collars was removed, and placed in a separate soil collar with a plastic dish glued to the bottom (Figure 1a). We capped the sealed soil collar with the flux chamber and measured the H$_2$ flux in the chamber. The flux chamber was moved back to the intact soil collar, where we remeasured the flux of H$_2$ in the soil collar, then removed a few cm of soil. The removed soil was placed in the sealed collar and the H$_2$ flux was measured. This process was repeated to establish the H$_2$ uptake capacity of individual soil layers (and of the remaining soil profile as layers were removed).

2.5. Soil Properties

[13] We measured the temperature of soils at 5 and 10 cm depth at each soil collar during each flux experiment. Soil samples from the top 5 cm were also collected near the collars, sealed in plastic vials and frozen. These samples were later used to calculate volumetric water content of the surface soils. Soil samples collected in September 2005 were analyzed for percent C and N.

[14] Soil temperature and moisture were measured continuously after February 2005 at the forest and desert sites using integrated temperature sensors from 0 to 5 cm depth (Model 107-L, Campbell Scientific, Logan, UT) and time domain reflectometry (TDR) sensors at 5 and 20 cm depth (Model 616-L, Campbell Scientific, Logan, UT). Data were averaged every 1/2 h and stored on CR10X data loggers (Campbell Scientific, Logan, UT). Southern California received an anomalously high amount of precipitation over the winter of 2005, and our sites received 100 cm (forest), 21 cm (desert), and 40 cm (marsh) of precipitation between September 2004 and May 2005 (Western Regional Climate Center (WRCC) station observations from Idyllwild, California, Twentynine Palms, California, and Newport Beach, California [WRCC, 2007]).

3. Field Results

[15] The loss of H$_2$ from the chamber headspace was initially quite rapid, and slowed as the mixing ratio of H$_2$ in the chamber decreased. The H$_2$ flux was therefore modeled as first-order loss process using a negative exponential relationship (equation (1)). An example time series from the forest site on 4 November 2004 is shown in Figure 2. The forest and desert H$_2$ fluxes exhibited similar ranges of variability with deposition velocities ranging from 0.01 to 0.1 cm s$^{-1}$ (Figure 3). No clear seasonal pattern was evident in our data. We observed substantially smaller deposition velocities in the forest streambed site in January 2005 due to a flooding event that deposited ~5 cm of litter and sediment over our collars (Figure 3a). The deposition velocities recovered to preflood levels by April 2005. In March 2005, H$_2$ deposition velocities at the desert site were substantially higher than at any other time (Figure 3b), and corresponded to a period when soil moisture remained relatively high and soil temperatures were relatively warm (Figure 4). Deposition velocities at the marsh were generally lower (0.015 to 0.054 cm s$^{-1}$) than at the forest and desert sites and were less variable (Figure 3c). Mean H$_2$ flux rates and standard deviations were $-7.9 \pm 4.2$, $-7.6 \pm 5.3$ and $-7.5 \pm 3.4$ nmol m$^{-2}$ s$^{-1}$ for the forest, desert, and marsh, respectively (Table 3).

[16] CO$_2$ fluxes were consistently higher at the forest streambed site than the hillside site (Figure 5a and Table 3) and the organic carbon content of the streambed soils was higher than that of the hillside (Table 2). At the desert site, mean CO$_2$ fluxes were a factor of 5 higher in the high SOM collars than in the low SOM collars (Tables 2 and 3 and Figure 5), but no similar pattern existed for H$_2$ fluxes. Soil temperature steadily increased at the forest and desert sites.
between January and July (Figures 4a and 4b). Volumetric water content of soils decreased at the forest site after the last rain event in May 2005 (Figure 4c). Soil moisture decreased at the desert site after March 2005 (Figure 4d). At both sites the soil moisture was higher at 20 cm depth than at 5 cm depth.

Our soil profile measurements showed that, at the forest and desert sites, average $\text{H}_2$ mixing ratios decreased rapidly with depth, were between 3% and 51% of atmospheric levels at 10 cm, and were always less than 10% of atmospheric levels at 40 cm (Figure 6). From March 2005 through July 2005, $\text{H}_2$ at the desert site penetrated progressively deeper into the soil profile. This coincided with decreases in surface $\text{H}_2$ fluxes (Figure 7a). The mixing ratio of $\text{H}_2$ at 5 cm depth increased along with a decrease in the volumetric water content of soils (Figure 7b), and surface fluxes decreased as the volumetric water content at 5 cm depth decreased (Figure 7c). A similar, although smaller change, occurred at the forest hillside site in July 2005. Soil $\text{H}_2$ mixing ratios at a depth of 40 cm were substantially higher at the marsh site (Figure 6c), which may be due to the anaerobic production of $\text{H}_2$ in saturated soils below our deepest soil gas sampler.

At the forest site, soil removal experiments showed that grass and litter layers did not significantly contribute to

Table 3. Mean $\text{H}_2$ and CO$_2$ Fluxes at Field Sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean $\text{H}_2$ Flux (nmol m$^{-2}$ s$^{-1}$)</th>
<th>Mean CO$_2$ Flux [Deposition Velocity] (cm s$^{-1}$)</th>
<th>Mean CO$_2$ Flux (mmol m$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest streambed</td>
<td>$-7.8 \pm 4.2 [0.060 \pm 0.027]$</td>
<td>7.6 $\pm$ 2.4</td>
<td></td>
</tr>
<tr>
<td>Forest hillside</td>
<td>$-8.0 \pm 4.3 [0.065 \pm 0.031]$</td>
<td>3.6 $\pm$ 1.8</td>
<td></td>
</tr>
<tr>
<td>Desert high SOM</td>
<td>$-6.8 \pm 3.1 [0.048 \pm 0.022]$</td>
<td>3.3 $\pm$ 1.6</td>
<td></td>
</tr>
<tr>
<td>Desert medium SOM</td>
<td>$-8.3 \pm 7.5 [0.053 \pm 0.053]$</td>
<td>1.4 $\pm$ 0.8</td>
<td></td>
</tr>
<tr>
<td>Desert low SOM</td>
<td>$-7.6 \pm 4.6 [0.052 \pm 0.029]$</td>
<td>0.6 $\pm$ 0.5</td>
<td></td>
</tr>
<tr>
<td>Marsh all sites</td>
<td>$-7.5 \pm 3.4 [0.035 \pm 0.013]$</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. CO$_2$ flux rates ($\mu$mol m$^{-2}$ s$^{-1}$) at the (a) forest and (b) desert field sites.
observed at the surface (Figure 8). After the is time (s), \( \frac{C_0}{C_2} \) in the soil \( \frac{C_2}{cm} \) (Figure 9b). Reducing the diffusivity of \( H \) to is the fractional air space \( \frac{H_D}{s} \) at 40 cm depth at the marsh field site (Figure 6c) may be due to anaerobic production of \( H_2 \) in layered soils by a factor of 10 from 1.25 \( \frac{C_0}{C_2} \) s to 1.25 \( \frac{C_0}{C_2} \) s penetrates deeper with depth from 5 \( \frac{C_0}{C_2} \) to 1.25 \( \frac{C_0}{C_2} \) s penetrates deeper with depth (cm) and soil air filled porosity. Air filled porosity is primarily determined by soil structure and moisture content, which leads to a strong control of soil texture and saturation on the diffusivity of hydrogen in soils \[ \text{Yonemura et al., 1999, 2000b; Smith-Downey et al., 2006} \]. The uptake of hydrogen by soils (\( \lambda \)) is biologically controlled and varies with soil moisture and temperature \[ \text{Fallon, 1982; Conrad and Seiler, 1985; Smith-Downey et al., 2006} \]. Using the finite difference solution to this model, we explored the effect of changes in \( D_s \) and \( \lambda \) on the distribution of \( H_2 \) with depth and on surface flux rates (Figure 9).

[21] Assuming a constant \( D_s \) of 0.1 cm\(^2\) s\(^{-1}\), a surface \( H_2 \) mixing ratio of 530 ppb and an \( \varepsilon \) of 0.3, we tested the effect of decreasing the biological uptake capacity (\( \lambda \)) uniformly with depth from 5 \( \times \) \( 10^{-2} \) s\(^{-1}\) to 5 \( \times \) \( 10^{-4} \) s\(^{-1}\). As \( \lambda \) decreases by 2 orders of magnitude, \( H_2 \) penetrates deeper into soils (Figure 9a) and as a consequence more soil volume is exposed to elevated levels of \( H_2 \). The net effect is a much smaller reduction in surface fluxes, with fluxes decreasing by only a factor of 6 from \(-38 \) nmol m\(^{-2}\) s\(^{-1}\) to \(-6 \) nmol m\(^{-2}\) s\(^{-1}\) (Figure 9b). Reducing the diffusivity of soils by a factor of 10 from 1.25 \( \times \) \( 10^{-2} \) cm\(^2\) s\(^{-1}\) to 1.25 \( \times \) \( 10^{-4} \) cm\(^2\) s\(^{-1}\) (and assuming a constant \( \lambda \) of 2.5 \( \times \) \( 10^{-2} \) s\(^{-1}\) that is uniform with depth) results in shallower \( H_2 \) penetration into soils (Figure 9c), and decreases in surface flux rates (Figure 9d). The reduction in surface fluxes, however, is again smaller than the initial change in diffusivity (a

4. Modeling Diffusive Properties of Soils

[19] To demonstrate the role of diffusion in the uptake of \( H_2 \) by soils, we adapted the parameterization developed by \textit{Smith-Downey} [2006] to describe \( H_2 \) uptake as a function of the diffusivity of soils (\( D_s \)) and biological uptake capacity (\( \lambda \)). In general, the flux of \( H_2 \) at the surface is proportional to the concentration gradient

\[
F_{H_2} = D_s \left. \frac{\partial [H_2]}{\partial z} \right|_{z = \text{soil surface}},
\]

where \( z \) is depth (cm). The gradient in [\( H_2 \)] with depth is driven by both the biological uptake of \( H_2 \) in the soil profile, and the diffusive structure of soils. It can be described by the diffusion equation with a first-order loss term

\[
\frac{\partial [H_2]}{\partial t} = \frac{\partial}{\partial z} \left( D_s(z) \frac{\partial [H_2]}{\partial z} \right) - \frac{\lambda(z)}{\varepsilon} [H_2],
\]

where \( t \) is time (s), \( z \) is depth (cm), \( D_s \) is the diffusivity of hydrogen in soil as a function of depth (cm\(^{-2}\) s\(^{-1}\)), \( \lambda \) is the biological uptake rate (s\(^{-1}\)), and \( \varepsilon \) is the fractional air space (unitless).

[20] The diffusivity of hydrogen in soils (\( D_s \)) varies with depth and is a function of the diffusivity of \( H_2 \) in air (\( D_a \)) and soil air filled porosity. Air filled porosity is primarily determined by soil texture and moisture content, which leads to a strong control of soil texture and saturation on the diffusivity of hydrogen in soils \[ \text{Yonemura et al., 1999, 2000b; Smith-Downey et al., 2006} \]. The uptake of hydrogen by soils (\( \lambda \)) is biologically controlled and varies with soil moisture and temperature \[ \text{Fallon, 1982; Conrad and Seiler, 1985; Smith-Downey et al., 2006} \]. Using the finite difference solution to this model, we explored the effect of changes in \( D_s \), and \( \lambda \) on the distribution of \( H_2 \) with depth and on surface flux rates (Figure 9).

[21] Assuming a constant \( D_s \) of 0.1 cm\(^2\) s\(^{-1}\), a surface \( H_2 \) mixing ratio of 530 ppb and an \( \varepsilon \) of 0.3, we tested the effect of decreasing the biological uptake capacity (\( \lambda \)) uniformly with depth from 5 \( \times \) \( 10^{-2} \) s\(^{-1}\) to 5 \( \times \) \( 10^{-4} \) s\(^{-1}\). As \( \lambda \) decreases by 2 orders of magnitude, \( H_2 \) penetrates deeper into soils (Figure 9a) and as a consequence more soil volume is exposed to elevated levels of \( H_2 \). The net effect is a much smaller reduction in surface fluxes, with fluxes decreasing by only a factor of 6 from \(-38 \) nmol m\(^{-2}\) s\(^{-1}\) to \(-6 \) nmol m\(^{-2}\) s\(^{-1}\) (Figure 9b). Reducing the diffusivity of soils by a factor of 10 from 1.25 \( \times \) \( 10^{-2} \) cm\(^2\) s\(^{-1}\) to 1.25 \( \times \) \( 10^{-4} \) cm\(^2\) s\(^{-1}\) (and assuming a constant \( \lambda \) of 2.5 \( \times \) \( 10^{-2} \) s\(^{-1}\) that is uniform with depth) results in shallower \( H_2 \) penetration into soils (Figure 9c), and decreases in surface flux rates (Figure 9d). The reduction in surface fluxes, however, is again smaller than the initial change in diffusivity (a
factor of 6 versus a factor of 10) (Figure 9d). Finally, to test the effect of inactive layer depth \( d_i \), we set \( \lambda \) of the surface soil layer to zero, and the remaining soil profile to \( 2.5 \times 10^{-2} \) cm\(^{-1}\). As \( d_i \) increased from 0 to 20 cm, \( \text{H}_2 \) penetrated deeper into the soil profile (Figure 9e) and surface fluxes rapidly decrease from \(-31\) nmol m\(^{-2}\) s\(^{-1}\) to \(-2\) nmol m\(^{-2}\) s\(^{-1}\) (Figure 9f).

5. Discussion and Conclusions

Our field observations provide evidence that ecosystem type is not a strong controller of soil \( \text{H}_2 \) flux rates and that the vertical distribution of \( \text{H}_2 \) uptake capacity and diffusive properties of soils have important effects on surface flux rates. The rate of \( \text{H}_2 \) consumption was nearly equal at the forest and desert sites, suggesting that uptake rates in low productivity ecosystems such as deserts may not scale with net primary production or soil organic matter, key variables that have been used to describe spatial patterns of soil CO\(_2\) fluxes. Our soil profile experiments demonstrated that the vertical distribution of \( \text{H}_2 \) uptake with depth changed over time in response to a decrease in soil moisture, which is consistent with previous work suggesting that \( \text{H}_2 \) uptake requires a minimum moisture level for microbial activation [Fallon, 1982; Conrad and Seiler, 1985; Smith-Downey et al., 2006]. The profile measurements show that the surface layer of soil at the desert site became inactive with respect to hydrogen between March
uptake by microbes within the soils, is a powerful local control on soil moisture availability.

At all of our sites, the H₂ mixing ratio at depth appeared to be nonzero (Figure 6), which would suggest a steady state equilibrium between H₂ production and consumption in soils. We cannot rule out contamination during sample collection and analysis, but our data were corrected for the leak rates we observed in the lab. The local maximum observed at 40 cm depth at the marsh site in October, and the general higher steady state mixing ratio with depth at this site certainly suggests both production and consumption of H₂ occurring simultaneously in these soils.

At the forest streambed site, a flooding event deposited ~ 5 cm of sediment and litter over our collars in January 2005. This led to a dramatic decrease in H₂ fluxes, which subsequently recovered by April 2005. This suggests that soil disturbance, particularly disturbance that impedes the diffusion of H₂ into soils, is a powerful local control on soil H₂ uptake.

Generally, there was little observable difference between fluxes at the forest and desert sites, but the marsh site exhibited slightly lower fluxes. We hypothesize that this is primarily due to differences in soil structure. The soils at the forest and desert sites were relatively porous, whereas the marsh was dominated by fine-grained, clay-rich, and less porous soil.

At the desert site, we designed our experiments to test the effect of organic carbon on H₂ fluxes by placing our soil collars along a gradient in SOM and vegetation from directly under oak shrubs to bare sand. Although CO₂ fluxes were substantially higher under the oak, and decreased as we moved to bare sand, no such trend was apparent in the H₂ flux data. This suggests that soil organic carbon content is not a strong controller of H₂ uptake, which is similar to patterns that have been observed for the uptake of methane by desert soils [Striegl et al., 1992]. Yonemura et al. [1999] reported increased H₂ fluxes after organic material was plowed into study plots, but the physical disturbance of plowing may have increased the diffusivity of H₂ into the soil. Smith-Downey et al. [2006] report that in laboratory experiments, soil from the boreal forest, with very high organic carbon content (39%) has a higher uptake capacity than soils from the same desert site studied here. It appears that if soil organic matter does play a role in the uptake of H₂, it is secondary to other factors such as diffusion and moisture availability.

Soil removal experiments showed that the litter layer at the forest site had an H₂ flux that was nearly zero. We attribute the small flux we did observe to a small amount of soil that was intermixed with the litter in the soil collar. Once the litter layer was removed, the flux at the surface increased. This is consistent with the removal of a diffusive barrier, which enhances the supply of H₂ to the underlying soils, and is similar to observations of CO deposition onto soils after litter removal [Sanhueza et al., 1998]. Layers of soil that we removed from the soil profile had progressively higher flux rates when we measured them in a sealed collar.
Figure 9. Sensitivity experiments for changes in the biological uptake capacity and diffusivity of soils. (left) The H$_2$ mixing ratio with depth in the soil profile under different conditions, and (right) the associated changes in the surface flux rates. (a) Reducing the strength of biological uptake ($\lambda$) uniformly in the soil profile causes H$_2$ to penetrate deeper into the soil profile. (b) As $\lambda$ increases, surface fluxes increase rapidly at first, then more slowly as the total flux becomes diffusion limited. (c) Decreasing the diffusivity ($D_s$) of H$_2$ in soils (analogous to filling pore space with water) results in an increased concentration gradient at the surface and shallower penetration of H$_2$ into soils. (d) As $D_s$ increases, fluxes at the surface increase. (e) Increasing the depth of an inactive layer of soil ($d_i$), where $\lambda = 0$ s$^{-1}$, results in a smaller concentration gradient at the surface and a shallower penetration of H$_2$ into soils. (f) As $d_i$ increases, the fluxes at the surface rapidly decrease because consumption of H$_2$ becomes limited by diffusion through the inactive layer.
In some cases the flux of H$_2$ into the removed soil layer was larger than that of the intact profile. In removing the soil layers from the surface and transferring them to the sealed collar, we disturbed the soil structure and thus greatly enhanced the exposure of soil microbes to atmospheric H$_2$ levels.

[28] At the desert site, we observed an inactive layer of soil at the top of the profile in our soil removal experiments. When this layer was removed, the surface flux of H$_2$ increased from $-6 \text{ nmol m}^{-2} \text{s}^{-1}$ to $-10 \text{ nmol m}^{-2} \text{s}^{-1}$. After a second layer of soil was removed, the surface flux increased to $-14 \text{ nmol m}^{-2} \text{s}^{-1}$. This experiment highlights the importance of the diffusive structure and vertical distribution of H$_2$ uptake capacity on surface flux rates. As soil that did not consume H$_2$ was removed, a diffusive barrier was also removed, which increased the availability of H$_2$.

[29] Modeling analysis provides further evidence that soil diffusivity and the vertical distribution of biological uptake interact to regulate surface flux rates. Because the system is diffusion limited, however, it is more sensitive to changes in the diffusive properties of soils than to changes in the biological uptake. Our results show that if $\lambda$ decreases by a factor of 100 (from $5 \times 10^{-4} \text{ cm s}^{-1}$ to $5 \times 10^{-5} \text{ cm s}^{-1}$) the surface fluxes are reduced by only a factor of 6 ($-38 \text{ nmol m}^{-2} \text{s}^{-1}$ to $-6 \text{ nmol m}^{-2} \text{s}^{-1}$). In contrast, increasing the inactive layer depth from 0 to 5 cm increases the diffusive barrier to biological uptake and reduces surface fluxes from $-31 \text{ nmol m}^{-2} \text{s}^{-1}$ to $-10 \text{ nmol m}^{-2} \text{s}^{-1}$, or 68%. Our observations show that, as even during summer the deep subsurface soil layers retained enough soil moisture to facilitate biological uptake. Most of the flux variability observed at this site appeared to be related to variations in the inactive layer depth. The increases in H$_2$ penetration depth we observed during summer (Figure 6b) were qualitatively similar in shape to that expected from an increasing surface inactive layer (Figure 9c). This may explain why observations at the forest hillside and marsh sites did not vary substantially over the course of the growing season. As long as the entire soil profile is consuming H$_2$ and remains well drained, variability in $\lambda$ will not drive large changes in the surface flux rates. This also implies that in a future H$_2$ emissions scenario, if the diffusive properties and $\lambda$ of soils remain the same, the flux of H$_2$ into soils will decrease linearly with concentration. If $\lambda$ increases in response to increasing H$_2$, the effect on surface fluxes will be small because of compensating decreases in the penetration of H$_2$ into the soil profile.

[30] Our results suggest that both the diffusive properties of soil, which regulate H$_2$ supply to soil microbes, and the vertical distribution of biological uptake control the surface fluxes of H$_2$. These results are consistent with previous observations from several groups [Conrad and Seiler, 1985; Yonemura et al., 1999, 2000a, 2000b; Smith-Downey et al., 2006] and we propose that in order to predict future changes hydrogen fluxes, it is necessary to model how both the diffusive properties of soils (e.g., changes in snow cover or soil moisture) and rates of microbial uptake respond to changing environmental conditions.

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