Temperature and moisture dependence of soil $\text{H}_2$ uptake measured in the laboratory

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[1] The soil sink of molecular hydrogen is the largest and most uncertain term in the global atmospheric $\text{H}_2$ budget. Lack of information about the mechanisms regulating this sink limits our ability to predict how atmospheric $\text{H}_2$ may respond to future changes in climate or anthropogenic emissions. Here we present the results from a series of laboratory experiments designed to systematically evaluate and describe the temperature and soil moisture dependence of $\text{H}_2$ uptake by soils from boreal forest and desert ecosystems. We observed substantial $\text{H}_2$ uptake between $-4^\circ\text{C}$ and $0^\circ\text{C}$, a broad temperature optimum between $20^\circ\text{C}$ and $30^\circ\text{C}$, a soil moisture optimum at approximately 20% saturation, and inhibition of uptake at both low and high soil moisture. A sigmoidal function described the temperature response of $\text{H}_2$ uptake by soils between $-15^\circ\text{C}$ and $40^\circ\text{C}$. Based on our results, we present a framework for a model of the soil $\text{H}_2$ sink. Citation: Smith-Downey, N. V., J. T. Randerson, and J. M. Eilert (2006), Temperature and moisture dependence of soil $\text{H}_2$ uptake measured in the laboratory, Geophys. Res. Lett., 33, L14813, doi:10.1029/2006GL026749.

1. Introduction

[2] Molecular hydrogen (H2) is the second most abundant reduced gas in the troposphere (after methane), with a concentration of approximately 530 ppb during the 1990s [Novelli et al., 1999]. Sources of $\text{H}_2$ to the troposphere include photolysis of formaldehyde, which is primarily generated from the oxidation of methane and non-methane hydrocarbons, and emissions from fossil fuel combustion and biomass burning. Sinks of hydrogen include oxidation by OH and uptake by soils [Novelli et al., 1999]. The soil sink is the largest and most uncertain term in the $\text{H}_2$ budget. Estimating the magnitude of the soil sink has proved challenging and the calculated proportion of $\text{H}_2$ uptake by soils to total loss has varied from 62% to 92% [Seiler and Conrad, 1987; Warneck, 1988; Ehnhall, 1999; Novelli et al., 1999; Gerst and Quay, 2001; Hauglustaine and Ehnhall, 2002]. The prospect of a global hydrogen economy has sparked interest in the environmental impact of substantial increases in $\text{H}_2$ emissions. A hydrogen economy may be accompanied by reduced NOx emissions, which would increase the atmospheric lifetimes of CH4 and CO due to decreases in OH, and decrease tropospheric O3 levels in polluted urban areas [Schultz et al., 2003]. Tromp et al. [2003] and Warwick et al. [2004] found that replacing fossil fuels with hydrogen fuel cells would lead to a decrease in stratospheric ozone because $\text{H}_2$ mixes freely across the tropopause and forms water in the stratosphere. A critical aspect of this problem is the response of the soil sink. Because neither the mechanism nor the environmental controls on soil uptake of $\text{H}_2$ are well defined it is difficult to predict both temporal and spatial variability in the magnitude of this sink and how it may respond to future changes in climate or anthropogenic emissions.

[3] Schuler and Conrad [1991] studied the temperature response of $\text{H}_2$ uptake by soils from a temperate forest, compost bin, and a private garden. They found that at $\text{H}_2$ concentrations of 1 ppm, the uptake was optimized at a temperature of $30^\circ\text{C}$ whereas at higher $\text{H}_2$ concentrations (3000 ppm) $\text{H}_2$ uptake was optimized at $65^\circ\text{C}$. At 1 ppm, rates of soil $\text{H}_2$ uptake doubled when temperature was increased from $5^\circ\text{C}$ to $30^\circ\text{C}$. In an incubation experiment that measured soil uptake for $\text{H}_2$ concentrations between 100 and 500 ppm, Trevors [1985] found a lower temperature optimum ($20^\circ\text{C}$) for aerobic soils at 60% water holding capacity (WHC) and observed a 3-fold increase in uptake between 5 and $20^\circ\text{C}$. Another experiment by Yonemura et al. [2000b] found a similar temperature optimum, and a factor of 2 difference in uptake rate between $1^\circ\text{C}$ and $25^\circ\text{C}$ at a single soil moisture level.

[4] Previous work suggests that soil moisture also plays an important role in determining the uptake rate of $\text{H}_2$. Experiments by Conrad and Seiler [1981; 1985] and Fallon [1982] show that in very dry soils, uptake is stimulated by the addition of water. Godde et al. [2000] measured the $\text{H}_2$ oxidation capacity of soils from a temperate forest, agricultural field and meadow in Germany, and found that uptake was generally higher in drier soils (at 30% WHC) than in wetter soils (at 60% WHC). Field studies from a forest and arable field in Japan show that at high soil moisture levels (> 30% volumetric water content) $\text{H}_2$ uptake decreases with increasing soil moisture [Yonemura et al., 1999; 2000a], probably from limited $\text{H}_2$ diffusion through water filled soils [Yonemura et al., 2000b].

[5] Although several experiments on the temperature and moisture response of $\text{H}_2$ uptake by soils exist, there are insufficient data to parameterize a mechanistic model that predicts soil $\text{H}_2$ fluxes across the full range of environmental conditions found in Earth’s major biomes. Such a model would be useful in exploring the sources of variability in the atmospheric $\text{H}_2$ record and could be used to predict changes in the $\text{H}_2$ cycle due to changing climate or emissions. To construct a mechanistic model of $\text{H}_2$ soil uptake, more information is needed about the interaction...
between soil temperature and soil moisture, the sensitivity of soil H₂ uptake to soil moisture under unsaturated conditions, rates of soil H₂ uptake at temperatures below 0°C, and differences in uptake between different biomes.

We measured rates of H₂ uptake by soils across a wide range of temperatures and soil moisture levels using a flow-through chamber system. In our experiments we used two different surface soils, one from a mature black spruce boreal forest in interior Alaska and another from the Mojave Desert in California. Our experiments imply that there is 1) a strong soil temperature control on H₂ uptake, 2) a minimum soil moisture requirement for biological activation, 3) maximized uptake at approximately 20% saturation, 4) decreasing uptake at higher soil moisture levels, 5) substantial H₂ uptake occurring between −4°C and 0°C and 6) that soil type affects the shape of the moisture response. We propose a framework from which global H₂ uptake by soils can be modeled based on these data.

2. Methods

2.1. Soil Collection and Preparation

Approximately 500 mL of the top 5 cm of soil was collected from a black spruce (Picea Mariana) forest near Delta Junction, Alaska (63°53′N, 145°44′W) and from the University of California Burns Piñon Ecological Reserve in the Mojave Desert (34°08′N, 116°27′W). From 1961 to 1990 the mean annual temperature was −2.3°C at the boreal forest site and 20°C at the Mojave Desert site. Mean annual precipitation was 30 cm/yr at the boreal forest site and 11 cm/yr at the Mojave Desert site. Mean annual precipitation was 30 cm/yr at the Mojave Desert site. Mean annual precipitation was 30 cm/yr at the Mojave Desert site.

2.2. Flux Measurements

Hydrogen calibration gases between 5 and 2000 ppb H₂ were generated by diluting a standard gas containing 5070 ± 25 ppm H₂ (Scott-Marrin, Riverside, CA) with ultra-pure N₂. Samples from cylinders of compressed air were measured following calibration of the instrument and these cylinders were used as secondary standards throughout the experiment.

We created a flow through apparatus for measuring H₂ uptake by insetting a 1/2" OD glass tube into a 2L beaker and filling the tube with soil (Figure 1). Gas from a compressed air cylinder containing 1585 ± 21 ppb H₂ flowed, in order, through a mass flow controller (MKS, Wilmington, MA), through a flask filled with water to control humidity, through the 1/2" glass tube filled with the soil sample, through a dry ice loop to remove moisture and finally to the inlet of a TA 3000R Reducing Gas Analyzer (Ametek Process Instruments, Newark, DE) at a rate of 10 standard cubic centimeters per minute (scm). The TA3000R RGA is a continuous flow instrument with a Unibead 1S and an MS 13X column for separation of H₂ and CO. Ultra-torr fittings (Swagelok, Solon, OH) were used at each joint, and the system was leak tested with an 80% H₂ source. The TA 3000R instrument measures H₂ with a relative precision of 1.5%.

2.3. Temperature and Moisture Experiments

In preparation for the temperature and moisture manipulation experiments, soils were thinly spread out in plastic pans and allowed to dry at room temperature (23°C) overnight. Soil samples were then split into 5 equal portions and water was added to each sample in increments. In these experiments, soil moisture was described as ‘% saturated’, which was calculated as the ratio of water (g) contained in soils to the amount contained after soils are fully submerged in pure H₂O and allowed to drain for 10 minutes. The soils were stirred to evenly incorporate the added water and stored in 50 mL test tubes sealed with Parafilm for at least 3 days before experiments began. The manipulation of the soils may have changed the soil porosity and existing
The outgoing \( H_2 \) concentration had remained constant for at least 30 minutes, because a gas-tight seal was necessary at each joint. Each soil sample was placed in the soil during the flow through experiments. We used a stir bar to avoid temperature stratification within the soil column. The drop in \( \left[H_2\right]_{\text{out}} \) between \(-4^\circ C\) and \(-15^\circ C\) corresponds with a warm temperature excursion due to the exchange of the salt-water solution from the beaker with an ethanol/ice solution.

Microbial communities and, for this reason, our results may not be representative of in situ fluxes.

For each soil moisture level, the column was filled with 10 mL of soil with a cone of filter paper at each end. The beaker was filled with water of different temperatures, and the concentration of outgoing \( H_2 \) was measured every 3.5 minutes. Temperatures were cycled through in the following order: 23, 30, 37, 10, 0, \(-4\), \(-15^\circ C\) (Figure 2). We used a hot plate to maintain \( 30^\circ C \) and \( 37^\circ C \), an ice water bath to maintain \( 0^\circ C \), an ice/salt water bath to maintain \(-4^\circ C\), and an ice/ethanol/water bath to maintain \(-15^\circ C\). The water in the beaker was drained and replaced between each temperature level to ensure a quick transition. We used a stir bar to avoid temperature stratification within the beaker. We conducted one set of temperature manipulations on soils with a thermocouple embedded in the soil and another in the water bath. The temperature of the soil equilibrated with the water bath temperature within minutes, and there was no observed temperature offset between the soil and the water bath. The thermocouple wire could not be placed in the soil during the flow through experiments because a gas-tight seal was necessary at each joint. Each temperature/moisture level was considered stable after the outgoing \( H_2 \) concentration had remained constant for at least 30 minutes (e.g., Figure 2).

2.4. Uptake Rate Estimates

The uptake rate (pmol cm\(^{-3}\) soil s\(^{-1}\)) of each soil sample was calculated using the measured difference between the incoming and outgoing \( H_2 \) concentrations:

\[ H_2\text{uptake} = \frac{\left[H_2\right]_{\text{in}} - \left[H_2\right]_{\text{out}} \cdot f \cdot P}{V_{\text{soil}} \cdot R \cdot T \cdot 1 \times 10^9} \quad (1) \]

where \( f \) is the flow rate (cm\(^3\)/s), \( P \) is the pressure (Pa), \( V_{\text{soil}} \) is the volume of soil (cm\(^3\)), \( R \) is the gas constant and \( T \) is the temperature (K). Pressure was assumed to be 1.01325 \( \times 10^5 \) Pa.

3. Results

Our experiments showed a dependence of \( H_2 \) uptake on soil moisture and temperature in both soils (Figure 3). The maximum flux from the boreal forest soil (0.8 pmol cm\(^{-3}\) soil s\(^{-1}\)) was approximately twice as large as the maximum flux rate from the Mojave Desert soil (0.35 pmol cm\(^{-3}\) soil s\(^{-1}\)). We observed a broad temperature maximum between 10\(^\circ C\) and 35\(^\circ C\) (Figure 3). Substantial uptake continued at \(-4^\circ C\) (especially for intermediate soil moisture levels), but was nearly eliminated by \(-15^\circ C\). The uptake rate increased sharply with increasing temperature between \(-4^\circ C\) and 0\(^\circ C\) for the boreal forest soils at intermediate saturation levels, whereas the changes in uptake rate with temperature were more gradual in the Mojave Desert soils. In a similar experiment on soils from a California forest, fluxes decreased substantially when the temperature was increased to 65\(^\circ C\) (Figure S1) suggesting uptake inhibition at high temperatures.

We observed both high and low soil moisture inhibition of \( H_2 \) uptake with soils from both sites (Figure 3). For the boreal forest soils, increasing the saturation level from \( 4\% \) to \( 10\% \) caused uptake to increase by \( 300\% \) at 23\(^\circ C\). Similarly, increasing the saturation from \( 11\% \) to \( 19\% \) for the Mojave Desert soils caused the uptake rate to increase from approximately zero to the maximum uptake levels (Figure 3). The boreal forest soils continued consuming substantial \( H_2 \) at higher saturation levels than the Mojave Desert soils, and did not show evidence of moisture inhibition until \( 59\% \) saturation.

We constructed normalized contour plots of the boreal forest and Mojave Desert fluxes as a function of both temperature and soil moisture (Figure 4). Contour values ranged between 0 and 1 and were scaled by the maximum observed flux at each site. The maximum flux occurred at 23\(^\circ C\) and 23\(^\circ C\) for the boreal forest soil, and at 30\(^\circ C\) and 19\% saturation for the Mojave Desert soil.

The response to temperature, when normalized to the maximum flux at each soil moisture level, was similar between the two sites and can be described by a sigmoidal function with the following parameters (Figure S2):

\[ f(T) = \frac{1}{1 + \exp(-0.1718 \cdot T + 46.938)} \quad (2) \]

where \( T \) is the temperature (K). This function is valid for temperatures between \(-15^\circ C\) and 40\(^\circ C\) (with an \( r^2 \) of 0.72). At temperatures above 40\(^\circ C\), our results suggest that uptake decreases with increasing temperature (Figure S1).

The moisture response cannot be characterized by a simple function, largely due to the effect of soil moisture on the diffusion of \( H_2 \) into soils, which varies considerably with soil type. It is clear, however, that a minimum level of soil moisture must be attained before uptake is possible. To account for the effects of soil moisture as it fills pore space,
hydrogen uptake must be modeled as a diffusion process where the uptake rate is scaled according to the results presented here:

\[
\lambda = f(T)g(M) \times \lambda_{\text{max}} \times [H_2] \times \frac{P}{R \times T}
\]

where \(f(T)\) and \(g(M)\) are functions of soil temperature (T) (Equation 2) and moisture (M) respectively that range between 0 and 1, \(\lambda_{\text{max}}\) is the maximum possible \(H_2\) uptake (1/s) under ideal soil temperature and moisture conditions (i.e., when \(f(T)\) and \(g(M)\) are equal to 1), \([H_2]\) is the available hydrogen concentration (ppb), \(P\) is pressure (Pa), \(R\) is the gas constant, and \(T\) is temperature (K). We assumed that the reaction was first order based on chamber measurements of \(H_2\) uptake in the field. This framework can be used to estimate \(H_2\) uptake as a function of soil moisture and temperature.

4. Discussion and Conclusions

[18] We systematically defined the temperature and moisture controls on soil \(H_2\) uptake over a wide range of environmental conditions and identified, for the first time, uptake at subzero temperatures (from \(-4^\circ C\) to \(0^\circ C\)). Our results provide additional evidence that a minimum moisture level is required for biological activation of microbes utilizing \(H_2\) [e.g., Conrad and Seiler, 1981; Fallon, 1982; Conrad and Seiler, 1985], but that once pore spaces are filled with water, diffusion of \(H_2\) into the soil becomes limited and fluxes decrease [e.g., Yonemura et al., 2000b].

Figure 3. Hydrogen uptake rates as a function of temperature for different soil moisture levels. (a) Boreal forest soils collected near Delta Junction, AK and (b) Mojave Desert soils collected near Yucca Valley, CA. Note that the scale in Figure 3a is twice that of Figure 3b. Uptake rate at 23°C was measured twice for the boreal forest soils at 10% and 23% saturation, and in both cases the difference between measurements was less than 5%. Standard deviations were calculated as \(\sqrt{\sigma_{\text{in}}^2 + \sigma_{\text{out}}^2}\) where \(\sigma_{\text{in}}\) and \(\sigma_{\text{out}}\) are the standard deviation of the measurement of incoming and outgoing \([H_2]\) respectively. The negative values observed probably do not represent an actual production of \(H_2\), but illustrate the level of internal noise in our measurement system.

Figure 4. Contour plots of normalized uptake rate at each site as a function of temperature and moisture. Data were normalized by the maximum flux at each site. Grey dots represent locations of the data points used to generate the contour plots. (a) For boreal forest soils there was a relatively strong gradient between 0% and 10% saturation and \(-4^\circ C\) and \(0^\circ C\). (b) For Mojave Desert soils there was more symmetry about the moisture maximum as compared to the boreal forest soils. In constructing this plot, we assumed negative flux values measured in the Mojave Desert soils (Figure 3b) were equal to zero.
The low soil moisture inhibition of H₂ uptake has important implications for desert soils, and may lead to maximum H₂ uptake in wetter months despite the possibility of lower temperatures.

[19] The shape of the temperature and moisture response (Figure 4a) suggests that in boreal forest soils most of the variability in H₂ uptake by soils occurs under relatively low (−4°C to 15°C) temperatures and low soil moisture conditions. These observations may have important implications for the seasonal cycle of H₂ uptake globally. Northern soils routinely experience shifts in temperature over the range −4°C to 15°C seasonally. The timing of the spring drawdown of H₂ (beginning in May) and buildup (beginning in October) at northern latitudes [Novelli et al., 1999] may be sensitive to the sharp increase in uptake that we observed between −4°C to 15°C (Figure S2). It is possible for northern soils to consume H₂ through the warmer parts of the winter, although the effect of snow cover, which may limit diffusion of H₂ into soils, must be measured and accounted for. Additionally, the seasonal and interannual soil moisture changes at these latitudes will affect the timing and magnitude of H₂ uptake.

[20] Boreal forest soil fluxes are approximately twice as large as Mojave Desert soil fluxes at the same temperature and soil moisture content. We hypothesize that this is due, in part, to differences in organic carbon content and soil structure. The two soils we examined have carbon contents near the extremes observed in common soils (0.02 to 38.5%) but more data is needed to clearly define the dependence of uptake on organic carbon content of soils. Although our laboratory measurements provided evidence that on a volumetric basis, boreal soils consume more H₂ than desert soils, chamber observations at these two locations do not show a large difference between surface flux rates per m² ground area [Rahn et al., 2002] (N. Smith-Downey et al., manuscript in preparation, 2006). The net uptake at the surface is a product of the maximum uptake capacity of a soil (Lₐₘₐₓ), the temperature and moisture controls defined here, along with the diffusion of H₂ into the soil profile. It is possible that despite a higher capacity for H₂ uptake per cm³ soil, the boreal forest uptake is diffusion limited due to higher soil moisture or differences in soil structure. Constructing a model that takes all of these factors into account will allow us to examine sources of variability in the observed atmospheric H₂ record and to assess how climate change will influence future atmospheric levels of H₂.

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