



A novel source of atmospheric H₂: abiotic degradation of organic material

H. Lee¹, T. Rahn², and H. L. Throop³

¹Climate and Global Dynamics Division, National Center for Atmospheric Research, Boulder, CO 80307, USA

²Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

³Department of Biology, New Mexico State University, Las Cruces, NM 88003, USA

Correspondence to: H. Lee (hannal@ucar.edu)

Received: 5 June 2012 – Published in Biogeosciences Discuss.: 18 July 2012

Revised: 25 October 2012 – Accepted: 29 October 2012 – Published: 12 November 2012

Abstract. Molecular hydrogen (H₂) plays an important role in atmospheric chemistry by competing for reactions with the hydroxyl radical (OH[•]) and contributing to the production of H₂O in the stratosphere, indirectly influencing stratospheric ozone concentrations. The dominant pathway for loss of H₂ from the atmosphere is via microbially-mediated soil uptake, although the magnitude of this loss is still regarded as highly uncertain. Recent studies have shown that abiotic processes such as photochemically mediated degradation (photodegradation) of organic material result in direct emissions of carbon (C) and nitrogen (N)-based trace gases as well as H₂. This H₂ production has important implications on source-sink dynamics of H₂ at the soil-atmosphere interface and thus it is important to quantify its variability over a range of plant types and materials. Here, we show laboratory observations of H₂ production and its temperature dependence during abiotic degradation of four plant litter types as well as pure cellulose and high lignin content woody material. A greater amount of H₂ was produced in the absence of solar radiation than from photodegradation alone, verifying that low temperature thermal degradation of plant litter is a source of H₂. In addition, we measured a significant release of H₂ both in the presence and absence of O₂. Our results suggest that abiotic release of H₂ during organic matter degradation is ubiquitous in arid ecosystems and may also occur in other terrestrial ecosystems. We propose that because these processes occur at the soil-atmosphere interface, they provide a previously unrecognized proximal source of H₂ for microbial uptake and confound interpretation of direct measurements of atmospheric uptake that are important for constraining the global H₂ budget.

1 Introduction

Atmospheric H₂ is one of the most abundant reduced gases in the atmosphere, with a seasonally varying dynamic equilibrium of approximately 530 ppb. The known sources of atmospheric H₂ are photochemical oxidation of methane and non-methane hydrocarbons (40 ± 16 Tg yr⁻¹), biomass burning (16 ± 5 Tg yr⁻¹), fossil fuel burning (15 ± 10 Tg yr⁻¹), N fixation (3 ± 1 Tg yr⁻¹), and ocean degassing (3 ± 2 Tg yr⁻¹) (Novelli et al., 1999). Once emitted to the atmosphere, H₂ is either oxidized by OH[•] (19 ± 5 Tg yr⁻¹) or consumed through microbially-mediated soil uptake (56 ± 41 Tg yr⁻¹), thus maintaining a seasonally dependant dynamic equilibrium in the troposphere (Novelli et al., 1999). H₂ is not considered a direct greenhouse gas species. However, it is considered an indirect greenhouse gas because its OH[•] mediated oxidation reaction reduces the amount of OH[•] available for reaction with CH₄ and oxidation of H₂ in the stratosphere produces H₂O. Among the known source-sink dynamics at the soil-atmosphere interface, the dominant pathway for loss of H₂ from the atmosphere is via microbially-mediated soil uptake (Novelli et al., 1999; Ehhalt and Rohrer, 2009) although the magnitude of this loss is still regarded as highly uncertain (Constant et al., 2009; Ehhalt and Rohrer, 2009).

Recent studies suggest that photodegradation of plant litter and soil organic matter can be an important mechanism of decomposition in ecosystems with a high solar radiation load and low precipitation (Austin and Vivanco, 2006; Rutledge et al., 2010). Much of the mass loss from litter photodegradation appears to be from CO₂ release (Brandt et al., 2009; Lee et al., 2012; Rutledge et al., 2010), but release of various

other gases has also been documented, including CO (Lee et al., 2012; Schade et al., 1999; Tarr et al., 1995; Derendorp et al., 2011c), CH₄ (Lee et al., 2012; Vigano et al., 2008; Bruhn et al., 2009; Keppler et al., 2006), CH₃Cl (Derendorp et al., 2011b, 2012; Hamilton et al., 2003), C₂–C₅ hydrocarbons (Derendorp et al., 2011a, b), and H₂ (Derendorp et al., 2011c). In addition, several studies have reported small but significant C, N, and H- based trace gas release from organic matter in the absence of solar radiation (Conrad and Seiler, 1985; Lee et al., 2012; McCalley and Sparks, 2009; Tarr et al., 1995; Vigano et al., 2008; Derendorp et al., 2011c), with strong positive correlations between the rate of gas release and temperature. These studies suggest that abiotic degradation of organic matter may occur not only from photodegradation, but also from thermal degradation processes at relatively low temperatures (< 100 °C) that are well below the ignition point.

The mechanisms driving abiotic trace gas production from organic matter are still poorly understood. Proposed mechanisms include photochemical oxidation of organic compounds (Armstrong et al., 1966; Miller and Zepp, 1995; Valentine and Zepp, 1993) and direct cleavage of chemical groups by radiative energy absorption (Keppler et al., 2008; Schade et al., 1999; Tarr et al., 1995; Vigano et al., 2008). Among these, CH₄ release via direct cleavage of methoxyl groups abundant in pectin and lignin from live and dead plant material was recently documented (Keppler et al., 2008; Vigano et al., 2008). Based on these observations, CO and CO₂ release during abiotic degradation of plant material have been proposed to result from direct cleavage of carbonyl and carboxyl groups, respectively (Lee et al., 2012; Tarr et al., 1995). Some support for this methoxyl groups as a source of H₂ is found in a recent wood burning study (Röckmann et al., 2010), where, relative to water, the isotopic composition of bulk biomass was slightly depleted while it was strongly depleted in both methoxyl groups and H₂. This isotopic fractionation indicates that a small portion of H₂ may have originated from methoxyl groups. Given the nature of the chemical groups and bonds composing plant tissue, we speculated that H₂ would be produced during abiotic degradation of plant litter [e.g., $2C_nH_m + nO_2 + h\nu \rightarrow 2nCO + mH_2$: as a byproduct (mH₂) of partial oxidation (nO₂) of methyl groups (2C_nH_m) under radiation energy (hν) absorption]. Such thermal and photo production of H₂ has recently been documented using a single plant species (*Sequoiadendron giganteum*) (Derendorp et al., 2011c).

In our study, we quantified the steady state production rate of H₂ from different plant materials in a factorial manipulation of solar radiation (+rad: solar radiation present, –rad: solar radiation absent) and temperature (15 to 55 °C). We used four plant litter types that varied in chemical and structural composition to investigate the range of abiotic H₂ release from plant derived organic material: two grass species (C₃ Indian ricegrass, *Oryzopsis hymenoides* and C₄ little bluestem grass, *Schizachyrium scoparium*), leaves of

two woody species common in the desert in the southwest USA (velvet mesquite, *Prosopis velutina* and piñon pine, *Pinus edulis*), and proxies for pure cellulose (cellulosic filter paper, 92 % pure cellulose) and high lignin woody material (thin sheets of basswood, *Tilia* sp.). For the plant material with the highest H₂ production rate (basswood), we extended measurements to 80 °C. We also assessed the role of atmospheric O₂ on H₂ release (+O₂: aerobic conditions and –O₂: anaerobic conditions) with the high lignin woody material.

We hypothesized that (1) there would be detectable abiotic production of H₂ and the production rates would be positively correlated with temperature as potential energy and oxidative potential increase with temperature, (2) the rate of H₂ production would be close to zero in the absence of O₂ if abiotic production of H₂ is via partial oxidation of methyl groups, and (3) abiotic production of H₂ from plant litter would vary among plant materials due to species- and tissue-specific differences in chemical composition (e.g., the presence and abundance of methyl groups).

In this study, we define H₂ produced in the absence of solar radiation as *thermal degradation* (temperatures below 100 °C). The H₂ produced in the presence of solar radiation was considered total abiotic degradation, thereby, we define *photodegradation* as the difference in H₂ production between total abiotic and thermal degradation. It is important to note that both thermal degradation and photodegradation could be thermally enhanced (i.e., H₂ production increasing with temperature).

2 Materials and methods

To assess the patterns of H₂ production across a wide range of plant materials differing in chemical and structural composition, we used plant materials from four species collected from their native habitats in the southwestern US [dried leaflets of velvet mesquite (*Prosopis velutina*), culms and leaves of a C₃ grass (Indian ricegrass, *Oryzopsis hymenoides*) and a C₄ grass (*Schizachyrium scoparium*, little bluestem grass), and piñon pine needles (*Pinus edulis*)] and two proxies for cellulose and lignin end members [cellulosic filter paper (92 % pure cellulose, Whatman 42, GE Healthcare Inc., Piscataway, NJ, USA) and 1.6 mm thick sheets of wood from basswood (*Tilia* sp., high lignin content, National Balsa, Ware, MA, USA)]. The materials were air dried at 35 °C for two days before the incubation. Filter paper and basswood sheets were precut to fit inside the chamber area; grass materials and piñon pine needles were cut to 1 cm lengths to facilitate distributing the litter in a non-overlapping monolayer. Mesquite leaflets were used without cutting. Due to differences in litter density, the mass of materials used to fill in the experimental surface varied (e.g., typical mass to fill in the chamber area was approximately 1 g cellulosic filter paper, 5 g basswood sheet, 3 g piñon pine needles, and 2 g mesquite and grasses). However, gas production was sensitive to area

of solar radiation exposure rather than mass (e.g., exposing multiple layers of filter paper did not influence the rate of gas production during photodegradation; data not shown).

We did not pre-treat the litter materials to eliminate microbial activity, but experiments took place under conditions where materials were completely dry and were exposed to intense solar radiation, thus minimizing the possibility of microbial activity (Johnson, 2003). Pre-treating of the material to completely negate the possibility of any biological activity was not feasible due to the potential for chemical alteration during certain sterilization treatments (e.g., autoclaving). Chemical sterilization was also ruled out since these techniques may add compounds that are vulnerable to breakdown under heat and/or UV radiation, thus confounding our H₂ production measurements. Consequently, we did not completely rule out the possibility of some microbial activity, although the abiotic conditions suggest that it would be either non-existent or extremely low.

The plant materials were exposed to a factorial manipulation of solar radiation (+rad and -rad) and temperatures (15, 25, 35, 45, and 55 °C) to quantify the rates and patterns of H₂ release during abiotic degradation of plant material. We used basswood sheets, which exhibited the highest rate of H₂ production in the presence of O₂, to quantify the rate of H₂ production during abiotic degradation of plant material at a higher temperature (80 °C) and to quantify the rates and patterns of H₂ production in the presence and absence of O₂ in combination with solar radiation (+rad and -rad) and temperature (15, 35, and 55 °C).

The plant litter incubation experiments were conducted in a custom built quartz chamber (Blue Flame Technologies, McKinney, TX) that was transparent to over 85 % of the radiation generated from the solar radiation simulator across all wavebands. Solar radiation was simulated with a 300 W xenon lamp and lamp housing equipped with an atmospheric attenuation filter (Oriol Instruments, Newport Corp., Irvine, CA). The xenon lamp emitted a wavelength range of 0–2400 nm, but the atmospheric attenuation filter eliminated the shorter and longer wavelengths (< 290 and > 1600 nm), thus representing the range of radiation wavelengths reaching the surface of Earth. The intensity of radiation relative to natural sunlight varied with wavelength; UV-B (50 μW cm⁻²) was generated at a similar intensity as the solar radiation, but UV-A was much lower (1 mW cm⁻²) than natural solar radiation (e.g., measured UV radiation intensity of cloud-free solar noon during early August in Los Alamos, NM, USA was approximately 55 μW cm⁻² for UV-B and 5 mW cm⁻² for UV-A). Ozone production and accumulation in the chamber from the xenon lamp was likely minimal, as the atmospheric attenuation filter eliminated UV-C (100–280 nm) and the residence time of gases in the chamber was on the order of 10 s.

The area of solar radiation exposure was defined by a Viton-core O-ring (53.5 cm² and 10.5 ml), which was clamped between the top and bottom halves of the quartz

chamber, making an airtight seal. The outflow of the chamber was attached to a CO-H₂ analyzer (Peak Performer 1 RCP, Peak Laboratories LLC, Mountain View, CA, USA). A controlled flow of headspace gas (zero air or N₂ at 50–70 ml min⁻¹) flowed through the chamber and to the analytical system. The zero air we used contains little or no H₂, so we cannot rule out the possibility of H₂ outgassing from the substrate in the zero air. However, emissions did not diminish through time as would be expected from outgassing. Instrument calibration was performed with a suite of natural air standards and mixtures (NOAA ESRL and Scott Marrin, Riverside, CA, USA) that were routinely tested for internal consistency in order to establish stability in H₂ concentrations. Data were corrected for instrument non-linearity and a reference gas was analyzed every 35 min during the course of the automated analytical sequence. Instrument precision was ± 5 % or better at H₂ concentrations < 100 ppb and ± 2 % or better at concentrations > 100 ppb. The detection limit for observed H₂ production was ± 0.01 nmol m⁻² hr⁻¹.

The chamber temperature was controlled using a water bath integrated into the bottom of the chamber and connected to a chiller/heater (ThermoCube 200/300/400, Solid State Cooling Systems, Wappingers Falls, NY, USA). The chamber temperature was continuously monitored with a thermocouple (error range ± 0.5 °C) and radiation influences on chamber temperature (approximately 2 °C) were controlled with the water bath. A hotplate was used to assist the temperature increase to 80 °C. The exposed litter material was exchanged after one full set of temperature and radiation manipulations (temperature increase from 15 to 55 °C and ±rad), although reusing the material did not change the rate of gas production (one set of measurements was approximately equivalent to one afternoon of exposure of solar radiation).

The rate of H₂ production during thermal degradation of plant material for a given temperature was estimated by excluding incident radiation with an aluminum foil shroud over the chamber. We then subtracted the H₂ concentration measured from the empty chamber at the same temperature (empty chamber values were considered “blanks”). To estimate the rate of H₂ production during photodegradation of plant material, we measured the H₂ concentrations at a given temperature in the presence of solar radiation and subtracted the H₂ production during thermal degradation at the same temperature. Again, H₂ production during photodegradation was corrected using blanks, e.g., the empty chamber exposed to the solar radiation simulator over the same range of temperature and light conditions as samples. In all cases, the blank values were < 5 % of the values measured with plant material in the chamber. Changes in H₂ concentrations in response to changes in temperature and solar radiation were essentially instantaneous, but we waited between 30 to 60 min after changing conditions before taking the mean H₂ (Fig. 1). The final 3 to 4 analyzes of a sequence were typically used to

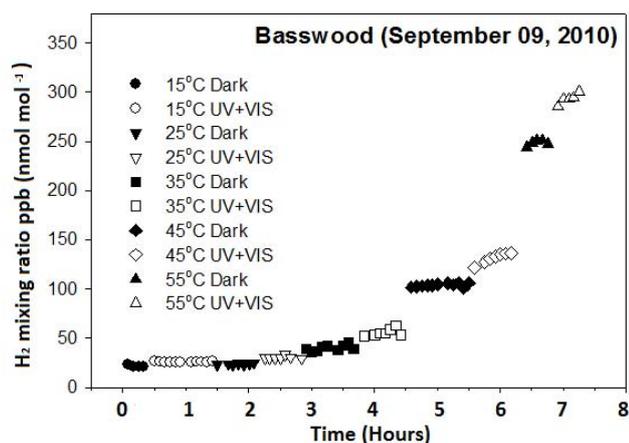


Fig. 1. Example of an analytical sequence exhibiting increasing H₂ concentrations with increasing temperature and light conditions (dark and UV+visible light). The automated GC system ran on a five minute sequence with analysis of a reference gas every 35 min. Open symbols indicate stabilizing period and filled symbols indicate period used for averaging. Note the nearly instantaneous response of the plant material, in this case of Basswood, to changes in temperature.

estimate the steady state H₂ production rate. Each measurement set was replicated three times for each litter type.

To quantify the rate of H₂ production during anaerobic thermal degradation and photodegradation of basswood sheets, we followed the same basic procedure used for measurements in the presence of O₂ with ultra high purity N₂ substituted for zero air. Measurements were taken at 15, 35, and 55 °C.

The H₂ production rates during thermal degradation and photodegradation of plant litter were normalized in two ways: per area (nmol H₂ m⁻² s⁻¹) and per mass (nmol H₂ kg⁻¹ s⁻¹): however, we suggest that H₂ production rate by thermal degradation is most appropriate on a mass basis because temperature would affect litter biomass as a whole. In contrast, photodegradation is most appropriately reported per unit area, as the UV radiation effects would only apply to the area of litter exposed to UV.

Activation energy of H₂ production during thermal degradation and photodegradation of litter under temperature manipulation was calculated using the Arrhenius equation (Eq. 1):

$$k = A \exp(-E_a/RT) \quad (1)$$

where k is the reaction rate coefficient, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature. We also estimated Q_{10} of the reaction according to Eq. (2) to better understand temperature sensitivity of the reaction.

$$Q_{10} = (P_n/P_{n-1}) \exp(10/(T_n - T_{n-1})) \quad (2)$$

where P_n is H₂ production rate at time n and T_n is chamber temperature at time n . Statistical analyzes including repeated measures analysis with mixed effects and regression analyzes were conducted using R 2.11.1 (R Development Core Team). The differences in H₂ production rate within the plant litter types were analyzed using repeated measures analysis.

3 Results

Thermal degradation of plant litter typically led to a higher H₂ production rate (range = 0.00069 to 2.17 nmol m⁻² s⁻¹ across all materials and temperatures) than did photodegradation alone (Fig. 2 and Supplement 1; range = 0.0036 to 1.01 nmol m⁻² s⁻¹). This difference was particularly pronounced at temperatures higher than 45 °C (Table 2). Averaged across all materials, the molar ratio of thermal degradation to photodegradation rose from 0.52 to 4.07 as temperature increased from 25 to 55 °C, implying that production of H₂ is more sensitive to changes in temperature than solar radiation alone. When temperature was raised to 80 °C for the high lignin proxy (basswood), total H₂ production rate reached 7.01 nmol m⁻² s⁻¹ (4.58 nmol m⁻² s⁻¹ from thermal degradation and 2.43 nmol m⁻² s⁻¹ from photodegradation).

We identified measurable H₂ production during abiotic degradation of plant litter with behavior typical of reactions following the temperature-dependent Arrhenius equation. The reactive energy (E_a) for H₂ production during thermal degradation of plant litter ranged from 60 to 146 kJ mol⁻¹ and those of photodegradation ranged from 40 to 88 kJ mol⁻¹ among the 6 different litter types (Table 1). The Q_{10} values for all materials during thermal degradation and photodegradation exhibited normal values ranging from 2 to 3 (Davidson and Janssens, 2006) with a few notable exceptions (Table 1). Both C₃ grass and mesquite litter exhibited high Q_{10} values during thermal degradation (5.7 and 7.1, respectively). Even with the elimination of a potential outlier in the C₃ grass data at 25 °C, Q_{10} remained high at 3.7. Both the cellulose proxy filter paper and C₄ grass exhibited low Q_{10} of 1.3 and 1.1 during photodegradation over the full temperature range and again when potential outliers were excluded at 55 °C, Q_{10} remained low at 1.6 and 1.1, respectively.

When the H₂ production rates were normalized by mass, the general temperature sensitivity patterns were similar with the exception of an increased relative rate of H₂ production for filter paper, the cellulose proxy (cf., Fig. 2a and b to c and d, Supplement). On a per-mass basis, the rate of H₂ production during thermal degradation of plant litter ranged from 0.0055 to 1.77 nmol kg⁻¹ s⁻¹ across all materials within the temperature range of 15 to 55 °C. The H₂ production rate during photodegradation of plant litter ranged from 0.029 to 1.03 nmol kg⁻¹ s⁻¹.

The rate of H₂ production varied among litter types representing different litter chemical compositions. Basswood

Table 1. The activation energy (E_a : kJ mol⁻¹) and the Q_{10} values of H₂ production during thermal degradation and photodegradation of litter for the six plant litter types calculated by Arrhenius equation over the 15 to 80 °C temperature range for E_a and 25 to 55 °C temperature range for Q_{10} .

Process	Type	Filter paper	Mesquite	C ₃ grass	C ₄ grass	Piñon	Basswood
Thermaldegradation	E_a	69.19	125.62	60.47	146.21	81.21	81.98
	Q_{10}	2.33	5.70	7.07	2.44	2.69	4.09
Photodegradation	E_a	48.03	85.42	39.70	88.20	70.74	71.06
	Q_{10}	1.29	2.23	1.93	1.07	2.09	2.31

Table 2. Mean (standard error: SE) molar ratios between H₂ production rate during thermal degradation and photodegradation of six plant litter types ($n = 3$). Only the lignin proxy (wood sheets of basswood) was used for the 80 °C exposure.

T (°C)	Molar ratios of H ₂ production rate (thermal degradation/photodegradation)					
	Filter paper	Mesquite	C ₃ grass	C ₄ grass	Piñon	Basswood
25	1.11 (0.78)	0.18 (0.00)	0.65 (0.37)	0.13 (0.10)	0.51 (0.03)	0.57 (0.15)
35	0.87 (0.09)	0.21 (0.16)	2.44 (1.02)	0.78 (0.15)	1.54 (0.05)	1.01 (0.12)
45	1.16 (0.23)	0.68 (0.06)	2.06 (0.46)	1.85 (0.18)	1.97 (0.10)	1.94 (0.45)
55	2.91 (0.63)	4.45 (3.40)	8.81 (6.38)	3.20 (0.28)	2.09 (0.59)	2.96 (0.74)
80	–	–	–	–	–	3.62 (0.63)

sheets exhibited the highest H₂ production rates, followed by piñon pine needles. The remaining four materials (filter paper, mesquite, C₃ grass, and C₄ grass) showed H₂ production rates that were much lower than those of basswood or piñon needles ($F_{1,79} = 18.22$, $P < 0.0001$) and were not observed to be statistically different from each other ($F_{1,49} = 1.57$, $P = 0.22$). The H₂ production rates for basswood and piñon pine needles diverged from that of the other materials with increasing temperatures (Fig. 1).

H₂ production was observed under anaerobic conditions, ranging from 0.060 to 1.05 nmol m⁻² s⁻¹ for basswood sheet within the temperature range of 15 to 55 °C. This production was on the order of half that produced under aerobic conditions at any given temperature and radiation combination (Fig. 3).

4 Discussion

Previous work on trace gas production during thermal degradation and photodegradation of plant litter showed that various C- and N- based trace gases are released during abiotic degradation of litter (Brandt et al., 2007; Conrad and Seiler, 1985; Schade et al., 1999; Viganò et al., 2008). A recent study suggested that this may be attributed to direct breakdown of various chemical compounds and chemical groups within the organic material (Lee et al., 2012) by absorbing the activation energy from the heat or solar radiation. In addition to various C-based gas species, measurable H₂ release was previously reported from *S. giganteum*, but thermal degradation was reported only at temperatures above 45 °C

and photodegradation was reported only in anaerobic conditions (Derendorp et al., 2011c). In this study, we identified and quantified the rate of H₂ release during abiotic degradation of various plant litter types and showed that the rate of H₂ production increases exponentially with temperature (Fig. 2, Tables 1 and 3). Additionally, we identified release of H₂ from dry litter under intense UV radiation, high chamber temperatures (Fig. 2), and in both the presence and absence of O₂ (Fig. 3) and that the temporal response to changing temperature is essentially instantaneous (Fig. 1) suggesting that the mechanism involved in the release of H₂ is abiotic.

The positive exponential response of H₂ production to temperature (Fig. 2 and Table 1) suggests that H₂ release during abiotic degradation of plant litter will be particularly high in hot and dry environments where microbial activity is minimal. In our experiment, we did not completely exclude the possibilities of H₂ production from anaerobically fermenting bacteria and aerobically by fungi. However, we suggest that this would be minimal. In addition, an E_a greater than 50 lends additional supports that the process involved in H₂ release in our observations is abiotic (Schonknecht et al., 2008). Substantial production of H₂ in the absence of O₂ (Fig. 3) contradicted our hypothesis that anaerobic H₂ production would be close to zero since oxidation of methyl groups would not occur in anaerobic conditions and indeed, our observation of anaerobic H₂ production confirmed the findings of Derendorp et al. (2011c). On the other hand, Derendorp et al. (2011c) observed no H₂ production in the presence of O₂, whereas our results suggest roughly equal production for aerobic (total minus anaerobic) and anaerobic processes in the case of high lignin basswood for the

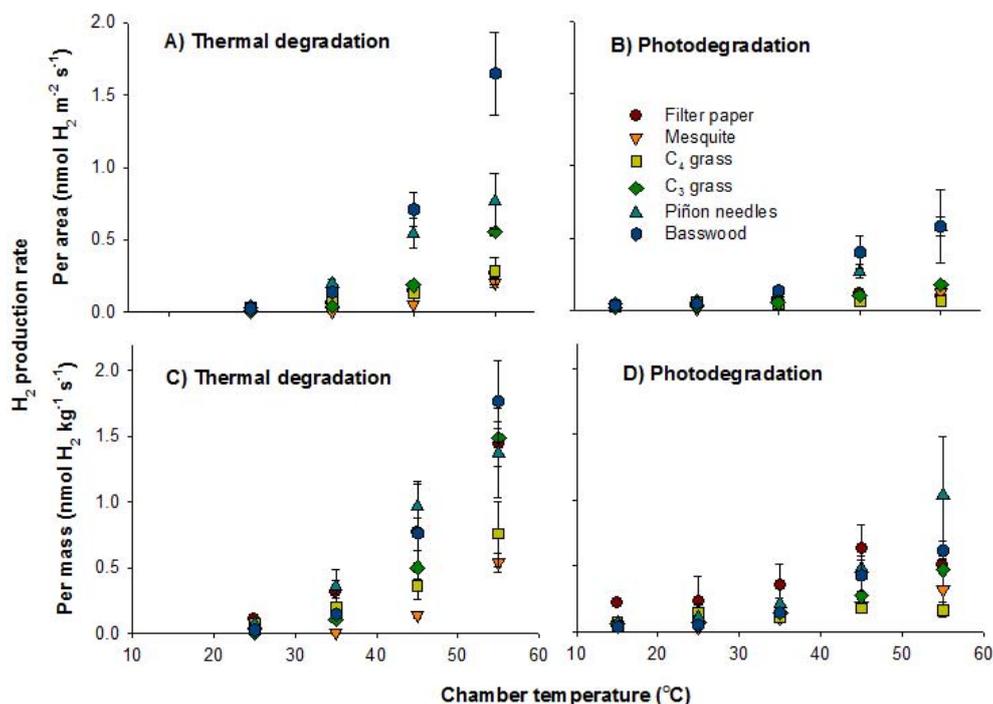


Fig. 2. The rate of H₂ production from abiotic degradation of plant litter across a range of temperatures. Abiotic degradation is divided into (a) and (c) thermal degradation (H₂ production in the absence of solar radiation minus blank) and (b) and (d) photodegradation (H₂ production in the presence of solar radiation minus thermal degradation). Six plant litter types were used. Means and standard error ($n = 3$) are depicted.

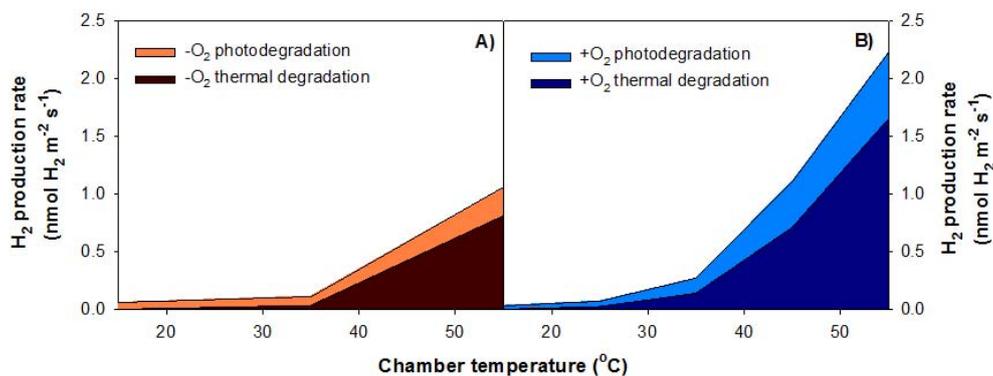


Fig. 3. The rate of H₂ production during thermal degradation (dark colors; measured in the absence of solar radiation) and photodegradation (light colors; H₂ production in the presence of solar radiation minus thermal degradation) of high lignin proxy basswood sheet in the (a) absence of O₂ and (b) presence of O₂.

total abiotic H₂ production. It is unclear at this time why the experimental results differ, but it is possible that there is a difference in plant species response between *S. giganteum* and the basswood studied here or that there is a fundamental difference in experimental setup that is not readily obvious. Regardless of this difference, our results suggest that multiple mechanisms drive the abiotic release of H₂ from plant litter. We speculated in previous experiments with C-based trace gases that both photochemical oxidation (via reaction

with O₂) and direct breakdown of carboxyl, carbonyl, and methoxyl groups could lead to production of CO₂, CO, and CH₄ (Lee et al., 2012). In our observations, typical H₂:CO mole fraction ratios across all litter samples were 0.14–0.59 for thermal degradation and 0.02–0.07 during photodegradation. The variability shown in the E_a and Q_{10} values of H₂ production rate across the six different plant litter types (Table 1) suggests that different chemical composition of these plant litter types (Lee et al., 2012) have varying rates

of reactivity (Davidson and Janssens, 2006). Similarly, the higher rate of H₂ production in the presence of O₂ may be due to partial photo-oxidation of organic compounds. Taken together, our results suggest that the plant litter pool is a previously unrecognized source of atmospheric H₂.

Our findings have substantial implications with respect to the most important loss process for atmospheric H₂. For instance, a previous field observation of soil H₂ uptake from different soil layers showed that the rate of H₂ uptake increased when the surface litter and organic matter layers were removed (Smith-Downey et al., 2008). The original interpretation of this observation was that litter and organic matter removals eliminated a diffusive barrier and increased access to atmospheric H₂ for soil microbes. Interpretation of these data in light of our results, however, would suggest that the litter removal eliminated a proximal source of H₂ that subsurface microbes had previously been consuming. We suggest that in this previous study, the observed uptake of H₂, occurred even though H₂ was likely produced within the chambered system, but consumption was simply greater than production.

The range of H₂ production rates during thermal degradation of plant litter in vitro observed in our study (0.02–33.62 ng H₂ gdw⁻¹ h⁻¹ within a 15–80 °C temperature range across the six different materials) corresponds well with the single species from which H₂ release was previously reported (Derendorp et al., 2011c; approximately 0–60 ng gdw⁻¹ h⁻¹ within a 20–80 °C temperature range). While Derendorp et al. (2011c) reported measurable rates of H₂ from *S. giganteum* only over 45 °C, for most litter types we detected measurable H₂ release beginning at 35 °C. In contrast to previously published findings, we observed substantial release of H₂ during photodegradation of litter both with and without O₂, whereas Derendorp et al. (2011c) only observed photo-induced H₂ release in anaerobic conditions. We expect that if H₂ release is due to direct breakdown of chemical groups within the organic material, H₂ release should be observed in both cases of thermal and photodegradation process unless the H₂ produced in Derendorp et al. (2011c) was somehow oxidized during the measurement.

Our observations of abiotic H₂ release suggest that this may be a substantial flux relative to the documented range of soil uptake of H₂ (0.2–12.0 nmol m⁻² s⁻¹; Conrad and Seiler, 1985; Gerst and Quay, 2001; King, 2003; Rahn et al., 2002; Smith-Downey et al., 2008; Yonemura et al., 2000). A detailed estimate of the global abiotic H₂ production would require up-scaling our results to account for global patterns of litter chemistry and pools, surface temperatures, and solar radiation reaching the soil surface. Geographically widespread arid and semi-arid lands comprise over 40 % of the global land surface (Bailey, 1996); these systems likely produce measureable amounts of H₂ due to the typically high surface temperatures, high radiative loads, and in many cases large amount of standing dead and surface litter. Although the majority of this H₂ is likely lost immediately to soil microbiota due to proximity to the most important atmospheric

H₂ sink, in the case of standing dead biomass, H₂ produced might indeed yield H₂ directly to the atmosphere. Given differences in reported H₂ flux response to O₂ between our study and that of Derendorp et al. (2011c), we suggest future research assessing the role of O₂ on abiotic release of H₂ and the correlation between UV intensity and the rate of H₂ release from various organic materials. In addition, future field work measuring H₂ flux from litter isolated from soil substrates will be required to verify and quantify field flux rates.

In summary, we quantified direct abiotic production of H₂ from plant litter resulting from both thermal- and photo-induced processes and have shown that these processes exhibit classic temperature dependence evidenced by approximate doubling of gas production rate per every 10 °C (Table 1). These results indicate that abiotic degradation of plant material is a ubiquitous source of H₂, especially under arid conditions. Because these processes occur at the soil-atmosphere interface, they provide a previously unrecognized proximal source of H₂ for microbial uptake and confound interpretation of direct, chamber based, measurements of atmospheric uptake that are important for constraining the global H₂ budget. An exploration of the varying UV intensity effects would be an important future step for understanding H₂ release through photodegradation. In addition, the importance of abiotic processes in the overall budget of land-atmospheric boundary layer H₂ is yet to be determined. Given projected increases in atmospheric temperatures and drought in some parts of the world (IPCC, 2007; Overpeck and Udall, 2010), and detailed investigation from field and large scale observations is warranted to further extrapolate the effects of abiotic processes on a global scale.

Supplementary material related to this article is available online at: <http://www.biogeosciences.net/9/4411/2012/bg-9-4411-2012-supplement.pdf>.

Acknowledgements. This research was funded by a LANL-NMSU Memorandum of Understanding grant (HLT and TR), the LANL Institutes, and NSF DEB 0815808 to New Mexico State University (HLT).

Edited by: G. Wohlfahrt

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