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Dry deposition of molecular hydrogen in the presence of H_2 production

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In a recent paper, we derived an analytical expression for the deposition velocity, v_d, of molecular hydrogen on soil that includes the action of a dry top soil layer without H_2 removal (Ehhalt and Rohrer, 2013). This expression is based on the solution of the vertical diffusion equation in a two-layer model and takes the following form:

$$v_d = \frac{1}{\frac{\delta}{D_{S,I}} + \sqrt{\frac{1}{D_{S,II} \cdot k_s \Theta_a}}} \tag{1}$$

The two-layer model was first suggested by Yonemura et al. (2000), and it assumes uniform conditions in the respective layers. δ is the depth of the dry top layer, D_S is the diffusivity of H_2 in the soil ($D_{S,I}$ in the dry top layer, $D_{S,II}$ in the moist, deeper soil layer), k_s is the rate constant for removal of H_2 from soil air, and Θ_a is the fraction of soil volume filled with air. Expressions for D_S, δ, k_s Θ_a, that is, their dependences on soil moisture, Θ_w, and temperature, T, are also given in the earlier paper (Ehhalt and Rohrer, 2013). Thus, eq. (1) can be used to describe the dependence of v_d on Θ_w and T. This description is more complete and more realistic than that derived from the one-layer model used so far (Yonemura et al., 2000; Smith-Downey et al., 2008; Morfopoulos et al., 2012).

Yet, eq. (1) does not treat all situations. In particular, it does not include the impact on v_d of a production of H_2 within the soil. Such H_2 production has been shown, for instance, to accompany the fixation of nitrogen by bacteria (Conrad and Seiler, 1980). Further evidence of H_2 production within the soil is provided by the occasional observation of non-zero asymptotic H_2 mixing ratios at greater soil depths (*cf*. Smith-Downey et al., 2008).

With this short note, we would like to point out that eq. (1) can be easily expanded to include a production of H_2 within the soil. This expansion is given by the factor $(1 - M_e/M_a)$, such that the deposition velocity, $v_{d,p}$, including soil production is given as

$$v_{d,p} = v_d \cdot (1 - M_e/M_a), \tag{2}$$

where v_d is given by eq. (1). M_a is the H_2 mixing ratio in the atmosphere and $M_e = P/(k_s\,\Theta_a \cdot \rho)$ is the equilibrium mixing ratio established in the soil between the production with the rate P and the destruction $k_s\,\Theta_a$. ρ is the number density of air. For v_d derived from the one-layer model, this relation has already been shown to hold (Yonemura et al., 2000). In Appendix A, we show that it also holds for the two-layer model.

Clearly, the dry deposition velocity defined by eq. (2) is no longer independent of the atmospheric mixing ratio of H_2. This has implications for the geographical distribution of $v_{d,p}$ which is especially important when the global uptake of H_2 by soil is derived from inverse modelling. We further note that M_e can be obtained from the field measurement of $v_{d,p}$ by the chamber method by allowing the H_2 mixing ratio in the chamber to drop to its asymptotic value (*cf*. Conrad and Seiler, 1985; Rice et al., 2011).

Appendix A

Derivation of $v_{d,p}$

By definition, the flux of H_2 from the atmosphere into the soil is given by

$$F_a = v_{d,p} \cdot \rho \cdot M_a, \tag{A.1}$$

where F_a is given in units of molec cm^{-2} s^{-1}, $v_{d,p}$, the dry deposition velocity in the presence of H_2 production, has the units of cm s^{-1}, ρ, the number density of air is in molec cm^{-3}, and M_a the atmospheric mixing ratio has the units of molec molec^{-1}.

The top soil layer, layer I, is assumed to be so dry that neither bacterial destruction nor production of H_2

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can take place. Thus, throughout layer I the vertical H_2 flux, F_I, remains constant and equal to F_a. The gradient in $M_S(z)$, the mixing ratio in the soil, is therefore linear and

$$F_I = \rho \cdot D_{S,I} \cdot \frac{M_S(0) - M_S(\delta)}{\delta} \qquad (A.2)$$

Here, $M_S(0) = M_a$ and $M(\delta)$ are the H_2 mixing ratios at depth $z = 0$ (the surface) and at $z = \delta$, the depth of the dry layer. $D_{S,I}$ is the diffusivity in layer I, its units are $cm^2\ s^{-1}$.

For $z \geq \delta$, that is, in layer II, the vertical profile of $M_S(z)$ is given by the one-dimensional vertical diffusion equation

$$\Theta_a \cdot \rho \cdot \frac{\partial M_S}{\partial t} = \frac{\partial}{\partial z} \cdot \rho \cdot D_{S,II} \cdot \frac{\partial M_S(z)}{\partial z} - \rho \cdot M_S(z) \cdot k_s \Theta_a + P, \qquad (A.3)$$

where $D_{S,II}$ is the diffusivity in the deeper soil layer II, units of $cm^2\ s^{-1}$, P is the production rate of H_2 per soil volume in molec $cm^{-3}\ s^{-1}$, k_s is the rate constant for the removal of H_2 from soil air, units of s^{-1}, and Θ_a is the fraction of soil volume filled with air. Assuming steady state, that is, $\partial M_S/\partial t = 0$ and $D_{S,II}$, ρ, Θ_a, k_s, P to be constant with depth equation (A.3) can be solved analytically:

$$M_{S,II}(z) = M_0 \cdot \exp\left(\frac{-(z-\delta)}{\zeta}\right) + M_e, \qquad (A.4)$$

where the characteristic decay length $\zeta = \sqrt{D_{S,II}/k_s\Theta_a}$ and $M_e = P/(k_s\Theta_a \cdot \rho)$ is the equilibrium H_2 mixing ratio established between in soil production and destruction of H_2 in the absence of transport.

To determine the free parameter M_0, we calculate the H_2 flux into layer II, F_{II} (δ), and use the fact that at the immediate boundary the flux into layer II is identical to the flux in layer I. The flux into layer II is given by Fick's law

$$F_{II}(\delta) = -\rho \cdot D_{S,II} \cdot \left.\frac{\partial M_{S,II}(z)}{\partial z}\right|_{z=\delta} \qquad (A.5)$$

Inserting eq. (A.4) for $M_{S,II}(z)$ yields

$$F_{II}(\delta) = \rho \cdot D_{S,II} \cdot M_0/\zeta. \qquad (A.6)$$

Remembering that $F_a = F_I = F_{II}(\delta)$ we can rewrite eq. (A.6)

$$F_a = \rho \cdot D_{S,II} \cdot M_0/\zeta \qquad (A.7)$$

$$\text{or } M_0 = (F_a \cdot \zeta)/(\rho \cdot D_{S,II}). \qquad (A.8)$$

The H_2 mixing ratio at depth δ, $M_S(\delta)$, is then

$$M_S(\delta) = M_0 + M_e = (F_a \cdot \zeta)/(\rho \cdot D_{S,II}) + M_e. \qquad (A.9)$$

Inserting eq. (A.9) into eq. (A.2) and remembering that $F_I = F_a$, we obtain

$$F_a = \frac{\rho \cdot D_{S,I}}{\delta} \cdot \left(M_a - M_e - \frac{F_a \cdot \zeta}{\rho \cdot D_{S,II}}\right). \qquad (A.10)$$

Collecting the terms with F_a gives

$$F_a \cdot \left(\frac{\delta}{D_{S,I}} + \frac{\zeta}{D_{S,II}}\right) = \rho \cdot (M_a - M_e), \qquad (A.11)$$

and since $F_a = v_{d,p} \cdot \rho \cdot M_a$ [see eq. (A.1)]

$$v_{d,P} = \left(1 - \frac{M_e}{M_a}\right) \cdot \left(\frac{1}{\frac{\delta}{D_{S,I}} + \frac{\zeta}{D_{S,II}}}\right) \qquad (A.12)$$

or

$$v_{d,P} = \left(1 - \frac{M_e}{M_a}\right) \cdot v_d \qquad (A.13)$$

since the second term on the right-hand side of eq. (A.12) is identical to v_d from eq. (1).

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