Dry deposition of molecular hydrogen in the presence of H₂ production

By DIETER H. EHHALT and FRANZ ROHRER*, Forschungszentrum Jülich, Institut IEK-8: Troposphäre, 52425 Jülich, Germany

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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 H₂ 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:

\[
\frac{v_d}{\delta} = \frac{1}{D_{S,1} + \sqrt{D_{S,1} k_s \Theta_a}}
\]

The two-layer model was first suggested by Yonemura et al. (2000), and it assumes uniform conditions in the respective layers. \( \delta \) is the depth of the dry top layer, \( D_S \) is the diffusivity of H₂ in the soil (\( D_{S,1} \) in the dry top layer, \( D_{S,II} \) in the moist, deeper soil layer), \( k_s \) is the rate constant for removal of H₂ from soil air, and \( \Theta_a \) is the fraction of soil volume filled with air. Expressions for \( D_S \), \( \delta \), \( k_s \), \( \Theta_a \), that is, their dependences on soil moisture, \( \Theta_w \), 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 \( \Theta_w \) 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 H₂ within the soil. Such H₂ production has been shown, for instance, to accompany the fixation of nitrogen by bacteria (Conrad and Seiler, 1980). Further evidence of H₂ production within the soil is provided by the occasional observation of non-zero asymptotic H₂ mixing ratios at greater soil depths (Smith-Downey et al., 2008; Morfopoulos et al., 2012).

With this short note, we would like to point out that eq. (1) can be easily expanded to include a production of H₂ within the soil. This expansion is given by the factor \( \left(1 - \frac{M_e}{M_a}\right) \), such that the deposition velocity, \( v_{d,p} \), including soil production is given as

\[
v_{d,p} = v_d \cdot \left(1 - \frac{M_e}{M_a}\right),
\]

where \( v_d \) is given by eq. (1), \( M_e \) is the H₂ mixing ratio in the atmosphere and \( M_e = P / (k_s \Theta_a \rho) \) is the equilibrium mixing ratio established in the soil between the production with the rate \( P \) and the destruction \( k_s \Theta_a \rho \) 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 H₂. This has implications for the geographical distribution of \( v_{d,p} \) which is especially important when the global uptake of H₂ 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 H₂ 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 H₂ from the atmosphere into the soil is given by

\[
F_a = v_{d,p} \cdot \rho \cdot M_a,
\]

where \( F_a \) is given in units of molec cm⁻² s⁻¹, \( v_{d,p} \), the dry deposition velocity in the presence of H₂ production, has the units of cm s⁻¹, \( \rho \), the number density of air is in molec cm⁻³, and \( M_a \) the atmospheric mixing ratio has the units of molec cm⁻³⁻¹.

The top soil layer, layer I, is assumed to be so dry that neither bacterial destruction nor production of H₂
can take place. Thus, throughout layer I the vertical H₂
flux, \( F_I \), remains constant and equal to \( F_a \). The gradient in
\( \text{M}_S(z) \), the mixing ratio in the soil, is therefore linear and
\[
\frac{\partial \text{M}_S(0)}{\partial z} - \frac{\text{M}_S(z)}{\delta} = \frac{\partial \text{M}_S(0)}{\partial z} - \frac{\text{M}_S(z)}{\delta} = (F_a \cdot \zeta) \quad (A.2)
\]
Here, \( \text{M}_S(0) = \text{M}_a \) and \( \text{M}(\delta) \) are the H₂ mixing ratios at
depth \( z = 0 \) (the surface) and at \( z = \delta \), the depth of the dry
layer. \( \text{D}_{S,I} \) is the diffusivity in layer I, its units are \( \text{cm}^2 \text{s}^{-1} \).

For \( z \geq \delta \), that is, in layer II, the vertical profile of \( \text{M}_S(z) \)
is given by the one-dimensional vertical diffusion equation
\[
\Theta_a \cdot \frac{\partial \text{M}_S}{\partial z} = \frac{\partial}{\partial z} \left( \rho \cdot \text{D}_{S,II} \cdot \frac{\partial \text{M}_S(z)}{\partial z} - \rho \cdot \text{M}_S(z) \cdot k_a \cdot \Theta_a + P \right), \quad (A.3)
\]
where \( \text{D}_{S,II} \) is the diffusivity in the deeper soil layer II, units
of \( \text{cm}^2 \text{s}^{-1} \). \( P \) is the production rate of H₂ per soil volume
in molec \( \text{cm}^{-3} \text{s}^{-1} \). \( k_a \) is the rate constant for the removal
of H₂ from soil air, units of \( \text{s}^{-1} \), and \( \Theta_a \) is the fraction of
soil volume filled with air. Assuming steady state, that is,
\( \partial \text{M}_S/\partial t = 0 \) and \( \text{D}_{S,II} \cdot \rho \cdot \Theta_a \cdot k_a \cdot P \) to be constant with depth
equation (A.3) can be solved analytically:
\[
\text{M}_S(z) = \text{M}_0 \cdot \exp \left( \frac{-z - \delta}{\zeta} \right) + \text{M}_e, \quad (A.4)
\]
where the characteristic decay length \( \zeta = \sqrt{\text{D}_{S,II}/k_a} \) and
\( \text{M}_e = P/(k_a \cdot \Theta_a \cdot \rho) \) is the equilibrium H₂ mixing ratio established
between in soil production and destruction of H₂ in the
absence of transport.

To determine the free parameter \( \text{M}_0 \), we calculate the H₂
flux into layer II, \( F_{II}(\delta) \), 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
\[
F_{II}(\delta) = -\rho \cdot \text{D}_{S,II} \cdot \frac{\partial \text{M}_S(z)}{\partial z} \bigg|_{z=\delta} \quad (A.5)
\]
Inserting eq. (A.4) for \( \text{M}_S(\delta) \) yields
\[
F_{II}(\delta) = -\rho \cdot \text{D}_{S,II} \cdot \text{M}_0 / \zeta. \quad (A.6)
\]
Remembering that \( F_a = F_I = F_{II}(\delta) \) we can rewrite eq. (A.6)
\[
F_a = \rho \cdot \text{D}_{S,II} \cdot \text{M}_0 / \zeta \quad (A.7)
\]\nor \( \text{M}_0 = (F_a \cdot \zeta) / (\rho \cdot \text{D}_{S,II}) \). \quad (A.8)
The H₂ mixing ratio at depth \( \delta \), \( \text{M}_S(\delta) \), is then
\[
\text{M}_S(\delta) = \text{M}_0 + \text{M}_e = (F_a \cdot \zeta) / (\rho \cdot \text{D}_{S,II}) + \text{M}_e. \quad (A.9)
\]
Inserting eq. (A.9) into eq. (A.2) and remembering that
\( F_i = F_a \), we obtain
\[
F_a = \rho \cdot \text{D}_{S,II} \cdot \left( \frac{\text{M}_a - \text{M}_e - \frac{F_a \cdot \zeta}{\rho \cdot \text{D}_{S,II}}}{\rho \cdot \text{D}_{S,II}} \right), \quad (A.10)
\]
Collecting the terms with \( F_a \) gives
\[
F_a \cdot \left( \frac{\delta}{\text{D}_{S,II}} + \frac{\zeta}{\text{D}_{S,II}} \right) = \rho \cdot (\text{M}_a - \text{M}_e), \quad (A.11)
\]
and since \( F_a = v_{d,p} \cdot \rho \cdot \text{M}_a \) [see eq. (A.1)]
\[
\begin{align*}
\text{v}_{d,p} & = \left( 1 - \frac{\text{M}_a}{\text{M}_e} \right) \cdot \rho \cdot \text{D}_{S,II} \cdot \text{v}_d \quad (A.12)
\end{align*}
\]
or
\[
\text{v}_{d,p} = \left( 1 - \frac{\text{M}_a}{\text{M}_e} \right) \cdot \text{v}_d \quad (A.13)
\]
since the second term on the right-hand side of eq. (A.12) is identical to \( v_d \) from eq. (1).

References

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