Isotopic signature of production and uptake of H_2 by soil

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Introduction

Molecular hydrogen (H_2) is the second most abundant reduced gas in the atmosphere (~550ppb). Our studies focus on the microbial production and uptake of H_2 by soil. The biogenic soil sink of molecular H_2 is the largest (~75%) and most uncertain term in the global atmospheric H_2 budget. The biological N_2 fixation on land is a poorly understood minor source (~4%) of H_2, but it has potentially a large local effect on the isotopic composition of H_2, due to its very deuterium-depleted source signature. To better understand the soil sink and source, one possibility is to investigate the isotopic fractionation processes involved.

Sampling and experimental set-up

Air samples were collected from a soil chamber at two contrasting locations in the Netherlands: a grass field (Cabauw) and a forest site (Speuld). Two types of ground cover, with and without clover, were sampled at Cabauw; while three types of forest (Douglass fir, beech and spruce) were selected in Speuld.

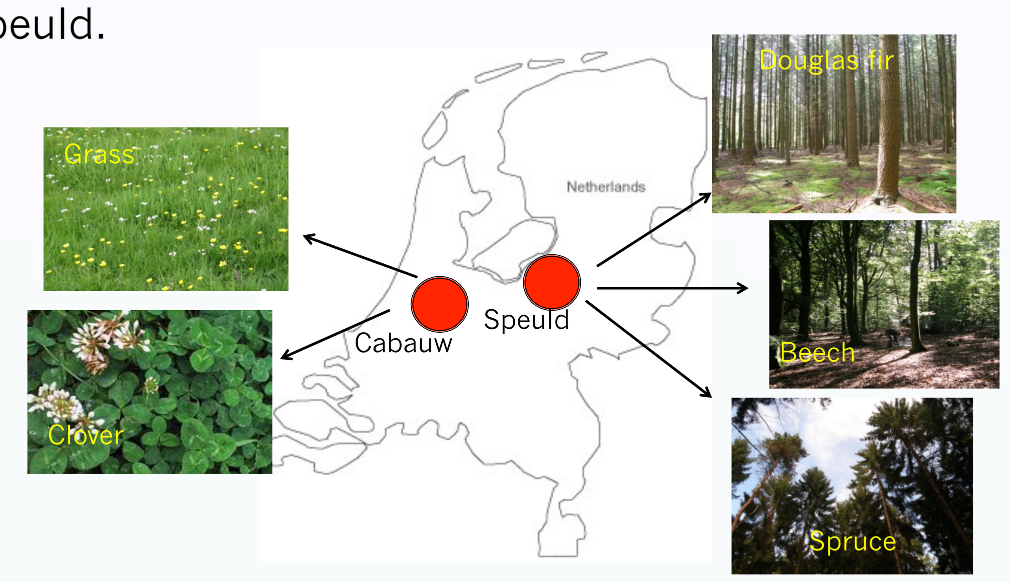


Fig. 1a Sampling sites.

We used a closed-cycle sampler designed at IMAU (Fig. 1b). Air samples were collected from the chamber in 1L glass flasks at 0, 10, 20 and 30 minutes after the start of sampling (time interval changed to 5 min in Speuld). The mole fraction and deuterium content of H_2 were measured with a GC/IRMS (Batenburg et al., 2011).

Fig. 1b Flask sampler and soil chamber

Mass balance model

Based on mass balance of H_2 (Rice et al., 2011)

Time evolution: $$\frac{dc}{dt} = P - kc \quad (1)$$

Solution for HH: $$c = (c_i - c_e)e^{-kt} + c_e \quad (2)$$

Solution for HD: $$c' = (c_i' - c_e')e^{-k't} + c_e' \quad (3)$$

Combined: $$\ln\frac{c'-c_e'}{c_i'-c_e'} = \frac{k'}{k}\ln\frac{c-c_e}{c_i-c_e} \quad (4)$$

where c, c_i and c_e (=P/k) are the mole fraction of H_2 at time t, initially and at equilibrium; c′, c_i', and c_e' are those for HD; P is the production rate and k is the uptake rate constant for H_2; k′ is the uptake rate constant for HD.

References

Batenburg, A.M., et al, Temporal and spatial variability of the stable isotopic composition of atmospheric molecular hydrogen: observations at six EUROHYDROS stations, *Atmos. Chem. Phys.*, 2011.

Rice, A., et al, Isotopic fractionation during soil uptake of atmospheric hydrogen, Biogeosciences, 2011

Results

1. Time evolution of H_2 and HD

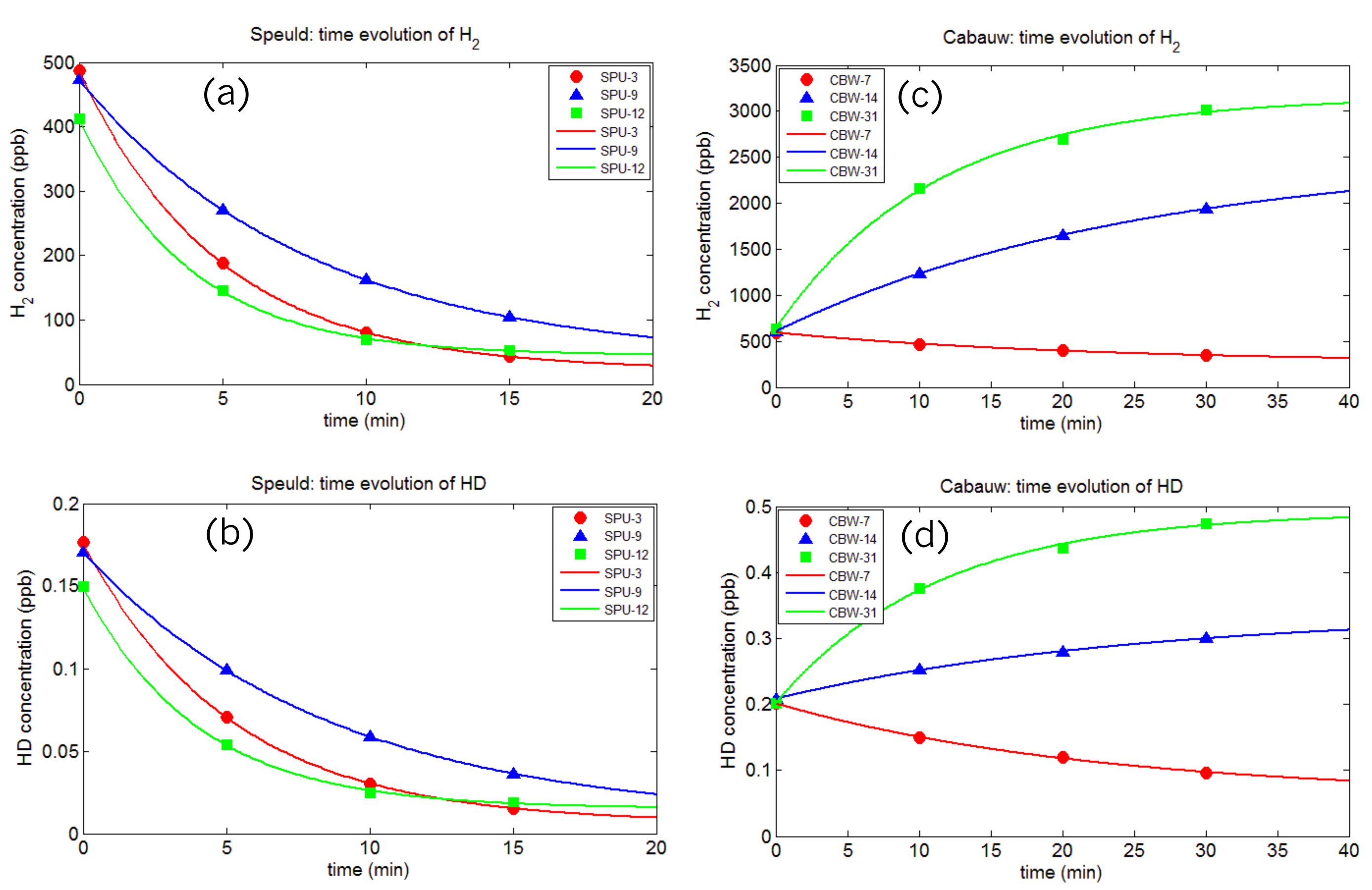


Fig. 3 Time evolution of (a) H_2 in Speuld, (b) HD in Speuld, (c) H_2 in Cabauw, and (d) HD in Cabauw, fitting with exponential functions (2) and (3).

· Cases with strong soil uptake of H_2 were observed in Speuld, while cases with strong H_2 emission were observed in Cabauw. In all experiments both a (apparent) source and a sink were present.

· Exponential functions of Eq. (2) and (3) fit well the data, supporting the constant source and first-order mole fraction dependent sink assumptions in Eq. (1).

2. Fractionation during soil uptake

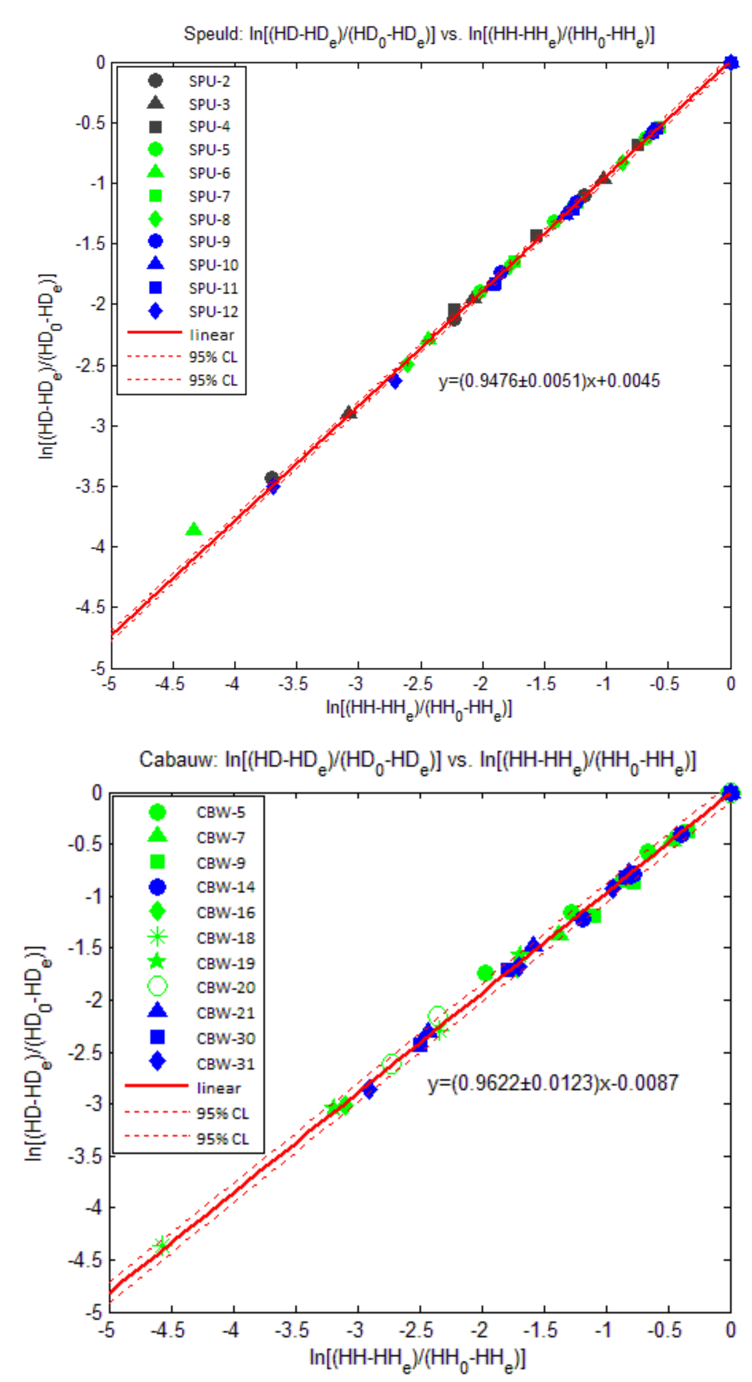


Fig. 5 The calculation of mean fractionation constant based on the mass balance model (Eq. (1)-(4)) for Speuld (upper panel) and Cabauw experiments (lower panel).

Table. 1 The uptake rate (k, k′), deposition velocity (v_d), fractionation constant (α), kinetic isotope effect (ε) and soil cover for each Speuld sampling.

	k (1/min)	k'(1/min)	α=k'/k	v_d (cm/s)	KIE ε (‰)	soil cover
SPU-2	0.232	0.219	0.942	0.155	-58	D. fir, needles
SPU-3	0.206	0.194	0.944	0.137	-56	D. fir, moss
SPU-4	0.152	0.139	0.913	0.101	-87	D. fir, moss
SPU-5	0.138	0.128	0.930	0.092	-70	D. fir, moss
SPU-6	0.257	0.240	0.935	0.171	-65	D. fir, moss
SPU-7	0.119	0.112	0.940	0.079	-60	beech, leaves
SPU-8	0.176	0.168	0.957	0.117	-43	leaves removed
SPU-9	0.124	0.116	0.935	0.083	-65	beech, leaves
SPU-10	0.131	0.123	0.941	0.087	-59	spruce, moss
SPU-11	0.129	0.118	0.918	0.086	-82	spruce, needles
SPU-12	0.261	0.250	0.957	0.174	-43	needles removed
MEAN	0.175	0.164	0.937	0.117	-63	
STDEV	0.052	0.050	0.014	0.034	14	

·The average fractionation constant α (=k′/k) is 0.94 for forest soil in Speuld, and 0.96 for grass field in Cabauw.

·There is no obvious observed dependence of kinetic isotope effect (KIE) on deposition velocity v_d, which disagrees with the positive correlation suggested by Rice et al. (2011).

· The removal of soil cover (needles/leaves) results in larger deposition velocity and less negative KIE, which suggests the important role of diffusion during isotopic fractionation processes by soil uptake of H_2.

3. δD of soil emission

Keeling plot: $\delta_{measured} = \delta_{source} + \frac{1}{c_{measured}} c_{bg}(\delta_{bg} - \delta_{source})$

where $\delta_{measured}$, δ_{source}, δ_{bg}, $c_{measured}$ and c_{bg} are measured δD, δD of the source, δD of the backgound, measured H_2 mole fraction and background H_2 mole fraction respectively.

Selected cases with strong H_2 emission rate (P>1.6 μmol/(min m^2)) and weak uptake rate constant (k<0.1 /min) (Fig. 6).

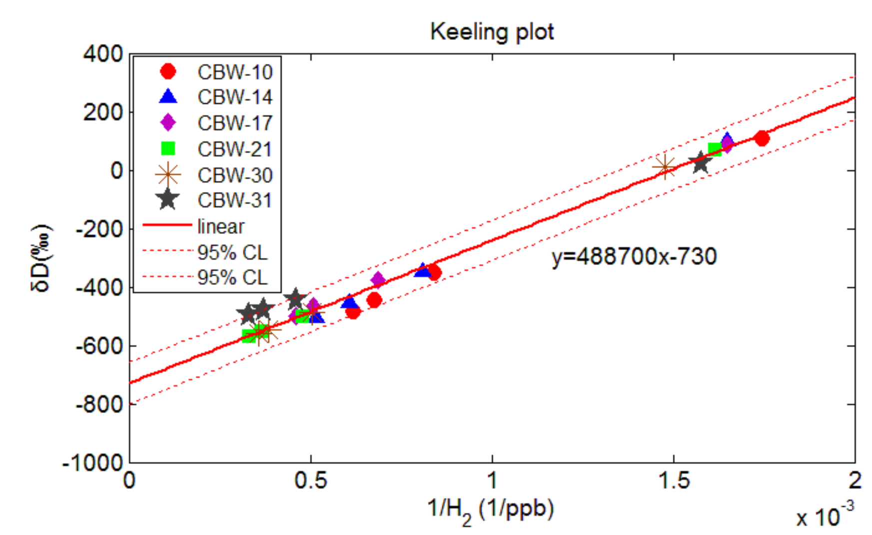
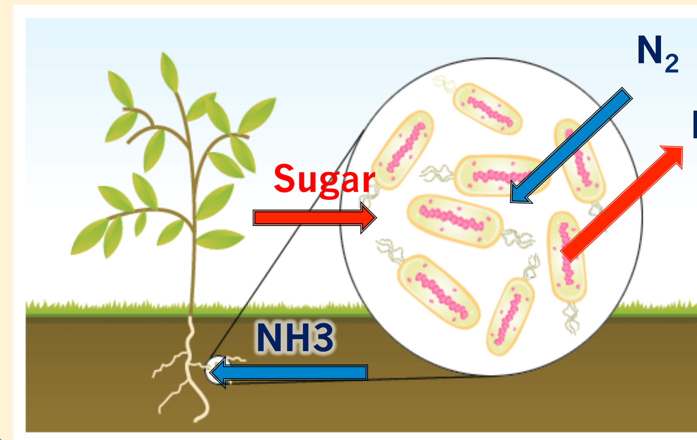


Fig. 6 Keeling plot to obtain isotopic signature of biogenic H_2 emission.

The intercept of the Keeling plot shows the δD of the source to be about -730‰.

H_2 emission during N_2 fixation



$$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$$

Fig. 2 Scheme: Nitrogen fixation leads to H_2 emission. Symbiosis: plant (legume) – bacteria (Rhizobium).