

## Hydrogen soil deposition in northern boreal zone

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Deposition velocities ( $v_d$ ) of molecular hydrogen were measured in the northern boreal zone in Pallas. Three separate methods were used to estimate the soil uptake rate. For soil chamber measurements, three sites (forest, wetland and above tree line) were selected according to different soil properties. The deposition velocity was calculated with radon tracer method taking advantage of nocturnal radon build-up and hydrogen decrease in the shallow mixing layer above ground. A two dimensional model was used to estimate corresponding night time values for  $v_d$  and radon exhalation rate. The radon tracer and two-dimensional model results were in the range of 0.18–0.52 mm s<sup>-1</sup>. All results were obtained for unfrozen soils, and there was no clear temperature dependence related to  $v_d$ . Soil chamber results were in the range of 0.06–0.52 mm s<sup>-1</sup> excluding the wetland site which had negligibly small  $v_d$  due to water saturation.

### Introduction

Different areas of the world are suffering serious degradation of air quality over the past decade. This is connected to the climate warming, which is a consequence of elevated mixing ratios of greenhouse gases produced e.g., from fossil fuel combustion and biomass burning, which are also sources of molecular hydrogen. Alternative methods to produce greenhouse gas emission-free energy deserve more attention. Molecular hydrogen as an energy transport medium is one of the options. The possible impacts of the large-scale hydrogen economy could lead to changes in the atmospheric composition (Schultz *et al.* 2003). The sinks of atmospheric hydrogen are the soil uptake and a reduction reaction with the hydroxyl radical by photochemical reaction. The remnants of microbes consisting of soil hydrogenases are responsible for the soil uptake of

atmospheric hydrogen (e.g., Conrad 1996). The hydroxyl radical is also involved in the methane oxidation process. The elevated mixing ratio of hydrogen decreases the atmospheric capacity to remove methane through oxidation reaction.

There are uncertainties in the strength of hydrogen sources and sinks (e.g., Novelli *et al.* 1999, Rhee *et al.* 2006). The estimation of the soil sink strength is an important target and only few measurements exist in the boreal zone (Rahn *et al.* 2002, Smith-Downey *et al.* 2006, Lallo *et al.* 2008). The hydrogen sink is stronger in the northern hemisphere in summer than in winter (Rhee *et al.* 2006). Previous results show that the deposition velocity of hydrogen is controlled by the soil moisture and temperature (Conrad and Seiler 1985, Yonemura *et al.* 2000, Lallo *et al.* 2008). The porosity and soil type as well as the thickness of the soil layer have also an effect on the deposition velocity.

The strength of the soil sink can be evaluated by using e.g., soil chamber measurements, radon tracer method and atmospheric modeling. Soil chamber technique is a direct method to measure the deposition flux inside a closed chamber. At Pallas, three different field locations were selected to distinguish the effect of different soil types representing the northern boreal forest zone. The radon tracer method (e.g., Schmidt *et al.* 2001) utilizes the simultaneous change in the radon activity and in the hydrogen mixing ratio inside the nocturnal boundary layer. In addition, the radon soil exhalation rate is needed to estimate the hydrogen deposition velocity. To estimate radon and hydrogen fluxes, simulations were made using a simple atmospheric two-dimensional model. All three methods were used in parallel to support and clarify individual results from each method.

## Material and methods

### Measurement sites

The Pallas site is located in the Pallas-Yllästunturi National Park in northern Finland. The region is sparsely populated and relatively unpolluted. The nearest population centre of 2500 inhabitants is located at 19 km distance, and the nearest public road (< 500 cars in a day) is about 2 km distance from the site. The atmospheric monitoring station is located on the treeless top of the arctic hill Sammaltunturi (67°58'24"N, 24°06'58"E, 565 m a.s.l.). The ground on Sammaltunturi is revealed and fractured bedrock (quartzite) partly covered with a thin layer of organic soil (in chamber plots 4–13 cm), populated with mosses, lichens and low vascular plants (ericaceous shrubs). The terrain around the site is characterized by patches of boreal forests, wetlands and lakes. In the nearest 20 × 20 km<sup>2</sup> area, lakes and wetlands comprise 22% of the land cover. There are two other sites nearby Sammaltunturi, a wetland (sedge fen) site Lompolojänkki (67°59'50"N, 24°12'33"E, 269 m a.s.l.) about 6 km distance from the hill site and a forest site Kenttäröva (67°59'14"N, 24°14'36"E, 347 m a.s.l.) at about 5-km dis-

tance from the hill site and 2-km distance from the wetland site. The forest mainly consists of old growth Norway spruce (*Picea abies*), and the soil is haplic podsol covered with *Hylocomium-Myrtillus* type of vegetation (Kalliola 1973). In all the sites ground is covered with snow usually from October to May. Mean temperature of the year is -1.6 °C at Sammaltunturi. In December–January, there is a period when the sun is continuously below the horizon due to the site being located north of the Arctic Circle. In summer, the sun is continuously above the horizon from 26 May to 18 July. This may affect the diurnal boundary layer dynamics so that a stable nighttime mixing layer may not be fully formed. Some photochemical reactions may also continue during night, though radiation intensity is less than 5% of the daytime maximum values.

### Chamber measurements

Soil chambers can be used for the determination of hydrogen uptake into the soil. Two three-day campaigns were held in the Pallas area in September 2007 and August 2008, covering three measurement sites within 6-km maximum distance. The sites were selected according to the different soil characteristics, and two chambers were used for the determination of  $v_d$ . In Kenttäröva and Lompolojänkki chambers were within 10 m from each other. On the top of Sammaltunturi, the chambers were about 150 m apart. One measurement cycle included five individual air samples which were collected inside the cover-closed soil chamber. After one measurement cycle, the cover was opened and kept open for a few minutes to ensure the satisfactory ventilation and for the recovery of initial conditions. At all three sites, three measurement cycles for each chamber were made in sequence. The first sample of each measurement cycle was taken immediately after lowering the cover. The following samples were collected after 2–5 min intervals, comprising five samples during about 15 minutes. In addition, one ambient air sample was taken at each site for reference purposes. Stainless steel frames (60 cm × 60 cm × 20 cm with aluminium cover) were fixed in the ground

in about 5–10 cm depth. A small battery-operated fan was attached inside the cover to ensure proper mixing in the chamber. Air samples were collected through the silicon tube into plastic syringes (BD Plastipak, 20 ml) with three-way stop-cock valves. The soil temperature was measured using thermistors or thermocouples.

The air tightness of the soil chamber was tested in laboratory conditions. The chamber was filled with a gas standard, in which the hydrogen concentration was two times higher than the ambient concentration. The syringes used in the field measurements were also tested for the leakage, which was found to be 4 ppb h<sup>-1</sup>. Air samples were analyzed during the same day to minimize the effect of leakage and the photochemical reactions.

### Concentration measurements

Hydrogen concentrations were measured using an automated gas chromatographic system based on the Peak Performer (PP1) instrument equipped with a reductive gas detector (RGD, RGA, RCP) for the detection of hydrogen. The instrument relies on the same basic detection principle first introduced by Schmidt and Seiler (1971). Sample air is delivered through the HgO bed. Mercury oxide is reduced to mercury gas, which concentration is proportional to the concentration of the hydrogen or carbon monoxide. The concentration is determined by detecting the absorption of UV light into mercury gas. The system takes five minutes to analyze one sample, and a working standard is measured after every four or five samples. The mixing ratio of hydrogen working standard was 911 ppb. The reproducibility of the instrument was estimated using the ten consecutive working standard samples, and the resulting standard deviation was 0.6%.

Hydrogen measurements were calibrated using a working standard gas, which was calibrated against four primary calibration standard gas cylinders. Primary hydrogen standards (407 ppb, 494 ppb, 600 ppb and 695 ppb) were acquired from Max-Planck Institute in Jena, Germany. The quality of the measurements was verified by intercomparison in the EUROHYDROS

project in 2008, showing good agreement with the other hydrogen measurements made in the European network.

The radioactive radon isotope <sup>222</sup>Rn is measured at the Sammaltunturi station with the radon instrument of FMI (Finnish Meteorological Institute). The system continuously collects aerosols onto a filter and from which beta activity is measured. The hourly mean values are calculated by assuming that the beta activity on the filter is only from short-lived <sup>222</sup>Rn progeny in equilibrium with radon (Paatero *et al.* 1998, Hatakka *et al.* 2003). The FMI's radon instrument was operated in parallel with the radon instrument of the University Heidelberg (Levin *et al.* 2002) for four months in 2005 at Pallas. Based on the intercomparison results the radon activities measured at Pallas were multiplied by a factor of 0.57. It has to be noted that if this calibration correction was not applied, the modeled radon exhalation rates would be higher by roughly a factor of 1.7. Consequently, the hydrogen deposition velocities from the radon tracer method would also be higher by the same factor. This would lead to disagreement with the independent experimental flux results, and thus the use of the calibration factor to correct Pallas results towards lower radon activities can be considered justified.

### Analysis of the results

The calculation of mixing ratios from the raw data was made using our own software based on the Matlab® platform, as well as the mathematical analyses concerning chamber hydrogen  $v_d$  and radon tracer method calculations. Nocturnal hydrogen deposition velocities were estimated using the model developed by Aalto *et al.* (2006), based on the Fluent® platform utilizing finite element methodology. Trajectories were generated using NOAA HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model accessed via NOAA ARL READY (Real-time Environmental Applications and Display sYstem of R.R. Draxler and G.D. Rolph, NOAA Air Resources Laboratory, Silver Spring, MD, available at <http://www.arl.noaa.gov/ready/hysplit4.html>).

## Soil chamber method

The decrease in molecular hydrogen mixing ratio inside the closed chamber is assumed to follow first-order kinetics for gas concentrations at atmospheric levels (Conrad and Seiler 1985, Yonemura *et al.* 2000).

The deposition velocity  $v_d$ , which is defined as a ratio of hydrogen flux and ambient mixing ratio, is calculated using Eq. 1 by making exponential fit to the concentration record obtained from the closed chamber.

$$C(t) = (C_0 - y\tau)\exp(-t/\tau) + y\tau, \quad (1)$$

where  $t$  is time,  $C_0$  is hydrogen mixing ratio at time zero,  $\tau$  is the decay constant and  $y$  is a production term. Deposition velocity is calculated as  $v_d = h/\tau$ , where  $h$  is the chamber height. The gas concentration  $C(t)$  decrease follows exponentially decreasing function, which is modified with the production term  $y$ , describing the hydrogen emissions from the soil. The  $y$  in the exponential fit (Eq. 1), was sufficiently small to justify the assumption of zero production. This was derived from several-hour-long measurement time series that resulted in very low concentrations (10–20 ppb).

## Radon tracer method

Tropospheric radon observations can be used for estimating the surface deposition and emission rates of other species (Schmidt *et al.* 2001) through a simple data-oriented method where time consuming simulations with a full atmospheric model are not needed. Radon is particularly suitable for this, since its sources and sinks are relatively well known. Much of the short term variation in radon activity is caused by diurnal changes in atmospheric mixing conditions. Due to solar heating, the atmospheric boundary layer grows in the morning to several hundred meters in depth and may further during day exceed two kilometers. When the solar heating ends and the radiative cooling and surface friction stabilize, the lowest part of the atmospheric boundary layer — a stable nocturnal layer — is formed just above the surface. It is usually of some tens

to hundreds of meters thick. The soil exhalation rate of radon is rather constant over the day and night. During the night, radon accumulates in the shallow nocturnal layer. The trapping inversion is released in the morning leading to lower daytime radon mixing ratios. At the same time, hydrogen is taken up by the soil and the mixing ratios decrease in the nocturnal layer. The airborne photochemical reactions are not considered to be significant in producing or consuming hydrogen in low irradiance conditions. The increase of radon during the night can be plotted against decrease in hydrogen, and the resulting hydrogen soil flux,  $j_{H_2}$ , can be estimated using the following formula:

$$j_{H_2} = j_{Rn} \frac{\Delta c_{H_2}}{\Delta c_{Rn}} \left( 1 - \frac{\lambda_{Rn} c_{Rn}}{\Delta c_{Rn} / \Delta t} \right), \quad (2)$$

if the radon flux,  $j_{Rn}$ , is known. Here  $\Delta c_{H_2}/\Delta c_{Rn}$  is the ratio between hydrogen concentration difference,  $\Delta c_{H_2}$ , and radon concentration difference,  $\Delta c_{Rn}$ . The radioactive decay of radon is taken into account by the correction term in brackets, where  $\lambda_{Rn} c_{Rn}(t)$  is the decay rate including radioactive decay constant for radon  $\lambda_{Rn}$  and radon concentration  $c_{Rn}(t)$ . A mean correction factor of 0.965 was used here (Schmidt *et al.* 2001).

In processing of the results, only those nights were used when there was a clear decrease in hydrogen ( $> 5$  ppb) and increase in radon ( $> 0.5$  Bq m<sup>-3</sup>), and they were highly correlated ( $R^2 > 0.8$ ). Slopes were determined using a geometric-mean regression model. The wind direction and trajectories were examined to avoid using mixing ratio measurements during changes in synoptic transport patterns. Change in air mass origin e.g., from marine to continental can change mixing ratios significantly due to their different source signature. They might bring other effects than plain soil deposition into the calculated hydrogen mixing ratios. In general, the applicability of radon tracer method is regional, depending on the integration time of the fluxes, measurement site topography and average wind speeds, etc. Typical range is from several tens to over one hundred kilometers (Levin *et al.* 1999).

## Two-dimensional model

A simple three-dimensional atmosphere–vegeta-

tion model developed for Pallas region (Aalto *et al.* 2006) was utilized for estimating the hydrogen deposition velocities. For hydrogen, the accurate description of vegetation and topography is probably not as critical as for example for CO<sub>2</sub>, because hydrogen is mainly taken up by boreal soils, which show relatively uniform uptake rates in optimal moisture and temperature conditions (Lallo *et al.* 2008). Thus, for conserving computational time the topography was removed and the model was converted into two-dimensional with vertical extent of 3 km (12 layers) and horizontal extent of 10 km (10 grid boxes) to allow for adjustment of profiles and boundary layer. The surface roughness length was 0.1 m and the all-sided vegetation leaf area index was 1 according to Sammaltunturi conditions. The model also included a 5-m-thick soil layer. Regarding species transport the soil acted as a passive solid, and fluxes of species were defined only at the soil-air interface.

Fluxes and concentrations in the model domain were solved using the commercial fluid dynamics software Fluent<sup>®</sup>. Surface exchange formulations and boundary conditions were programmed as user defined C codes and inserted into the basic simulation system. Energy, turbulence, fluid and species transport equations were solved in segregated mode. Turbulence inside the domain was simulated with the standard *K-ε* theory (Launder and Spalding 1972). The model was non-hydrostatic, i.e. pressure changes were allowed in addition to the meteorological input pressure. CO<sub>2</sub> and H<sub>2</sub>O were simulated in order to produce realistic transpiration fluxes and canopy conductances for heat balances and species transport, though for LAI of 1 their effect was limited. Lateral boundary input for CO<sub>2</sub> and H<sub>2</sub>O was taken from Sammaltunturi measurements. For air pressure, temperature and wind entering the model domain a typical stable conditions vertical profile from earlier results was used, scaled with Sammaltunturi surface observations.

The model was run only for the nighttime, when photochemistry of hydrogen was assumed negligible. For comparison, radon activity was also simulated. The radioactive decay of radon was simulated by a constant volumetric removal rate corresponding to its half life of 3.82 days. In order to simulate the regional soil exhalation/

deposition instead of synoptic transport phenomena, only those nights were chosen which were suitable also for the radon tracer method, showing an hour by hour increase in radon and decrease in hydrogen with no significant change in the wind direction or trajectories.

The model was allowed to spin up for few hours before the actual period of interest. The simulation time-step was 10 minutes, using corresponding boundary input interpolated from the measurements. The hydrogen and radon boundary condition during the simulated hours was periodic, i.e. the outflow vertical profile from the last time step was used as new input. Simultaneously, the lowest (5-m) level boundary concentrations of hydrogen and radon were forced towards the Sammaltunturi observations by adjusting the surface fluxes. The hydrogen deposition velocities and radon exhalation rates were solved at every time step during the simulation in order to let the modeled outflow concentration meet the Sammaltunturi observations. The hydrogen and radon surface fluxes were thereby inverted from the concentration observations. Stabilized flux values at the end of each hour were saved as a result of the simulation.

## Results

Hydrogen chamber measurements were performed during a three-day campaign on 3–5 September 2007 (Table 1). At the top of the arctic hill, Sammaltunturi, the mean deposition velocity  $\pm$  SE for both chambers was  $0.12 \pm 0.02$  mm s<sup>-1</sup>. At Kenttäröva, the corresponding value was  $0.070 \pm 0.004$  mm s<sup>-1</sup>. At the wetland site, Lompolojänkkä, the water table level was high during the measurements, thus soil moisture was 100% and the surface was saturated with water. As a result soil uptake was negligible. Therefore, the site was left out of comparisons. The difference in the deposition velocities between Sammaltunturi and Kenttäröva were significant (two-sided *t*-test:  $t = 2.62$ ,  $df = 11$ ,  $p < 0.05$ ). During a five-day period before the campaign the lowest nighttime temperature at Sammaltunturi was 0 °C. During the campaign, the temperature varied between 0–8 °C, the warmest day being 4 September 2007. Moderate winds between east-

ern and northern directions brought occasional weak rains. At Kenttäröva (and Lompolojänkä), nighttime temperatures varied between  $-2$  and  $2$  °C and the coldest night was the one before start of the campaign. In general, the temperature varied between  $-2$  and  $10$  °C.

On 5–7 August 2008, a three-day campaign was repeated at same locations (Table 1). At the top of the arctic hill Sammaltunturi the mean deposition velocity  $\pm$  SE including both chambers was  $0.45 \pm 0.04$  mm s<sup>-1</sup>. At Kenttäröva, the corresponding deposition velocity value was  $0.17 \pm 0.02$  mm s<sup>-1</sup>. At the Lompolojänkä wetland site, soil moisture was 95%–100% and the surface was saturated with water. As a result soil uptake was, as in the previous year, negligible. Therefore, the site was again left out of comparisons. The differences in the deposition velocities between Sammaltunturi and Kenttäröva were again significant (two-sided *t*-test:  $t = 6.68$ ,  $df = 10$ ,  $p < 0.05$ ). During a five-day period before the campaign, the lowest nighttime air temperatures were around  $4$  °C. Including campaign days, the temperature varied between  $4$  and  $15$  °C. During the campaign, the temperatures increased to  $9$ – $15$  °C during daytime (measured at Kenttäröva). There were weak rains and local showers on 7 August 2008.

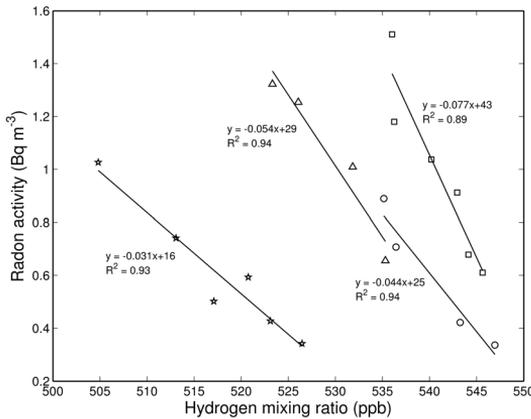
The radon activity at Sammaltunturi was low, averaging about  $1.02$  Bq m<sup>-3</sup> between the years 2007 and 2008. Peak values were observed ten times between December 2007 and March 2008, when elevated radon concentrations ranging from

$2.5$  to  $3.65$  Bq m<sup>-3</sup> were detected. Variations in radon concentrations were small as compared with those at sites at lower altitudes. During night, the hill top is often above the surface inversion layer (e.g., Aalto *et al.* 2006) and the observed air masses are well-mixed and represent a large source area. Therefore, only few nights were found since 2006 when simultaneous radon increase and hydrogen decrease were clearly visible at the Sammaltunturi hill top (Fig. 1). During four such typical summer fair weather nights, when temperatures were around  $8$ – $16$  °C and weak-moderate eastern or southwestern winds prevailed.

The two-dimensional model results for these four nights indicated an average hydrogen deposition velocity of  $0.30 \pm 0.11$  mm s<sup>-1</sup> (mean  $\pm$  SE) and radon exhalation rate of  $32 \pm 6$  Bq m<sup>-2</sup> h<sup>-1</sup> (mean  $\pm$  SE) (Table 2), as inferred from the model inversion results. To further validate the radon result, the exhalation rate was modeled for ten intense radon accumulation nights in June–August 2006–2008. The average from these results was  $31 \pm 11$  Bq m<sup>-2</sup> h<sup>-1</sup> (mean  $\pm$  SE). The modeled hydrogen deposition rates did not have a clear temperature dependence in the narrow range studied. With current settings, the model developed a turn in the potential temperature profile indicating a local inversion in  $80$ – $120$  m altitude. In reality, the boundary layer structure may be somewhat different due to the hill topography and surrounding land cover, but the current value is realistic for nighttime studies. The average

**Table 1.** Mean deposition velocities of molecular hydrogen ( $v_d$ )  $\pm$  SE in the Pallas region [Sammaltunturi hill (S), Kenttäröva forest (K), and Lompolojänkä wetland (L)] in September 2007 and August 2008.  $M$  = volumetric water content.

Date	Location	$v_d$ (mm s <sup>-1</sup> )	Soil temp. (°C)	Air temp. (°C)	Soil $M$ (%)
3 Sep 2007	S1	$0.12 \pm 0.04$	5	3	43
3 Sep 2007	S2	$0.12 \pm 0.01$	6	3	43
4 Sep 2007	K1	$0.062 \pm 0.004$	5	8	25
4 Sep 2007	K2	$0.078 \pm 0.003$	5	8	27
5 Sep 2007	L1	$-0.004 \pm 0.005$	5	5	100
5 Sep 2007	L2	$-0.007 \pm 0.006$	5	5	100
5 Aug 2008	L1	$0.02 \pm 0.01$	8	12	95
5 Aug 2008	L2	$-0.02 \pm 0.01$	8	12	100
6 Aug 2008	S1	$0.52 \pm 0.02$	9	11	34
6 Aug 2008	S2	$0.39 \pm 0.04$	10	11	34
7 Aug 2008	K1	$0.16 \pm 0.04$	9	11	20
7 Aug 2008	K2	$0.18 \pm 0.02$	9	11	27



**Fig. 1.** Hourly mean hydrogen mixing ratio vs. radon activity during four nighttime events at Pallas (June–August 2007).

hydrogen deposition velocity for the four nights according to the radon tracer method was  $0.29 \pm 0.17 \text{ mm s}^{-1}$  (mean  $\pm$  SE) (Table 2). Here we used the mean modeled radon exhalation rate of  $32 \text{ Bq m}^{-2} \text{ h}^{-1}$ , which was the same as the experimental average for northern Finland (Szegvary *et al.* 2007). Individual deposition rates using the corresponding modeled radon exhalation rates were also calculated (Table 2).

The results from the radon tracer method did not show a clear dependence on temperature or other environmental variables. All results shown here were obtained during the snow free period for unfrozen soils. Only two nights fulfilling the selection criteria occurred during winter in January and December 2007. The air temperature had

been below  $-5 \text{ }^\circ\text{C}$  for over a week before the nights in question and there was  $> 10 \text{ cm}$  snow cover. Considering the freezing temperature and thick snow cover, it is improbable that these winter time results refer to actual regional hydrogen soil deposition, rather to a synoptic or long range transport event. However, there was no direct evidence for that (e.g., significant change in the trajectory paths).

## Discussion

Hydrogen deposition rates from the chamber measurements were in the same range with the earlier results for the boreal soils. In this study,  $v_d$  ranged from near 0 to  $0.52 \text{ mm s}^{-1}$ . Rahn *et al.* (2002) presented deposition fluxes of  $2\text{--}12 \text{ nmol m}^{-2} \text{ s}^{-1}$  for a boreal forest soil in Alaska. The value of  $0.5 \text{ mm s}^{-1}$  for  $v_d$  corresponds to a flux of  $10 \text{ nmol m}^{-2} \text{ s}^{-1}$  in NTP conditions. Lallo *et al.* (2008) presented values of 0 to  $0.7 \text{ mm s}^{-1}$  for  $v_d$ , including the snow-free and winter seasons. The thin soil layer at the top of the Sammaltunturi hill appeared to be as active in absorbing hydrogen as the southern Finland boreal forest floor. Earlier results (Yonemura *et al.* 2000) support this by suggesting that hydrogen uptake takes place in the first few centimeters of soil. The wetland site expectedly showed very small deposition velocities due to the saturating water table level which prevents the gas diffusion into the soil.

**Table 2.** Hydrogen soil deposition velocities ( $v_d$ ) at Pallas according to radon tracer method and two-dimensional model. Varying  $j_{\text{Rn}}$  refers to varying radon soil exhalation rate from the model results in the last column, and  $32 \text{ Bq m}^{-2} \text{ h}^{-1}$  is the model average. RTM denotes to radon tracer method and MOD to two-dimensional model, respectively.

Date	Air temp. (Sammaltunturi) ( $^\circ\text{C}$ )	Soil temp. (Kenttäröva) ( $^\circ\text{C}$ )	$v_d$ RTM $j_{\text{Rn}} = 32 \text{ Bq m}^{-2} \text{ h}^{-1}$ ( $\text{mm s}^{-1}$ )	$v_d$ RTM varying $j_{\text{Rn}}$ ( $\text{mm s}^{-1}$ )	$v_d$ MOD ( $\text{mm s}^{-1}$ )	$j_{\text{Rn}}$ ( $\text{Bq m}^{-2} \text{ h}^{-1}$ )
12 Sep 2006	8.5	7.5	0.18			
19 Sep 2006	9.7	8.5	0.19			
26 Sep 2006	-0.1	3.3	0.20			
11 Jun 2007	8.6	5.9	0.35	0.32	0.29	28.7
4 Jul 2007	15.2	9.5	0.33			
16 Jul 2007	13.4	10.4	0.29	0.31	0.30	33.6
18 Jul 2007	10.6	10.2	0.31			
8 Aug 2007	15.2	11.6	0.20	0.24	0.19	38.0
23 Aug 2007	9.9	8.5	0.52	0.44	0.41	26.2
31 Aug 2007	1.5	6.4	0.36			

The radon tracer method delivered results mainly during summer, which was expected due to the high soil uptake of hydrogen gas and weather conditions favoring calm nights. The hydrogen deposition rates were in range of the recent results for the boreal soils (Lallo *et al.* 2008) and agreed with the two-dimensional model results, giving in most cases slightly higher values. The results were within 8% for three of the four nights, when the radon flux was adjusted case by case. Without adjustment, the results were within 22%. The two-dimensional model and radon tracer method results were also similar to the soil chamber results, and the range of variability was acceptable given the integrative nature of the atmospheric methods and variation in chamber plots. Over 20% of the Pallas region is comprised of wetlands and lakes, which have only a negligible contribution to hydrogen deposition and could lead to low  $v_d$  result by the radon tracer method. However, as opposed to the two-dimensional model and chamber results, the effect of these low activity patches could not be seen from the radon tracer results.

In winter, the hydrogen deposition velocities are low or even negligibly small due to frozen ground and snow cover (Lallo *et al.* 2008). The soil microbial activity may also be weaker in low temperatures. During the September 2007 chamber campaign,  $v_d$  was lower than in August 2008 at the Sammaltunturi and Kenttäröva sites. In 2007, the soil temperatures were close to 5 °C which, according to Lallo *et al.* (2008), is the limit where  $v_d$  starts to decrease. During several preceding nights air temperature had been close to zero, which may also induce the long-term drawdown of  $v_d$ . The soil humidity was also slightly higher at Sammaltunturi in 2007, but still in optimum range (6 to 50 m<sup>3</sup> m<sup>-3</sup> by water volume). The radon tracer results were obtained on 26 September 2006 and 31 August 2007 (Table 2), when the air temperatures were close to zero. In 2007, however, the soil temperatures were above 6 °C and the preceding days had been warm. The  $v_d$  was at an average summer level. In 2006, the soil temperature was around 3 °C, and had been decreasing towards this value for several days while the air temperature was close to zero. However, no significant decrease in  $v_d$  was observed. There might be suitable data

for the radon tracer method during the autumn and spring periods when the soil activity is low, but the weak signal is difficult to extract from the background variation. The comprehensive research material collected in different climatological conditions would shed more light on the temperature regulation of the local hydrogen deposition.

Our modeled radon exhalation rates were strikingly similar with experimental soil chamber results of Szegvary *et al.* (2007) for northern Finland (Rovaniemi region). Their average exhalation rate was the same as our model result average, 32 Bq m<sup>-2</sup> h<sup>-1</sup>. However, according to Szegvary *et al.* (2007), the exhalation rate varied significantly from one plot to another covering range of 2–95 Bq m<sup>-2</sup> h<sup>-1</sup>. Dörr and Münnich (1990) measured radon exhalation rates from cultivated fields and undisturbed forest soils. The radon fluxes were between 500 and 6500 dpm m<sup>-2</sup> h<sup>-1</sup> (8.3–108.3 Bq m<sup>-2</sup> h<sup>-1</sup>, 1 dpm = 1/60 Bq) in West Germany, the average being 3200 dpm m<sup>-2</sup> h<sup>-1</sup> (53.3 Bq m<sup>-2</sup> h<sup>-1</sup>). This corresponds to radon emission of 0.7 atoms cm<sup>-2</sup> s<sup>-1</sup>. Schüßler (1996) observed the radon exhalation rate of 56.7 Bq m<sup>-2</sup> h<sup>-1</sup> with seasonality of ±25% for the Heidelberg area. Nazaroff (1992) obtained 79 Bq m<sup>-2</sup> h<sup>-1</sup> for a characteristic surface flux density in samples collected from North America. Schery *et al.* (1984) found that reduction in diffusion and <sup>222</sup>Rn flux occurs in rainy conditions due to capping effect of the top layer of soil. Results by Levin *et al.* (2002) indicate low rates for moist boreal soils (3.3–7.9 Bq m<sup>-2</sup> h<sup>-1</sup>) in Fyodorovskoye, Russia. Only during very dry summer the exhalation rates increased close to, or above our values. These results should be considered also for Pallas because of the weak radon variability. The current results may actually be overestimating the exhalation rate due to selection of only the most obvious cases with strong change in radon activity and thus limited extent of the data set. To confirm the current results, the two-dimensional model simulations should be made for all radon accumulation nights. It is necessary to use a realistic value for the radon exhalation rate in the radon tracer method in order to obtain unbiased results for hydrogen deposition rates. The current measurement technique there might also be affected by radon not being in equilibrium

or by local cloud droplet formation cleaning the aerosol before measurement. However, in the presented cases there were no clouds present. Most probably the inversion development was so slow that radon inside the layer, possibly transported from the lower altitude, and had aged for a couple of hours and thus equilibrium conditions could be assumed.

## Conclusions

Hydrogen deposition velocities into the northern boreal soil were determined using the soil chamber method, the radon tracer method and the atmospheric modeling. The deposition velocities were well in range of earlier results and all methods agreed with each other. According to this study, the thin unfrozen soil layer in an arctic hill and in northern boreal forest consumed hydrogen. The soil chamber measurements showed different deposition rates between two campaigns possibly indicating regulation by soil temperature and moisture. However, the regulation was not clearly seen from the radon tracer method or two-dimensional model results. In the future, results could be specified and verified by applying modeling to all radon accumulation nights and finding more hydrogen deposition events, as well as continuing field work at different climatological conditions. Similar approach could also be applied to different sites in the boreal region.

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