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Hydrogen soil deposition at an urban site in Finland

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Abstract

Hydrogen deposition velocities (v_d) were estimated by field chamber measurements and model simulations. A closed-chamber method was used for soil deposition studies in Helsinki, Finland, at an urban park inhabited by broad-leaved trees. Radon tracer method was used to estimate the $v_d$in nighttime when photochemical reactions were minimal and radon gas was concentrated to shallow boundary layer due to exhalation from soil. A two-dimensional atmospheric model was used for calculation of respective v_d values and radon exhalation rate. v_d and radon exhalation rates were lower in winter than in summer according to all methods. The radon tracer method and two-dimensional model results for hydrogen deposition velocity were in the range of 0.13 mm s^{-1} to 0.90 mm s^{-1} (radon tracer) and 0.12 mm s^{-1} to 0.61 mm s^{-1} (two-dimensional). The soil chamber results for v_d were 0.00 mm s^{-1} to 0.70 mm s^{-1}. Both models and chamber measurements revealed relation between one week cumulative rain sum and deposition velocity. Lower v_d values were usually measured in high soil moisture conditions. Precipitation occurring a few days before chamber measurements decreased v_d values. The snow cover also lowered v_d.

1 Introduction

There is a need to better understand interactions of molecular hydrogen in the atmosphere. The interest to develop carbon dioxide free energy production methods promotes the hydrogen economy goals to utilize hydrogen as an energy transport media. Energy produced using cleaner methods (e.g. wind power) can be used to split water to hydrogen (and oxygen) electrochemically.

The interest in hydrogen in the past few years has accelerated and steered the research to find out the processes, where hydrogen is participating, these include stratospheric (Rahn et al., 2003; Röckmann et al., 2003) and tropospheric studies (Barnes et al., 2003). Rhee et al. (2006) estimated that soil uptake is the largest sink being

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responsible for 82% of tropospheric hydrogen turnover globally and that the soil uptake is higher in northern hemisphere due to larger land coverage. An extensive review of tropospheric hydrogen cycle was made by Ehhalt et al. (2009). A companion article by Aalto et al. (2009) is focused on atmospheric variations and to the traffic emission of hydrogen. Recent field measurements to estimate the soil uptake of hydrogen were made in agricultural area in Heidelberg (Schmitt et al., 2008), in forest, marsh and desert area in California (Smith-Downey et al., 2008), in northern boreal zone (Lallo et al., 2008) in Alaska (Rahn et al., 2002). Yonemura et al. (1999, 2000) made field studies in temperate forest and in arable field in Japan. Earlier field measurements were made by Conrad and Seiler (1980, 1985) in Germany and in Africa. Soil microbes and free soil enzymes are responsible for hydrogen uptake (Conrad, 1996; Constant et al., 2008, 2009), and soil hydrogenases that are responsible for hydrogen uptake have recently been extracted by Guo and Conrad (2008) and Constant et al. (2008). Photochemical production and destruction of atmospheric hydrogen is hydroxyl radical controlled. (Simmonds et al., 2000).

Radon tracer method is suitable for estimating various greenhouse gas emissions (Zahorovski et al., 2006) including nitrous oxide (Schmidt et al., 2001), methane (Levin et al., 1999) and carbon dioxide (Langendörfer et al., 2002), and has recently been applied for hydrogen by Hammer and Levin (2009). The regional representability of radon tracer method depends on integration time of the fluxes, site topography and meteorological parameters (Levin et al., 1999). The results are dependent on radon exhalation rate, which varies depending mainly on grain size distribution and soil porosity. The high soil moisture/water content is also known to hinder the radon exhalation (Levin et al., 2002) Latitudinal distribution of ^{222}Rn flux is examined by Conen and Robertson (2002). A simple two-dimensional atmospheric model, based on earlier work by Aalto et al. (2006) and Lallo et al. (2009), was utilized to estimate local radon exhalation and hydrogen uptake rates by inverting the soil fluxes from atmospheric measurements. These two models and chamber measurements were used to evaluate the soil sink strength and were compared against each other.

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2 Materials and methods

The urban park near the center of Helsinki in Kumpula (60°12′13″ N, 24°57′40″ E) was selected for studies of soil uptake of molecular hydrogen. The vegetation consists mainly of broad-leaved trees and low grass species. The location is under influence of local traffic and adjacent sea. The closest high traffic volume roads Hämeentie 44 700 and Mäkelänkatu 45 000 cars a day were in the minimum distance of 350 m and 700 m, respectively.

2.1 Soil chamber measurements

The soil texture of measurement site including surface vegetation is fine sandy till (sandy loam) according to maps provided by Geological Survey of Finland, (a geological map available at: http://geomaps2.gtk.fi/geo/, 2009). In the south direction soil texture changes to clay 100 m away from the measurement site. The detailed soil type was determined (in laboratory studies , Soil Analysis Service in Mikkeli, Finland) to be gravely sandy loam (fractionated soil type) in the first 7 cm. The 7 cm to 20 cm layer was determined as fine sandy till (coarse soil type).

The field measurement setup included a stainless steel chamber (60 cm×60 cm) fixed into ground about 5 cm in depth. One chamber was normally used, except on 30 October 2007, when two chambers were used for comparison. The low grass species vegetation was removed inside the chamber. Both the chamber and aluminium cover was 20 cm in height. A small battery-operated fan was attached inside the cover to ensure mixing in the closed-chamber. The first sample was taken immediately after lowering the cover. The following samples were taken after 2 to 5 min intervals. The sampling from the closed chamber was made through a silicon tube mounted on the top of aluminium cover. A 20 cm^3 plastic syringe with three-way stop-cock valve was attached to the silicon tube during the sampling. The total length of the one measurement cycle was 15 to 20 min, which included 5 samples. The cover was opened after a cycle and chamber was ventilated for a few minutes. Three to four cycles were made

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in sequence. One ambient air sample was taken about 2 m height for reference purposes during one arbitrarily chosen cycle. The soil temperature was measured using thermistors and thermocouples. Volumetric soil moisture concentration was measured by ThetaProbe ML2x sensor. Both soil temperature and moisture was measured four times outside of the chamber. The air samples were analyzed during the same day.

The closed chamber setup was tested in a laboratory. The chamber was filled with hydrogen in air gas, with concentration two times higher than ambient hydrogen mixing ratio. The hydrogen mixing ratio inside the closed chamber did not change during the 20 min test. The leakage from the syringes was measured and it was found to be 4 ppb h^{-1}.

2.2 Atmospheric measurements

The sampling inlet was 2 m above the roof of FMI (Finnish Meteorological Institute) institute building and the roof 25 m above the ground level (53 m a.s.l.). Sample air was first transferred through plastic tubing at flow speed 10 m/s, with residence ca. 1 s. A sideflow to hydrogen analyzer was filtered with 1.0 µm Gelman filter and delivered through stainless steel tubing to flow restrictor and pressure relief valve, which was adjusted to pass about 200 cm^3 min^{-1} to analyzer.

A modified RGA5 instrument with RGD detector is used for the detection of molecular hydrogen. After chromatographic separation of sample air, molecular hydrogen is delivered through the mercury oxide bed. During the chemical reaction of hydrogen and the mercury oxide, it was reduced to mercury gas, which concentration is proportional to concentration of hydrogen. Same detector is also able to detect CO. The detection is based on the absorption of UV light into mercury gas.

A measurement cycle consists of four ambient air samples after which a working standard sample was measured. Each analysis took 5 min. The system was calibrated according to four standards (scale 400–700 ppb) acquired from Max-Planck Institute in Jena. The reproducibility of RGA5 instrument was estimated by taking into account ten consecutive working standard samples, and it found to be 1.1% (range 915–950 ppb).

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The linearity of the RGA5 instrument was checked using a series of known mixing ratios over the atmospheric range, resulting in R^2 of 0.97. The quality of measurements was verified by the intercomparison samples of the EU-project EUROHYDROS.

The radioactive radon isotope ^{222}Rn is measured at the roof of FMI (Finnish Meteorological Institute) building. The sampling inlet is the same used for hydrogen. The determination of radon is based on the short-lived ^{222}Rn progeny assumed to be in equilibrium with radon. The air samples are collected onto a filter and one hour means are calculated. The analysis method is similar than described in Paatero et al. (1998) and Hatakka et al. (2003).

The weather parameters were monitored with an automated weather station MILOS 500. Wind parameters were measured with a two component ultrasonic anemometer at a 32 m high mast next to the FMI institute building and temperature with a shielded Pt100 detector at 2.5 m above ground.

2.3 Analysis of results

2.3.1 Soil chamber method

The hydrogen concentration decrease inside a closed-chamber follows exponentially decreasing function. The hydrogen uptake into the soil follows first-order kinetics as explained by Yonemura et al. (1999). The exponential fit in Eq. (1) was applied to concentration values.

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

where t is time, C_0 is hydrogen concentration at time zero. y is a production and τ a decay term. The deposition velocity is calculated as $v_d = h/\tau$, where h is the chamber height. Hydrogen emission from the soil is taken into account in the production term y. Hydrogen mixing ratio decreased to 10–20 ppb, when the chamber was kept closed for three hours in a field test, thus zero hydrogen production can be used.

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2.3.2 Radon tracer method

The radon tracer method (Levin et al., 1999; Schmidt et al., 2001) is suitable for the tropospheric determination of emission rates of trace gases (e.g. H_2, CH_4, N_2O). There is a strong covariance between ^{222}Rn, CH_4 and also CO_2 summer and autumn nighttime mixing ratios (Levin et al., 1999). This indicates that the changes in trace gas mixing ratios originated from the variability of diurnal atmospheric conditions rather than short-term changes of trace gas emissions (Levin et al., 1999). The radon tracer method was used only during the nights, when a stable nocturnal boundary layer was formed. The height of nocturnal boundary layer is usually a few hundreds of meters, in which radon is accumulating.

During the nighttime, photochemical processes affecting the hydrogen concentration are minimal since the intensity of solar irradiation in summer in Helsinki is less than 5% of the daytime values. The major sink of hydrogen is soil and hydrogen is consumed in the first few centimeters of the soil (Schmitt et al., 2008). The photochemical reactions, e.g. due to hydroxyl radical formation from ozone, are not significant in low irradiance conditions during the nighttime. The hydrogen flux can be calculated using Eq. (2).

$$j_{H2} = j_{Rn} \frac{\Delta c_{H2}}{\Delta c_{Rn}} \left(1 - \frac{\lambda_{Rn} c_{Rn}}{\Delta c_{Rn} / \Delta t} \right) \quad (2)$$

if the radon flux j_{Rn} is known (Schmidt et al., 2001). The $\Delta c_{H2}/\Delta c_{Rn}$ is a ratio between the hydrogen concentration difference, Δc_{H2} and radon concentration difference, Δc_{Rn}. $\lambda_{Rn} c_{Rn}(t)$ is the decay rate for radon including radioactive decay constant λ_{Rn} and radon concentration c_{Rn}. For the radon tracer method calculations, only those nights were accepted when hydrogen mixing ratio decreased more than 5 ppb and radon activity concentration increased more than 0.6 Bq m^{-3} between 23:00 and 5:00 LT. Only high correlation R^2>0.8 events which had five or six hours of data were selected.

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2.3.3 Two-dimensional model

The hydrogen deposition velocities were also determined by a two-dimensional model. The model was built for support, comparison and verification of other methods described earlier. It has been applied for hydrogen soil deposition studies in Northern Finland by Lallo et al. (2009). The model is based on the three dimensional atmospheric model (Aalto et al., 2006). The variation in vegetation, land use and topography is suppressed to one specified type to gain faster simulation run times, while the surface fluxes are inverted from atmospheric concentration observations. By aiming to estimate regionally averaged soil surface fluxes, and assuming that the boundary layer height can be adequately simulated, then the detailed vegetation and topography description is less important for the current study. A 5 m thick surface layer was built in the model, where the soil acted as a passive solid and fluxes were defined only in the air-soil interface of the model. The model was run with setup of 3 km vertical extent (12 layers) and horizontal extent of 10 km (10 grid boxes) to allow for adjustment of boundary layer and profiles.

The commercial fluid dynamics software Fluent® was used to solve fluxes and concentrations of radon and hydrogen. The mass and energy exchange formulations in the soil-air surface were modeled by user defined codes added to the model (Aalto et al., 2006). The necessary boundary conditions were also given based on local observations. The turbulence inside the domain was simulated using the standard K-epsilon theory by Launder and Spalding (1972). The model equations for energy, turbulence, fluid and species transport were solved in segregated mode. The model allowed changes to the initial value of meteorological pressure i.e. the model was non-hydrostatic.

As in the case of radon tracer model, the nighttime simulations were made to avoid indirect photochemical degradation of hydrogen. The model was initialized few hours before the selected time range to achieve balanced state. During the simulation, the hydrogen and radon outflow vertical profile from the preceding time step was used as

a new input to following time steps. The deposition velocities and radon exhalation rates were solved at every time step to let the modeled outflow concentration meet the observed concentrations at Kumpula site. The hydrogen and radon surface fluxes were thereby inverted from the concentration observations. Simulation results consist of stabilized flux values obtained at the end of each simulation hour. For hydrogen, only those nights were accepted when there was at least four hours of monotonous increase in radon and decrease in hydrogen mixing ratios. In the case of radon, also nights with no hydrogen decrease were accepted. These selection criteria are somewhat different from radon tracer method and result in a larger number of events. Our aim was to obtain an extensive data set especially for radon, so that we could estimate the radon exhalation rate separately for winter and summer.

The boundary layer height simulated by the two-dimensional model was compared to ceilometer data at about 2 km distance from the Kumpula site. The model produced a turn in the potential temperature profile, which was interpreted as the top of the boundary layer. On 13 July 2007, at 02:00 to 04:00 LT the turn occurred at 124 m height, while on 18 July 2007 at 00:00 to 05:00 LT it appeared at the next model level, 198 m above ground. The ceilometer boundary layer (BL) estimate for these nights showed high variability which could not be reproduced by the model, on 13 July 2007, 80–240 m, and on 18 July 2007, 310–590 m, respectively. On contrasting winter night conditions (−15°C) in 10 February 2007, the model simulated the first inversion at 75 m model level, and second at 198 m level, while ceilometer results indicated 70–200 m for the BL height. Generally, when the observations showed lower BL height, also the model indicated a shallow BL. However, the model results were in the lower end of the range given by observations, and therefore the simulated BL height may be somewhat too low. This would result in underestimation of the inverted hydrogen and radon fluxes.

3 Results

3.1 Hydrogen deposition velocities from soil chamber measurements

The chamber measurements were performed between 28 October 2005 and 30 October 2007 at the urban park site in Kumpula. The automatic weather system (AWS) data collected from Helsinki area (Kaisaniemi and Kumpula) was used in the interpretation of chamber and model results. Hydrogen v_d values are shown in Fig. 1. The lowest close to zero v_d values were measured in January to March 2006 and highest 0.70±0.02 mm s^{-1} on 15 June 2006. The winter (12 field days from November to April) v_d values ranged from 0.00 mm s^{-1} to 0.42 mm s^{-1} with mean value of 0.20±0.05 mm s^{-1} and in summer (10 field days from May to October) from 0.13 mm s^{-1} to 0.70 mm s^{-1} with mean value of 0.34±0.06 mm s^{-1}.

The lowest values occurred when snow covered the ground, as indicated by Lallo et al. (2008). The highest v_d value (0.18±0.04 mm s^{-1}) with permanent snow cover was measured on 2 February 2007 (Fig. 2). Snow depth was then 16 cm, soil temperature +0.5°C and soil volumetric water content 0.27 m^3 m^{-3}. When snow depth exceeded 20 cm, v_d values were close to zero. When snow layer thickness was between 10 cm and 20 cm, v_d mean values were lower than 0.20 mm s^{-1}.

Hydrogen v_d values are shown together with corresponding air and soil temperatures in Fig. 3a. There is large scatter in v_d, but it tends to get lower values in freezing temperatures. In Fig. 3b hydrogen v_d is plotted against soil volumetric water content showing lower values at high soil moistures. In general, the lower limit of v_d values from chamber measurements was 0.24 mm s^{-1} and the upper limit was 0.45 mm s^{-1}, provided that no exceptional weather conditions (e.g. drought or intense rain) occurred. The soil volumetric water content ranged in this region from values 0.29 m^3 m^{-3} to 0.41 m^3 m^{-3}. The soil and air temperature varied in this group between 2°C to 8°C and 2°C to 12°C, respectively.

According to measurement records, heavy rain showers decreased soil uptake when

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there had been precipitation within three days before. An intensive thundershower (13.8 mm) two days before hindered the soil uptake on 24 August 2007, lowering v_d to 0.13±0.01 mm s^{-1}, which was the lowest summer time v_d value in the whole measurement period. On 2 August 2007 weather conditions were favoring strong soil uptake. Soil temperature and volumetric water content was 15°C and 0.24 m^3 m^{-3} respectively, but only 0.33±0.01 mm s^{-1} was recorded. Three days before 20.4 mm rain was recorded. The total amount of 24.1 mm precipitation was recorded on 31 October 2006 with v_d value of 0.34 mm s^{-1}. Compared to high summer values recorded in 2006, soil uptake was significantly reduced. Soil volumetric water content was 0.41 m^3 m^{-3}.

There was a four-month drought in 2006 in Helsinki area, during which high v_d values of 0.509±0.004 mm s^{-1} (2 August), 0.55±0.02 mm s^{-1} (31 May) 0.70±0.02 mm s^{-1} (15 June) were measured. Soil volumetric water content values were between 9 m^3 m^{-3} and 25 m^3 m^{-3}, while the typical soil volumetric water content values obtained in the field measurement were higher than 0.29 m^3 m^{-3}. The cumulative rain sum between 26 May and 29 September 2006 was only 51.6 mm (287.3 mm in 2007 and 265.2 mm in 2008) in Helsinki area. In May 2008 rain sum was significantly lower (7.5 mm) than in May 2006 (41.6 mm) and 2007 (58.9 mm) (Fig. 4).

3.2 Hydrogen deposition velocities and radon exhalation rates from two-dimensional model simulations

The two-dimensional model results covered the time period between June 2007 and July 2008, when atmospheric hydrogen mixing ratios were continuously measured at Kumpula. The modeled winter (17 nights) v_d values ranged from 0.12 mm s^{-1} to 0.46 mm s^{-1} with mean value of 0.26±0.02 mm s^{-1} and in summer (31 nights) from 0.13 mm s^{-1} to 0.61 mm s^{-1} with mean value of 0.35±0.02 mm s^{-1} (Fig. 1). The modeled mean radon exhalation rate in winter (from November to April) was 22±1 Bq m^{-2} h^{-1} and in summer (from May to October) 45±3 Bq m^{-2} h^{-1} with highest values occurring in August 2007 (Fig. 5). The highest exhalation rates were observed

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during northerly winds when air masses traveled above continent and captured high radon activities before arrival to the site. The northerly-northeasterly winds dominated during August 2007 high radon exhalation nights. Generally, the conditions were favorable for radon exhalation in summer when the soil was not saturated with water despite of short rain periods which lowered radon exhalation rates. Radon exhalations are depicted against one week cumulative precipitation in Fig. 6a. Pearson product moment correlation for Fig. 6a is −0.321. Correlation is significant at the 0.01 level (2-tailed). Over 100 Bq m^{-2} h^{-1} emission values were reached in dry conditions, while 25 mm precipitation lowered the radon emission down to 50 Bq m^{-2} h^{-1}. Correspondingly, one week dry period raised the hydrogen soil uptake to hydrogen deposition velocity values up to 0.7 mm s^{-1} and 30 mm precipitation decreased the v_d values down to about 0.3 mm s^{-1} (Fig. 6b). Pearson product moment correlation for Fig. 6b is −0.293. Correlation is significant at the 0.05 level (2-tailed), when outliers were excluded. The winter soils were typically moister than the summer soils due to lower evapotranspiration regulated by global irradiation, which had a maximum of over 600 W m^{-2} in June, while in December less than 100 W m^{-2} (Fig. 4) was reached (see also Vesala et al., 2006). This can be seen in the yearly cycle of radon exhalation rates in Fig. 5, as well as in the hydrogen results in Fig. 1, where lower chamber v_d values were recorded during winter.

3.3 Hydrogen deposition velocities from radon tracer method

The radon tracer method results covered the time period between June 2007 and July 2008. According to radon tracer method, in winter (November to April, 9 nights), modeled v_d values ranged from 0.14 mm s^{-1} to 0.68 mm s^{-1} with a mean value of 0.34±0.07 mm s^{-1} and in summer (May to October, 28 nights), modeled v_d values ranged from 0.13 mm s^{-1} to 0.90 mm s^{-1} with a mean value of 0.41±0.04 mm s^{-1} (Fig. 1). The radon tracer method is dependent on the radon exhalation rate, which was estimated by the two-dimensional model. The average winter rate was used for

November to April and summer rate for May to October. The annual cycle of hydrogen deposition velocities was similar than the one simulated with the two-dimensional model, but there were cases when radon tracer method indicated higher values than two-dimensional model, which can be seen in Fig. 1 and Fig. 6b. The range of both radon tracer method and two-dimensional model results was in good agreement with the chamber results.

All methods delivered results on 30 October 2007, the radon tracer method and two-dimensional model v_d values were 0.68±0.16 mm s^{-1} and 0.39±0.18 mm s^{-1} respectively, while soil chambers indicated a v_d of only 0.19±0.02 mm s^{-1}. Soil water content was 0.33 m^3 m^{-3} and soil temperature was 9°C. There was rain during 30 October 2007 which may have affected the soil chamber result, measured at midday, while the other estimates refer to earlier nighttime observations from drier soils. In general, the October 2007 rain sum was significantly lower, 56 mm, than in October 2006, 183.6 mm and in 2008, 166.6 mm. The results also had a lot of statistical variation. The difference between radon tracer method and two-dimensional model was probably due to choice of data. For example, if only three hours with the largest change in hydrogen and radon are selected from the two-dimensional model simulations, the resulting v_d increases to 0.65 mm s^{-1}.

4 Discussion

4.1 Radon exhalation rate

The radon tracer method is dependent on pre-calculated radon exhalation rate j_{Rn}, which is based on regional radon emission estimates. The radon exhalation rates were measured by Dörr and Münnich (1990) in cultivated fields and undisturbed forest soils. The fluxes were in the range 500 dpm m^{-2} h^{-1} and 6500 dpm m^{-2} h^{-1} (8–108 Bq m^{-3}, 1 dpm=1/60 Bq) in West Germany and the average value was 3200 dpm m^{-2} h^{-1} (53 Bq m^{-2} h^{-1}). Szegvary et al. (2007) measured exhalation rates at 8 locations in

southern Finland by using soil chambers. There were significant variations in radon exhalation rates, which were between 51 Bq m^{-2} h^{-1} and 134 Bq m^{-2} h^{-1} including one peak value of 189 Bq m^{-2} h^{-1}. An average value of 100±17 Bq m^{-2} h^{-1} was obtained when eight locations in southern Finland was included to calculations (88 Bq m^{-2} h^{-1} if peak value was excluded). Levin et al. (2002) measured radon exhalation rates for moist boreal forest using closed-chamber technique at Fyodorovskoye in Russia. ^{222}Rn exhalation rates were in the range 3.3 Bq m^{-2} h^{-1} to 7.9 Bq m^{-2} h^{-1}, while water table depth were from 5 cm to about 70 cm. Strong relation between water table depth and radon fluxes was found. (Levin et al., 2002; Conen and Robertson, 2002). Conen and Robertson (2002) measured ^{222}Rn flux using closed-chamber technique. They found that radon flux was at the highest in mineral soil type with no humic layer, decreasing towards more humic and organic soil type.

A modeled radon exhalation rate can also be used as an input to the radon tracer method. Our radon fluxes simulated with the two-dimensional model were lower in comparison to the southern Finland and Germany chamber results, but higher in comparison to Fyodorovskoye. The highest values were obtained during northerly winds from the continent. Thus the proximity of the sea may have a lowering effect on the mean values. Also, the two-dimensional model can provide only a crude estimate of the boundary layer height which has a direct effect on the magnitude of the inverted flux. However, it is not probable that the mean radon fluxes are heavily underestimated. According to radon tracer method the hydrogen deposition velocity values are proportional to the radon exhalation rate (Eq. 2) and the method would yield unrealistically high deposition velocities if radon fluxes were multiplied by e.g. a factor of two.

4.2 Comparison between the methods

The results of chamber measurements were in the same range with the earlier measurements made in boreal zone (Rahn et al., 2002; Smith-Downey et al., 2008). According to chamber measurement results, hydrogen soil deposition increased on May to August 2006 after long drought. During that time soil volumetric water content varied

between 0.09 $m^3\,m^{-3}$ and 0.25 $m^3\,m^{-3}$, which was significantly lower than typical values (0.29 $m^3\,m^{-3}$ to 0.41 $m^3\,m^{-3}$) recorded in 2005 and 2007–2008. Highest v_d values 0.5 mm s^{-1} to 0.7 mm s^{-1} were measured in high soil temperature conditions from 10°C to 17°C, which was usually recorded from May to August. Negligibly small v_d values were measured, when air and soil temperatures were near-zero and soil surface was snow covered. The soil volumetric water content was usually higher in winter than in summer. The dependency of v_d to soil volumetric water content (in this study R^2 was 0.47) might be more important than to soil temperature (Schmitt et al., 2008). The dryness of soil is in correlation with the high soil temperature. The high soil water content effectively hindered the hydrogen diffusion into ground.

The modeled hydrogen deposition values were compared against chamber measurements and using several parameters, such as air/soil temperature and soil volumetric water content. The modeled and measured v_d values were in good agreement with each other and their annual cycles were similar (Fig. 1). The radon tracer v_d values were distributed more evenly in summer time (May to October), yielding values from 0.13 mm s^{-1} to 0.9 mm s^{-1}. The v_d values of two-dimensional model were distributed to more narrow range (0.12 mm s^{-1} to 0.61 mm s^{-1}) than radon tracer method. In winter time both radon tracer and two-dimensional model produced v_d values lower than 0.33 mm s^{-1}. Within the modeled period the lowest air temperature was −5°C and highest 21°C. Among both models, results did not show clear temperature dependency in above zero temperatures. Hammer and Levin (2009 and references therein) used also radon tracer method for the estimation of nocturnal soil uptake rate and respective hydrogen deposition velocities in urban/suburban environment. Estimated v_d values ranged from 0.1 mm s^{-1} to 0.8 mm s^{-1}, which is close to our results.

4.3 Precipitation and v_d

A strong solar irradiation during summer (May to July) above 600 W m^{-2} is capable to dry the top soil layer allowing higher soil uptake. In fall, low solar irradiation and more

frequent rain periods keep the soil volumetric water content level high. Chamber measurements made on rainy weather conditions indicate low hydrogen deposition rates. Field measurement made on 24 August 2007 was affected by intensive thunderstorm two days before. All field measurements where v_d was less than 0.2 mm s^{-1} were snow results, except 24 August and 30 October 2007. However, soil volumetric water content at 24 August was not higher than typical values. There is not a single factor, which fully explains the lowest v_d value, but the soil surface may have compacted after rain, hindering gas diffusion into ground. On the other hand high v_d values were occasionally measured in high soil volumetric water content conditions. In these cases, the probe may have overestimated the soil volumetric water content, especially when the soil surface was moist due to small amount of rain. In snowy winter conditions, v_d values were small at sub-zero temperatures. This is supported by results of Lallo et al. (2008), who made field measurements in winter with snow cover. Snow cover hinders the gas diffusion into ground resulting in lower v_d as shown in Fig. 2. Rhee et al. (2006) found out that seasonal variation is mainly controlled by snow cover in Northern Hemisphere based on deuterium ratio measurements and estimating effective land surface. Yonemura et al. (2000) found, based on modeling and measurements, that diffusion into soil is an important factor controlling hydrogen and carbon monoxide soil uptake.

The comparison of v_d values and radon exhalation rates with rain records showed a decreasing trend towards increased one week cumulative precipitation. The decreased soil uptake rate and radon exhalation was possibly due to higher water table level and/or higher soil volumetric water content. Precipitation has effects to short-term variations to ^{222}Rn flux (Szegvary et al., 2007). Szegvary et al. (2007) found during the long-term measurements (June to November 2006) in Basel, that while the prolonged dry period decreased the soil volumetric water content, the ^{222}Rn flux increased about 100% until the beginning of August. The ^{222}Rn flux was enhanced due to increased diffusion and air-filled porosity and decreased soil volumetric water content. Later measurements on September in three rainy days showed that ^{222}Rn flux decreased immediately with the beginning of precipitation, preventing ^{222}Rn diffusion into atmosphere

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(Szegvary et al., 2007). In Finland there was a dry period from June to August 2006. Lowest soil volumetric water content in conjunction with high temperature increased the hydrogen soil uptake, v_d values were $>0.5\,mm\,s^{-1}$, due to enhanced diffusion into the soil layers. Schery et al. (1984) found also that radon flux and its diffusion into ground is reduced in rainy conditions due to capping effect of the top soil layer. Rain seals the upper surface pores, thus retarding the radon exhalation. Soil exhalation values show significant spatial variation, correlated to soil water content.

5 Conclusions

Hydrogen deposition velocities in urban environment were measured. The field measurements were made using closed-chamber technique. The results calculated from the field measurements were further compared and verified with the modeled hydrogen deposition velocity values applying two-dimensional model and radon tracer method. Hydrogen deposition velocity values obtained from all three methods were in good agreement with each other. Based on the chamber measurements in rainy conditions the decreased deposition velocity suggests that increased soil volumetric water content hinders the gas diffusion into ground leading to decreased hydrogen deposition velocity rate. The soil volumetric water content values did not vary enough to see clear moisture dependency among hydrogen deposition velocity values. However a good agreement was found between the modeled and measured hydrogen deposition values compared to one week cumulative rain.

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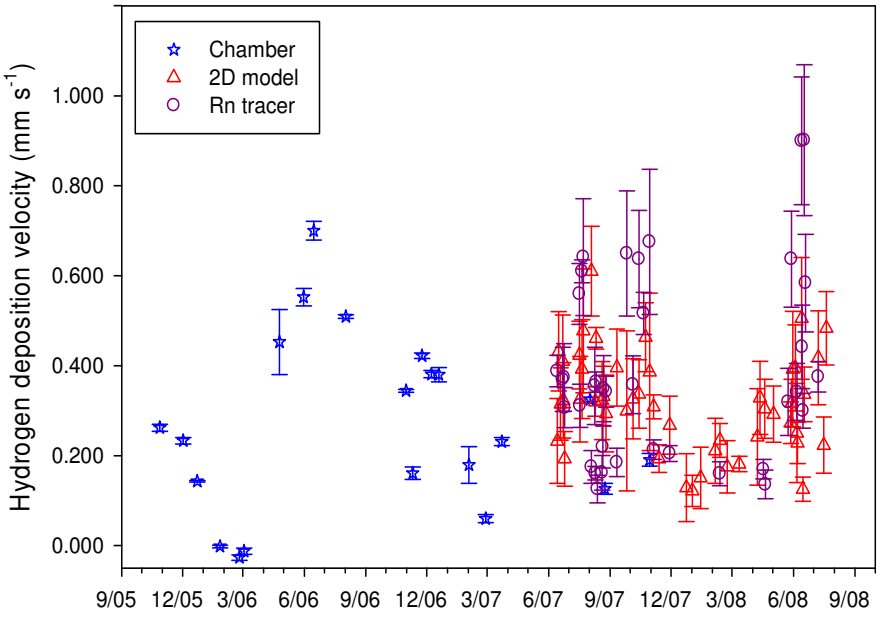

Fig. 1. Hydrogen deposition velocity (v_d) values from the chamber measuements, and using radon tracer method and two-dimensional model. v_d values are presented as mean ± standard error of the mean (SE).

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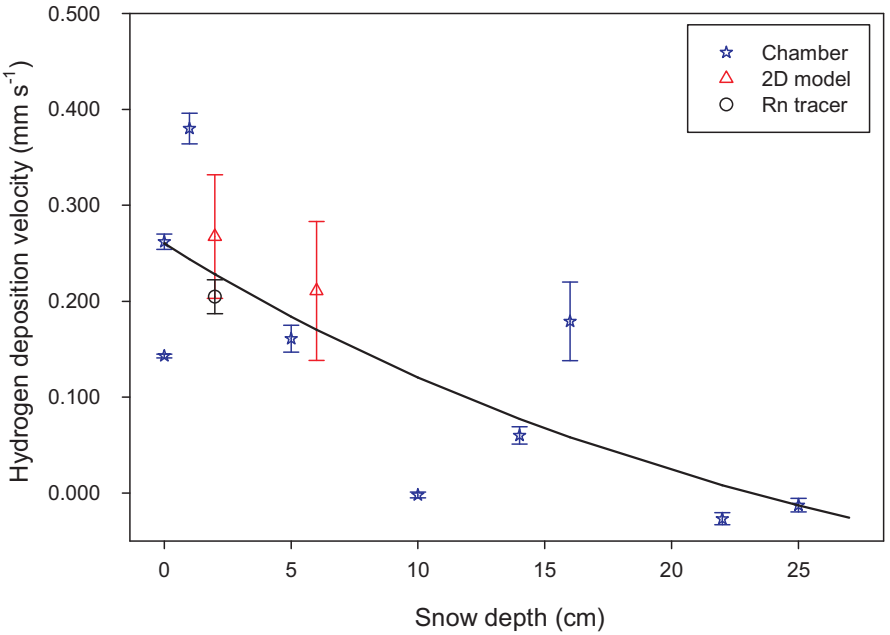

Fig. 2. The effect of snow depth to soil uptake rate. R^2, i.e. squared correlation coefficient, is 0.62.

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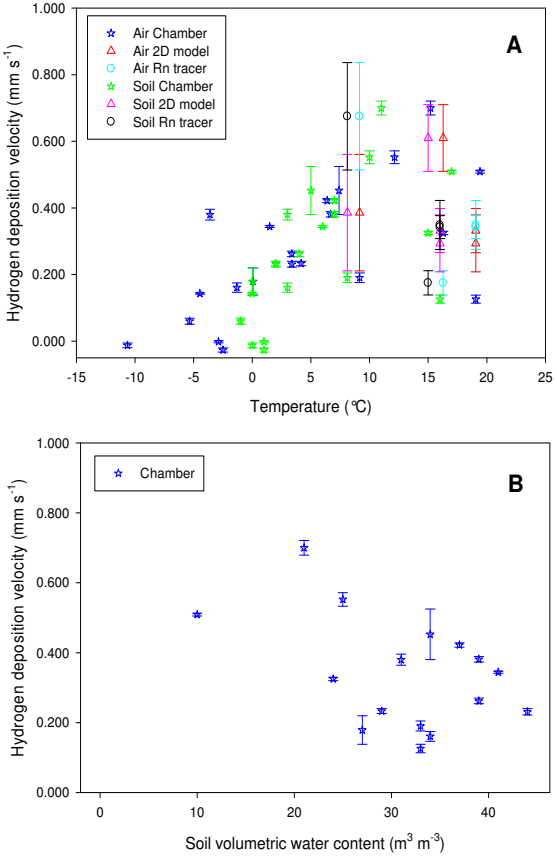

Fig. 3. **(a)** The dependency of measured and four modeled hydrogen deposition velocity values to air/soil temperature of chamber measurements and **(b)** the dependency of measured hydrogen deposition velocity to soil volumetric water content of chamber measurements.

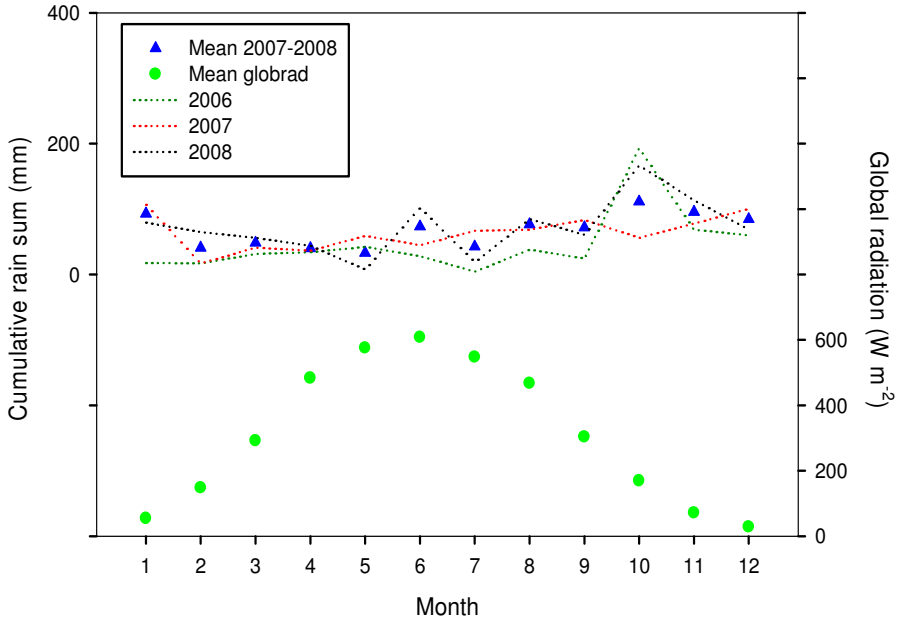

Fig. 4. Biannual global radiation average obtained at 12:00 UTC and biannual cumulative monthly precipitation 2007–2008 and monthly rain sum for years 2006 to 2008.

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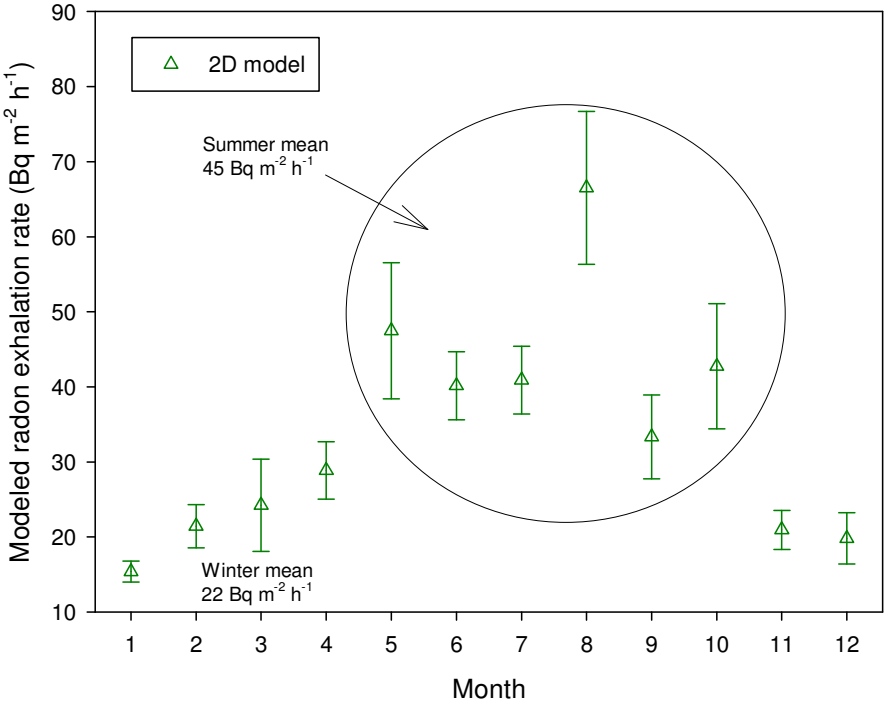

Fig. 5. Two-dimensional model results for ^{222}Rn exhalation rate j_{Rn}.

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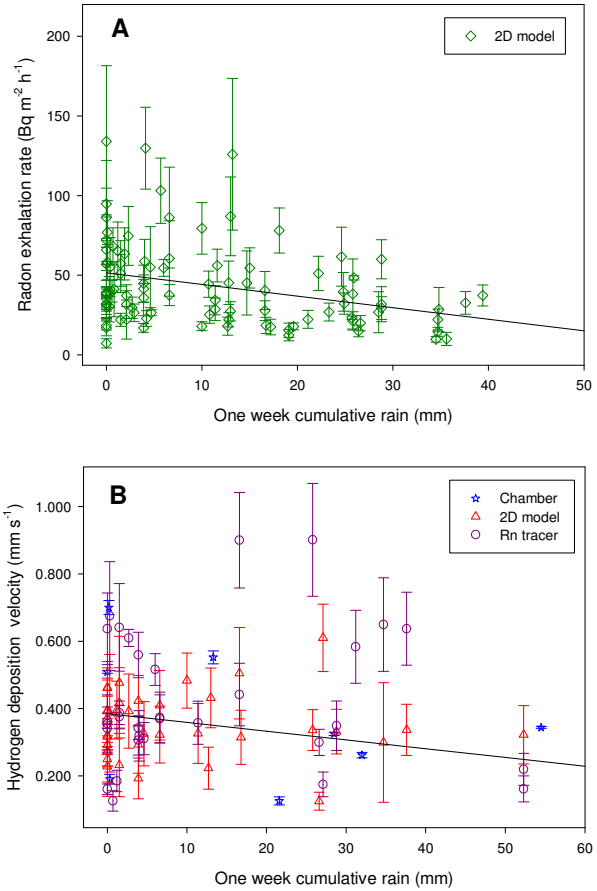

Fig. 6. The effect of one week cumulative rain to **(a)** the radon exhalation rate ($p<0.01$) and **(b)** the modeled and measured hydrogen deposition velocities ($p<0.05$).

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