Atmos. Chem. Phys. Discuss., 9, C5766–C5781, 2009
www.atmos-chem-phys-discuss.net/9/C5766/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hydrogen soil deposition at an urban site in Finland" *by* M. Lallo et al.

M. Lallo et al.

marko.lallo@fmi.fi

Received and published: 9 October 2009

Author Response to Referee #1 comments: Anonymous Referee #1 Received and published: 3 September 2009

*General comments:

*The manuscript presents bottom-up measurements and inverse (top-down) model estimates of the uptake rate (deposition velocity) of molecular hydrogen on a vegetated soil area in southern Finland. Soil uptake is the most important sink of atmospheric hydrogen and the results presented here are particularly useful, as measurements at high latitudes (of the northern hemisphere) are very rare. The authors use independent methods to determine the soil sink which makes the study particularly useful. However, the two top-down methods, modeling and the radon-tracer-method, are not really independent from each other, and this needs to be made clear to the reader. Also, there

are a number of other issues (see specific comments) which need to be addressed before the manuscript is suitable for publication. Besides these scientific points, the English language requires some improvement, ideally by a native speaker. In fact, if the presentation would be a bit streamlined, e.g. by putting detailed findings explained at length in the text into tables or more illustrative figures (see specific comments) this would make the manuscript more easily digestible for the readership of ACP.

*Specific comments:

Answer: The use of two-dimensional model will be clarified in the revised manuscript. The English language will also be checked. Some figures are corrected and are now more informative.

*Introduction

*Several earlier papers (before Rhee et al., 2006) came to the conclusion that the soil uptake is the larges sink of H2 (e.g. Novelli et al. JGR 1999, Hauglustaine and Ehhalt, JGR 2002), and the number of 82% without giving any uncertainty values suggests that we know this sink already very accurately, which is misleading. Instead a range of recent estimates with references should be given here.

Correction:

Several authors have reported that soil uptake is the largest sink, which is responsible for 73-82% of total hydrogen turnover (Novelli et al., 1999; Hauglustaine and Ehhalt, 2002; Rhee et al., 2006).

*The same is true for the OH source/sink reference, here also earlier publications other than Simmonds et al. (2000) need to be cited.

Correction:

Photochemical production and destruction of atmospheric hydrogen is hydroxyl radical controlled. (Schmidt, 1974; Sanders, 2006; Simmonds et al., 2000).

*The Schmitt et al. reference was published in 2009 not 2008.

Correction:

Recent field measurements to estimate the soil uptake of hydrogen were made in agricultural area in Heidelberg (Schmitt et al., 2009), 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).

*2. Materials and Methods

*Closed chamber method: I am wondering how the authors could avoid advective flux from the soil caused by the under-pressure in the chamber when taking the samples with a syringe. Sampling of three or four cycles: As closing the chamber does not only cause a large decrease of mixing ratios at the air-soil interface, but also influences the soil air profile,

Answer: The syringe volume was 0.020 L and the closed-volume inside the chamber was about 100 L, which is large enough to minimize disturbances. The disturbance of pressure differentials can not totally avoid, but the effect of these can be minimized using short measurement time and large chamber volume.(Davidson et al. 2002). For this reason, chamber was kept closed only 15.minutes (sometimes 20 minutes) and large closed-volume (about 100 L) chamber was used. During the sampling, only about 0.4 dm3 is removed from the chamber headspace.

*I am wondering if only a few minutes time for adjustment in between sampling events is sufficient to bring the sampling place back into steady state. Both these points need to be discussed.

Answer:

When examining the deposition velocity values of consecutive measurements, all values were scattered randomly and usually all values were close to each other. Systematic trends between the repetitive measurements were not observed. In addition,

according to Hutchinson and Livingston (2001) repetitive chamber measurements is not a major source of error.

*A short description of the H2 analysis system (for the chamber samples), the measurement uncertainties and the non-linearity correction (at mixing ratios much below ambient air) should be given.

Answer:

The analysis sequence differed from the method used in atmospheric samples. The sample inlet line was detached before syringe samples. The syringe samples were injected directly to the RGA5. At least three working standard samples were analyzed before and after syringe samples.

The linearity was checked within the broad range (200 - 2000 ppb).In this range the squared correlation (R2) for linear fit was . 0.995 and for the second order fit 0.997. Within the atmospheric range (400-700 ppb) the squared correlation for linear fit was 0.973 and for the second order 0.974. We correlate a peak area against mixing ratio.

A response curve was made in the concentration range between the 200 - 2000 ppb. By plotting the mixing ratio against peak area, it is possible to construct a linear or second order fitting, which can be used for non-linearity correction. A concentration in the chamber decreased under 200 ppb usually after 15 minutes. A difference between linear and non-linear fit varied in a range 0.02 mm s-1 – 0.05 mm s-1. Corresponding difference value between non-corrected value and second order fit was in a range 0.03 mm s-1– 0-06 mm s-1.

*Also the description of the ambient air measurement should give a few more details or a respective reference. Please explain and specify what is meant with the remark “the quality of measurements was verified by the intercomparison samples of the EU-project EUROHYDROS”.

Answer:

The description of the ambient air measurement is given in a companion article by Aalto et al. (2009). The sampling line was checked using two flask samples, taken at the roof of institute building. Normal ambient air samples (through the inlet line) and flask samples were compared with each other. Three sample average was close to flask samples (difference: 2 ppb). Calibration was made according to EUROHYDROS standards provided by Max Planck Institute.

*222Radon observations: The same intake as for H2 is used for the radon daughter measurements: Did the authors check loss of aerosols in the intake line?

Answer: A loss of aerosols was not checked during the EYROHYDROS campaign. Long term radon measurements are performed continuously using the radon instrument.

*How good is the assumption of radioactive equilibrium between 222Radon and its daughters (e.g. Levin et al., 2002) quote 214Po/222Rn disequilibrium of around 0.7 at about 30m above local ground).

Answer: Most probably inversion layer development was so slow that radon had aged couple of hours and thus equilibrium condition could be assumed.

*How does the uncertainty of the assumption of no disequilibrium translate into the uncertainty or systematic bias of the 222Radon flux?

Answer: Since we assume that nighttime layer formation is slow and radon has aged couple of hours, we did not excpect systematic biases due to disequilibrium.

*2.3. Analysis of results *Eq. (1) allows also taking into account H2 production when estimating H2 deposition fluxes from the change of H2 in the chambers during the experiment. Only one experiment yielded zero production. Did the authors still use Eq. (1) for all evaluations or a more simplified version? It may well be that there is production only in certain times of the year.

Answer:

A production term is usually dropped for the calculations. When depositions or emissions were measured using the chamber technique, emissions were not detected in the field site. There was not e.g. clover vegetation in the field site, which could produce hydrogen.

*Radon-tracer-method: The sampling/atmospheric measurement site is close to very busy streets and even during night or early morning hours there may be some contribution of H2 emissions from traffic. How did the authors correct for this (potential) contribution ?

Answer:

For the method, those hours were selected when the difference between maximum and minimum hydrogen concentration was at least 5 ppb. The possibility for H2 emissions is then lowest.

*Two-dimensional model: The first two paragraphs of this section are not clear. May be the authors want to say that the uncertainty to model boundary layer height is much larger than the error associated with not including the changing vegetation and topography?

Answer:

The uncertainty related to estimation of the model boundary layer is much larger than the error associated with the changing vegetation. A more clear explanation will be added to manuscript.

*What is the purpose of the 5m surface layer?

Answer:

The purpose of the 5m surface layer is created for the calculations of the energy balance. This requires realistic values for soil density and thermal conductivity. The modeled layer could also be thinner.

*What “adjustments were made to boundary layer and profiles”?

Answer:

A user can not alter the profiles or boundary layer features during the simulation. The model generates new value for these in the calculation.

*A reference should be given for the software Fluent.

Answer:

CFD Flow Modeling Software & Solutions from Fluent http://www.fluent.com/software

*Which local observations are available to provide the boundary conditions?

Answer:

Following boundary conditions are included in the two-dimensional model: Hydrogen and radon outflow profile is transferred to inflow profile (a periodic boundary condition). Weather parameters (air temperature, humidity, atmospheric pressure, wind speed) are controlled in the inflow, where adjustments were made in 5 minutes steps. These were also local observations.

*The information from the last paragraph of this section (page 14881, lines12ff), i.e. the comparison of simulated and measured boundary layer height should be presented in a figure or at least as a table.

Answer:

The model estimates smoothly boundary layer values, but the measurements were more scattered. Table values still needs explanation, which is already given in the text.

*3. Results

*Figure 3A: The measurements under exceptional weather conditions should be given a different symbol. Is it possible that the low deposition velocities measured at temperatures below zero °C are influenced by snow cover (compare Fig. 2)?

Answer:

Figure 3A is divided into two separate figures, which shows now air and soil temperatures in separate graphs. Snow, rain and drought points were marked to the graph. Soil temperature and deposition velocity is better correlated than air temperature. In some cases, when air temperature was decreased to subzero values, the soil temperature may have been over zero. This means also higher vd values, typically over 0.16 mm s-1. When there was snow cover vd values were usually lower than this.

*Lines 24-26 on page 14882 are not clear.

Answer:

These lines and the current paragraph will be rephrased: Higher vd values (above 0.50 mm s-1) were only recorded in drought conditions, when soil moisture was between 0.10 - 0.25 below and soil temperature was 10 °C or higher. Low vd values (below 0.20 mm s-1) were often associated with sub-zero or close to zero values and snow cover. Soil temperature was then usually below 4 °C.

*Fig. 4 is not really helpful and the respective section (upper part of page 14883) is confusing.

Answer:

The purpose of this figure is to show the difference of the year 2006 and also to show the effect of solar heating and evapotranspiration, which helps to decrease the soil water content (soil moisture).

*For clarification I would suggest to replace this figure by a plot which shows all chamber measurements vs. time together with the rain events.

Answer:

For this purpose, we have modified the Figure 3, which shows better the effect of rain and snow.

*Then Figure 1 which shows all results (chamber, model and radon-tracer from 2005 to 2008) could be replaced by a figure showing the mean seasonal cycle of all measurements in better resolution than given in the present figure 1 (because in figure 1 it is very difficult to distinguish the different measurement points obtained from the different methods).

Answer:

Figure 1 is replaced by a new graph with mean seasonal cycle of all methods.

*Section 3.2

*The uncertainties given for the mean summer or winter H2 deposition velocities and likewise for the radon exhalation rates seem to be derived only from the variance of individual determinations. When the authors then report standard errors of the means these become unrealistically small. In this error estimate also uncertainties in the model, e.g. of the boundary layer height and potentially other uncertainties need to be included.

Answer:

The two-dimensional model estimates the boundary layer height. The uncertainty of flux values calculated by the model varies from 10% to a few tens. This affects to the hydrogen flux estimation. The model estimates smoothly the boundary layer height. The variability of two-dimensional model results are acceptable, when compared to radon tracer and chamber results and also due to integrative nature of the atmospheric methods. The uncertainties related to fixed vegetation layer is small compared to boundary layer estimation.

*Also, it seems very unrealistic that the radon exhalation rate changes abruptly from summer to winter by a factor of two. Figure 5 gives more the impression that there is a smooth change of radon exhalation during the year, and a respective smooth curve should be estimated and used as input for the radon tracer method.

Answer:

A smooth trend line was fitted and added to the Figure 5. Also hydrogen deposition velocity values produced by the radon tracer model were estimated using the smooth curve, which gives slightly different values.

*It is also difficult for me to believe that a rain event of a few centimeters a few days ago can still significantly influence the current radon exhalation rate. From the magnitude of the reported radon fluxes, i.e. 20 - 50 Bq m-2 h-1 the water table depth which is the limiting parameter for the total exhalation rate, must be much deeper than about half a meter. In this case 2-5 cm of rain water will be distributed quickly over the unsaturated soil depth and will not be able to close off pores reducing the exhalation flux (it will change soil moisture, though).

Answer:

Radon exhalation with respect to one week cumulative rain sum shows a slightly but significantly decreasing trend. This does not mean that precipitated rain fully blocks all air-filled pores in the soil. In this case hydrogen deposition velocity could have been only minimal. Although water permeates through the soil layers this however affects to soil moisture, which will change leading to increased soil water content. In addition an intense rain showers could change the physical structure of the soil surface, which compacts the soil surface and blocks partially the air channels.

*Possibly (also) other parameters such as the meteorological conditions are responsible for the apparent change of the radon exhalation rate with rain? For example the authors mention that the radon exhalation rate estimated in the model depends on the path the air mass takes before arriving at the sampling point. The argument that rain events a few days before the measurement should influence deposition velocity of H2 seems even more unlikely, as the H2 sink is located in the first few cm of the soil which are quickly dried after a rain event.

Answer:

Air masses, which are coming from the southern direction, are influenced with sea. This may have an effect to radon exhalation rates. In the case, where all air channels are blocked with precipitated water, a hydrogen deposition velocity will be close to zero. Due to partial water-filled porosity H2 deposition velocity is decreased in some extend, but not being negligible. In addition an intense rain showers could change the physical structure of the soil surface, which compacts the soil surface and partially blocks the air channels.

*Also, the method how “outliers have been excluded” in Figure 6b should be explained.

Answer:

Outliers were excluded based on calculation of standard deviation. A distance of individual point was calculated and compared to mean value. The tools for heteroscedasticity are needed for data calculation.

*Section 3.3

*For this study the radon tracer method to estimate H2 deposition velocities should on average yield the same results as the model because they are not independent (the underlying radon exhalation rates have been obtained with the same model as H2 deposition velocity, and are thus subject to the same potential systematic biases). It is not clear to me why the authors applied the radon tracer method at all, as it does not provide any new information (because the radon flux was not independently determined).This point is confusing for the reader and has to be clarified

Answer:

The two-dimensional model is used to estimate hydrogen deposition velocity using the meteorological input values and hydrogen mixing ratio. In addition same two-dimensional model is used separately for the estimation of radon exhalation. Only the radon flux is estimated based on the radon concentration measurements (initial profile).

After that, model changes the radon concentrations according to model controls.

*On page 14885 lines 7ff the authors should discuss the different scales and representativeness of the chamber measurement (less than 1 m2) compared to the model/radon tracer method (more than several km2).

Answer

*Different scales will be explained in the discussion section.

*Section 4.3

*Why should snow cover hinder diffusion of H2. I would suspect than the permeability in non-compacted snow is similar to that in the soil air. May be the interface between snow and soil is blocked by ice (which may also be one of the reasons why the H2 deposition velocity decreases at very cold temperatures)?

Answer:

In a frozen soil surface case, the gas exchange is effectively blocked by ice. The soil temperature could also be above zero under the thick snow cover. Increased soil water content changes the radon diffusion coefficient. The decreased deposition velocity in snow conditions measurements is possibly due to higher soil moisture. Also when thicker snow layer is formed, it becomes more layered due to changing weather conditions. The permeability of snow differs from the gas permeability of thinner snow layer. These are also different compared to soil (according to porosity of snow) without the snow cover where free air diffusion coefficient is applicable.

*On page 14888 line 14ff the authors cite Rhee et al. (2006). But this study did not look at the processes but just looked at the different potential parameters which may explain their atmospheric findings. This is very misleading !

Answer:

Rhee et al. reference will be removed from the manuscript. Lallo et al. (2008) reference

will be added to manuscript.

*It would be important to know the water table depth at the sampling site, see also comments on Section 3.2.

Answer:

A suitable data for water table depth is not available for the sampling site.

*Page 14889 lines 5ff: Again I cannot believe that rain “seals” the upper surface pores for much longer than a few hours, and this time should not be relevant to the top-down estimates.

Answer:

The word “seal” is too strong word and is also rephrased in the manuscript. Rain precipitation increases the soil water content. According to Nazaroff (1991), radon diffusion coefficient is a function of soil water saturation. Radon diffusion coefficient is a gently decreasing slope until 0.5 and after that more steeply decreasing. The hindered gas permeation is due to increased amount of water-filled porosity in the soil.

*Certainly, rain increases soil moisture and decreases free soil volume, and thus decreases radon exhalation rate, but the arguments concerning the correlations with rain itself seem to be too strong and not really justified from the findings of this study.

Answer:

Corresponding sentences will be rephrased as explained in the previous answer.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 14873, 2009.

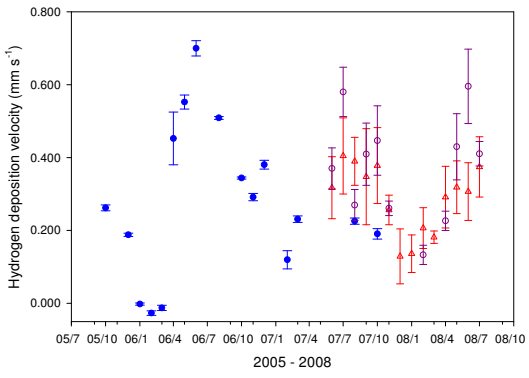

Fig. 1. Mean hydrogen depositon velocity (vd) values from the chamber measurements, and using radon tracer and two-dimensional model. vd values are presented as mean ± standard error of the mean (SE).

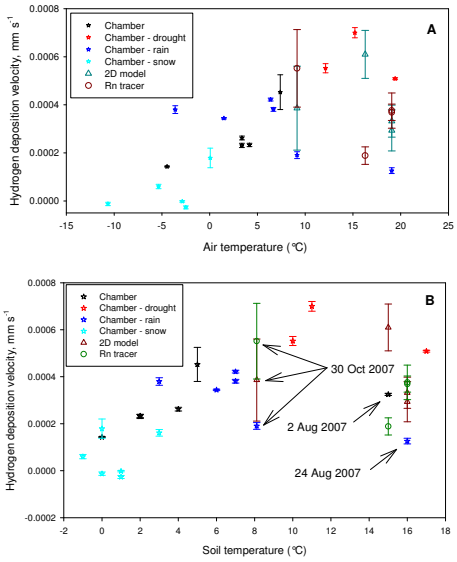

Fig. 2. 'Fig 3 (a) The dependency of measured and modeled hydrogen deposition values (a) to air (b) to soil temperature ...'

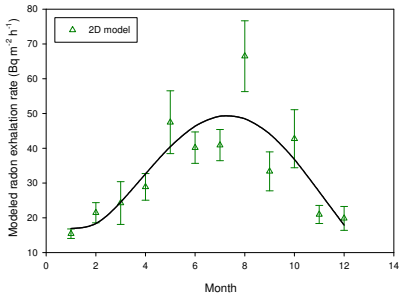

Fig. 3. 'Fig. 5 Two-dimensional model results for 222Rn exhalation rate jRn'