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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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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:

1. 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. The same is true for the OH source/sink reference, here also earlier publications other than Simmonds et al. (2000) need to be cited. The Schmitt et al. reference was published in 2009 not 2008.

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, 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.

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. 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".

222Radon observations: The same intake as for H2 is used for the radon daughter

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measurements: Did the authors check loss of aerosols in the intake line? 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). How does the uncertainty of the assumption of *no disequilibrium* translate into the uncertainty or systematic bias of the 222Radon flux?

2.3. Analysis of results

Eq. (1) allows also 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.

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 ?

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 ? What is the purpose of the 5m surface layer? What "adjustments were made to boundary layer and profiles"? A reference should be given for the software Fluent. Which local observations are available to provide the boundary conditions? 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.

3. Results

Figure 3A: The measurements under exceptional weather conditions should be given

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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)? Lines 24-26 on page 14882 are not clear.

Fig. 4 is not really helpful and the respective section (upper part of page 14883) is confusing. For clarification I would suggest to replace this figure by a plot which shows all chamber measurements vs. time together with the rain events. 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).

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. 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.

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). Possibly (also) other parameters such as

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

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

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).

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)? 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

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findings. This is very misleading !

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

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