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Interactive comment on "The overwhelming role of soils in the global atmospheric hydrogen cycle" *by* T. S. Rhee et al.

T. S. Rhee et al.

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We thank the reviewer for the careful reading and the comments on our paper. The reviewer numerates literature (including a manuscript submitted) that deals with estimates of the H_2 uptake by soils. As the reviewer pointed out, our estimate of soil sink is within the values mentioned literature above. Since the range of those estimates is extremely wide, of course our estimate complies. The cardinal point is that our estimate is based on new measurements and using a new method. Independent estimates are essential, particularly since soils are extremely complex and heterogeneous. The reviewer is concerned about the temporal and spatial resolution of the data, the inferred large photochemical production of H_2, and the isotopic signature of H_2 from biomass burning determined from this study. We reply to these 3 points below:

1. As the reviewer questioned whether the stations of Mauna Loa and Cape Grim represent the background air in the NH and SH, respectively, we add in Figure 2 the hemispheric mean values for the year 2000 as provided by Paul Novelli for the NOAA/CMDL dataset (see Figure 2). There is not much difference between these two sets (the station data and the mean values), in particular in the NH. Furthermore, apart from what the reviewer pointed out, the amplitude of the sinusoidal curve from the NH mean values is not larger than the value from our data. Although we attempted to find the seasonal amplitudes in the references mentioned by the reviewer, we couldn't. Novelli et al. (1999) only stated the amplitude of seasonal H_2 cycle in the NH is 3 times larger than in the SH, which we do not see in the hemispheric mean values for 2000 (Figure 2).
The latitudinal ranges in the NH covered in this study are from 10°N to 50°N, lacking high latitudes. This leads the reviewer to be concerned because of the large fraction of land in the high latitudes. It is generally accepted that the timescale of meridional mixing within the hemisphere is about 1 - 2 month and that of zonal mixing is about 2 weeks. Unless a strong source or sink are located in a specific region, we do not expect a large gradient of H_2. Indeed, Hauglustaine and Ehhalt (2002) showed in a 3-D model result no gradient of H_2 in January and a little gradient (about 10 - 20 ppb) in July in the free troposphere. A strong gradient was found near the PBL in July, which was also observed in inner Siberia (Lloyd et al., 2002). Our sampling altitude is located at 9-12 km in the free troposphere. As stated in the introduction, this high sampling altitude has the effect of excluding sampling biases that take place when sampling inside the PBL.

2. Photochemical production of H_2 in the atmosphere is the largest source in the H_2 budget. However its uncertainty is substantial because the yield of H_2 from CH_2O is a

function of several parameters which may vary spatially and temporally, and the atmospheric burden and lifetime of non-methane volatile organic compounds (NMVOCs) are poorly understood. In addition, the chemical yields of CH_2O from these NMVOCs are unknown. Under these circumstances, we argued that photochemical production from NMVOCs would fill the difference between our estimate and the value by Novelli et al. (1999) on the basis of the recent finding of large quantities of oxygenated volatile organic compounds (OVOCs) by Singh et al. (2001; 2004). The direct emission rate (excluding airborne production from hydrocarbon oxidation) of these OVOCs ranges 100 - 400 Tg C/yr, which is slightly lower than isoprene emissions. However, note that, as Singh et al. (2004) stressed, the estimates of OVOCs emissions are poorly confined at present. Although we do not have a firm value of H_2 production from these OVOCs due to the lack of the yield of H_2 from them, their contribution to the H_2 budget should not be ignorable. We expect that photochemical oxidation of the OVOCs also contributes to CO budget, too.

3. We are preparing a separate manuscript to describe a persistent biomass burning emissions in the northern Africa using a large body of data including the isotopic compositions of CO. Since the main objective of this paper is not the discussion on biomass burning impact, we did not present the data of ^{13}CO, C^{18}O, and ^{14}CO in this paper. However, Mühle et al. (2002) has already shown the capture of large biomass burning impact to the flight altitude in July applying the emission ratios of non-methane hydrocarbons and the isotopic ratios of CO, supporting our argument.
Derivation of the characteristic δD value of H_2 from biomass burning is based on the isotope mass balance as described in equations (2) and (3). This signature does not change along the dilution with the background air and is not a subject of fractionation, either. When the δD value of H_2 from fire is -290 per mil and that of the background air is 135 per mil, the biomass burning signature is -290 per mil and what to be observed will be between these two values depending on the dilution factor. We do not understand the reviewer's point how the stable isotope ratios of CO could be used

to estimate mixing in the upper troposphere. Andreae and Merlet (2001) present the emission factors in their Table 1 for the characteristic fire types and we derived the emission ratios from the table. As mentioned in the text, the H_2 mixing ratios we observed are the result from the combination of emissions from biomass burning and destruction on soil surfaces while CO rarely reacts on the soil surface (slower bacterial uptake in soils). Therefore, ER for H_2 cannot be determined from the measurements. We note that following the terminology defined by Andreae and Merlet (2001), the term "enhancement ratio" in the text and figure captions is changed to emission ratio.

Other comments:

Abstract: I question the statement 'The large airborne production of H2 helps explain the fairly homogeneous distribution in the troposphere'. The H2 time series determined by CSIRO and NOAA show considerable spatial and temporal variations.

We intended in this sentence to emphasize the substantial role of photochemical production in H_2 budget compared with other chemicals most of which have their primary sources on the surface. Several papers reported the horizontally and vertically homogeneous distribution of H_2 (e.g., Ehhalt et al., 1977; Schmidt, 1978). The similar seasonality of CARIBIC and NOAA/CMDL observations also supports this (see Figure 2). Of course there are spatial and temporal variations in time series with their magnitude depending on the locations of sampling stations.

P. 11216, 5. Note that both NH and SH δD are used in this study. line 6. It is stated that a 'better constrained estimate' is determined in this work. This is debatable. Simply say 'independent estimate'.

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We stated the phrase 'better constrained estimate' because both the spatial coverage of our observation is larger than the previous spot measurements of soil uptake rate and two independent isotope species were used to constrain soil sinks.

P.11217, 15. 'effect' should be 'effects'

Agreed and corrected.

P.11218, section 2, Methods. Samples were collected during the flight and transferred to ss canisters later. What materials were used in the original collection? How long were the samples stored before analysis? How were the containers tested for stability of H2 and HD?

The original canisters are large volume stainless steel tanks, and the air was processed within a week after the flight. Due to their large volume (21 L), and high pressure (17 bar), the surface/gas ratio is much more favorable than in systems used elsewhere. The smaller canisters are made of electro-polished stainless steel. The samples had been stored for 2 - 3 years in a freezer at -25C. We were not able to test the stability of H_2 and HD for this period because no instrument was available yet. However, since any substantial deviation of H_2 mixing ratio or the δD value was not observed (see Table 2), we do not expect significant contamination during storage.

P.11219, 0-14. This section describes the binning of the data into equatorial, NH and SH subsets. It is unclear if the equatorial subset was included in the NH and SH averages upon which the bulk of the discussion revolves. It would be helpful if another column was added to Table 2 indicting the results used in the analysis.

The binning of the data is indicated in Figure 1 with different colors for different segments of regions.

P.11219, 0-7, Figure 1a. Although the upper atmosphere measurements extend from 30S to 50N, data used in the analysis apparently ranges from 30S to 32N, 42N and 38N (May, July and December respectively). This should be stated explicitly (see comment above).

As mentioned above, the sampling locations and binning of the NH and SH segments are shown in Figure 1.

The authors state (p. 11219, 14-24) "The H2 mixing ratios (determined in the study) show almost the same seasonal cycle as Mauna Loa and Cape Grim ... The agreement in both phase and magnitude of the seasonal cycle confirm the spatial homogeneity of H2..." However, the curves in Figure 1b show significant differences in both timing and magnitude of the seasonal maximum in both hemispheres. The mean H2 from the many NOAA monitoring locations would provide a better reference for comparison to the data reported here.

The hemispheric mean H_2 calculated by P. Novelli (personal communication) is now included in Figure 2.

P. 11220, 20-28. The suggestion that the NH seasonal cycle is dominated by ice cover requires further examination. The annual extent of snow cover in the NH is highly variable, yet has been decreasing over the past decade. Is the variability and trend in snow observed in the CSIRO and NOAA time series at high latitude stations? How can snow cover be separated from temperature?

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This is an interesting point, but to our knowledge no interpretation has been made yet on the relation between CSIRO or NOAA time series of H_2 and the annual variation of the snow-cover extent. We do not know how to separate the snow cover from (soil) temperature, but the snow cover extent should be a rough indicator for soil temperature variation.

P. 11221-11222 Section 4.2. Equation (1) uses the seasonal maximum and minimum H2 and δD to determine the percentage total NH sink due to soil uptake. This is then used to compute the absolute sink. I questioned above the validity of the seasonal cycles derived from the sinusoidal fit. If the simulated seasonal fit to the limited data does not represent the atmosphere, then the calculated sink is incorrect.

We show that the sinusoidal fits of the H_2 mixing ratios are very similar to the seasonal variations observed by NOAA/CMDL, suggesting that a potential bias of our estimate should be minimal.

P. 11226, 18. ER is undefined. The definition on line 23 should be given here. Eq. (4).

Agreed and corrected

Why is the ratio of [H2]ob/[CO]bb used rather than [H2]bb/[CO]bb? Shouldn't ? be ?bb.

In view of derivation of the equation, the equation is correct because in Eq. (4) the emission ratio (ER) is introduced, which is not in (2) and (3). Since we do not know [H2]bb, we introduced ER in Eq. (4).

P. 11228, 5. The statement 'observations over the past decade show no significant variation or trend in either hemisphere' is not quite correct. Both the CSIRO and NOAA time series show considerable inter-annual variation in both the seasonal maximum and minimum.

This may or may not be true. According to Novelli et al. (1999) there is no considerable variation except the years of 1991 and 1992. In addition, the authors also mentioned the calibration issue at evaluating the inter-annual variation between NOAA and CSIRO.

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