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

Anonymous Referee #2

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In the paper "The overwhelming role of soils in the global atmospheric hydrogen cycle", Rhee, Brenninkmeijer and Rockmann use measurements of H2 and its deuterium isotope (HD) to study the global hydrogen budget. Previous works have shown greater H2 mixing ratios in the Southern Hemisphere (SH) relative to the Northern Hemisphere (NH); and there are four major sources (fossil fuel combustion, biomass burning, methane oxidation and oxidation of other volatile organic compounds). Two major sinks are recognized - oxidation by OH and destruction in soils. The South to North gradient has been attributed to strong uptake by soils on northern continents. Reaction with OH is believed responsible for 20-25 percent of the total sink, with soils accounting for the balance.

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In this work air samples were collected from the upper troposphere between Germany and Southern Africa in May, July and December 2000. H2 and D/H were measured by continuous-flow mass spectrometry. The authors conclude that H2 uptake by soils accounts for 82 percent of the global sink. This estimate is not new. It falls within those previously reported based upon 1) emission estimates and tropospheric chemistry (Seiler and Conrad, 1987; Warneck 1988; Novelli et al., 1999; Hauglustaine and Ehhalt, 2002), 2) measurements of H2 and ?D (Gerst and Quay 2001, Rahn at al. 2003), 3) inverse modeling of NOAA/CMDL and AGAGE data (AGAGE, manuscript submitted). Only Ehhalt (1999) suggests smaller soil uptake in the global sink. Rhee at al. assert the global soil flux is equivalent to 88 (11) Tg CO a-1 - considerable greater than recent estimates by Novelli, Ehhalt, and Hauglustaine and Ehhalt, but within the uncertainties of Seiler and Conrad and Warneck. In light of previous research this report either adds to the uncertainty or clarifies the budget, depending upon one's point of view. Still, the authors do make several unique conclusions: the NH seasonal cycle is driven by the seasonal variation in snow cover, the isotopic signature of biomass burning is much heavier than previously recognized, and the SH winter maximum is controlled by NH-SH exchange.

The data presented in this paper are clearly of high quality and add to the limited measurements of atmospheric D/H. Additional measurements of H2 and ?D by this group are encouraged. However, the data presented here are sparse and related issues need to be addressed.

1) The work is based upon results of three inter-hemispheric flights made during May, July and December 2000. Measurements in the troposphere span 30S to 40N along 6-16E, and the data are discussed in terms of NH and SH averages. Measurements made in May, July and December were used to define the seasonal cycle using a sinusoidal fit. The conclusions depend strongly upon how well the limited data set and curve represent tropospheric H2 and HD. The approach is validated by comparing the curve to the seasonal cycles at Mauna Loa and Cape Grim, sites presumed to rep-

resent the NH and SH, respectively. They probably do not. The seasonal amplitudes reported in Table 3 for the NH and SH (18.2 ppb and 8 ppb, respectively) are smaller than those reported by NOAA and CSIRO (see Novelli et al., Langenfelds et al, 2002).

The latitudinal extent of the data is also a concern, particularly in the NH. Much of the arable northern land mass is between 40N and 70N and the strongest H2 seasonal cycle is found in the high latitudes of the NH. The tropospheric data extend to 40 N. I suspect if high northern hemisphere seasonal cycle was included it would further increase their estimate of the fractional soil sink. The temporal and spatial density of the data limit the conclusions that can be made.

2) Rhee et al. determine that soil uptake accounts for 88 Tg H2 loss a-1 and photochemical destruction = 19 Tg a-1. H2 is in quasi-steady-state thus this sink must be balanced by a 107 Tg a-1 source. The authors conclude from the measured ?D that 64 Tg H2 a-1 is due to photochemical oxidation (Table 1). Photochemical production in the SH = 23 Tg a-1, most of which is from CH4 oxidation. Forty one Tg are produced in the NH from CH4 and other VOCs. As CH4 oxidation is similar in both hemispheres, production of H2 from NH NMVOCs must be 20 Tg a-1. Over the past decade a better understanding of the emissions and the photochemistry and heterogeneous chemistry of NMVOCS indicates smaller yields of H2 and CO. A H2 NMVOC source equivalent to that of CH4 is difficult to reconcile. The authors must discuss these new findings in light of the old. How can the larger photochemical production of H2 be explained in terms of CH4 and NMVOC emissions and oxidation? Is this greater H2 source consistent with the budgets of CO and CH4?

3) In section 4.5 Rhee et al. determine the ?D from biomass burning. The authors contend that samples of high CO represent air parcels containing emissions from surface fires. They state the 13CO, C18O and 14CO in the samples confirm this. These data should be presented and discussed further as they are crucial to the author's argument. The measured ?D is accepted as representing fractionation during burning and suggest much smaller fractionation from biomass burning than previously reported (-90

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per mil compared to -290 per mil). CO mixing ratios originating from burning would be much greater than 200 ppb, therefore the air parcel must have undergone significant mixing with cleaner air before reaching the upper troposphere and the H2 signature would have been diluted. Emissions from fires with ?D on the order of -290 per mil, when mixed with background air of +135 per mil, would suggest a biomass burning signature much heavier. Perhaps the stable isotopes of CO can be used to estimate the effect of mixing on the upper troposphere ?D. I found the text description and caption of Figure 3a confusing. How were ER (ppb ppb-1, H2 excess/CO excess) taken from Andreae and Merlet when no mixing ratios were given in that paper. Why weren't ER calculated from the measurements?

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.

P. 11216, 5. Note that both NH and SH ?D 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'.

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

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?

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.

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).

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.

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?

P. 11221-11222 Section 4.2. Equation (1) uses the seasonal maximum and minimum H2 and ?D 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.

P. 11226, 18. ER is undefined. The definition on line 23 should be given here. Eq. (4). Why is the ratio of [H2]ob/[CO]bb used rather than [H2]bb/[CO]bb? Shouldn't ? be ?bb.

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.

Summary statement. The H2 and ?D measurements provided in this paper are unique. They add to a very limited data set. Unfortunately I feel the data are insufficient to draw conclusions as to the global H2 cycle and budget. The authors not sufficiently address, and provide reasonable explanations, for the differences between their new results and the large body of previous work.

Citations:

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11215, 2005.

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