

Author's Response to the comments of Anonymous Referee #2

Responses to the specific comments:

“Page 10089, Line 5: Include Xiao et al. (2007) J. Geophys. Res., 112, D07303.”

We initially did not include all the literature estimates of the H₂ budget, since this paper focuses on the isotopic composition of H₂, and not so much on all the different budget estimates that were made. We agree, however, that those papers should be cited to guide the interested reader to them. Therefore, we will add Xiao et al. (2007), as well as Hauglustaine and Ehhalt (2002), Sanderson et al. (2003), and Yashiro et al. (2011) to the list of references on line 5, but we will remove Novelli et al. (1999) and Ehhalt and Rohrer (2009) from Table 1 for brevity.

“Page 10090, Line 1: Include Rhee et al. (2006b)”

We will remove the citations in line 1 altogether since all the works cited there are also, and more appropriately, cited in the paragraphs that follow.

“Page 10090, Line 4: I recommend omitting the bracket in “d(D)” in the equation and in the text following the convention of isotopic nomenclature.”

The $\delta(D, H_2)$ notation is recommended in a new (unpublished) draft of IUPAC on isotope nomenclature. In the rest of the paper, the “,H₂” is omitted because no confusion can occur when only molecular hydrogen is discussed. We agree that the brackets are not necessary either in this abbreviation, and we will omit them as well.

“Page 10090, Line 8: Cite literature for the value of RVSMOW”

We use a value of $(155.75 \pm 0.08) \times 10^6$ for RVSMOW, as in Gonfiantini et al. (1993) and De Wit et al. (1980). These references will be added to the paper.

“Page 10090, Line 23: Include Mar et al. (2007) J. Geophys. Res., 112, D19302.”

We will include Mar et al. (2007) in the list of citations on line 18.

“Page 10091, Line 14: It needs more information on how to treat inside of the glass flasks before dispatching for sampling, how to collect air sample, whether or not use a scrubber or a pump, etc. Have you checked any potential artifacts such as leaking or H₂ production inside the flask?”

The flask samples analyzed within this project are provided by three institutions (UHEI-IUP in Heidelberg, MPI-BGC in Jena and LSCE in Gif-sur Yvette) that run leading European trace gas monitoring programs. Air sampling strictly follows the established sampling protocols of these institutions. The final revised paper will include more details on the sampling procedures.

The used glass flasks with Kel-F stopcocks are known to be stable for a variety of trace gases (see Rothe et al. 2004). Extensive storage tests performed at the MPI-BGC in Jena in the framework of the EUROHYDROS project indicated that $m(H_2)$ is stable in flasks of this type. No long-term stability tests were performed for δD , but we consider it likely that if the flasks are stable for $m(H_2)$, they are also stable for δD .

Most flasks were covered with a black plastic hose, and all flasks were stored in closed metal boxes when not in use, minimizing photochemical production after sampling.

“Page 10093, Line 22: How did you determine the factor 1.064 and how did you apply it for correction of the original data?”

This factor was determined from the measurements of the mixtures of synthetic air with H₂ of known composition.

In the correction of the original data, it is assumed that the GC-IRMS system follows a linear response curve. Following this assumption, this factor is then used to inter- or extrapolate the corrected value starting from the 5-day moving average values for the reference gases on that day. This will be reformulated in the revised version.

“Page 10095 Line 4: Equation (2) considers only seasonality. Have you included an inter-annual trend function to fit the measurements?”

Given the still relatively short timeseries of $m(H_2)$ and δD from our measurements, it seems premature to investigate interannual changes quantitatively, and therefore we have not included an inter-annual trend in the fit function. Other institutes have produced longer time series (for $m(H_2)$), which are better suited for deriving interannual trends.

“Page 10095, Line 21: Not all sources are “deuterium-depleted”. Photochemically produced H₂ contains more deuterium than the ambient air (see Table 1). The authors should consider this in interpreting seasonal variations of δD and H₂ in the text.”

We do not think that the wording of this specific sentence implies that *all* sources are deuterium-depleted. This could however be stated more clearly. We will replace “deuterium-depleted” by “mainly deuterium-depleted”.

The net source in the NH is strongly depleted in D (see for example Price et al. (2007) or Pieterse et al. (2011)). Photochemically produced H₂ has an isotopic composition that is close to that of H₂ in ambient air. Therefore, photochemically produced H₂ in general does not have a large effect on δD of H₂. This is also shown in the TM5 model (Figure 8 in Pieterse et al. 2011).

“Page 10098, Line 10: How often have the air samples been taken in Mace Head? What

would be optimal time interval of sampling to pick up the full variability of δD and H₂?”

Here, “time interval” is intended to mean the three-year time period over which samples have been collected. To make this clearer “interval” will be replaced by “period”.

“Page 10098, Line 24: Conrad and Seiler (1980) reported that H₂ emission from N₂ fixation in soil is strong between April and June. However, time series of δD at Schauinsland station does not seem to show this seasonal variation although the authors speculated it. It needs explanation why the authors speculate.”

As written in the preceding paragraph in the paper, the seasonal variations observed in Schauinsland are not the same between 2007 and 2008/2009 and it is not easy to explain this observation. The source from nitrogen fixation is mentioned, since small contributions from this source could in principle have a large effect on δD , which may affect the local reservoir especially during the growing season. However, if this is a systematic effect, it should also occur each year. Therefore, the paragraph may appear a bit inconclusive, but we feel that it is adequate to at least mention this source.

“Page 10099, Line 12: Why do the maximum of H₂ and minimum of δD occur in summer rather than in spring, which is different from what is typically observed in the northern hemisphere? The maximum of dD was observed in winter not late summer or early autumn. Why is it so at Cape Verde? As shown in Fig. 7, the authors argued strong photochemical destruction of H₂ at Cape Verde (~70% of H₂ sink). However, it is hard to imagine that strong chemical destruction in winter rather than in summer, which needs clear explanation.”

We thank the referee for this insightful comment, which has led us to rephrase some of the argumentation around the Rayleigh fractionation plots. From the measurements, it

appears that, moving from Alert to Mace Head to Cape Verde, the cycles shift to later in the year. This can also be seen in the phases obtained from the cosine fits (Table 3). In response to this comment, we will discuss possible contributors in the revised version. It is possible that the seasonal cycle in Cape Verde is affected by seasonal variation in the sources (e.g. tropical biomass burning) or transport (interhemispheric exchange), in addition to the sink processes. Due to the dominant NNW wind direction (trade winds), Cape Verde receives much air from Mauretania and surrounding countries. The biomass burning season in this region is in winter, but we do not see the expected $m(\text{H}_2)$ increase and concomitant δD decrease in this season. Most interhemispheric mixing occurs in summer, when Cape Verde is close to the edge of the ITCZ. Increased transport from the SH should result in higher δD values (see Fig. 4(b)), but this is not observed. Therefore, we cannot identify individual source or transport signatures that cause the cycles in Cape Verde to be delayed with respect to the Alert cycles.

The approach of Rhee et al. (2006) has been derived to infer the relative sink strengths from the slope of the Rayleigh plot fit line to measurements. We apply this approach to the observations at Alert, Mace Head and Cape Verde, although it is not clear whether the seasonal variation at all three stations is similarly driven by the sink processes (and the phase shift observed indicates that this may not be the case). The formal application of the approach yields a surprisingly high relative fraction of the OH sink ($67\pm15\%$). Whereas this number may be an overestimate (due to the assumptions that sinks are the dominating factor), and the conclusion about this trends depends largely on one measurement station, the general trend towards a higher OH fraction with decreasing latitude is in accordance with expectations and model results (Figure 8 in Pieterse et al., 2011).

Therefore, our findings indicate that the soil sink fraction of 88% derived by Rhee et al. (2006) from a limited number of samples in the tropopause region is likely an overestimate. To investigate this further, it would be useful to analyze samples from subtropical northern latitudes, for example the Iberian Peninsula, the Canary Islands or Morocco.

These additional considerations are important for the conclusions that are drawn in section 3.3 and will be added to the paper.

“Page 10100, Line 1: Some literature pointed out that biomass burning in the southern hemisphere dominates seasonal variation of trace gases. For instance, Novelli et al. (1999) argued that seasonal variation of the southern hemispheric H_2 is driven by biomass burning. Gross et al. (1999) observed clear seasonal variation of CO at Amsterdam Island which was attributed to the emission of biomass burning. However, time series of δD here does not reveal the effect of biomass burning emission of H_2 . Why is it so?”

Indeed, no large seasonal cycle is seen in δD or $m(\text{H}_2)$ at Amsterdam Island. Other $m(\text{H}_2)$ time series from locations in the Indian Ocean, such as the timeseries from the Seychelles that is shown in Novelli et al. (1999), also show very small seasonal cycles. Yashiro et al. (2011) concluded from the timing of the $m(\text{H}_2)$ seasonal cycle that photochemical production is a dominant driver of the seasonality in $m(\text{H}_2)$ south of 30°S , which is in accordance with the conclusions that Rhee et al. (2006) drew from δD observations. Since the δD value of photochemically produced H_2 is close to ambient values, this does not cause a large seasonality in δD . The Amsterdam Island results are in agreement with these findings.

It is likely that some depleted H_2 from the spring maximum (July-October) in SH biomass burning reaches Amsterdam Island. That this does not lead to an observable seasonal depletion indicates that the depleting effect is offset by the enriching effect of photochemical H_2 destruction that likely takes place in summer. This discussion will be added to the revised paper.

“Page 10100, Line 19: In summer, photochemical destruction of H₂ can also occur as the authors ascribed it to the large amplitude of δD at Cape Verde. If so, δD should be high in austral summer which is not the case at Neumayer station. Why is it so?”

That δD at Neumayer shows so little variation, despite the expected enrichment from the H₂ destruction processes, means that a process that depletes the H₂ reservoir in D compensates this enrichment. The budget calculations in Pieterse et al. (2011) suggest that a seasonality in emissions and transport of depleted H₂ from lower latitudes are significant contributors to the δD changes in the extratropical SH. This will be reformulated in the revised version.

Page 10100, Line 23: Does the horizontal transport of air mass from the low latitude take place all the year? Or does it happen in summer only?

Pieterse et al. (2011) estimate that the horizontal transport of H₂ happens all year, but actually has a minimum in December for latitudes south of 30° S. This will be mentioned and the related argumentation will be rephrased accordingly in the revised manuscript

“Page 10101, Line 2: Describe what stand for DJF, MAM, JJA, and SON.”

This explanation will be added to the text.

“Page 10101, Line 26: Replace “Atlantic” with “Pacific”. “

This will be corrected.

“Page 10106, Line 14: Does “anthropogenic combustion source” mean fossil fuel combustion only, or fossil fuel combustion and biomass burning together? The δD minimum was observed at Cape Verde in summer season which the authors attributed to the emission of anthropogenic source. This argument needs to show supporting evidence.”

It was intended to mean fossil fuel combustion only. To make that clearer, “anthropogenic combustion source” will be replaced by “anthropogenic fossil fuel combustion source”.

“The δD minimum” will be replaced by “The smallest yearly average of δD ”.

“Page 10115, Fig. 2: Scale of y-axis needs to be blown up. It is very hard to distinguish symbols. How big is the error bar in Figure 2? It looks smaller than that in Figure 4 of Pieterse et al. (2011) in spite of the same data.”

The resolution of the figures is large enough to see the symbols after zooming in, but we agree that ideally the symbols should be distinguishable on an A4 printout of the paper. The y-axis scale is quite small as a result of our choice to plot all data on the same scale to allow easy comparison. We will revise this figure for the final version of the paper for better readability.

The error bar plotted here is the estimated standard error in the measurements, which was determined to be 4.5 %. In the (Pieterse et al. 2011) figure, the error bars are based on the total variation in the data in the latitude bin, including the seasonal variation. The (Pieterse et al. 2011) error bars are therefore more representative of the natural variation in δD , whereas the error bars in this paper are solely an estimate of measurement error.

“Page 10118, Fig. 5: Add standard deviation of the intercept.”

The standard error of the intercept will be added to the figure.

“Page 10119, Fig. 6: It is very hard to match the month and symbol. It needs to make plot clearly.”

The figure will be revised for the final version for better readability.

References

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