

## ***Author's Response to the comments of Anonymous Referee #1***

### **Responses to the specific comments:**

“Page 10091, line 14: Could you provide more information about sampling? Did you preevacuate the glass flask and fill air sample or did you flush the flask several times with air sample? What's the initial pressure in the glass flasks after the sampling? Did you wrap the flask with something such as aluminum foil to prevent photochemical production since  $\text{CH}_4/\text{VOC}$  oxidation is  $\text{H}_2$  source?”

**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. The final revised paper will include more details on the sampling procedures.**

**The initial pressure in the glass flasks was generally between 1.5 and 2 bar absolute pressure. Most flasks were covered with a black shrink hose, and all flasks were stored in closed metal boxes when not in use, minimizing photochemical production after sampling.**

“Page 10092, line 1: Have you tested the stability of  $\text{H}_2$  in the glass flask since “several months passed between sample collection and isotope analysis”? What's the initial pressure in the glass flasks before isotope analysis?”

**These 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  $\text{H}_2$  is stable in flasks of this type. No long-term stability tests were performed for  $\delta\text{D}$ , but we consider it likely that if the flasks are stable for  $\text{H}_2$ , they are also stable for  $\delta\text{D}$ .**

**The pressure in the flasks before isotope analysis was usually a little lower than the initial pressure after sampling, due to the analysis with reduction gas analyzers at the partner institutes.**

“Page 10093, line 14: What's the  $\delta\text{D}$  value of the blank? If it is very different from that of the air samples, the 4% blank signal will have a significant impact on the results. Is this blank always taken into account and subtracted from the air sample signal?”

**The peak area of the blank measurements was used in the calculations of the sample  $\text{H}_2$  mixing ratios (that were not discussed in the paper, but used for measurement quality assessment). Unfortunately, due to the very small peak area of the blank peak, the  $\delta\text{D}$  value of the blank could not be determined reliably. Since the blank  $\delta\text{D}$  value is not known, it cannot be taken into account in the calculation of sample  $\delta\text{D}$  values. The contribution of the blank signal to the random scatter is already included in the 4.5‰ reproducibility that is obtained for repeated measurements of the laboratory reference bottle, as stated in the paper. However, the blank may cause a systematic error that is not quantified. This information will be added in the revised version of the paper.**

“Page 10094, line 18: Is there any criteria used to determine the outliers instead of “visual inspection”? Sometimes special local events such as wildfires could give a very strong signal.”

**For some observations at the northern mid-latitude stations that seemed to deviate from observations in other years (see section on Mace Head), we have looked into back-trajectory calculations to determine the origin of air parcels in the samples that appear to be outliers, but no clear conclusions could be derived from this analysis. Therefore, the outliers were selected by visual inspection only.**

“Page 10095, line 22: VOC oxidation also has a seasonal variation. Will this contribute the seasonal variations of the signals at Alert except for the combustion source and removal processes? For example, in winter, H<sub>2</sub> accumulates from depleted combustion source and contribution from VOC oxidation (enriched source) is very small, thus leading to the H<sub>2</sub> peak and  $\delta D$  minimum in spring.”

**Although the precise isotopic composition of H<sub>2</sub> from tropospheric chemical production is not well-known, most recent studies conclude that it is not much different from the isotopic composition of ambient H<sub>2</sub>. Therefore, it does not contribute much to isotope variations, whereas it can be relevant for the mixing ratio changes (see e.g. Pieterse et al., 2011).**

“Page 10099, line 21-22: I am not sure if it is appropriate to compare the amplitude in the harmonic fit at Cape Verde with that at Mace Head and Alert. Since it is pointed out that “This is in contrast to the TM5 model results (Pieterse et al., 2011) where the seasonal variation in  $\delta D$  at Cape Verde is somewhat smaller than for Mace Head and Alert” and “The harmonic fit does not seem to underestimate the amplitudes as it does for the Alert and Mace Head datasets”, it seems more reasonable to compare the original data instead of the harmonic fits. From the original data and on visual inspection, the seasonal variability of  $\delta D$  at Cape Verde is not larger than that at Mace Head or Alert. The interannual variations at Mace Head and Alert indicate comparison of original data is more reasonable.”

**We agree that in the case of Cape Verde comparing the original data is more appropriate. This will be changed in the revised manuscript.**

“Page 10100, line 1: Can you explain why the trend of mixing ratio and  $\delta D$  of H<sub>2</sub> at Amsterdam Island is like that? Is it related to sources, sinks, or transport?”

**The time series from Amsterdam Island shows only a very weak cycle in  $m(H_2)$ . This may be due to the remoteness of this location; it is far from densely populated areas where anthropogenic H<sub>2</sub> is produced, and far away from large land areas where deposition to soil can occur (in fact, there is little snow-free soil surface in the SH overall). Other  $m(H_2)$  timeseries 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  $m(H_2)$  seasonal cycle that photochemical production is a dominant driver of the seasonality in  $m(H_2)$  south of 30° S, which is in accordance with the conclusions that Rhee et al. (2006) drew from  $\delta D$  observations. Since the  $\delta D$  value of photochemically produced H<sub>2</sub> is close to ambient values, this does not cause a large seasonality in  $\delta D$ . Nonetheless, in austral summer photochemical H<sub>2</sub> destruction will occur, with a D-enriching effect on the reservoir. That we see no seasonal cycle in  $\delta D$  probably means that a D-depleting process compensates this enrichment. Transport of depleted H<sub>2</sub> from lower latitudes (from tropical biomass burning in SH spring and interhemispheric exchange) is a likely explanation. This will be reformulated in the revised version.**

“Page 10105, line 6: Can you define “ $\alpha_{app}$ ”?”

**We will add the following sentence before “To make...” on page 10103 line 6: “This “apparent” fractionation factor does not quantify the inherent isotope fractionation in one single reaction, but is calculated from atmospheric data collected in a complex situation that involves more than one sink reaction, as well as other processes such as contributions from sources and mixing, and we denote this apparent fractionation factor by  $\alpha_{app}$ .”**

**References:**

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