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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emission ratio and isotopic signatures of molecular hydrogen emissions from tropical biomass burning" *by* F. A. Haumann et al.

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We thank the anonymous Referee 2 for the positive review of our manuscript and the constructive remarks. Please find our responses to his or her comments below:

Referee 2: It might help to have a slightly more detailed assessment of the stability of CO and H_2 in the flasks, which were kept for up to 300 days. While such delays are normal in all labs, they can have significant effects and the point needs to be treated at a little more length.

Response: We agree that some more information would be helpful. We have already

mentioned the stability of CO and its effect on our results (p. 11219 | 12). Detailed information is provided by Andreae et al. (2012). Additionally, we have added the following details (p. 11219 | 1, before "Flask analysis results [...]"):

→ Between the time of sampling and the measurements the samples were kept in 1 l borosilicate 3.3 glass flasks which were sealed with PCTFE valves (Batenburg et al. 2011; Andreae et al. 2012). In order to avoid any photochemical production of H_2, the flasks were enclosed by black flexible tubes and stored in closed metal boxes. The stabilities of several species were tested at the MPI-BGC Gaslab. Most of the species showed no significant drift except for CO which increased by 2.6 to 6.5 ppb during the storage period (Andreae et al., 2012).

Referee 2: How linear is the RGA in the range of the high end sample that is a significant drive to the Keeling plot?

Response: Although a clear biomass burning signature is evident from the samples, H_2 and CO mole fractions are not extremely high in these aircraft samples. CO mole fractions range between about 82 and 317 ppb (one sample with 524 ppb) for our flasks, and H_2 mole fractions between about 475 and 579 ppb (one sample with 666 ppb). Therefore, all flasks are within the calibrated range of the RGA used at MPI-BGC for these analyses, where the non-linearity was explicitly corrected for by a suite of reference gases. We have added the following (p. 11219 | 20):

→ The range of the H_2 and CO mixing ratios in the samples that we analyse in this study is within the calibrated range of the RGA and the non-linearity was explicitly corrected for by a suite of reference gases.

Referee 2: I've probably missed it in the text but are the data to be deposited publicly somewhere?

Response: Yes, we will make the mixing ratios and H_2 isotopic composition available. We have added the following sentence (p. 11217 | 13):

→ The CO and H_2 mixing ratios as well as the H_2 isotope data used for our analysis in this study are available in the supplementary material.

Referee 2: 1. It is interesting there is no correlation between H_2 and CH_4 – this is presumably in the dry season and it will be interesting to consider the results of the wet season flights. Note: my experience of tropical fires and wetlands is based on Africa, not Amazonia, and my travel to South America is limited to a brief trip to Venezuela, so the comments here are those of an interested outsider, not from direct experience.

Response: We also analysed some of the wet season samples and did not find a biomass-burning signal. Consequently, we do not include these samples here. For a detailed analysis of methane sources and sinks during the BARCA campaign the reader is referred to the study by Beck et al. (2012). Our interpretation that other sources and sinks influence the methane mixing ratio of the considered samples (p. 11226 | 1-12) is consistent with the findings by Beck et al. (2012).

Referee 2: 2. page 11224 – my observation of large grassfires in Africa in dry season is that the fires frequently pierce the dry season inversion and plume upwards to >1000m above ground level – indeed they can often be smelled at regional passenger jet altitude. But in the quiet weather of the dry season this is more a consequence of the natural upward pluming of the fire itself, making its own chimney which pierces the inversion, rather than being driven by the daily mixing of the broader convective mixed boundary layer during diurnal afternoon heating.

Response: In the manuscript we argue that probably both the normal convection and the heat from the fires cause such high rising plumes. It is beyond the scope of this paper to test which of these mechanisms is responsible for the high reaching signal. The fact that natural convection occurs at this time of the year (end of the dry season) is supported by the cited studies by Fu et al. (1999) and Fu and Li (2004).

→ We reformulated p. 11224 | 2-9 to make this clearer: In contrast, the source signal from the vegetation fires can reach high up in the atmosphere due to convection. This

high uplift of air masses influenced by the biomass-burning source is caused either by the heat produced by these extensive fires themselves, by natural convection occurring at this time of the year, or by a combination of these two effects. During November and December – at the end of the dry season – the atmospheric stratification over the Amazon basin is mostly unstable and frequent convection is very likely to occur (Fu et al., 1999; Fu and Li, 2004). Also the circulation pattern shown in Fig. 1a, that is dominantly easterly, suggests a transition period to the wet season and favourable conditions for convection.

→ We also reformulated p. 11233 | 1-2: In contrast, the strong convection induced by the heat from the fires and the naturally unstable boundary layer results in high-reaching biomass-burning plumes.

Referee 2: 3. page 11226. Rainforest?? – is this really closed canopy rainforest fire? Surely these emissions are from grass fires dominantly? C4, not C3 plants. The figures seem to show fires in the areas that are either dominantly savanna or wholly or partly cleared ex-forest, rather than in the rainforest proper. What proportion of the fire pixels are in virgin closed canopy forest?

Response: Thank you very much for pointing this out. From our data, we cannot derive the plant type or even fractions of different plant types that burned in these fires. Most of the samples were collected along the Amazon basin (Fig. 1b), where rainforest (C3 plants) is the major vegetation type (Saatchi et al. 2007, Simon et al. 2009), but the biomass-burning plumes may indeed be influenced by air masses advected from savanna areas (C4 plants) that dominate the south-eastern part of the domain. This has been clarified in the revised manuscript (see below).

Referee 2: Could the use of wind vectors be explained in a little more detail in Fig. 1? In Fig 1a is the red mainly in the grassland, not the closed-canopy forest? I'm not fully clear how the red patterns in the box of Fig 1a scale across to the rather different distribution pattern in Fig 1b – can this be explained in a little more detail?

Response: The ECMWF ERA-Interim 800 hPa wind vectors illustrate the large-scale circulation patterns in the sampling region at that time of the year. Air masses are clearly advected from the east or north-east over the locations where the samples were collected. Thus, we expect that samples are mostly influenced by the fires to the east of the sampling locations. The area displayed in Fig. 1b is a zoom-region of the box indicated in Fig. 1a to better see the sampling locations (circles). The coloured patterns in Fig. 1b show exactly the same distribution as the coloured areas in Fig. 1a (since they were calculated from that distribution), but show the estimated H_2 surface emissions from these fires (a detailed description on how this is calculated is given by Kaiser et al. (2012)). Most samples were collected over the Amazon basin that is mostly rainforest (Saatchi et al., 2007; Simon et al., 2009). However, some of the area in the south-east of the displayed domain is savanna (Saatchi et al., 2007; Simon et al., 2009). This has probably only little influence on our samples when considering the circulation. We have made several changes for clarity:

→ Reformulated p. 11218 | 5-7: Further, the European Centre of Medium Range Weather Forecast (ECMWF) ERA-Interim reanalysis (Dee et al., 2011) 800 hPa-level mean wind vectors illustrate the large-scale circulation pattern. Easterly or north-easterly winds imply an advection of air masses from the major biomass-burning region over the interior of the continent and the sampling region. Figure 1b shows an enlargement of the box in Fig 1a. The coloured area in Fig. 1b shows the estimated H_2 emissions that are associated with the biomass burning. These GFASv1.0 H_2 emissions were retrieved by scaling the burned matter with emission factors from Andreae and Merlet (2001) for tropical rainforest (Kaiser et al., 2012).

→ Added/reformulated sentences on p. 11218 | 15-16 (after "[. . .] indicated by circles in Fig. 1b."): Black circles indicate high-altitude samples (above 1100 m a.s.l.) and white circles low-altitude samples (below 1100 m a.s.l.). They were all either collected directly in the wildfire region visible in Fig. 1 or down-wind of this region. The area where the samples were collected and the region to the east is mostly covered by

dense forest (Saatchi et al., 2007; Simon et al., 2009). Thus, we expect a biomass-burning influence mainly from C3 plants. However, in the south-eastern corner of the enlarged box in Fig. 1b the dominant vegetation cover is savanna grassland (Saatchi et al., 2007; Simon et al., 2009). This could have a small influence on some of the samples.

→ Added sentence in caption to Fig. 1 after "(b)": Enlargement of the box in (a).

Referee 2: 4. It might be interesting to use NOAA Ascension Island data as a background for the Amazonian Keeling plots, as all this air has come from the little-varying SE Trades that previously passed over Ascension. The transit time to South America is probably a few days so not much H_2 chemistry will occur before landfall (and which could be factored in to mixing ratios).

Response: In principle, this is a very useful approach, but unfortunately no δD(H_2) data are available from Ascension Island. So, we cannot use data from this station for the Keeling plots.

Referee 2: 5. page 11244 Fig 3 pink dot TM5 Region – is this -265 per mil (text implies -262)?

Response: Yes, the regression analysis through the sampled points of the TM5 region at about 1300 m a.s.l. results in a Keeling plot intercept of -265 ‰ (cf. figure legend). On the other hand, the model was forced at the surface with a biomass burning signature of -262 ‰ as described in the caption and in the text. We conclude from the very good agreement between these two numbers that we can indeed derive the isotope signature of the H_2 emitted from the fires from the samples at this altitude. We have changed the text to clarify:

→ Reformulated p. 11231 | 21-27: In the surface layer (blue line in Fig. 4f), the data points seem to carry a biomass-burning signature. However, the Keeling plot intercept is with -290 ‰ somewhat lower than the original source value of -262 ‰ that was

applied in the model. This discrepancy may be caused by interfering effects from the soil sink near the surface, for example. If we perform the Keeling plot analysis at higher model levels, the intercept increases towards the input value. At the sixth model level, the value (-265 ‰) is the closest to the input value (-262 ‰) and the correlation coefficient between δD_{bb} and the inverse H_2 mixing ratio is highest (cf. red line in Fig. 4f). This confirms that at this level the distortion of the biomass-burning signal by the soil uptake has nearly vanished completely and that the fixed input value for the biomass-burning emissions at the surface can be recovered at this altitude.

→ Reformulated caption of Fig. 3 (last two sentences): The pink points that show TM5 results at about 1300 m a.s.l. are from Fig. 4. Regression analysis for these points results in a δD_{bb} signature of -265 ‰ which is close to the model input value at the surface of -262 ‰ .

Referee 2: 6. page 11245 Fig 4. Intense green box at about 12S 55W in the heavily agricultural Mato Grosso state – is this cerrado grassland? – the area is now significantly deforested and a world-class producer of agricultural crops.

Response: It is important to note that the analysis done with the TM5 model in Fig. 4 is performed with data from a previous model run that uses emissions from the year 2003, as stated in the figure caption and the text. So, this is not the situation that we had during the BARCA-A campaign. In addition, the biomass-burning signature enforced in the model runs does not distinguish between plant functional types and is fixed at -262 ‰ . Therefore, the type of biomass that burns in the fires depicted in Fig. 4 has no influence on our results. The important point is that in the model we recover the input value for biomass burning at an altitude similar to our flask sampling altitude, as clarified in the answer to the previous comment. This suggests that the isotopic signature that we measure at this altitude is representative of the emission source, but does not allow investigating in more detail from which material the H_2 originated. We have added a sentence to make this clear (p. 11230 | 18, after "[. . .] (indicated by the green box)."):

→ Furthermore, it should be noticed that this region is at a different location to the sampling region (cf. Fig. 1b) with, probably, a very different vegetation cover (mixed grassland, secondary forest, and rainforest; Saatchi et al., 2007; Simon et al., 2009). However, this will not affect our results since the model does not distinguish C3 and C4 plants in terms of their δD signature, which has a fixed input value for biomass burning of -262 ‰ .

Referee 2: The most obvious general question is whether this the main bulk of the H_2 and D/H, and CO, signatures are from burning rainforest or burning grass and crop waste? Perhaps the grass may be in clearings in forest, but nevertheless is the main source C4 grass, not C3 trees?

Response: As we have stated above, we cannot distinguish between plant type (C3 or C4) from our data. According to Saatchi et al. (2007) and Simon et al. (2009), the area where the samples were collected and the region to the east is mostly covered by dense forest. However, in the south-eastern corner of the enlarged box in Fig. 1b the dominant vegetation cover is savanna grassland (Saatchi et al., 2007; Simon et al., 2009). Fortunately, the bulk deuterium content is not very different between C3 and C4/CAM plants, with slightly (about 20 ‰) lower values for C3 plants (Leaney et al., 1985; Vigano et al., 2010). We expect that the isotopic composition of H_2 from biomass burning should also be similar between these plant types. The reported δD difference between "pure" C3 and C4 plants of about 20 ‰ is within the error estimate of ± 41 ‰ for fires given in our study. Overall, we think that deviations related to the plant type (Leaney et al., 1985; Vigano et al., 2009, 2010) and to the precipitation or combustion-efficiency effects (Röckmann et al., 2010a) are within the uncertainty range that we provide. Therefore, the reported value should be a robust estimate for δD of H_2 from biomass burning in the Amazon region. We also discuss in detail in the manuscript how our values compare to other estimates.

→ We have reformulated the paragraph on p. 11229 | 1-7: The regional δD_{bb} depends mainly on the latitude due the variations of δD in the precipitation, on the combustion

efficiency, and the plant type. The precipitation effect leads to an enriched δD_{bb} in the tropics compared to the global mean value. The combustion efficiency is extremely variable between different ecosystems, seasons, primary and secondary forests, and natural and anthropogenic fires (Seiler and Crutzen, 1980). It is determined (among other factors) by the availability of oxygen and the temperature of the combustion process (Röckmann et al., 2010a). In terms of plant type, C3 plants are depleted in δD compared to C4 plants (Leaney et al., 1985; Vigano et al., 2009, 2010).

→ We have moved the paragraph p. 11229 | 8-14 ("The highly depleted [. . .]") to p. 11228 | 17 for a better structure and changed the last sentence of the paragraph to: The offset might not only be due to the uncertainty of the measurement but could also include the effect of the combustion efficiency (see below) on the δD value.

→ We have reformulated the sentence on p. 11229 | 18-19: The comparatively high δD values of the precipitation at lower latitudes would result in a slightly higher estimate from our samples than the global mean value.

We would like to thank the Referee again for creating an interesting discussion. All corrections will be included in the final version of the manuscript.

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