

***Interactive comment on “Molecular hydrogen (H<sub>2</sub>) combustion emissions and their isotope (D/H) signatures from domestic heaters, diesel vehicle engines, waste incinerator plants, and biomass burning” by M. K. Vollmer et al.***

**M. K. Vollmer et al.**

martin.vollmer@empa.ch

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Authors reply to: Anonymous Review #1

Title: Molecular hydrogen (H<sub>2</sub>) combustion emissions and their (D/H) signatures from domestic heaters, diesel vehicle engine, waste incinerator plants, and biomass burning  
Authors: Vollmer et al.

The submitted manuscript presents measurements of hydrogen (H<sub>2</sub>), its isotope signature (dD), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) sampled

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from a wide range of combustion sources. This manuscript reports detailed analysis of samples from all major emission sources of anthropogenic H<sub>2</sub>: domestic oil, gas and wood heaters, diesel vehicle engines and waste incinerators. Using the H<sub>2</sub>/CO ratios of these sources detailed global emission estimates of H<sub>2</sub> are reported. A new method of calculation of H<sub>2</sub> emissions is also used in this manuscript where the H<sub>2</sub>/CH<sub>4</sub> ratio from biofuel and biomass burning is used with CH<sub>4</sub> inventories to estimate global H<sub>2</sub> emissions. My general comment on this paper is that it deserves to be published in ACP since it provides a wealth of new information constraining sources of H<sub>2</sub>. These are the first measurements of H<sub>2</sub>, CO and other gases taken directly from the exhaust of specific combustion sources. These data fill a large void in the information available on H<sub>2</sub> and these data should enable a more accurate estimate of H<sub>2</sub> emissions using global models. This is becoming increasingly important in light of the potential use H<sub>2</sub> as a large scale energy carrier. The manuscript is scientifically sound and needs only minor revision before publication (see comments below).

Answer: Thank you for the positive and constructive comments

Specific Comments: p6841, L13: replace with 'past 15 years'

Answer: done

L18: Yver et al, is quoted here but not in Table 1. This is inconsistent. Need to include this in the table reference if it is referred to in the text.

Answer: done

p6842, L18 change to 'recognising' Answer: We have left the 'recognizing' as we believe that this is correct in American English, in which we have written the entire manuscript.

p6844, L19-23: This sentence is unclear and needs to be reworded and/or split up. Answer: We assume that the reviewer means p. 6843, and not p. 6844. We have added another sentence and re-worded the existing one, we hope this is now more

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clear. The text reads now:

\cite{Ehhalt09} find a different explanation for the lower observed urban  $\Delta\text{H}_2/\Delta\text{CO}$  (compared to the traffic signal of  $\sim 0.5$ ) than \cite{Hammer09}. They argue that the differences in lifetimes (essentially the rapid  $\text{H}_2$  removal by soil) is negligible in suburban observations, and explain the lower observed urban ratios (compared to pure traffic) by a mixture of a non-traffic fossil fuel source ( $\Delta\text{H}_2/\Delta\text{CO}$  of 0.2) with the pure traffic signal.

p6844, L14: replace 'The present' to 'This' Answer: We prefer to keep 'The present' because the expression 'This' is often confusing as it is not readily clear, to what 'this' refers to. We want to make sure our statements aren't interpreted as relating to any of the other studies mentioned before this sentence.

p6845, L24 to p6847 L22: This Instrumental part should be in a separate section in Methods and be placed before or after all the sampling site descriptions. It is confusing to the reader place here.o

Answer: We have deliberately placed the analytical details of each sampling campaign after the respective section because these analytical methods are rather different for the heater campaign, the waste incinerator campaign, and the diesel exhaust campaign. Also, for several compounds (CO, CH<sub>4</sub>) there were multiple measurement techniques involved, and not all applied to the same samples. For example, the H-sense instrument was only used for the diesel exhaust samples, so it seems to make sense to mention this directly in the section where the methods for the diesel-powered vehicles is described. We believe that it would be more confusing to have one single analytical section later, in which we would then have to split up the description for the individual campaigns again, and specify the details for each campaign again.

p6846, L7: '2%'. It needs to be specified which gas this number applies to. If both gases, this also needs to be specified.

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Answer: This is now specified, the sentence now reads: The overall accuracies, including calibration scale and nonlinearity uncertainties, are estimated at  $\sim 5\%$  for each  $\text{H}_2$  and CO. Note that we have re-assessed the accuracy and found that the 2% is too optimistic, mainly because of the uncertainties involved with RGA nonlinearities.

p6847, L24: this should read 'at 6 waste incinerator facilities'

Answer: We agree that the word 'waste' should be spelled with a small 'w' but we disagree that the number 6 should be numerically listed. We believe that numbers up to twelve should be written as words, not numbers. This now reads: '... at six waste incinerator facilities ...'

L26/27: Reorganise this sentence to '(...equipped to one to four boilers, they have a yearly waste throughput of 90,000-220,000 t). The incinerators are equipped with a ...'

Answer: We have reorganised this sentence. It reads now: These incinerators are equipped with one to four boilers and a sequence of filter systems to remove most particles and toxic substances. These incinerators are designed for the combustion of household and industrial waste on a regional scale with yearly waste throughputs of typically 90'000 – 220'000\,t.

p6848, L1: replace with '...incinerators were sampled..'

Answer: We believe that 'was' is correct as it refers to 'set', which is singular.

L10 replace with '...in Tedlar bags for less than...'

Answer: done, added the word 'for'

p6849, L22: replace with '(parts per million, 10-6)

Answer: We are not sure if the reviewer states that the dashes in the expression should be omitted, i.e. parts per million instead of parts-per-million. We believe that the version with the dashes is correct, 'parts-per-million', and refer to

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[http://en.wikipedia.org/wiki/Parts-per\\_notation](http://en.wikipedia.org/wiki/Parts-per_notation) . However, this may not be the correct source for spelling question, so we would be grateful if the reviewer could guide us to the correct location for the rules on that matter, or if the typesetters of copernicus could shine some light on this. We have for now kept the original spelling, but we have moved the definition to an earlier part in the manuscript, to the introduction, where 'ppm' is first mentioned. There we changed it to (parts-per-million, micromol/mol) as suggested by the other reviewer.

p6850, L2: The value of 0.05-0.2 quoted here is different to the value quoted in the table 3. Could you correct it if it is wrong or explain the difference between this value and that in the table. It would also be useful to quote the dH<sub>2</sub>/dCO value for gas heaters in the text if this value refers to oil heaters only.

Answer: Thank you for spotting this. We have now corrected this and made it more consistent so the ranges in the text and table agree. In the text we are now also mentioning the range in the delta notation for the fossil fuel heaters. The text reads now: 'Consequently, the absolute H<sub>2</sub>/CO is small, typically 0.03–0.2 and even lower with some negative ratios (–0.1 to 0.13) when using the  $\Delta$  notation (differences to background).'

p6850: Section 3.1.2: Are residential wood heaters classed as biofuel in Table 3? If so you need to make this clear in this paragraph.

Answer: We have clarified this now but not in this paragraph (here we only discuss the measurement results) but we mention now in paragraph 3.4.2 that the wood heaters are classed under biofuel in Table 3.

p6850-1 L25/26-L1/2: This long sentence beginning 'There are a few exception..' ending '...at the time of sampling.' is confusing and needs to be split up and reworded.

Answer: We have now split this sentence up and reformulated the second part. We hope it will be clear now. The sentences now read: 'At plant 1-2 much higher mole

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fractions of H<sub>2</sub> ( $\sim 2$ , ppm) and CO ( $\sim 30$ , ppm) were observed. This is likely a result of a poor adjustment of a natural gas heater for NO<sub>x</sub> removal, which this plant had in operation (downstream of all filters) when our samples were collected.

p6851, L19: reword to '...but also the H<sub>2</sub>/CO ratios are also smaller.'

Answer: done

p6852, L7: '(dD +130 per mil)'. This is not any of the values quoted in Table 3 as ambient air. You must quote where this value has come from.

Answer: We are now quoting the following four references for this: Gerst and Quay, 2001, Rhee et al, 2006b, Rice et al., 2010, Batenburg et al., 2011.

L10: 'fuel-air ratio' is referred to in this sentence. This is very confusing as on p6851 L 24 the 'fuel-air ratio' is described in detail and then the terminology changed in the following section. Need to keep to the same terminology or else highlight that this value is the inverse of the last described fuel-air ratio.

Answer: We have now adopted all mentioning of this ratio to 'air-fuel' throughout the entire text, so here it was reversed (and the second mentioning in this paragraph deleted as not necessary). This part now reads: 'The  $\Delta$  and the H<sub>2</sub> mole fractions for the gas and oil heater samples both decrease with decreasing air-fuel ratio, represented by increasing CO<sub>2</sub> mole fractions.'

L26-28, L1 p6852: Sentence beginning and ending ' In such a one-source.....case for our samples.' The discussion of results in relation to the Keeling plot needs to be described in further detail to make it a useful addition to the discussion.

Answer: We have now re-written this paragraph (see text)

L28: '...specific end-member isotopic signature..' This terminology is confusing and needs to be replaced/clarified.

Answer: We have now re-written this paragraph. However the term 'end-member' is

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still used, but we hope that its meaning is much clearer now.

p6854, L2: 'The ratios from our wood-fire exhaust (2.4 and 3.9) bracket this ratio with reasonable agreement.' It needs to be clarified is these values are included in the 3.3 value for biomass.

Answer: We have now clarified this: The sentence reads now: 'The ratios from our high-mole-fractions wood fire exhaust (2.4 and 3.9), which were not used to derive the above ratio, bracket this ratio with reasonable agreement.'

p6854, L24 'a less pronounced imbalance'. Rephrase this eg. more diesel emission/vehicles than previous years.

Answer: We have changed this now, the sentence reads: '... its contribution relative to gasoline increased in the later years.'

L26: 'above mentioned 4 yr' specify the years as the sentence sounds incomplete.

Answer: We have changed this now but instead of writing out the years (2000, 2005, 2010, and 2015) we write: '... estimate road traffic diesel CO emissions for the above-mentioned four years at  $\sim 40\%$ ,  $35\%$ ,  $30\%$ , and  $25\%$ , respectively, ...'

p6855 L3: Replace with 'despite little change in the relative'

Answer: Done

L5: Replace with 'are likely to be due to the'

Answer: Done

L7: replace 'and combine these'

Answer: Done

L18-24: These sentences are difficult to read and need to be structured differently to clearly get across the point that is being made.

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Answer: This paragraph has been now been rephrased — we hope it is clearer now.

p6856, L22: Remove 'While such'.

Answer: We don't think that a proper sentence would remain if these two words are removed. We have now altered the sentence slightly and broken it into two sentences.

p6857, L17 L22: Replace Fig. 5 with Fig. 5a.

Answer: done

p6858, L24: 'there is confirmatory indication' Rephrase this to for example 'evidence'

Answer: done

p6859, L10: change to 'unlikely to be applicable'

Answer: done

L16: 'signatures of these exhausts' Specify which exhaust type eg. oil, gas, biofuel etc.

Answer: done, the sentence now reads: '... and the isotopic hydrogen signatures of fossil fuel heater exhausts suggest that our understanding of the ...'

Table 1: Place a + sign in front of the positive isotope signatures as you have in the text.

Answer: done

Table 3: f: highly variable: This should be defined with a range or values in the key

Answer: done

Figure 1: This plot does not come out clearly when printed. The black outline of the waste incinerator needs to be removed. The grey + symbol needs to be defined in the key on this plot.

Answer: We tested the blue diamonds without black outline but it became impossible

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to recognize the data points when there is an entire assemblage. We now replaced the dark blue by cyan throughout all figures for the waste incinerators. We also tested removing the black lines for the wood (red) and diesel (green) data points but found it clearer to leave these in. We have now add the grey plus symbol to the legend. We will carefully work with the graphical editors to ensure the figure will have a reasonable size in the final version.

Figure 2: The axes and text on this plot are all too small to be read and need to be made bigger for the plot to be useable.

Answer: Our submitted figure had exactly the width of 1 column in ACPD, but the typesetter had decided to make this figure smaller in this manuscript version. We will work with the typesetter to ensure that in an updated version, the figure has the full column width, and if this doesn't make the plot any better, we will enlarge it for a 2-column width figure.

Figure 4: The grey + needs to be defined in the key.

Answer: done

Figure 5: The blue square for GFED H2 cannot be easily seen on the plot. This point needs to be changed in colour.

Answer: We re-arranged symbol types and colors. We hope that all records can now be seen better.

We thank the reviewer again for his/her comments and suggestions

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6839, 2012.