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Atmospheric
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Discussions

Interactive comment on “Molecular hydrogen (H_2) 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.

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Authors reply to:

Interactive comment on “Molecular hydrogen (H2) 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.

Anonymous Referee #2 Received and published: 5 April 2012

This is a very valuable study where data have been collected that help to close a data

gap in quantifying different contributions to the global hydrogen budget. It is a well written paper providing data of H2 emissions by various combustion sources as well as the respective isotopic signatures of the emitted isotopes. The paper concludes with a thorough bottom-up quantification of hydrogen emission processes mainly based on literature data. The subject and the quality of the manuscript makes it well suited for ACP and I strongly recommend its publication. In addition to very few editing issues there are several points, though, which I would like the authors to address beforehand.

Answer: We thank the reviewer for his/her thorough review and for the positive feedback.

p. 6841: replace 10-6 by μmole/mole

Answer: done

p. 6845, l. 13: Change: "For each location, two samples (A and B) were taken typically 5min apart." to "If not specified differently in the supplementary information, two samples (A and B) were taken at the same location, typically 5 min apart".

Answer: done

p. 6846, l. 8: "Some of the samples’ H2 and/or CO exceeded the detector’s response or the range characterized for nonlinear system behavior." What is the calibrated range for the respective species and over which range and how has the detector linearity been characterized?

Answer: This is now described in the supplementary material, to which we refer now in the main text. The supplementary material now reads:

Analysis on the RGA-3: Analysis was conducted on the Empa laboratory RGA (RGA-Frog). This instrument was characterized for nonlinear system response using a series of flasks containing various dilutions of a high-concentration mixture. For the dilutions, synthetic air was used from which traces of H$_2$ and CO were removed using a catalyst (Sofnocat 514, Molecular Products, Thaxted, UK). Based on the measurements of these flaks samples, the nonlinearities were characterized and correction functions derived. A function of the form $y = a + b\times x + c\times x^{0.5} + d\times x^{0.3333} + e\times x^{0.25}$ was applied (available within the GCWerks software used for all RGA measurements), where x is the normalized peak height (with respect to the bracketing standard), and y is the normalized sensitivity, see e.g.\ \citet{Vollmer02a}. The ranges, for which these functions were applicable, were approximately 50\,ppb to 3.5\,ppm for H$_2$ and 20\,ppb to 1.2\,ppm for CO. The dilutions were made based on pressure measurements using a Keller (Switzerland, www.keller-druck.com) pressure gauge (–1 to 3\,bar) with a stated accuracy of 0.1\,\% of the full scale.

l.24: ..at six waste incinerators..

Answer: corrected

p. 6848 l.4: ..cryogenically transferred.. I am not familiar with the term cryogenic transfer- is the steel flask put to temperatures such that the entire gas sample is condensing in this flask or is this rather to say the following? "Some of these Tedlar bag samples were transferred through a cryogenic water-trap (which temperature?) (>0.6Lmin−1) into evacuated stainless steel flasks."

Answer: The former is correct, the flasks were immersed in liquid nitrogen. This is now stated in the text. In the supplementary material, we also state the transfer flow rates, which we believe were large enough to prevent back diffusion of H2. In the main text it now says: 'Tedlar bag samples were cryogenically transferred into evacuated stainless steel flasks, which were immersed in liquid nitrogen.' and in the supplementary material, the following is added: 'The transfer flow rates through the connecting 1/4\," OD stainless steel tube were $>$0.6\,L\,min^{-1}. We assume that back diffusion of H$_2$ becomes negligible under these conditions.

p. 6848: section 2.3 The emission data from diesel powered vehicles are not listed in a table of this manuscript (only in Figure 1) but a reference is made to the Bond et al. 2010 study. However, as is stated at the end of section 2.3 that paper did not include H2/CO ratios of diesel exhaust. I am at a loss to identify what kind of samples (vehicle type, driving cycle) actually are represented by the data points in Figure 1 and finally summarized in Table 3 of this manuscript. I would highly encourage the authors to add another table specifying the diesel vehicle emission data to make this more transparent.

Answer: A table has now been added to the Supplement, which lists all the details necessary to reproduce the results and calculations that we have made in the main text. It lists details to the 6 vehicles that were tested under 6 driving cycles (where measured H2 was above detection limits only for 4 of the driving cycles). It lists the results on all the episodes that were selected for the estimation of a diesel H2/CO ratio, and the text in the Supplement explains how the ratio is ultimately calculated.

p. 6851, l. 9 "We find H2/CO < 0.25" should refer to Fig. 1 (or the additional table containing the diesel emission data as suggested in my previous comment) not to Table 3. The author's approach to derive the number of 0.15 listed in Table 3 should be explained. In section 2.3 it is stated that only data from driving conditions resulting in high emissions are considered: in Fig 1 there are as many data points of H2/CO < 0.05 as data points with H2/CO ï′CÂÿs 0.1. There is a sentence on the low ratios representing cold starts and the higher values acceleration phases with a hot engine. Apparently the high H2/CO ratios are weighted stronger to yield an overall 0.15. If cold starts are insignificant for the global emission and hence are not included in calculating this ratio this should be made more transparent. To avoid a misleading impression from Figure 1 the authors might consider a differentiation of the "diesel" symbols in Fig 1 (e.g. open symbols for cold starts, filled symbol for accelaration).

Answer: We how refer to Fig. 1 and to the Supplement, where we provide a detailed table. In the supplement, we also have now more transparently calculated the H2/CO ratio. The ratio of 0.15 is now revised, it is only about 0.058. We have now calculated this ratio by using all 'events' that we have selected, and by weighing them with their duration and their H2 (or CO) concentration, so the resulting ratio is a better estimate of the ratio of the accumulated quantities that escape to the atmosphere. We have now also omitted a distinction with regard to the cold starts/ accelerating phases as this isn't sufficiently conclusive. As a consequence, we have removed the corresponding sentences from the main text.

line 14: compared to those for gasoline-powered vehicles

Answer: corrected

p. 6853, section 3.3 The authors could mention the fact that not only the wood fire emissions from this study result in a H2/CH4 ratio similar to literature values but also waste incinerator flue gases with high mixing ratios of these gases (apparently due to badly working cleaning techniques).

Answer: we have now revised that text accordingly. However note that it is not the incinerator results with the high CH4 and H2 mixing ratios that agree also (there were no CH4 measurements on these high mixing ratio samples). The few incinerator samples and the wood sample with the low CH4 emissions (all below background mole fractions) agree only if one assumes no 'presence' of background H2 and CH4. This finding is interesting but we find possible interpretations too speculative to pursue here. As a note on the side, the earlier found ratio of 3.3 has changed to 3.6 after we have found and added more data from the literature, now covering an impressively larger range of CH4 and H2 (Ward et al, 1992), and strenghtening our suggestion to use CH4 as a proxy for H2 emissions from biomass burning. In any case, the revised text is now: ' This resulted in ΔH$_2$/ΔCH$_4$=3.61 (corresponding to a weight-based ratio of 0.45) with 95\,\% confidence bounds 3.55–3.66 and R-square=0.99. Alternatively, a simple statistical averaging of all ΔH$_2$/ΔCH$_4$ yielded a ratio of 3.5 (1 stdv = 1.3). Our wood fire exhaust measurements were not used to derive the above ratio but they bracket this ratio with reasonable agreement. For the three high mole fraction samples we find ΔH$_2$/ΔCH$_4$ of 2.5, 3.8, and 5.9 (listed with decreasing CH$_4$ mole fraction, Fig.∼\ref{h2ch4ratio}).

Interestingly, some of the low CH$_4$ mole fraction (below background values) samples (fourth wood sample and some incinerator samples) also support this ratio if their uncorrected (for background) ratios H$_2$/CH$_4$ were used instead of ΔH$_2$/ΔCH$_4$.

p. 6855, l. 29: It seems pretty speculative to me that a similar H2/CO emission ratio can be assumed for train and ship diesel engines (to my knowledge the fuel type used for ships is not the same as for road vehicles) given that it has been mentioned that delivery vehicles and passenger cars have different H2/CO ratios under different driving conditions with trains and ships being run quite differently compared to road traffic. I would ask the authors to either omit this sentence, to provide evidence for the assumption or to make a clear statement that this assumption is rather uncertain.

Answer: We agree with the reviewer and omit the estimate of H2 emissions from rail and water transportation. We delete the corresponding line from Table 3, but keep a modified text, which now is: ' Diesel H$_2$ emissions are also expected to occur from diesel fuel use in water and rail transportation. According to \citet{Fulton04}, the fuel use for these categories are roughly the same as for the sum of freight trucks and buses. However there is no information on H$_2$/CO for ship and train emissions. Ultimately, H$_2$ emissions are also expected to occur from diesel combustion for other purposes (e.g.\ power generation), but with poor understanding on CO emissions and H$_2$/CO ratios. We therefore exclude these categories from our analysis.

p. 6856: It remains unclear to me where the allocation of residential CO emission for Switzerland originates from if these disaggregated emissions are not included in the UNFCCC CRF and EDGAR inventories. The source of this information should be mentioned.

Answer: We have now clarified this and also cited the relevant national report: 'The difficulty in extracting the various subtypes of emitters in this category 1A4b is that national emission inventories {\color{red} do not reach this level of detail in their UNFCCC

CRF tables, and access to the relevant data from individual countries is difficult.} For Switzerland for example, residential 1A4b emissions of CO are 45\,kt\,yr$ˆ{-1}$ according to the UNFCCC CRF. However, the largest fraction ($\sim$80\,$\%$) of these CO emissions derives from biofuel (wood) burning (for heating) and from seemingly minor applications ($\sim$8\,$\%$), such as gardening tools (2-stroke engines) with very large CO emission factors \citep{Leippert10}. The oil and gas heating systems' CO emissions for Switzerland are comparably small ($\sim$5\,$\%$), despite their dominance from an energy perspective \citep{Leippert10}.

Reference: Leippert, F., Kasser, F., and Heldstab, J.: Switzerland's Informative Inventory Report 2010 (IIR); Submission 585 under the UNECE Convention on Long-range Transboundary Air Pollution, Tech. Rep. Submission ofMarch 2010 to the United Nations ECE Secretariat, INFRAS Consulting group, Zurich, for Federal Office for the Environmennt (FOEN), Berne, Switzerland, 2010.

line 27: "..which we derive from the literature." Why isn't there any reference to the data from this manuscript (Figure 1)?

Answer: There is no reference because we are taking the ratio for biomass, as our analysis suggests that this best approximates biofuel emissions. However, we have only 4 wood samples for biomass burning, which seems too little to incorporate compared to the large body of data already available in the literature.

p. 6867: Table 1, footnote a) .. a mean isotopic composition of 120–132 ‰ (per mill sign missing)

Answer: Thank you for spotting this. Our originally submitted table did include the permil sign. However, the text editor had introduced numerous errors into this table when converting it to a suitable Copernicus format, and we seem to not have caught all errors. We will carefully re-check this table if this manuscript will be published.

Table 2: I would appreciate if the sample description in this table would not restrict to simple sample codes but include additional columns providing a more explicit description of the samples (e.g. S-8 and S-9 not only characterized by "W" but S-8A "wood pellet heater, start-up", S-8B "wood pellet heater, optimal burning"). This is especially needed where identical sample numbers actually refer to different sources or source conditions (e.g. S-1, S-5, S-8, S-9). In the way the data are presented now it is striking that there is a large deviation between apparent sample pairs, where it is hidden somewhere in the text (p. 6850, l. 10) or the supplementary information that S-8 A and B samples are not duplicates but refer to the start-up and optimal burning phase of a fire, respectively. It should be made clear within the table where the samples are replicate samples of an emission source under the same condition, and where they refer to different conditions. Likewise an additional column could provide the information which data refer to a discrete and integrated sample, respectively.

Answer: This has now been added to Table 2. It lists whether the sample was taken during startup or optimal burning phase, and it details whether the incinerator samples were discrete or integrated samples.

Table 3: Adding to my comment related to diesel, rail & water emissions: in contrast to the other emission sources the number H2/CO number presented here is not based on data but on an assumed equivalence to road vehicles. It remains absolutely unclear to me what the global emission numbers are based on. Is there any inventories of railway and ship based diesel consumption and related emissions relative to road emissions? The origin of the decline in road traffic emissions is advances in combustion and exhaust gas treatment technologies. I doubt that these advances have gone exactly in parallel for road vehicles and rail and water vehicles. As long as there is no better information basis I would request to omit the line for rail & water in this table.

Answer: Now omitted

Figure 1 caption: All measurements are shown on a log-log scale in (a) and a selection (delimited by dashed-dotted box) on a linear scale in (b).

Answer: Now changed according to these suggestions

Figure 2: "Samples with H2 mole fractions >1 ppm (I2) are omitted from b. It's not only I-2 but also I-4, I-5, I-8, S7-S9. The caption should clearly state which samples are represented and which are not for all the graphs.

Answer: This has now been added. The relevant caption of the figure now reads: 'Samples with H$_2$ mole fractions $>$1\,ppm (S7–S9, I-2, I-4A, I-5, I-8C) are omitted from (b) to better show the variability of the oil and gas heater measurements.

Figure 3: Why is the x-axis scaling selected such that some data points are excluded (S-2A, S-5A, S-3B)? This should be mentioned in the figure caption.

Answer: We have now extended the figure in the x-axis so that these 3 samples are also on the plot.

Figure 4: Molecular hydrogen (H2) versus methane (CH4) in combustion exhaust (note that most waste incinerator samples are not depicted because CH4 mixing ratios were below the detection limit).

Supplement line 5: Change: "For each location, two samples (A and B) were taken typically _5min apart." to "If not specified differently, two samples (A and B) were taken at the same location, typically 5 min apart".

Answer: done

line 34: "Finally, ambient air samples were also collected during this campaign in order to determine approximate concentrations of the air drawn for combustion." It is unclear which place and time "this campaign" refers to. Samples S-1 to S-9 all have been collected at different locations within two months so it should be specified when and where the air samples were collected.

Answer: This is now explained, the additional sentence is: 'They were collected in the vicinity of the sampled buildings, one air sample was collected at the end of the S-2 sampling, and two air samples were collected during the I-1 sampling.'

line 38: How has the dilution been made and have the dilution factors been determined? Dilution of sample 9B by the given dilution factor results in a mixing ratio that is exceeding the highest CO calibration point by a factor of 20. The authors should specify if the 2% uncertainty refers to analysis results within the calibrated range or include extrapolated values. I did not find any description of the calibrated range for hydrogen - given the non-linearity issues of the RGA technique any extrapolation is likely to create errors higher than the quoted 2 %.

Answer: After some more measurement campaigns we have now found that the 2% uncertainty may be too optimisitic because of nonlinearity issues, and we are now stating a 5% uncertainty. Please note that CO and also some of the other gases were measured on multiple instruments. While e.g. CO in higher concentration samples exceeded the nonlinearity ranges for the GC-RGA and the GC-ECD, where these data were not used, the FTIR measurement was taken. Depending on the species and samples, sometimes one, or two, or all three results from the 3 instruments could be used, sometimes less. We believe that the concept on how we proceed is eplained sufficiently in the text. We believe that it would be too detailed to start listing which result from which instrument was taken, and which wasn't.

line 73: I'd suggest to change to: "Flue gas samples were taken from a large set of incinerators from September 2010 to March 2011 (sample groups I-3 to I-9 (?)) by collection of integrated (1 week) dried.."

Answer: done

line 74: "Some of these Tedlar bag samples were cryogenically transferred (>0.6Lmin−1) into evacuated stainless steel flasks." I am not familiar with the term cryogenic transfer- is the steel flask put to temperatures such that the entire gas sample is condensing in this flask or is this rather to say the following: "Some of these Tedlar bag samples were transferred through a cryogenic water-trap (which temperature?) (>0.6Lmin$-$1) into evacuated stainless steel flasks."

Answer: this is now explained, see earlier comments about the same issue in the main text.

line 82 Exhaust gas samplesi (typo)

Answer: corrected

We would like to thank the reviewer again for his/her thorough job.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C3372/2012/acpd-12-C3372-2012-supplement.pdf

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