Atmos. Chem. Phys. Discuss., 12, C1296–C1301, 2012
www.atmos-chem-phys-discuss.net/12/C1296/2012/

Atmospheric
Chemistry
and Physics
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.

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.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

p. 6841: replace 10-6 by μmole/mole

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".

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?

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

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."

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.

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 ïĆş 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).

line 14: compared to those for gasoline-powered vehicles

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).

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.

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.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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

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.

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.

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).

Figure 2: "Samples with H2 mole fractions >1 ppm (l2) are omitted from b. It's not only

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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.

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.

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".

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.

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 %.

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.."

line 74: "Some of these Tedlar bag samples were cryogenically transferred

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

(>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."

line 82 Exhaust gas samplesi (typo)

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper