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Interactive comment on "Molecular hydrogen (H$_2$) emissions and their isotopic signatures (H/D) from a motor vehicle: implications on atmospheric H$_2$" *by* M. K. Vollmer et al.

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Reply to Referee #2

We thank the referee #2 for his useful suggestions and comments.

Following the referee's suggestion we have now added an explanation for the abundance of H2O (relative to H2) at the beginning of paragraph 2.4. Indeed, since H2O was measured, we do not need to 'assume' that H2O is the dominant pool, but can rather state this as a fact. Accordingly the sentence on original p. 3030, l. 14 was changed from '... assuming that H2O is the dominant hydrogen pool ...' to ' ... because H2O is the dominant hydrogen pool ...'

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With regard to the comment on the importance of the role of the water gas shift reaction the suggestion of the reviewer is intriguing but we believe that we see a similar problem as described in the Vollmer et al. (2007) paper on H2 in a highway tunnel, i.e. a large uncertainty in the H2O measurements. For example, the molar H/C ratio of all compounds in the exhaust should be that of the fuel plus a correction for the H2O in the intake air (see also comment to referee #1). The molar H/C ratio of the fuel we've used was determined at 1.97 (fuel analysis). Quantitatively, H2O and CO2 are the only relevant H and C compounds in our experiment, this would yield H2O/CO2 of 0.98, or if we add a 10% correction for additional H2O from the air intake, this would result in an H2O/CO2 ratio of ∼1.08. However our measured H2O/CO2 is only about 0.85 – 0.92. This suggests that the H2O measurements were inaccurate (these were not part of the main compounds of interest for the core experiment) or that there may have been H2O condensation in the lines leading to the FTIR instrument. For this reason, any calculations on the K value (for the water-gas shift reaction) become questionable and we have therefore excluded them. For the same reason the H2O results are excluded from Table 2.

The suggestion of the reviewer to use the concentrations of both H2 and H2O in the exhaust to help determine whether this is a strictly H2/H2O system is also hampered by the above-mentioned miss-match of calculated vs. measured H/C which is almost certainly caused by uncertain H2O measurements. Hence an accurate mass balance for H2 and H2O in intake and exhaust is impossible. There were many measurements of other H-containing compounds (total hydrocarbon, CH4, NH3 and selected hydro-carbons), all showing much lower concentrations than H2O, so quantitatively, H2O is the major H component. We do not conclusively know whether these other minor H-containing compounds have an isotope effect on H2O but we believe that this is un-likely. Hence the H2O isotope pool is probably a stable 'bank'. Then the fact that we find variable H2 isotopic compositions suggests that the H2âĂŦH2O is not always at equilibrium but that some reaction (like the catalytic removal that we suggest) causes the isotope fractionation in the H2.

original p 3029, l. 26âĂŤ28: It has now been added that Rahn et al (2002) also mention similar temperature-dependent equilibrium processes for various chemical and photo-biological systems.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3021, 2010.

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