

Interactive comment on “Molecular hydrogen (H₂) emissions and their isotopic signatures (H/D) from a motor vehicle: implications on atmospheric H₂” by M. K. Vollmer et al.

M. K. Vollmer et al.

martin.vollmer@empa.ch

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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 ...'

C3201

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 hydrocarbons), 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 unlikely. Hence the H₂O isotope pool is probably a stable 'bank'. Then the fact that we find variable H₂ isotopic compositions suggests that the H₂↔H₂O is not always at equilibrium but that some reaction (like the catalytic removal that we suggest) causes the isotope fractionation in the H₂.

C3202

original p 3029, l. 26–28: It has now been added that Rahn et al (2002) also mention similar temperature-dependent equilibrium processes for various chemical and photo-biological systems.

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C3203