

***Interactive comment on “Molecular hydrogen (H<sub>2</sub>) emissions and their isotopic signatures (H/D) from a motor vehicle: implications on atmospheric H<sub>2</sub>” by M. K. Vollmer et al.***

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Reply to Referee #1

We thank the referee #1 for his useful suggestions and comments.

Original p. 3030, l. 6: Comparison to Bottinga (1969) This is a very useful suggestion and we have incorporated this in the revised version. First, we have now altered the sentence l. 6 to reflect that the difficulty in the comparison with the Bottinga (1969) prediction is that we have not measured the isotopic composition of H<sub>2</sub>O in the exhaust. Secondly, following the suggestion of the referee, we have calculated the percentage of the exhaust H<sub>2</sub>O deriving from the moisture in the air by using the measured H<sub>2</sub>O

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concentration in the exhaust and the knowledge on the 50% relative humidity set in the air at the intake. This calculation results in almost exactly 10% of the total hydrogen in the exhaust, as the referee also suggested. Our experiment was conducted in January 2008 when the intake air was cold and dry. It therefore was moisturized using Zurich tap water for which we assume  $\delta D = -50$  permil to  $-100$  permil based on typical precipitation values (new reference added). These values are not drastically different from the  $\delta D$  of H<sub>2</sub> in gasoline and therefore it does not alter our conclusions. The corresponding effect on the shift of the 'Bottinga' line is maximally  $\sim 5$  permil. These calculations are now all incorporated into the text in a separate paragraph. Thirdly, as indicated by the referee, the effect of the  $\delta D$  in H<sub>2</sub>O affects the CH<sub>4</sub>-fuelled experiment more than the gasoline. For the  $\delta D$  values reported in the paper, the effect would be  $\sim 3$  times as large. Still this would not strongly affect our conclusions and. Furthermore, only one experiment with CH<sub>4</sub> was carried out and it is now explicitly mentioned that Figure 2 primarily targets at a comparison for gasoline.

Original p. 3032, l. 14. We are not entirely sure what the confusing point really is and have addressed this comment by clarifying the following point:

We like to emphasize that the numbers in the line below the equation ( $-300$  permil and  $-0.3$ , respectively) are only an example, and do not relate to a specific data point in the figure. We have slightly changed the text to make this clearer.

We now explicitly state that Figure 3 shows not the original  $\delta D$  values as in Figure 1 and 2, but  $\ln(\delta D + 1)$ , also expressed in permil. This is necessary since the isotope variations are so large that the conventional linear approximation  $\ln(\delta D + 1) \sim \delta D$  is not a good approximation anymore. This means that  $\delta D = -300\%$ , for example, corresponds to  $\ln(\delta D + 1) = -357$  permil.

p. 3029, l. 6: 'cocking' should be 'coking'. However, we have now changed this sentence to make it more understandable: 'One possible explanation for these observations is that the TWC's active sites are occupied by hydrocarbons thereby preventing

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adsorption of H<sub>2</sub>O required for the water-gas-shift reaction '

p. 3029, l. 26: The reference has now been added to the end of the sentence.

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