Atmos. Chem. Phys. Discuss., 10, C1970–C1971, 2010
www.atmos-chem-phys-discuss.net/10/C1970/2010/

Atmospheric Chemistry and Physics Discussions

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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Received and published: 22 April 2010

General comments: A very nice contribution that adds significantly to our knowledge of H2 production from internal combustion engines and the isotopic effects associated with engine operating conditions and air/fuel ratio. The paper also contributes to the body of literature related to exhaust emission ratios.

Specific comments: Regarding the adjustment factor for comparing the measured results to Bottinga, 1969 – since D of H2O was not measured, the assumption that H2O is the dominant hydrogen pool results in the shift of ∼100 per mil; however, since it is reported on p. 3026 line 23 that [H2O] was measured along with a full suite of other

exhaust gases, the [H2O]/[H2] ratio could be used to lend some insight into the validity of this assumption. In addition, this ratio would lend insight into the importance of the role of the water-gas-shift as well as the relative strength of the various other proposed controlling mechanisms. It would also, perhaps, alleviate the concerns of reviewer 1 regarding the role of H2O vapor introduced at the engine intake.

Regarding the suggestion of two separate isotope effects during the loss of H2 in the TWC – It may be that the same process, i.e. oxidation of H2 to H2O, is responsible for both observed effects. Not only are H2 and H2O attempting to reach thermodynamic equilibrium on a catalytic surface in a brief period of time but a fraction of the H2 is being converted to H2O, a reaction which may have a kinetic fractionation associated with it. Again, knowing the concentration of both species both entering and leaving the TWC would help determine if it is strictly the H2/H2O system that is driving the observed isotopic effects or if additional species are involved.

P 3029, line 26-28: Rahn et al., 2002 in their conclusions also suggested H2O:H2 temperature dependent equilibrium processes for the observed range of deuterium in terrestrial H2.

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