



## **Global budget of molecular hydrogen and its deuterium content: constraints from surface, aircraft, and oceanic cruise observations**

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To improve our understanding of the global budget of molecular hydrogen, we present a new simulation of molecular hydrogen and its deuterium component ( $\delta D$ ) using the GEOS-CHEM three dimensional global model of tropospheric chemistry. The primary sources of  $H_2$  (fossil fuel, biofuel, and biomass burning) used in the model are based on the GEOS-CHEM CO emissions inventory, scaled with the appropriate emission factors. Secondary sources from photochemical production arise from the photolysis of formaldehyde (resulting from oxidation of methane and biogenic volatile organic compounds, BVOCs) and account for an estimated 45% of the  $H_2$  source. There is considerable uncertainty in the source of  $H_2$  from formaldehyde, because of poor understanding of BVOC sources and chemistry. We also include a seasonally varying ocean source, based on a simulation of ocean nitrogen fixation. The main tropospheric sink, accounting for  $\sim 80\%$  of the total, is uptake by enzymes in soils, a process which is poorly understood. The remainder loss is through oxidation by the hydroxyl radical (OH). The observed deuterium component of tropospheric  $H_2$  (expressed as  $\delta D$ ) is enriched by  $\sim 130\%$ , relative to Vienna Standard Mean Ocean Water [Gerst and Quay, 2000]. The combustion and ocean sources of  $H_2$  are isotopically depleted, while the photochemical sources are thought to be isotopically enriched [Gerst and Quay, 2001]. The soil sink for  $H_2$  shows little fractionation, while the OH sink shows considerable fractionation. Furthermore, stratosphere-troposphere exchange is believed to isotopically enrich  $H_2$  [Röckmann et al. 2003; Rahn et al. 2002]. We use  $H_2$  observations from the CMDL network (seasonal cycle, latitudinal and longitudinal gradients, aircraft observations) to constrain the budget of  $H_2$  in the atmosphere, in particular, the

sink by soil uptake, the photochemical source, and ocean emissions. At the same time, we use observations of  $\delta D$  from ocean cruises, aircraft, and ground sites to further constrain the budget of  $H_2$  and provide new isotopic constraints on the enrichment due to the photochemical source and stratosphere-troposphere exchange.

Gerst S. and P. Quay, The deuterium content of atmospheric molecular hydrogen:

Methods and initial measurements, *J. Geophys. Res.*, 105, 26,433-26,445, 2000.

Gerst S. and P. Quay, Deuterium component of the global molecular hydrogen cycle, *J. Geophys. Res.*, 106, 5021-5031, 2001.

Rahn, T. et al., Extreme deuterium enrichment in the stratospheric hydrogen and the global atmospheric budget of  $H_2$ , *Nature*, 424, 2003.

Röckmann T., T. Rhee, and A. Engel, Heavy hydrogen in the stratosphere, *Atmos. Chem. Phys.*, 3, 2015-2023, 2003.