



## Temporal and spatial variability in the isotopic composition of atmospheric molecular hydrogen: measurement time series from six EUROHYDROS stations

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Molecular hydrogen ( $H_2$ ) is present in the atmosphere at levels of  $\sim 0.5$  ppm. Its sources are the oxidation of methane and other hydrocarbons, combustion processes, and production by nitrogen-fixing bacteria. About three quarters of the  $H_2$  thus produced is taken up by soils; the other quarter is oxidized by the hydroxyl radical (OH). But while the contributions to the global  $H_2$  budget are qualitatively known, large quantitative uncertainties remain.

This is now a pressing matter, since the anticipated use of  $H_2$  as an energy carrier –with potential benefits for air quality and climate–, will likely result in increased emissions of  $H_2$  to the atmosphere due to the inevitable leakage during production, storage and distribution. The associated rise of atmospheric  $H_2$  levels may affect the lifetime of greenhouse gases such as methane, and might also affect stratospheric ozone levels. The EUROHYDROS project aims to improve our understanding of the  $H_2$  cycle with the establishment of a global network for atmospheric  $H_2$  observations.

Isotope measurements can be a useful addition to hydrogen mixing ratio observations for constraining the terms in the global budget. In the research presented here, weekly to monthly air samples from six globally distributed locations in the EUROHYDROS network have been analysed for the stable isotopic composition (, i.e. the deuterium content,) of the  $H_2$  ( $\delta D-H_2$ ), in addition to the hydrogen mixing ratio ( $m_{H_2}$ ). This has resulted in time series of between one and five years long, which constitute the largest dataset of ground-based  $\delta D-H_2$  observations so far.

On average, the  $m_{H_2}$  and  $\delta D-H_2$  values are higher at the Southern Hemisphere (SH) than at the Northern Hemisphere (NH) stations. A  $\delta D-H_2$  minimum is observed at the NH mid-latitudes, which is likely an effect of anthropogenic emissions of deuterium-depleted hydrogen. The SH stations show small seasonal cycles in  $m_{H_2}$ , but no discernible seasonal cycles in  $\delta D-H_2$ . The three coastal/marine NH stations show larger cycles in  $m_{H_2}$ , and  $\delta D-H_2$  cycles that are five to six months out-of-phase with respect to the  $m_{H_2}$  cycles. These large relative seasonal variations have been used to make a rough estimate of the relative sink strength of the two sinks, and the results are in agreement with the expectation that on the NH the relative contribution of soil uptake to the total sink processes increases with latitude.

This dataset has now been used to validate the TM5 global chemistry transport model, in which the sources and sinks of deuterated and non-deuterated  $H_2$  have been implemented. The TM5 results agree well with  $m_{H_2}$  observations, but have a negative bias with respect to the  $\delta D-H_2$  observations that can be resolved by adjusting the values of a limited number of parameters within the range of uncertainty. However, to uniquely constrain the global  $H_2$  isotope budget, more data are needed than are available to date. The Gas Chromatography – Isotope Ratio Mass Spectrometry system used for the isotope measurements is currently being automated to facilitate the continuation of these observations, so that long-term  $\delta D-H_2$  time series can be obtained.