The stable isotopic composition of atmospheric molecular hydrogen at the Cabauw tall tower in the Netherlands

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Molecular hydrogen (H_2), though not a greenhouse gas itself, is chemically linked to the methane cycle and may have an indirect greenhouse effect by affecting the atmosphere's oxidative capacity. As increased use of hydrogen fuel is anticipated, a better understanding of the global, regional and local atmospheric H_2 cycles is needed. Since the H_2 source and sink processes have large isotope effects due to the large relative mass difference between `ordinary' hydrogen and deuterium, studying the stable isotopic composition of H_2 (δD(H_2)) is a promising way to achieve this. Over the last 15 years, studies of the isotope effects in H_2 source and sink processes have appeared, δD(H_2) has been incorporated into global chemical transport models and more environmental observations of δD(H_2) have been published. The latter, however, were mostly obtained from samples that were collected in remote regions of the atmosphere, which is not sufficient to fully characterize the H_2 cycle or to assess the possible environmental effects of H_2 leakage in urbanized regions. To address this gap, flask samples were collected at the Cabauw tall tower from the air inlets at 20, 60, 120, and 200 meter altitude for the analysis of H_2 mixing ratio (χ(H_2)) and δD(H_2). More than 250 samples were collected and analysed over a period of four years.

The H_2 mixing ratios in the samples show frequent excursions to high values above the background. Previously published continuous χ(H_2) observations at the Cabauw site showed a similar pattern. With the isotope observations, we can now see that these high χ(H_2) excursions are accompanied by very low δD(H_2) values; a result of anthropogenic emissions of deuterium-depleted H_2.

With a simple "Keeling plot" analysis, we obtained an apparent source signature (-285 ± 13 ‰) that is in the lower range of published values for H_2 emissions from the combustion of fossil fuels. The result of the fit, however, depended markedly on the selection of the samples that were included. Therefore, to obtain a more realistic picture of the uncertainty of the result, a bootstrap method was applied to this fit. The bootstrap results showed a wide distribution with a central value that was even lower than -300‰, suggesting that the H_2 cycle at Cabauw is under the influence of a source mix that is more deuterium-depleted than currently accepted values for fossil fuel combustion.

A comparison of the samples from different sampling heights shows that δD(H_2) values at the 200 m level are slightly but significantly higher than at the 20 m level. The sign of this difference shows that the uptake of H_2 by the soil, which preferentially removes "light" H_2, is relatively weak at the site.