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Isotopic evidence for biogenic molecular hydrogen production in the Atlantic Ocean

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Oceans are a net source of molecular hydrogen (H_2) to the atmosphere. The production of marine H_2 is assumed to be mainly biological by N_2 fixation, but photochemical pathways are also discussed. We present measurements of mole fraction and isotopic composition of dissolved and atmospheric H_2 from the southern and northern Atlantic between 2008 and 2010. In total almost 400 samples were taken during five cruises along a transect between Punta Arenas (Chile) and Bremerhaven (Germany), as well as at the coast of Mauritania.

The isotopic source signatures of dissolved H_2 extracted from surface water are highly deuterium-depleted and correlate negatively with temperature, showing δD values of (-629±54) ‰ for water temperatures at (27±3) ˚C and (-249±88) ‰ below (19±1) ˚C. The results for warmer water masses are consistent with biological production of H_2. This is the first time that marine H_2 excess has been directly attributed to biological production by isotope measurements. However, the isotope values obtained in the colder water masses indicate that beside possible biological production a significant different source should be considered.

The atmospheric measurements show distinct differences between both hemispheres as well as between seasons. Results from the global chemistry transport model TM5 reproduce the measured H_2 mole fractions and isotopic composition well. The climatological global oceanic emissions from the GEMS database are in line with our data and previously published flux calculations. The good agreement between measurements and model results demonstrates that both the magnitude and the isotopic signature of the main components of the marine H_2 cycle are in general adequately represented in current atmospheric models despite a proposed source different from biological production or a substantial underestimation of nitrogen fixation by several authors.