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Measuring fast variations of δ^{18}O and δ^{2}H in atmospheric water vapour using laser spectroscopy: an instrument inter-comparison and characterisation study

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Fast variations of stable water isotopes in water vapour have become measurable lately using novel laser spectroscopic techniques. This allows us to perform process-based investigations of the atmospheric water cycle at the time scales of significant weather events. An important prerequisite for such studies implying automatic field measurements lasting for several weeks or even months is a detailed knowledge about sources of uncertainty and instrument properties. We present a comprehensive characterisation and comparison study of two commercial laser spectroscopic systems based on cavity ring-down spectroscopy (Picarro) and off-axis integrated cavity output spectroscopy (Los Gatos Resarch). The old versions (L1115-i, WVIA) and the new versions (L2130-i, WVIA-EP) of both systems were tested. The uncertainty components of the measurements were assessed in laboratory experiments, focussing on effects of (i) water vapour mixing ratio, (ii) measurement stability, (iii) uncertainties due to calibration and (iv) response times of the isotope measurements due to adsorption-desorption processes on the tubing and measurement cavity walls. Knowledge from our laboratory experiments was used to setup a one-week field campaign for comparing measurements of the ambient isotope signals from the L1115-i and WVIA systems. The optimal calibration strategy determined for both instruments was applied as well as the correction functions for water vapour mixing ratio effects. Using this field measurement data we address the question of how well the deuterium excess (d=δ^{2}H-8δ^{18}O) of atmospheric water vapour can be determined with laser spectroscopy. The deuterium excess is an interesting parameter for process-based atmospheric water cycle studies, which depends on humidity and temperature conditions at source location of water vapour. Up to now only very few high-time-resolution measurements of deuterium excess exist. Our concurrent measurements of atmospheric isotopes in water vapour using the two analysers allow us to evaluate the precision and accuracy of atmospheric deuterium-excess measurements.