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Fast measurement of stable isotope profiles in the unsaturated zone – from equilibrium to flow

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Cavity ringdown spectrometers offer ways to analyze gaseous and liquid water phases in the unsaturated zone. Pioneering work on the comparison of vapour and water profiles in the unsaturated zone (Barnes & Allison, 1988), and on the methodological adaptation to equilibrium laser spectrometry for the saturated zone (Wassenaar et al., 2008) demonstrate the general feasibility of information transfer between vapour and water in the subsurface. A range of laboratory tests were performed in order to ascertain principles of gas water equilibrium fractionation in soils of different textures (sand, silt, loam and clay). Additional field experiments provided data on isotope profiles in different soil types (cambisol, vertisol), textures (silt, loam and clay) as well as in humid (Southern Germany) to semi-arid (Israel) climatic and hydrologic conditions. Results indicate that in principle, laser spectrometry yields relatively fast and high resolution data on isotope distribution of vapour and soil water in the unsaturated zone. Still, laboratory and field procedures need to be established and further developed in order to assure that isotope ratios can be reproduced and inter-compared. The calibration of results and comparison to mass-spectrometry standards revealed no significant bias for sand and silt and a weak but significant bias from standard equilibration fractionation in clays. Some general patterns apparent in the measurement of stable isotopes in soil water by laser spectrometry raise further research questions about the balance between equilibrium and flow processes in the unsaturated zone.