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In situ measurements of soil and plant water isotopes: a review of approaches, practical considerations and a vision for the future

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Table S1: Summary of *in situ* investigations of soil, xylem and transpired water isotope values (arranged by these four groups, within groups chronological order)

Author(s)	***Environment / Location***	***Isoflux measured in situ***	***Methods***	***Findings/ Recommendations Advantages (+) /Disadvantages (-)***
Soderberg et al. (2012)	Semiarid, Kenya	Soil water isotope values of depth-profiles	• Material: gas permeable membrane (Teflon) with open ending, packed with glass wool • Soil type: sandy loam • Pull-only system with additional dilution of 400 ml/min, diluted with ambient air • Calibration/Validation: No information provided	• Include soil water potential into Craig-Gordon model for soils + Includes modelling of results − Glass wool used might fractionate − Condensation issue not addressed − Dilution with non-dried ambient air
Volkmann and Weiler (2014)	Humid (southwest Germany)	Soil water isotope values of depth-profiles Evolution of evaporation front	• Material: gas permeable membrane (PE) with mixing chamber • Soil type: clayey silt • Both push-trough (flow rate not specified) and pull-only (30-35 ml/min) systems used, dilution with pure N_2 • Calibration: - boxes filled with soil and equipped with gas probes, water content, EC, temperature, soil water potential sensors - isotope standards added to water content of 20 vol.-% - linear two-point calibration & quality control standard - correction for vapor-concentration dependence - liquid–vapor equilibrium after Majoube (1971) - normalization to VSMOW and drift correction • Validation: depth profiles using cryogenic vacuum extraction	• First successful field study and comprehensive investigation of *in situ* soil water isotopes + Very flexible system + Both stationary and mobile use + Both push-through and pull-only methods tested + Control of condensation via dilution directly in probe − Complex system − Expensive probes
Rothfuss et al. (2015, 2013)	Laboratory	Soil water isotope values of depth-profiles	• Material: gas permeable membrane (PP) • Soil type: fine sand • Push-trough system with excess tube; dry synthetic air flow of 25 ml/min at inlet, dilution with dry synthetic air after passage through soil	• Potential isotope-effects introduced via gas permeable probe (difference of theoretical and observed values for δ^2H_{vap}) • Uncertainties when using CG-model

			• Calibration: - three standards prepared, added to dried soil and measured over a range of temperatures (8°C - 24°C) - constant water vapor concentration via dilution with dry synthetic air - drift correction and check for material changes of the soil gas probe • Validation: comparison to theoretically calculated vapor values	• Gas-permeable membranes can resolve rapid changes of isotope values • Provide improved equation for vapor-liquid conversion + Linear correction for non-reached isotopic equilibrium + Water vapor concentration kept constant + Checked for equilibrium conditions − Test limited to laboratory conditions − Isotopic equilibrium not reached
Gangi et al. (2015)	Laboratory	Soil water isotope values of depth-profiles and carbon dioxide δ^{18}O values	• Material: gas permeable membrane (PP) • Soil type: fine sand • Push-trough system with excess tube; dry synthetic air flow of 85 ml/min at inlet, dilution with dry synthetic air after passage through soil • Validation: comparison to theoretically calculated and modelled values	• No fractionation due to tubing for δ18O • Combined measurements of oxygen isotopologues in soils and atmospheric carbon dioxide + modelling involved (MuSICA) − No field testing
Gaj et al. (2016)	Semi-arid (Namibia)	Soil water isotope values of depth-profiles Evolution of evaporation front	• Material: gas permeable membrane (PP) • Soil type: medium sand • Pull-only at 95 to 110 ml/min, pre-flushing of probes using dry air; system changeable to push-through • Calibration: - four standards prepared in oven-dried soil material; 5 ml of standard solution added - drift and memory correction, quality control - conversion of the corrected vapor to respective liquid water isotopic compositions • Validation: depth profiles using cryogenic vacuum extraction	• First successful *in situ* study in semi-arid environment • Recommendations: - Organic contamination should be investigated further - Increase probe length under dry conditions - Use heating/dilution to avoid condensation - Further development of calibration strategies for clay-rich soils. + calibration in soil media + water vapor concentration controlled by sampling time + calculated influence radius for pull-only method and air volumes sampled − Not corrected for water vapor concentration − Strong deviations in upper soil layer

Pratt et al. (2016)	Humid (Canada)	Waste rock mining site unsaturated zone isotope values	• Material: HDPE tubes with 50-mm stainless steel mesh filter • Soil type: coarse textured sand tailings dyke • Pull-only, 30 ml/min, no dilution or flushing • Calibration: - 10ml of liquid water standards added to Ziploc bag - correction for water vapor concentration - conversion of the corrected vapor to respective liquid water isotopic compositions • Validation: comparison to bag equilibration method	• Direct *in situ* measurement of natural, water stable isotope profiles thick unsaturated mine waste is challenging • Bag equilibration as alternative • General agreement to samples collected in equilibration bags for some depths − Strong deviations in most depths
Oerter et al. (2019, 2017); Oerter and Bowen (2017, 2019)	Desert/Arid (Utah, United States)	Soil water isotope values of depth-profiles	• Material: gas permeable membrane (PP) • Soil type: coarse textured sand tailings dyke • Push-trough system with excess tube; dry N_2 for flushing and dilution; flow of 60 ml/min; dilution flow of 20 ml/min • Calibration: - oven dried (105°C for >12 h) soil material at 7%, 18%, 26% GWC (g water g^{-1} soil), n = 18 calibration standards (3 soil depth groups (7% to 11% clay content) × 3 GWC contents × 2 water types) - multi-linear regression for one-step correction of water isotope data derived from standards, variables used: clay content, water content, water vapor isotope value - CO_2 spectral interference correction • Validation: depth profiles using cryogenic vacuum extraction and bag equilibration	• Throughput rates greater than 7 samples/h^{-1} • Accuracy of the method to be equivalent to direct headspace equilibration and vacuum extraction techniques • measurement duration of ~5 min is typically sufficient to achieve >2 min of stable H_2O and δ^2H and $\delta^{18}O$ measurements • Most complete approach in terms of calibration and setup + water vapor concentration kept constant (20.000 ppm) + calibration carried out in same media as measured (=soil) + one-step calibration with different soil types and water contents; calibration can easily be extended to more variables - Effect of changing environmental conditions (temperature) not addressed, issue of condensation not addressed at all
Quade et al. (2019)	Humid (western Germany)	Soil water isotope values of depth-profiles	• Material: gas permeable membrane (PP), membrane length 20cm • Soil type: silt loam	• ET Partitioning study on sugar beet (*Beta vulgaris*) using additional data from destructive sampling and Eddy-Flux measurements • Large discrepancies between isotope values of evaporation derived destructively and non-

		Atmospheric isotope values	• Push-trough system with excess tube; dry synthetic air (N_2) flow of 85 ml/min at inlet, dilution with dry synthetic air (N_2) • Coated heating wire to avoid condensation	destructively from those of soil water were found to cause significant differences in T/ET
Kübert et al. (2020)	Humid (South West Germany)	Soil water isotope values of depth-profiles	• Material: gas permeable membrane (PP), membrane length 20cm • Soil type: upper soil layer: sand; below 40 cm: silt/clay • Push-trough system with excess tube; dry synthetic air flow of 110 ml/min at inlet, dilution with dry synthetic air (N_2) • System flushed before measurements to remove condensation • Vessel with standard solution embedded in soil at site	• Used rainout shelter to stimulate different water contents; isotope values by isotopic labelling via irrigation • Large mean absolute differences between cryogenic vacuum extraction and *in situ* vapor measurements • *in situ* soil water vapor method captures temporal dynamics in the isotopic signature of soil water well while the destructive approach also includes the natural lateral isotopic heterogeneity
Kühnhammer et al. (2020)	Laboratory	Soil water isotope values of soil column depth-profiles Transpiration water isotope values	• Material: gas permeable membrane (PP) and throughflow plant chamber • Soil type: silt loam • Plant species: *Centaurea jacea* (herbaceous) • Push-trough system with excess tube; dry synthetic air flow of 50 ml/min at inlet, dilution with dry synthetic air • Calibration: - two soil standards with gas permeable membranes integrated into automated system - calibration equation developed by Rothfuss et al (2013), drift correction, correction for effect of wvmr • Validation: - comparison of calculated liquid values with water added to soil column - agreement between soil and transpiration isotope values in dual isotope space - comparison root water uptake profiles and changes in soil water content	• Data set of 48 days monitoring isotopic changes in soil and plant water uptake + error propagation to estimate realistic value for measurement precision + combined continuous *in situ* measurement across soil profile and in plant transpiration + check for isotopic steady-state in plant transpiration + root water uptake modelling including additional parameters − No check for isotopic equilibrium in soil measurements − Not easily transferable to the field

Dubbert et al., (2013)	Semi-arid (Portugal)	Evaporation bulk water isotope values	• Material: Custom build soil chamber • Soil type: loamy sand • Open gas exchange system following the design of Pape et al. (2009) • Calibration: - liquid injection of 3 standards - water vapor concentration dependency from 5000-30000 ppmv considered	• First data set observing soil evaporation *in situ* under field conditions • Sensitivity analysis of the Craig and Gordon model for input parameters • Different conditions monitored (bare soil, root ingrowth, vegetated soil) • High impact of vegetation cover and root ingrowth on isotopic signature of soil evaporation
Quade et al. (2018)	Laboratory	Evaporation bulk water isotope values	• Material: Custom build soil chamber • Soil type: silty loam • Keeling plot approach • Calibration: - Vapor equilibration standards in the same soil as the experimental column	• Evaluating temporal dynamics of the kinetic fractionation factor • αK values within the range reported in the literature • prevalence of turbulent water vapor transport under water-saturated soil conditions and at soil water content significantly lower than saturation
Volkmann et al. (2016)	Humid (Southern Germany)	Xylem water isotope values	• Material: gas permeable membrane (PE) with mixing chamber • Plant species: deciduous maple trees (*Acer campestre L.*; 9m tall, 0.2m in diameter at breast height and $30m^2$ of crown projected area) • Mixed system; dry N_2 provided in throughflow line, set at the flow rate induced by laser spectrometer (30-35 ml/min); dilution with N_2 directly in probe; pre-flushing of system for 120s • Calibration: - three standards, headspace measured; conversion of xylem vapor values using Majoube equation and measured temperatures in tree • Validation: - comparison with vacuum-extracted xylem cores measured with IRMS	• First study of *in situ* measured xylem water isotopes • *In situ* monitoring of xylem water isotopes is feasible, but complicated • Good precision and repeatability, but accuracy needs to be improved • Longer-term study needed • Issue of organic contamination needs to be addressed + Condensation avoided via dilution directly in probe − No check if equilibration conditions were reached in probe − Partially large discrepancies between extracted values and in situ measured data − Complicated

Marshall et al. (2020)	Greenhouse	Xylem water isotope values	• Material: hole drilled through the stem of a tree, Swagelok connections on both sides (airtight); flush with acetone to avoid pitch and resin production • Plant species: Pine trees (*Pinus sylvestris* L. and *Pinus pinea* L.); first experiment: cut-stem tree; second experiment: intact-root experiment • First experiment: pull-only with ~35-40 ml/min and flush of system manually when needed; second experiment: push-through with 80 ml/min of dry air (diving air), 5min pre-flush and 15 min measurement time • Calibration: - four standards, headspace measured; conversion of xylem vapor values using Majoube equation and measured temperatures in tree • Validation: - comparison to source water isotope values	• Novel approach for measuring xylem water isotopes • Method requires testing for different tree species and under different environmental conditions + *In situ* monitoring of xylem water isotopes of natural abundances is possible + No gas-permeable membranes are required + No influence of organic contamination observed + fundamental aspects of *in situ* studies thoroughly evaluated by modelling − Systems needs to be simplified − possibility of liquid water reaching water vapor analyser if tree shows strong defence mechanism or 'backflow' of water occurs
Wang et al. (2013)	Great Plains, Oklahoma, USA	Evaporation bulk water isotope values Transpiration water isotope values Evapotranspiration water isotope values	• Material: modified commercial soil chamber, commercial plant chamber, custom build ET chamber • Soil type: not provided • Plant species: *Bromus arvensis L., Vicia sativa L., Solanum carolinense L., Euphorbia dentata Michx., Tridens flavus (L.) Hitchc.* • Keeling plot approach • Calibration: Liquid injections	• Testing chamber based bare soil observations vs modelled by Craig and Gordon model and impact on ET partitioning • Difference between approaches on T/ET • Demonstrate necessity for uniform partitioning approach
Wang et al. (2012)	Laboratory, arid (Kenia)	Transpiration water isotopes	• Material: custom build transpiration chamber, OA-ICOS • Plant species: *Spathiphyllum spp, Acacia spec.* • Open gas exchange system • Calibration: - verification of set up using a dew point generator - liquid injections to calibrate the laser spectrometer	• First publication of in-situ transpiration measurements + Observation of transit from non-steady state to isotopic steady state − Limited data set − Complex set up

Simonin et al. (2013)	Laboratory	Transpiration water isotope values	• Material: fully automated leaf gas exchange system (MPH1000, Licor 7600); Laser spectrometry • Plant species: Citrus, Tobacco • Open gas exchange system • Calibration: - Liquid water standards injected spanning the observed isotopic range - Concentration dependencies 3000-24000 ppmv	• Exposed leaves to changes in environmental conditions • Non-steady state effects dominate transpiration of both species • Even when leaves are already physiologically transpiring in steady state + Evaluated the rate of change in leaf water, determined leaf water turn-over time
Dubbert et al. (2014)	Semi-arid (central Portugal)	Transpiration water isotope values	• Material: Custom build branch chamber, Laser spectrometer • Plant species: cork oak (*Quercus suber L.*) • Open gas exchange system • Calibration: - liquid injection of 3 standards - concentration dependency from 5000-30000 ppmv	• Diurnal courses of isotopic signatures of transpiration during different seasons • Dominance of non-steady state effects • Sensitivity analysis of the Craig and Gordon/Dongmann based model
Song et al. (2015)	Laboratory	Transpiration water isotope values	• Material: Fully automated leaf gas exchange system (Licor 7600), Laser spectrometer • Plant species: Cotton • Calibration: - liquid injection, following Simonin et al., 2013	• Adapting existing non-steady state leaf water model to cuvettes, where delta atm is influenced by delta T

Table S2: Summary of physically-based models that are able to simulate water movement and water stable isotope values in different ecosystem water pools and specifically, different depths of the vadose zone and/or plant water

Model / Authors	*Applications/Further development*	*Focus/Objective*	*Scale*	*Advantages (+) /Disadvantages (-)*
EcH2O-iso *Kuppel et al. (2018)*	*Smith et al. (2019), Knighton et al. (2020)*	physically-based representation of energy-water-ecosystem coupling, vertical and lateral connectivity in the catchment explicitly resolved allrounder - spatially distributed	plot to catchment, spatially distributed	(+) flexible definition of spatial domain (+) simulation of spatial patterns and heterogeneity (+) coupled model of energy fluxes, water fluxes (includes both $\delta^{18}O$ and $\delta^{2}H$) and storage and vegetation state with age tracking (+) process-based linkage of spatial-temporal patterns in energy-water-ecosystem coupling across headwater (methodological middle path between detailed plot-scale, catchment rainfall-runoff models and land surface models) (-) high data requirements (-) limited resolution of vadose zone (3 layers)
HYDRUS-1D *Stumpp et al. (2012)*	*Stumpp, Hendry (2012), Huang et al. (2015), Sprenger et al. (2015), Brinkmann et al. (2018), Sprenger et al. (2018), Zheng et al. (2018)*	models water flow and solute transport in porous media	1D	(+) developed for soil water movement and solute transport in soils with different degrees of saturation (+) well-established and widely used model in soil hydrology (-) fractionation processes during soil evaporation not in corporated
MuSICA *Ogee et al. (2004)*	*Gangi et al. (2015), Hirl et al. (2019)*	model incorporates different vegetation layers and leaf classes, models both CO2 and H2O fluxes	1D	(+) different modules that can also be used independently (+) CO_2 and H_2O fluxes and their exchange modeled (next to energy) (+) different leaf-level variables predicted for plant parts with different light regime (sunlit/shaded), water status (wet/dry leaves) and age at different levels within canopy (understorey/canopy) (-) studies 'only' modeled $\delta^{18}O$ up to date
R-SWMS *Meunier et al. (2018)*	*Couvreur et al. (2020)*	mechanistic representation of root water uptake, focus on rhizosphere processes	plant/rhizotron 3D root system and soil,	(+) realistic representation of root architecture and its effect on RWU is accounted for, physical representation of water flow in roots (-) 3D root system architecture needs to be simulated separately (-)'only' $\delta^{18}O$ modeled up to date (-) only tested in rhizontrons so far (limited spatial extent) - more for lab studies then larger scale field investigations

SiSPAT-Isotope *Braud et al. (2005)*	*Braud et al. (2009), Rothfuss et al. (2012)*	solves couples heat and water (both liquid and vapor phase) transfer equations in the soil	1D	(+) modelling of isotopes in liquid soil water and vapor phase (-) only applied in laboratory studies (monolith experiments)
Soil-Litter-Iso (SLI) *Haverd and Cuntz (2010)*	*Haverd et al. (2011), Cuntz and Haverd (2018)*	focus on the impact of litter on soil evaporation, trade-off between efficiency (to enable use at regional scale) and accuracy representing coupled heat and water transport (vapor and liquid phase)	1D	(+) suitable for use in an isotope-enabled land surface model (+) optional litter layer with effect on soil evaporation (+) similar physical principles than SiSPAT-Isotope but faster numerical implementation
SWIS *Mueller et al. (2014)*	*Sprenger et al. (2018)*	investigate soil water movement and pools (vertical percolation on hillslopes and mobile vs immobile pore water)	1D	(+) relatively simple, focussed on water movement in the vadose zone (+) comparison with HYDRUS-1D simulations in Sprenger et al. (2018)
TOUGHREACT *Singleton et al. (2004)*	-	couples multiphase flow (water and air), heat flow, aqueous and gaseous species transport and kinetic and equilibrium mineral-water-gas reactions	flexible scale	(+) more for thicker soil layers and geochemical applications (+) applicable to 1-, 2- or 3-D domains (+) developed for assessing infiltration into soils and contaminant or mineral transport