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Special Section: Stable Isotope Approaches in Vadose Zone Research

Core Ideas

- Soil water stable isotope profiles can be used to quantify groundwater recharge.
- Climate conditions are recorded in water stable isotope profiles of the unsaturated zone.
- Soil water isotope profiles provide insight into the seasonality of recharge events.

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Using Water Stable Isotopes in the Unsaturated Zone to Quantify Recharge in Two Contrasted Infiltration Regimes

Florent Barbecot,* Sophie Guillon, Eric Pili, Marie Larocque, Elisabeth Gibert-Brunet, Jean-François Hélie, Aurélie Noret, Caroline Plain, Vincent Schneider, Alexandra Mattei, and Guillaume Meyzonnat

A reliable estimate of recharge is needed for the sustainable management of groundwater resources. Water stable isotope ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) profiles in the unsaturated zone are frequently used to quantify groundwater recharge based on the seasonality of water isotopic compositions in precipitation. A very simple approach consists of integrating the soil water content between peak values of soil water isotopic composition, typically corresponding to precipitation signatures from warm and cold seasons. When precipitation isotopic compositions are available, a conceptual surface water isotopes budget and lumped parameter dispersion model can be computed. These models were applied on two field sites with similar permeable soils with grass cover but contrasting recharge regimes and seasonality, one in the Paris Basin (France) with continuous recharge from autumn to spring and the other in the St. Lawrence Lowlands (Quebec, Canada) with episodic recharge in fall and after snowmelt. For the two sites, the peak-to-peak method and isotope surface budget led to comparable recharge intensities. At least at the Paris Basin site, evaporation was shown to slightly modify the average unsaturated zone and hence groundwater isotope composition. The proposed parameterization of isotope fractionation due to evaporation allows qualitative estimation of the fraction of evaporation, at least during the recharge seasons. In spite of its simplifications and limitations, the proposed parsimonious model can give estimates of recharge in a variety of sites even if they are not well characterized, as it benefits from the large availability of monthly isotopic compositions in precipitation.

Abbreviations: d-excess, deuterium excess; GNIP, Global Network of Isotopes in Precipitation; LMWL, Local Meteoric Water Line; lc-excess, line-conditioned excess; PB, Paris Basin; PET, potential evapotranspiration; SLL, St. Lawrence Lowlands.

The UNESCO World Water Assessment Program identified a gap in knowledge of the impact of climate change on groundwater resources. While numerous recent studies have attempted to bridge this gap, they have also demonstrated that we currently do not have the ability to quantitatively predict the impact of climate change on groundwater resources with a satisfying degree of confidence (Crosbie et al., 2013; Kurylyk and MacQuarrie, 2013). Recharge is a key parameter in groundwater management, and thus a reliable estimate of recharge is necessary for sustainable groundwater resource development (Rivard et al., 2014). To achieve accurate water budgets, recharge quantification has been investigated at local scales using lysimeters (Pflutschinger et al., 2012; Xu and Chen, 2005), water-table fluctuations (Hagedorn et al., 2011; Healy and Cook, 2002; Liang and Zhang, 2012), and baseflow analysis (McCallum et al., 2014). Independent of the method, the impact of all possible environmental stresses, meteorological variability, and changes in climate, land use, and water extraction on the recharge regime cannot be completely taken into account (Kurylyk and MacQuarrie, 2013).

Variability in the stable isotope signature of soil pore water collected at depths with suction lysimeters has been used to investigate subsurface processes (Darling and Bath,

1988; Stumpp et al., 2009a, 2009b; Thomas et al., 2013). As an alternative method, water stable isotopes in the unsaturated zone offer a time-integrated fingerprint of recharge and of subsurface water pathways (Darling and Bath, 1988; Bengtsson et al., 1987; Koeniger et al., 2016). Unsaturated zone stable isotope profiles under temperate climate conditions have thus been used to study groundwater recharge mechanisms (Lee et al., 2007; Li et al., 2007; McConville et al., 2001; Mueller et al., 2014; Saxena, 1984; Song et al., 2009; Stumpp and Hendry, 2012; Stumpp et al., 2009a, 2009b). Suction lysimeters are quite time consuming to use, with a sampling effort of at least 1 yr, while cryogenic extraction of soil water allows the collection of comparable stable isotope data within one or a few field work days. New, faster methods, such as direct equilibration, are also becoming widely used and raise issues regarding the possible biases between the various methods of soil water isotope analysis used (Orlowski et al., 2016).

The isotopic composition of precipitation is strongly correlated with air temperature. A distinct seasonal pattern therefore occurs in precipitation under temperate climates, with summer rainfall enriched in heavy isotopes and winter rainfall depleted (Rozanski et al., 1993). In addition to $\delta^{18}\text{O}$ and $\delta^2\text{H}$, line-conditioned excess (lc-excess) values (Landwehr and Coplen, 2004) are very sensitive to local evaporation and associated isotope fractionation occurring at the surface. These are therefore used in addition to $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to evaluate recharge processes and apparent mean residence times of soil water (Lee et al., 2007).

Even if transpiration predominates under temperate climates and is considered to not fractionate water stable isotopes, evaporation from plant interception or from the upper soil leads to fractionation and enrichment in heavy isotopes (Braud et al., 2005, 2009b; Sprenger et al., 2016; Sutanto et al., 2012). Water recharging during a given season can therefore be identified in deep unsaturated zone profiles, and recharge rates can be obtained from the displacement between successive seasonal inputs (Gehrels et al., 1998; Małozzewski et al., 2006; Małozzewski and Zuber, 1993; McConville et al., 2001; Saxena, 1984). On the one hand, this simple peak-shift method is easily applied (Adomako et al., 2010), even if the isotopic compositions of precipitation are not available (Gehrels et al., 1998). On the other hand, numerical models, such as SiSPAT-Isotopes (Braud et al., 2005, 2009a), Soil-Litter-Iso (Haverd and Cuntz, 2010), or a modified version of HYDRUS-1D (Stumpp et al., 2009a, 2009b; Stumpp and Hendry, 2012), are increasingly being used to understand the dynamics of water stable isotopic composition in the unsaturated zone (Sprenger et al., 2015). Such level of model refinement is associated with a high data requirement that can only be achieved for specific study sites, but less for more numerous and less known sites at the regional scale where there is a lack of recharge rate estimations.

The aim of this study was to apply a simple and parsimonious method to quantify the rate and seasonal pattern of recharge, based on water stable isotope depth profiles, applicable to sites under contrasted climate conditions and requiring a limited amount of additional data. The two study sites are in the Paris Basin (France)

and in the St. Lawrence Lowlands (Quebec, Canada), for which water stable isotopic compositions of both precipitation and the unsaturated zone are available. Recharge was calculated based on a simple peak-shift approach. A model coupling a surface water and isotope budget to a lumped parameter model is proposed for a more robust quantification of recharge but also to explain the evolution of water isotopic composition in the unsaturated zone, and particularly to investigate the influence of evaporation.

Materials and Methods

Study Sites and Sampling

The Paris Basin Site

The Paris Basin site (PB) is located 35 km south of Paris (France), in the very fine and well-sorted sands of the Oligocene Fontainebleau aquifer. This regional unconfined aquifer has a maximum thickness of 50 to 70 m. The total porosity of the aquifer is 25 to 40%, with volumetric water content in the unsaturated zone in the range of 7 to 28% (Schneider, 2005). The hydraulic conductivity reaches 1.10^{-5} to 6.10^{-5} m/s (Corcho Alvarado et al., 2007; Renard and Tognelli, 2016).

This study site is covered with grass, with a 60-cm-thick sandy soil layer overlying a clayey-sand layer from 60 to 100 cm and homogeneous sands below 100 cm (Fig. 1a). In May 2006, a 3-m-deep trench was dug in the unsaturated zone using an excavator. Soil sampling for pore water extraction and isotopic analysis was conducted immediately after opening the trench. Soil was sampled using a spatula, with a 2.5-cm spacing from the 0- to 137-cm depth and a 10-cm spacing from the 140- to 280-cm depth (Fig.

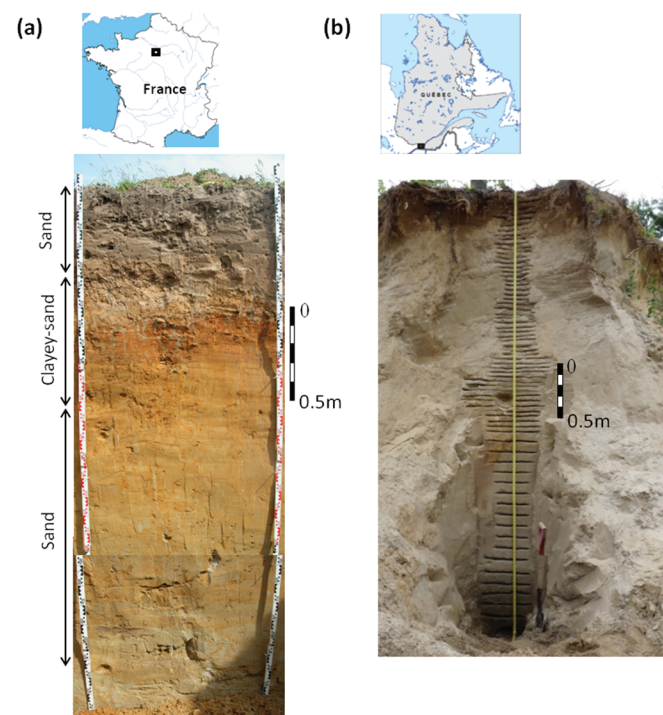


Fig. 1. Locations and photographs of the trenches where sand samples were taken for soil water extraction and water isotope analysis for (a) the Paris Basin and (b) the St. Lawrence Lowlands.

1a). Soil samples weighing on average 100 g were collected in polypropylene bottles and were stored in these airtight bottles until stable isotope analysis. Gravimetric water content was measured on the grab samples and converted into volumetric water content assuming a bulk density of 1500 kg/m³.

The water table below the site lies, on average, 6 to 8 m below the surface. Several groundwater samples were collected from nearby wells for stable isotope analysis.

Meteorological data, precipitation and temperature, were obtained with a 15-d time step from the nearby Trappes station (Meteo France). The average annual precipitation is 668 mm/yr, while average monthly temperatures fluctuate between 0 and 25°C. An average recharge rate of 100 to 150 mm/yr was calculated for the previous decades based on environmental tracers and at the regional scale around the study site (Corcho Alvarado et al., 2007) (Table 1) and confirmed by hydrological modeling in the Fontainebleau Sands (Renard and Tognelli, 2016).

Precipitation was collected 10 km away, at the GEOPS laboratory (Université Paris-Sud/Paris-Saclay, Orsay, France), from August 2002 to July 2012, using paraffin oil to prevent evaporation of water in the collector and isotopic fractionation. Cumulated bulk precipitation was sampled twice a month, and its isotopic composition was measured (Fig. 2–4). Deuterium excess ($d\text{-excess} = \delta^2\text{H} - 8 \delta^{18}\text{O}$) in precipitation was calculated to look for variable origins of air masses. The Local Meteoric Water Line (LMWL) was defined based on the isotopic composition of precipitation. Its equation ($\delta^2\text{H} = a \delta^{18}\text{O} + b$) was used to calculate lc-excess values ($lc\text{-excess} = \delta^2\text{H} - a \delta^{18}\text{O} - b$) for the soil pore water profile.

The St. Lawrence Lowlands Site

The St. Lawrence Lowlands site (SLL) is located 70 km southwest of Montreal, in the Vaudreuil-Soulanges area (Quebec, Canada), and in the medium sands of the Saint-Télésphore esker. These glaciofluvial sediments can reach up to 40-m thickness and lie above the regional bedrock aquifer (Larocque et al., 2015). The aquifer is locally unconfined, with a total porosity of 40% and a hydraulic conductivity on the order of 10⁻⁵ to 10⁻⁴ m/s. The study site is located in a flat area close to a sand quarry. The area is covered mainly by woodland, except on the site outcrops where the soil is covered with grass and where the unsaturated zone was sampled.

Table 1. Estimate of the amount of annual groundwater recharge at the Paris Basin (PB) and St. Lawrence Lowlands (SLL) using several methods.

Method	Groundwater recharge	
	PB	SLL
	mm/yr	
Unsaturated zone isotope profile	304	114
Hydro-isotopic water budget	203	200–370
Regional modeling	150†	189‡

† Corcho Alvarado et al. (2007).

‡ Larocque et al. (2015).

Taking advantage of an outcrop recently exposed on the border of the sandpit excavation, the entire unsaturated zone was sampled in May 2013 for the measurement of water content and pore water isotopic composition. The vertical outcrop was refreshed immediately before sampling by removing the 5 to 10 cm of sand exposed to the atmosphere. Sand samples were taken using a spatula, with a 5-cm spacing below the soil surface down to a depth of 2.5 m and then a 10-cm spacing down to the water table at the 4.5-m depth (Fig. 1b). Soil samples weighed on average 100 g and were stored in airtight polypropylene bottles until stable isotope analysis. The sand was homogeneous throughout the whole depth profile. Gravimetric water content was measured on the grab samples and converted into volumetric water content assuming a bulk density of 1500 kg/m³. Daily weather data (minimum and maximum temperature and precipitation) were obtained from the Coteau du Lac station (<http://www.mddelcc.gouv.qc.ca/climat/donnees/index.asp>), 20 km from the study site. Average annual precipitation in this area for the period 1980 to 2010 is 960 mm/yr (Larocque et al., 2015), with average monthly temperatures ranging from -11 to 23°C. An average recharge rate of 189 mm/yr was calculated for the period 1990 to 2010 using a regional surface water budget (Larocque et al., 2015) (Table 1).

Monthly isotopic composition values and precipitation amounts were obtained from the closest station of the Global Network of Isotopes in Precipitation (GNIP, http://www-naweb.iaea.org/naweb/ih/IHS_resources_gnip.html), namely Ottawa, from January 2010 to June 2012 (Fig. 4). Even though Ottawa is relatively far (130 km) from the study site, the climate is similar at Ottawa and the SLL site, with similar average temperatures and precipitation as well as altitude, and Ottawa precipitation isotope compositions can thus be used for the SLL site model. Discrete snowpack and rain samples were collected at SLL for measurement of isotope composition in 2012 and 2013. As was done for PB, the LMWL was determined and used to calculate the lc-excess for the soil pore water profile.

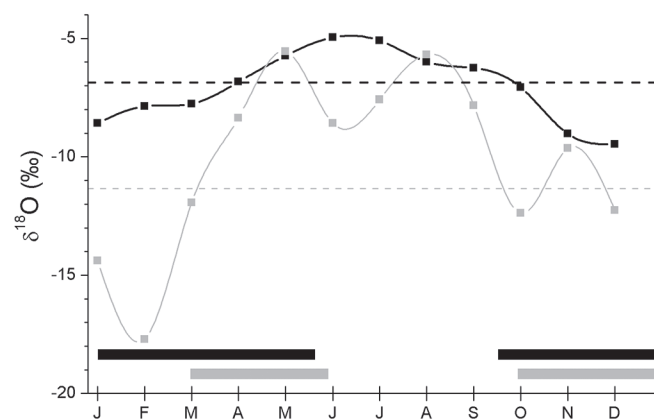


Fig. 2. Monthly average O isotopic composition of precipitation at the Paris Basin (PB, black) and the St. Lawrence Lowlands (SLL, gray). For each site, dashed lines represent the volume-weighted average O isotopic composition of the unsaturated zone profiles sampled in May 2006 for PB and May 2013 for SLL. Periods of recharge obtained from the water budget are represented by horizontal bars.

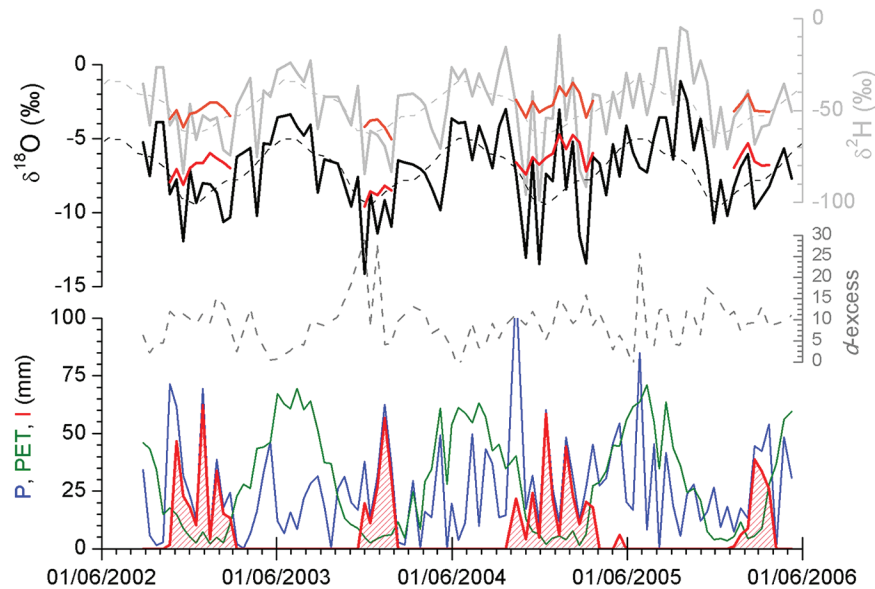


Fig. 3. Time series of water and isotope surface budgets for the Paris Basin site from 2002 to 2006: isotopic composition measured in precipitation (black and gray solid lines with monthly average as dashed lines), isotopic composition calculated in infiltrating water (red and orange), deuterium-excess in precipitation (dashed gray line), measured precipitation (blue), calculated potential evapotranspiration (green), and infiltration into the unsaturated zone (red).

Water Extraction and Isotopic Analysis

Stable isotopic analysis of the soil pore water was conducted on water extracted from the collected soil samples using cryogenic vacuum extraction. Because soils sampled for this study were mainly of sand type and relatively wet, water isotope composition from cryogenic extraction can be assumed to have limited bias. A small soil sample of around 100 g for PB (40 g for SLL) was introduced into a vacuum line. Pore water was extracted for 6 h for PB samples and 2 h for SLL samples and condensed in a collection tube maintained in liquid N₂ (Araguás-Araguás et al., 1995). The soil sample was heated to around 60°C during the extraction, under a vacuum of around 1 Pa. After extraction, the soil sample was weighed, heated overnight at 100°C, and then reweighed to determine the water extraction yield as well as the initial soil water content.

The isotopic signature of water condensed in the collection tube was shown to follow a Rayleigh distillation curve (data not shown), and >98% of pore water must be extracted to ensure the absence of isotopic fractionation in the pore water sample. For this study, extraction yields were monitored to be >98% for all samples.

Oxygen and H isotopic compositions of the extracted soil pore water as well as of the groundwater and precipitation were measured with a Thermo Finnigan Delta+ isotope ratio mass spectrometer in dual inlet mode, coupled to an equilibration bench, at the GEOPS laboratory (Université Paris Sud, France) for PB and on a Micromass Isoprime isotope ratio mass spectrometer in dual inlet mode, coupled to an Aquaprep system, at GEOTOP-UQAM (Montreal, Canada) for SLL. Each analysis required 200 μL of water, equilibrated at 40°C for 7 h with CO₂.

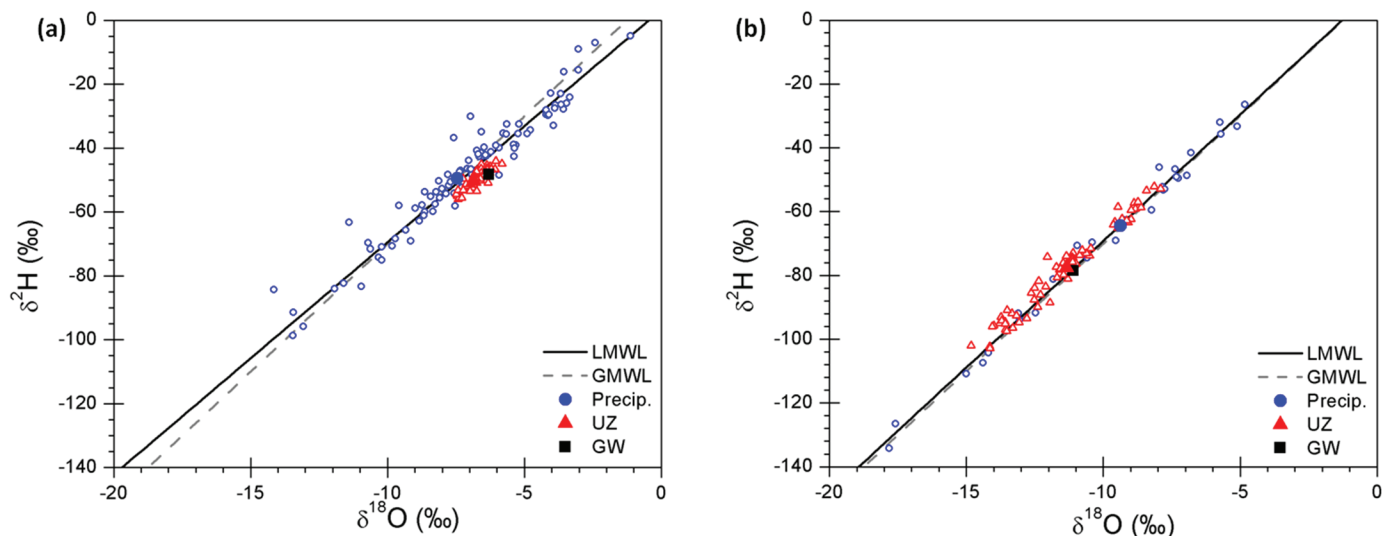


Fig. 4. Stable isotopic composition of water in precipitation (blue circles), in the unsaturated zone (UZ) pore water (red triangles), and in groundwater (GW, black squares) for (a) the Paris Basin and (b) the St. Lawrence Lowlands. For each site, filled symbols correspond to volume-weighted averages of individual empty data points. For each site, the Local Meteoric Water Line (LMWL) and Global Meteoric Water Line (GMWL) are represented by a black solid line and gray dashed line, respectively.

for $\delta^{18}\text{O}$, and equilibrated at 40°C for 4 h with H_2 with a Pt catalyst for $\delta^2\text{H}$.

Raw data were corrected using three internal working water standards, expressed in delta notation and normalized to the Vienna Standard Mean Ocean Water (VSMOW)–Standard Light Antarctic Precipitation scale:

$$\delta^{18}\text{O} = \frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \quad [1]$$

where

$$R_i = \left(\frac{[^{18}\text{O}]}{[^{16}\text{O}]} \right)_i$$

and i corresponds to the sample or VSMOW. Hydrogen isotopic composition is expressed similarly to $\delta^2\text{H}$, with $R_i = ([^2\text{H}]/[^1\text{H}])_i$. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are reported in per mil (‰) vs. the VSMOW international standard. The precision of liquid water analysis (1σ) was 0.05‰ for $\delta^{18}\text{O}$ and 1‰ for δD . To check that the uncertainty due to cryogenic extraction was small, dried soil samples were rewetted with standard water. The measured isotopic composition for the extracted water was equal to that of the standard water in the range of the analytical precision of the liquid water analysis.

Recharge Estimation from Water Isotope Profiles in the Unsaturated Zone

The seasonal variation in the isotopic composition of precipitation (Fig. 2), combined with a seasonal pattern of evapotranspiration, were directly linked to atmospheric temperatures. This led to a seasonal pattern of the amount and isotopic composition of infiltration and recharge. Even if the input function (i.e., rain isotopic composition) was unknown, a simple interpretation of water stable isotope depth profiles would allow the amount and periods of recharge to

be quantified. The successive recharge seasons (summer–autumn vs. winter–spring) were identified in water isotope profiles in the unsaturated zone due to their contrasting water isotopic compositions (enriched vs. depleted in heavy isotopes) (Fig. 2, 5, and 6). The amount of recharge I (in m/yr) that occurred during a certain time period T (in yr) was obtained by integrating the volumetric water content $\theta_w(z)$ over the depth interval $[Z_1, Z_2]$ (in m), corresponding to the time period T (equation after Leibundgut et al., 2009):

$$I = \frac{\int_{Z_1}^{Z_2} \theta_w(z) dz}{T} \quad [2]$$

For this method, the time period could be only roughly estimated, typically to one hydrological season or 1 yr, from the evolution of water isotope composition with depth.

Lumped Parameter Models for Water Isotopic Composition in the Unsaturated Zone

To explain the observed evolution of water isotopic composition in the unsaturated zone, a surface water and isotopic mass balance was used, combined with a lumped parameter model for isotope transport in the unsaturated zone. The successive steps of the model, from a time series of precipitation and its stable isotopic composition to the depth profile of water isotopes in the unsaturated zone, are described below.

Water Budget at the Subsurface

As a reference point from which to discuss the water budget at the surface, the traditional Thornthwaite method (Thornthwaite, 1948) was used to calculate the potential recharge fluxes. This conceptual box model applies to the soil layer from the surface to the root depth:

$$P(i) = \text{ET}(i) + R(i) + I(i) + [S(i) - S(i-1)] \quad [3]$$

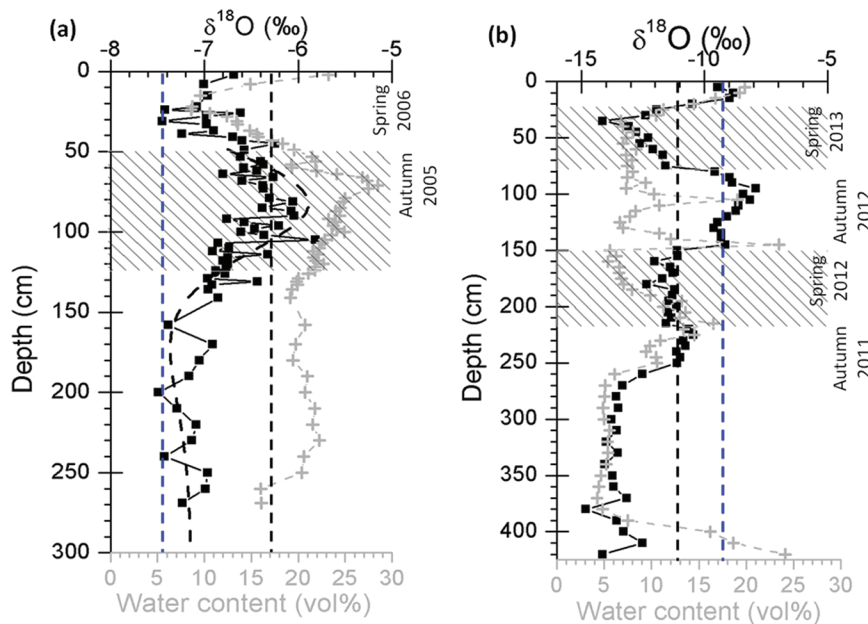


Fig. 5. Depth profiles of pore water O isotopic composition (black) and volumetric water content (gray) at (a) the Paris Basin and (b) the St. Lawrence Lowlands. Vertical dashed lines correspond to volume-weighted average isotopic composition in groundwater (black) and precipitation (blue). Annual or seasonal recharge is calculated through depth integration of water content in shaded areas. For the Paris Basin, the modeled depth profile of isotopic composition (dashed line) was calculated from the hydro-isotopic surface budget and the one-dimensional lumped parameter model.

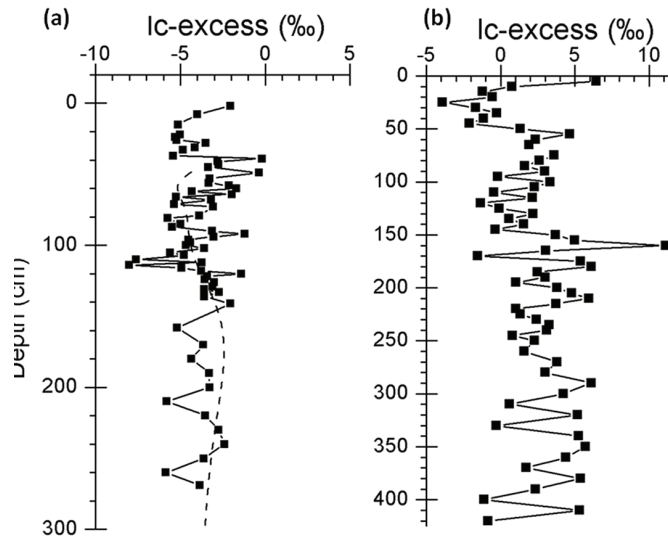


Fig. 6. Depth profiles of line-conditioned excess (lc-excess) in pore water at (a) the Paris Basin and (b) the St. Lawrence Lowlands. For the Paris Basin, the modeled depth profile of lc-excess (dashed line) was calculated from the hydro-isotopic surface budget and the one-dimensional lumped parameter model.

where i is the time step, P is precipitation (rain), ET is actual evapotranspiration, R is surface and subsurface runoff, I is percolation below the root depth, i.e., recharge, and S is soil storage, all expressed in millimeters.

This water budget was calculated at the smallest time step available for stable isotopes in precipitation (15 d for PB, 1 mo [i.e., 28–31 d] for SLL). Potential evapotranspiration (PET) was calculated following Turc (1961). Even if it was shown to tend to underestimate evapotranspiration (Fisher and Pringle, 2013), this method was originally developed for a monthly time step, close to the one used here, and could be applied solely with temperature data, hence well adapted for poorly instrumented sites. For both PB and SLL sites, surface and subsurface runoff was assumed to be negligible due to the flat topography and very permeable sandy soils. The conceptual soil storage reservoir, with a maximum capacity S_{\max} , corresponded to the upper soil down to the maximum rooting depth (0.1–0.2 m at both sites), where evaporation and transpiration occurred, and below which there was no more water abstraction. Water “overflowing” and leaving this soil reservoir percolated vertically in the unsaturated zone and finally recharged the underlying aquifer. At each time step i , precipitation $P(i)$ and soil water $S(i-1)$ were considered as available water for evaporation and transpiration. Actual evapotranspiration was calculated based on the demand on PET and this amount of water available in the precipitation and soil reservoir: $ET(i) = \min[PET(i), S(i-1) + P(i)]$. If some water remained available after subtraction of the actual evapotranspiration, it was added to the soil storage. Recharge was then calculated as overflow, water exceeding the threshold capacity S_{\max} of the soil storage reservoir. This could be summarized as $I(i) = \max\{S(i-1) + P(i) - \min[PET(i), S(i-1) + P(i)], 0\}$ and $S(i) = \max\{S(i-1) + P(i) - \min[PET(i), S(i-1) + P(i)], S_{\max}\}$.

Such a simple conceptual box model was assumed valid because the calculation time step was long, typically 15 to 30 d, and because the objective was to build a data parsimonious model.

For SLL, recharge was expected to occur in autumn and with snowmelt in the spring, the soil usually being frozen from mid-December to March. Hence, the water budget was modified, with evapotranspiration and recharge set to zero when the average monthly temperature remained below zero. The potential excess water then accumulated in the soil reservoir until positive temperatures occurred.

Hydro-isotopic Surface Budget

Following the traditional surface water budget (Eq. [3]), a simple mass balance approach was applied to determine the isotopic composition of the percolating water. At each time step, the water isotopic composition of the soil storage reservoir was calculated by weighting the isotopic composition of water in the soil reservoir at the previous time step and the isotopic composition of the precipitation at the current time step:

$$\delta_{\text{mix}}(i) = \frac{\delta_S(i-1)S(i-1) + \delta_P(i)P(i)}{S(i-1) + P(i)} \quad [4]$$

where δ is the isotopic composition of $\delta^{18}\text{O}$ or $\delta^2\text{H}$, δ_S and δ_P are the isotopic compositions of soil storage and of precipitation, respectively, and $S(i)$ and $P(i)$ are the amounts of water in the soil storage and in precipitation, respectively, at the i th time step.

Partitioning between evaporation and transpiration was not included in the model, neither based on field properties nor directly based on water stable isotopes as done by Sutanto et al. (2012). However, for grassland under northern latitudes as for the two sites, transpiration was shown to dominate with >60 to 65% of total actual evapotranspiration (Wei et al., 2017). As discussed below, the isotopic composition of water in the unsaturated zone was used as a simple proxy to identify whether some evaporation occurred during the recharge period(s), without going further into quantification. At PB, isotopic compositions clearly followed an evaporative trend, with negative lc-excess (Fig. 6a), while it was not the case at SLL with null or slightly positive lc-excess (Fig. 6b). In the model, isotopic fractionation was therefore assumed to occur due to evaporation of water in the soil reservoir. Soils of the two study sites were wet (Fig. 5, water content >10% v/v), consistent with a medium intensity of evapotranspiration fluxes, and the equations of isotopic fractionation for open water (Gonfiantini, 1986) were used, including equilibrium fractionation as well as kinetic enrichment. At each time step, the isotopic composition of water in the soil storage was calculated by

$$\delta_S(i) = \left[\delta_{\text{mix}}(i) - \frac{A(T, H_r)}{B(T, H_r)} \right] f^{B(T, H_r)} + \frac{A(T, H_r)}{B(T, H_r)} \quad [5]$$

where f is the fraction of water remaining after evaporation, and $A(T, H_r)$ and $B(T, H_r)$ are parameters defined by Gonfiantini (1986), which depend on both atmospheric temperature, T ,

and atmospheric relative humidity, H_r . Following Barnes and Allison (1983), in A and B terms, the kinetic enrichment is equal to $(1 - H_r)$, the relative difference of transport resistance in air between isotopes being neglected.

The outputs of the water budget (Eq. [3]) were used to calculate $\delta_{\text{inf}}(i)$, the isotopic composition of water percolating from soil storage into the unsaturated zone. The value of $\delta_{\text{inf}}(i)$ was determined for the time steps during which recharge occurred (Fig. 3) and was equal to $\delta_S(i)$, the isotopic composition of water in soil storage at this same time step.

The model was applied to PB from January 2002 to May 2006. For SLL, the hydro-isotopic surface budget was calculated from January 2010 to May 2013, with a monthly time step.

Transport in the Unsaturated Zone: Piston Flow with Dispersion

The second step of the model was the transport of water stable isotopes through the unsaturated zone. Considering the limited amount of data available with which to constrain the model, a conceptual input–output lumped parameter model based on transit time distribution was chosen in this study to identify the main processes. According to the literature (Barnes and Allison, 1988; Lindström and Rodhe, 1992) and in agreement with the observed variability in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ with depth (Fig. 5), transport of water stable isotopes in the unsaturated zone occurred by convection or piston flow, as well as dispersion, leading to attenuation at depth. The convolution integral method of Małoszewski and Zuber (1993) was chosen to reproduce and interpret soil depth profile data.

First, the amount of recharge, $I(i)$ (Eq. [3]), and the isotopic composition of the percolating water, $\delta_{\text{inf}}(i)$, obtained from the water and isotope budgets as a function of time (Fig. 3), were combined and transformed into $\delta_{\text{inf}}(q)$, a series of isotopic compositions for each increment of recharge water q (in mm). Water content was not constant with depth (Fig. 5), but the spatial and temporal variations of soil water content were not included in the model because it was intended only as a simple model for validation of the surface budget and main recharge processes and not as an investigation of transient processes. The assumption of homogeneous and constant water content by volume, θ_w , was made, corresponding to steady-state vertical flow of water. This assumption was required to apply the transit time distribution model. A simple mass balance, or piston flow model, was applied to propagate the series $\delta_{\text{inf}}(q)$ into a series $\delta'_{\text{inf}}(z)$ of isotopic composition as a function of depth in the unsaturated zone. This was done using the simple conversion

$$z = \frac{Q_{\text{max}} - q}{\theta_w} \quad [6]$$

where z is the depth (in mm) reached by the parcel of water after a cumulated amount of recharge of q (in mm), and Q_{max} is the cumulated recharge amount (in mm) calculated for the entire time series (2002–2006 at PB).

Second, the relationship between input and output soil water isotopic compositions was based on a transit time distribution

function. The dispersion model (Małoszewski et al., 2006) was chosen as the most appropriate for solute transport in soil columns. This dispersion model was retained also for its parsimony, with a dispersion parameter as the single parameter. However, the limitations of this model have to be kept in mind, especially through the steady-state assumption. The model proposed here aimed at giving a general estimate of water fluxes, not at explaining the transient dynamics of soil water isotopes.

Traditionally, the dispersion model was used to determine the temporal evolution of the isotopic composition of unsaturated zone water collected at a fixed depth with a lysimeter, based on the temporal evolution of the isotopic composition in precipitation. For the current application, the isotopic composition of unsaturated zone water for all depths had to be calculated at a fixed time, namely the time of sampling. The lumped parameter dispersion model was therefore modified as follows. For each depth Z , the isotopic composition after dispersion $\delta'_{\text{out}}(Z)$ was obtained by a convolution between the transit time distribution function with the theoretical non-attenuated depth profile $\delta'_{\text{inf}}(z)$:

$$\delta'_{\text{out}}(Z) = \int_{z=0}^{Z_{\text{max}}} \delta'_{\text{inf}}(z) g(Z, z) dz \quad [7]$$

where $Z_{\text{max}} = Q_{\text{max}}/\theta_w$ (in m) is the maximum depth reached by water that recharged at the real beginning of the time series, and g is the transit time distribution function of the dispersion model:

$$g(z) = \frac{\sqrt{Z} z^{-3/2}}{\sqrt{4\pi D}} \exp\left[-\frac{(Z-z)^2}{4DzZ}\right] \quad [8]$$

where D is the dispersion parameter (dimensionless), which corresponds to the inverse of the Peclet number (Małoszewski and Zuber, 1993) and hence can theoretically be linked to dispersivity.

The depth profile of the water content was not modeled, as it was not the main focus of the study and not adapted to the lumped parameter model.

The transport model was applied only at PB. For SLL, the surface budget was less well constrained, due to the lack of time series on snowpack and snowmelt, and the transport segment was not pursued.

Sensitivity Analysis and Calibration of the Model Parameters

Four years of data were available prior to sampling at PB. The model was thus run from July 2002 to May 2006. Isotopic compositions were observed to be constant below 2 m at PB (Fig. 5a). With such dispersion, the available 4-yr period of data was long enough so that the first and oldest recharged water isotopic compositions were attenuated at the 2-m depth. Especially, any data older than 2002 would have been attenuated. To ensure initialization of the model but keep its simplicity, the recharge time series, $\delta'_{\text{inf}}(z)$, was artificially extended into the past (corresponding to the deepest part of the unsaturated zone) using the measured average isotopic composition of the deep unsaturated zone. For cases

where shorter time series of meteorological data were available or if dispersion was lower, monthly average data of precipitation amounts and isotope compositions should be used for a spin-up period.

A simple sensitivity analysis was conducted to determine the influence of the hydro-isotopic budget parameters on the average isotopic composition and intensity of recharge (Table 2). The value of atmospheric relative humidity H_r did not influence much the isotopic composition of the recharged water but controlled the slope of the unsaturated zone data points relative to the meteoric water line in $\delta^{18}\text{O}$ – $\delta^2\text{H}$ space. The value of f strongly influenced the isotopic composition of the recharged water (Table 2), and the value of S_{max} also influenced it, albeit to a lesser extent. The values of these three latter parameters were determined by a simple inverse approach. The objective function φ that was minimized was defined as the difference between the calculated volume-weighted average $\delta^{18}\text{O}$ of recharge water and the measured volume-weighted average $\delta^{18}\text{O}$ in the unsaturated zone:

$$\varphi = \left| \frac{\sum_i [I(i)\delta_{\text{inf}}(i)]}{\sum_i I(i)} - \overline{\delta^{18}\text{O}_{\text{UZ}}} \right| \quad [9]$$

The calibration of the two parameters of the transport model, namely the dispersion coefficient, D , and soil water content, θ_w , was then performed. The transport parameter values depended on those of the parameters obtained from the surface budget. Soil water content θ_w was not very sensitive and was estimated by manual adjustment. For the dispersion coefficient, a coupled multiparameter calibration as in Sprenger et al. (2015) was not conducted, but rather a simple parameter adjustment based on the minimization of the objective function φ' , defined as the sum of the differences between the measured and calculated $\delta^{18}\text{O}$ in the unsaturated zone at each depth where measurement was available:

$$\varphi' = \left| \sum_{Z_0}^{Z_{\text{max}}} [\delta'_{\text{out}}(Z) - \delta^{18}\text{O}_{\text{UZ}}(Z)] \right| \quad [10]$$

The transport model applied only to water percolating below the active rooting depth. The upper 10 to 20 cm of the soil, which corresponded to the conceptual soil reservoir or at least where transient surface water fluxes occurred, were thus not handled by the transport model and not considered for the fit and interpretation.

Results

Water Budget

For PB, the average annual precipitation and potential evapotranspiration were 668 and 746 mm/yr, respectively. The surface water budget was calculated for a fitted S_{max} value of 52 mm, giving the best agreement for isotopic composition (see below). The actual evapotranspiration was 455 mm/yr, for an average recharge of 203 mm/yr (Table 1). Recharge was obtained almost continuously from September and October until April and May (Fig. 2 and 3). In that case, the value of S_{max} could be compared with the soil

Table 2. Sensitivity analysis of the hydro-isotopic surface budget to the parameters relative humidity (H_r), maximum storage capacity (S_{max}), and the fraction of water remaining after evaporation (f), and to potential evapotranspiration (PET) for the Paris Basin (PB) site.

Parameter	Avg. recharge	$\delta^{18}\text{O}$ -weighted avg.	$\delta^2\text{H}$ -weighted avg.	lc-excess†
	mm	-----‰-----		
Reference case‡	203	-6.86	-50.00	-3.35
$H_r = 0.1$	203	-6.95	-50.84	-3.55
$H_r = 0.5$	203	-6.72	-48.56	-2.90
$S_{\text{max}} \times 2$	147	-6.02	-46.31	-5.64
$S_{\text{max}}/2$	231	-7.41	-52.52	-1.95
$f = 0.99$	203	-8.13	-55.60	0.10
$f = 0.90$	203	-2.52	-30.40	-14.65
PET +10%	192	-6.88	-50.16	-3.36
PET -10%	217	-6.82	-49.75	-3.38
Unsaturated zone profile (PB site)		-6.86	-50.39	-3.74

† Line-conditioned excess.

‡ Parameter values: $S_{\text{max}} = 52$ mm, $H_r = 0.30$, $f = 0.97$.

moisture capacity, according to $S_{\text{max}} = \text{RD}(\theta_{\text{FC}} - \theta_{\text{WP}})$ (Renard and Tognelli, 2016), where RD is the rooting depth (0.2 m for the PB site), and θ_{FC} and θ_{WP} are the water contents of the soil at field capacity and the wilting point, respectively (around 5 and 2% v/v, respectively). Physical soil properties gave an S_{max} value of 6 mm, which was lower but compatible with the fitted value. The obtained intensities for the various components of the water budget were in agreement with those used by Renard and Tognelli (2016) for another site nearby in the Paris Basin.

For SLL, the average annual precipitation (rain and snow) and potential evapotranspiration for the 2010 to 2013 period were 922 and 630 mm/yr, respectively. The S_{max} value leading to the best agreement between the modeled and measured volume-weighted average isotopic composition was 300 mm, a large value that could not be linked to a physical interpretation of soil moisture content. It has to be emphasized here that S_{max} was a fitting parameter of the conceptual water budget, and that the link with field observations was not straightforward, especially as S_{max} depended on the model time step. The large value of S_{max} was thus consistent with the long time step (1 mo) of the model at SLL. The corresponding recharge was 200 mm/yr, in the same order of magnitude as the literature value (Table 1), but occurred only for snowmelt. The actual evapotranspiration was 608 mm/yr, almost equal to the potential evapotranspiration. At the regional scale, Larocque et al. (2015) obtained a lower value of 381 mm/yr, but this has to be considered carefully because they considered runoff. The water budget thus appeared to be somehow too simple to fully handle processes occurring in a cold climate and thus to be affected by large uncertainty. Larocque et al. (2015) used a more complex surface water budget better adapted to a cold climate and showed that recharge

occurred during two separate periods for SLL, from October to December and then from March to May. An S_{\max} value of 50 mm was also tested, similar to that for the PB site. This led to an actual evapotranspiration of 517 mm/yr and recharge of 372 mm/yr, with an acceptable fit of isotopic composition but this time with the two expected periods of recharge.

Stable Isotopic Composition of Precipitation

Monthly averaged, amount-weighted isotopic compositions of precipitation for the two sites are presented in Fig. 2. The entire time series of isotopic compositions and d-excess in precipitation from 2002 to 2006 for the PB site is presented in Fig. 3. A marked seasonal fluctuation existed for both sites due to temperature effects, with correlation coefficients (R^2) of 0.36 and 0.60 between $\delta^{18}\text{O}$ in precipitation and temperature for the PB and SLL sites, respectively. Isotopic compositions of both O and H were more depleted in heavy isotopes during winter and more enriched in heavy isotopes during summer. The amplitude of this seasonal fluctuation was greater for SLL (97‰ for $\delta^2\text{H}$ and 12‰ for $\delta^{18}\text{O}$) than PB (29‰ for $\delta^2\text{H}$ and 5‰ for $\delta^{18}\text{O}$) due to the larger underlying temperature amplitude. For SLL, the isotopic compositions of the local rain samples were fully consistent with the values from the GNIP station in Ottawa. The average isotopic composition of the snow samples was $-17.3 \pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $-126.1 \pm 1.0\text{‰}$ for $\delta^2\text{H}$, also in the range of the GNIP station data.

For both sites, the LMWLs were close to the Global Meteoric Water Line (Fig. 4a, $\delta^2\text{H} = 7.12 \delta^{18}\text{O} + 2.19$ for PB; Fig. 4b, $\delta^2\text{H} = 7.93 \delta^{18}\text{O} + 10.1$ for SLL). They compared well with LMWL equations in the same regions [see, for example, Millot et al. (2010) for PB and Arnoux et al. (2017) for SLL]. For PB, the d-excess varied throughout the year according to the variable sources of vapor masses and the continental recycling of water vapor. The lc-excess was therefore used to overcome this variability and to investigate local evaporation effects.

Stable Isotopic Composition of Pore Water in the Unsaturated Zone and Groundwater

Depth profiles of the water isotopic composition in the unsaturated zone are presented in Fig. 5a and 6a for PB and in Fig. 5b and 6b for SLL. Only $\delta^{18}\text{O}$ profiles are reported because $\delta^2\text{H}$ profiles show similar patterns of variability. At both sites, at least one cycle of pore water isotopic composition variation was observed: higher isotopic compositions corresponding to recharge at the end of summer and during autumn, and lower values corresponding to recharge during winter. The amplitude of soil water isotopic composition variability was dampened compared with that of precipitation, with 12‰ for $\delta^2\text{H}$ and 2‰ for $\delta^{18}\text{O}$ for PB and with 51‰ for $\delta^2\text{H}$ and 7‰ for $\delta^{18}\text{O}$ for SLL. At PB, the 4.5‰ $\delta^{18}\text{O}$ amplitude in precipitation was attenuated to 1‰ at the 1-m depth and to $<0.1\text{‰}$, in the range of noise, at the 2-m depth. Depth profiles of soil water content also showed some variability (Fig. 5), with higher water content in the finer layer at PB and at the surface at both sites because sampling was conducted in May following winter infiltration.

The average isotopic composition of water in the unsaturated zone, weighted by the water content at each depth, was equal to $\delta^{18}\text{O}_{\text{uz}} = -6.9\text{‰}$ and lc-excess = -3.7‰ for PB, and $\delta^{18}\text{O}_{\text{uz}} = -11.3\text{‰}$ and lc-excess = 2.3‰ for SLL (Fig. 5 and 6).

At PB, the average isotopic composition of the groundwater was $\delta^{18}\text{O} = -6.3\text{‰}$ and $\delta^2\text{H} = -48.3\text{‰}$ (Fig. 4a), while the measured isotopic composition of the groundwater in the regional surface aquifer of SLL was $\delta^{18}\text{O} = -11.1\text{‰}$ and $\delta^2\text{H} = -78.5\text{‰}$ (Larocque et al., 2015) (Fig. 4b).

Even if the two sites had contrasting recharge seasonality and mechanisms, the average isotopic composition of the unsaturated zone was close to that of the local groundwater (Fig. 4). For SB, it was quite close to the weighted average isotopic composition of the local precipitation, reflecting the continuous infiltration and recharge of precipitation from fall to spring. On the contrary, for SLL the average isotopic composition in the unsaturated zone was more depleted in heavy isotopes than the weighted average isotopic composition of the local precipitation, corresponding to the large amount of heavy-isotope-depleted snowmelt water infiltration as freshet. Comparison between $\delta^{18}\text{O}$ values in precipitation and in the unsaturated zone indicated that recharge occurred predominantly during late fall ($\delta^{18}\text{O}$ around -10‰) and spring ($\delta^{18}\text{O}$ of snow around -15‰) at SLL (Fig. 2 and 5b) and more continuously during fall, winter, and spring at PB (Fig. 2, 3, and 5a). At PB, lc-excess values in the unsaturated zone ranged between 0 and -5‰ (Fig. 6a), indicating that at least some evaporation occurs before or during infiltration, leading to a slight enrichment of the isotopic composition in recharge in the unsaturated zone. At SLL, the average lc-excess values in the unsaturated zone were positive (Fig. 6b), showing no evidence of evaporation and suggesting the existence of heterogeneity in precipitation sources between recharge and non-recharge periods.

Quantification of Recharge for the Two Contrasted Sites from Unsaturated Zone Profiles

Annual amounts of recharge were calculated following Eq. [2] for both the PB and SLL profiles and are reported in Table 1. The depths between which soil water content was integrated were chosen based on the visual observations of maximum and minimum as well as smooth or more abrupt changes in the isotopic composition vs. depth (Fig. 5) and on the expected seasonality of isotopic composition in recharge, from higher values in autumn to more negative values in spring. At PB, one cycle between two minima of $\delta^{18}\text{O}$ was identified between the 22- and 160-cm depths (Fig. 5a), corresponding to an annual recharge of 304 mm/yr (Table 1). More specifically, infiltration during autumn and winter 2005 could be identified by a relatively higher isotope composition between the 50- and 125-cm depths, while recent infiltration in spring 2006 would lie on top of the profile, down to the 50-cm depth (Fig. 5a). At SLL, relatively abrupt changes of $\delta^{18}\text{O}$ vs. depth allowed identification of spring snowmelt and autumn recharge for the two hydrological years preceding sampling (Fig. 5b). In the upper part of the profile, snowmelt recharge in 2013 was identified

with low $\delta^{18}\text{O}$ values between 22 and 72 cm and amounted to 48 mm, and a recharge in autumn 2012 of 66 mm was identified with high $\delta^{18}\text{O}$ values between 77 and 142 cm. This led to an annual recharge of 114 mm/yr (Table 1). Below that, low $\delta^{18}\text{O}$ were again observed from 147 to 212 cm, corresponding to spring snowmelt in 2012, with a calculated recharge of 68 mm. Below 217 cm, $\delta^{18}\text{O}$ values increased slightly and probably corresponded to recharge from autumn 2011, but the amplitude of variations was too dampened to allow quantification. Quantification of recharge based on the integration of water content vs. depth was based on a subjective identification of the depth range corresponding to a given period of recharge and thus subject to a large uncertainty. However, the results obtained in this study provide a straightforward first-order estimate of the amount of recharge and also a confirmation of the expected seasonality of recharge.

Modeling the Isotopic Composition Evolution from Precipitation to Infiltration and Recharge

For the PB site, Eq. [5] and isotope fractionation were at first not included in the model, but the minimization of the objective function φ never led to a good fit of the data (data not shown). As already identified with the negative lc-excess value in the unsaturated zone, this confirmed that some evaporation occurred at PB. Isotope fractionation was therefore included in the model. Minimization of the objective function φ then led to the determination of the surface water budget parameters (S_{max} and evaporation parameters f and H_r). The best fit (Fig. 5a and 6a) was obtained for $S_{\text{max}} = 52$ mm, $H_r = 0.3$, and $f = 0.97$. The obtained average annual recharge was then 203 mm/yr (Table 1), not fully similar to the values obtained from the depth integration method (above) and the literature but of the same order of magnitude and acceptable regarding the simplifications of the model and associated uncertainties. It has to be noted that the surface hydro-isotopic budget was self-sufficient to quantify the amount and seasonality of recharge. The transport model served as validation and confirmation of the major recharge processes.

Regarding the lumped parameter transport model for PB, the distance between the two $\delta^{18}\text{O}$ minima in the soil profile (Fig. 5a) was compared with the amount of recharge between the two $\delta_{\text{inf}}(r)$ series minima, and Eq. [6] was used to deduce an average water content of $\theta_w = 0.42$. This value was higher than the field value of 0.15 to 0.25 (Fig. 5a), but this parameter was not optimized automatically, was not very sensitive, and was thus affected by a large uncertainty. A dispersion parameter D of 0.06 gave the best fit between the observed and calculated profiles (Fig. 5a and 6a). This dispersion parameter was an effective bulk parameter for the whole profile, disregarding the spatial variations of dispersivity with depth, and was not interpreted in terms of dispersivity.

For SLL, as already guessed by the positive lc-excess values in the unsaturated zone, a model without evaporation and without isotope fractionation allowed minimization of the objective function and was thus retained. There was thus only one parameter, S_{max} , to calibrate. The best agreement between the average $\delta^{18}\text{O}$ and $\delta^2\text{H}$

calculated for recharge vs. measured values in the unsaturated zone profile was obtained for an S_{max} of 300 mm, leading to an annual recharge of 200 mm/yr (Table 1), again different from but on the order of magnitude of values obtained from the simple depth integration method (above) and from the literature. However, as already discussed above, an S_{max} value of 50 mm, similar to that for the PB site and more physical, led to a higher recharge of 372 mm/yr and emphasized the current limitations of the model for a cold climate.

Discussion

Processes to Include in Models of Soil Water Isotope Profiles

In this study, a conceptual water isotope budget was used at the surface, based on the traditional water budget, but also taking into account physical processes that alter the soil water isotopic composition, namely mixing and isotopic fractionation associated with evaporation. Regarding transport in the unsaturated zone, the choice of a lumped dispersion model to reproduce the measured $\delta^{18}\text{O}$ in the unsaturated zone was based on the limited availability of data with which to constrain the model. The simplified surface budget was consistent with a simplified transport model that did not incorporate the variations of water content with depth and with time. The influence of soil heterogeneity as well as of immobile water on the average isotopic composition of recharge water were considered to be negligible by several researchers (Barnes and Allison, 1988; Lindström and Rodhe, 1992) but were shown to occur by others (Gazis and Feng, 2004; Schoen et al., 1999). The use of a lumped parameter model allowed these processes to be taken somehow into account through the effective dispersion parameter.

Other modeling approaches with more physically based numerical models of surface water, isotopes, and heat budgets have been proposed, coupled with water and isotope transport in the unsaturated zone based on Richards' equation (Braud et al., 2005; Gehrels et al., 1998; Haverd and Cuntz, 2010; Melayah et al., 1996; Rothfuss et al., 2012; Sprenger et al., 2015; Stumpp and Hendry, 2012). Such physically based models handle the transient dynamics of flow and transport in the unsaturated zone as well as soil heterogeneity and help improve the calibration of soil transport parameters and the understanding of water residence time. However, they often lack detailed presentation of a surface isotope water budget. Non-fractionating transpiration is usually included in the models for sites in temperate areas (e.g., HYDRUS-1D; Stumpp and Hendry, 2012), but isotope-fractionating evaporation is less often taken into account (Haverd and Cuntz, 2010; Rothfuss et al., 2012; Sprenger et al., 2018). These modeling approaches can be more or less complex but always require many data and parameters. In opposition, the model proposed here is much more conceptual and simplified but includes this isotope fractionation in a simple way while requiring few data and parameters.

Parsimonious Models for Recharge Quantification and Uncertainties

The two sites considered in this study have contrasting recharge mechanisms and seasonality, with episodic recharge in

autumn and from snowmelt at SLL and more continuous recharge from autumn to spring at PB. The two models proposed here been proven to allow quantification of the recharge amount and possibly seasonality for sites that are not so well characterized and where only limited data are available to interpret the isotope composition of the pore water in the unsaturated zone.

The two methods give estimates of recharge intensity that are of the same order of magnitude as values given in the literature and obtained with hydrogeological modeling (Table 1). However, even if a precise quantification was not the scope of the study and uncertainties on annual recharge estimated from depth integration of water content as well as from our simple model are large, noticeable differences remain with literature values. Such uncertainties could not easily be handled by water managers, and the proposed models are not intended for their use. More generally, uncertainties on recharge estimations remain significant, especially when comparing methods and even with complex models, which emphasizes the need to further improve recharge quantification methods.

Limitations of the Proposed Water Isotope Budget and Transport Model for Recharge Quantification

The main limitation of the use of unsaturated zone water isotope profiles is the attenuation of the precipitation isotope signal at depth (Cook et al., 1992). As opposed to arid or semi-arid regions with deep unsaturated zones where several years of recharge intensity are stored, temperate areas generally have shallower unsaturated zones and higher recharge intensities that limit the preservation of the signals. The seasonal variability can clearly be observed at SLL but is smaller for PB (Fig. 5). The model shown here is intended to be theoretically applicable to any site under a temperate climate, even if sites characterized by strong seasonality, and especially by snow cover, are better suited to the quantification of recharge from soil water isotopes profiles.

Another limitation of the interpretation of soil water isotope profiles is that a long-term time series of precipitation isotopic composition is required. Monthly time step time series have been used because they are more easily acquired or available from GNIP stations almost all over the world. A monthly time step is shown here to enable the application of a hydro-isotopic surface budget and the identification of seasonal variations in recharge. If associated with soil sampling at a fine spatial resolution, typically every 5 cm or so, high-resolution precipitation data could allow the use of a two-component lumped parameter model, with both piston flow and dispersion models, to investigate the existence of preferential infiltration events, as proposed by Stumpp and Małozewski (2010).

Uncertainties in the surface water budget propagate also into the transport model. The major limitation of the transport model is the assumption of steady-state flow (homogeneous and constant soil water content), which is required to apply the lumped parameter dispersion model but which prevents any investigation of transient processes.

Finally, the surface water budget and transport models were calibrated in this study on one single profile taken at one

time, which is one of its strengths but also a limitation because it increases the uncertainties, from sampling and cryogenic extraction to model calibration.

Despite these limitations, the simple surface and transport models are complementary to the peak-to-peak method and are applicable to sites where little information is available.

Impact of Evaporation on Water Isotopic Composition in the Unsaturated Zone

Isotopic fractionation is associated with evaporation at the soil surface and is known to be an important control of the isotopic composition of water in soils (Barnes and Allison, 1983, 1988; Sutanto et al., 2012). The average negative lc -excess value in the unsaturated zone for PB indicates the role of local evaporation, and this was confirmed by the hydro-isotopic surface budget, where isotope fractionation had to be included to fit the data. For SLL, this is not the case; average lc -excess is positive and a good fit of the data is obtained without fractionation. The fitted f coefficient of 0.97 for evaporation at PB might not be directly transposed into evaporation partitioning but confirms that transpiration largely dominates water uptake for soil under a temperate climate and covered with grass. Evaporation occurring during the hot summers clearly leads to isotope fractionation, but because there is no recharge during summer, this fractionated signal is barely preserved in a small amount of soil moisture. When autumn rain is mixed with this small amount of fractionated water remaining in the soil reservoir, the evaporated signal is largely dampened. These values of f and evaporation therefore correspond to the recharge periods, namely autumn and spring. At SLL, where average temperatures are lower, evaporation from the unsaturated zone is negligible during the recharge seasons, spring and autumn, and hence does not impact the isotopic composition of recharge.

For both sites, lc -excess appears to be a robust indicator of local evaporation intensity. Water stable isotopes in the unsaturated zone have thus already been used to partition evaporation and transpiration fluxes (Sutanto et al., 2012). Surface budgets for water stable isotopes, including fractionation associated with evaporation, as proposed in this study, should be further developed and tested under temperate climates.

Equation [5] is proposed as a simple parameterization of the isotope fractionation associated with evaporation in soils, but it would require improvement and validation by future experimental and numerical studies. Equation [5] was originally established for open water and is adapted to sites such as PB where evaporation fluxes are small and kinetic fractionation is limited. Future work should focus more specifically on the validation of such isotope fractionation equation. One major issue would be to include a parameterization or a fit of a temporal evolution of the f parameter, which would require including partitioning of evapotranspiration.

Conclusion

Based on the results from two field sites with contrasting hydrologic and climate conditions, water stable isotope ($\delta^{18}\text{O}$ and

$\delta^2\text{H}$) profiles in the unsaturated zone were shown to permit the quantification and identification of seasonality in recharge, based on the seasonality of the water isotopic composition of precipitation. A very simple approach consists of integrating the soil water content between extreme values of soil water isotopic composition, typically corresponding to precipitation signatures during warm and cold seasons. When a time series of precipitation isotopic composition is available, even at only a monthly time scale, a water isotope budget can be calculated at the surface using a conceptual overflowing soil reservoir model including mixing of successive precipitation but also isotope fractionation due to evaporation. The intensity of evaporation, associated with enrichment in heavy isotopes, can be constrained by the lc -excess measured in the unsaturated zone. A first and simple parameterization is proposed to take this fractionation into account in the surface water budget. This water budget can be constrained with the volume-weighted average isotopic composition of pore water in the unsaturated zone and thus allows determination of the intensity and seasonality of recharge. This model and the peak-to-peak integration lead to similar values, consistent at first order with more complex methods but emphasizing the uncertainties remaining on recharge quantification. A lumped parameter dispersion model is then used to represent percolation of water and attenuation of the water isotope signal at depth. It allows the main variations of water isotope composition with depth to be reproduced and soil parameters and transport processes to be discussed.

Even if the attenuation of the precipitation isotopic signal during recharge limits the investigation to the two first meters of the unsaturated zone and to sites with contrasting recharge periods, the approaches proposed in this study could be applied to a large number of sites and are very promising for the investigation of spatial and temporal variability of recharge as well as for drawing recharge maps at the local to regional spatial scales.

Data Availability

All data are available on request to the corresponding author.

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