

Special Section: Stable Isotope Approaches in Vadose Zone Research

Core Ideas

- This special section focuses on stable isotopes approaches in the vadose zone.
- Recent advances and challenges in stable isotope approaches are summarized.
- Isotopes are used to study flow, transport, geochemical, and ecohydrological processes.
- The articles present key findings in analytical and modeling developments.
- Results can improve understanding of water flow and contaminant transport in the critical zone.

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Stable Isotope Approaches in Vadose Zone Research

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Recent developments in the measurement, modeling, and application of stable isotope tools to provide insights on water flow, transport, biogeochemical, and ecological processes in the vadose zone have motivated a special section in *Vadose Zone Journal*. We give an overview of recent advances and challenges in stable isotope approaches in the vadose zone and present the key findings from the five manuscripts in this special section. These five manuscripts advance our understanding of (i) analytical developments in water stable isotope analysis, (ii) modeling of water and transport within the soil matrix using water stable isotopes, and (iii) using compound-specific isotope analysis for identifying the fate of nonaqueous-phase liquids in the unsaturated zone.

Stable isotopes are frequently used as environmental or artificial tracers to study water flow, transport, and biogeochemical processes in soils and the unsaturated zone. In recent years, new analytical and technical developments have transformed the field of isotope hydrology and isotope biogeochemistry and widened the scope of questions that can now be tackled. In particular, it is now possible to measure and parameterize isotope dynamics within soils at increasingly finer temporal resolution or at increasingly larger scales. At the same time, smaller sample volumes are required for stable isotope analysis, and the cost of analysis itself has become much cheaper with new laser technologies relative to isotope ratio mass spectrometry in the past. In addition, new automated systems that can provide high-resolution in situ measurements and real-time data analysis have now been developed. These technological breakthroughs are thus poised to improve our understanding and the modeling of water and matter fluxes in the atmosphere–plant–soil–groundwater continuum. This special section of *Vadose Zone Journal* summarizes examples of current analytical and modeling developments that have been applied to improve understanding of water flow and contaminant transport in the unsaturated zone.

Stable Isotope Approaches in the Vadose Zone

Isotopes of an element have the same number of protons but different numbers of neutrons, for example in the case of the water stable isotopes ^1H and ^2H and ^{18}O and ^{16}O , thus causing water molecules to differ in atomic mass. In contrast to radioactive isotopes such as ^3H , stable isotopes do not decay with time. Because molecules with different mass have different physical properties such as rates of diffusion or equilibration kinetics but participate in the same chemical reactions, shifts in the isotopic composition of molecules can change during such reactions and phase changes, causing isotope fractionation. In isotope hydrology and biogeochemistry, we make use of these stable isotope fractionation events to trace water and nutrient cycling and to identify sources, mixing ratios, and specific transformation processes in and between soils, water bodies, and the atmosphere. Of particular interest for hydrologists or biogeochemists are the environmental isotopes of H, C, N, O, and S that are naturally found in the environment with different abundances—some of which are highlighted in this special section.

Water Flow and Transport

As introduced above, the stable isotopes of water molecules (^2H and ^{18}O) are powerful tracers of water around the planet and between different materials and organisms. Many of the fractionation processes that cause variations in the stable isotope composition of water have a seasonality linked to them. This originates from both changes in solar radiation received at the Earth's surface that drives evaporation and cloud formation and the rain-out history. Consequently, a strong spatial distribution in precipitation isotopes is observed at the Earth's surface, with more isotopically depleted rains found in the cooler regions and months of the year while more enriched values are measured during the warmer seasons and in hotter ecosystems (Clark and Fritz, 1997; Dansgaard, 1964). In regions closer to the equator, the rainfall amount mainly drives the annual differences in the isotopic composition of rainfall, with isotopically depleted rains in the months with higher rainfall and more enriched values in months with lower rainfall (Dansgaard, 1964; Bowen, 2008). Consequently, precipitation events have specific isotopic fingerprints that can be followed as water flows through an ecosystem. Measuring such seasonal changes in the stable isotope composition of vadose zone water inputs, and how its composition subsequently changes within the soil matrix, provides integrative information about changes in the rates of water flow and transport processes with time and depth below ground.

In the past, water isotopes have been widely used for identifying processes of groundwater recharge. It is, for example, possible to distinguish with isotope methods whether net recharge or net evaporation occurs in an area of the soil profile (DePaolo et al., 2004; Robertson and Gazis, 2006; Gaj et al., 2016) and whether transport is dominated by either advection, dispersion, or diffusion (Singleton et al., 2004; Hendry et al., 2011; Stumpp and Hendry, 2012; Beyer et al., 2015). Additionally, patchy infiltration patterns, flows, and transport heterogeneities can be identified when comparing isotope data in space or with time (Stumpp et al., 2007; Garvelmann et al., 2012; Stumpp and Hendry, 2012; Baram et al., 2013; Mueller et al., 2014). For drying soils, water isotopes give information about evaporation rates caused by fractionation processes occurring close to the soil surface. Thus, from vertical profiles of water content and stable isotope composition, evaporation rates can be estimated (Allison, 1982; Allison et al., 1983). Similarly in humid or semiarid regions, groundwater recharge rates can also be calculated from vertical depth profiles of stable water isotopes (Saxena and Dressie, 1983; Scanlon et al., 2002; Li et al., 2007; Adomako et al., 2010; Chesnaux and Stumpp, 2018; Barbecot et al., 2018). When stable water isotope data are combined with modeling approaches, some more quantitative information is added. For example, isotopes can be used to calibrate numerical flow and transport models (Małoszewski et al., 2006; Braud et al., 2009; Vogel et al., 2010; Stumpp et al., 2012; Huang et al., 2015; Sprenger et al., 2015b, 2018; Groh et al., 2018). More specifically, mean transit times and transit time distributions can also be calculated from variations in isotope compositions

and have shown that transit time distributions can vary according to land use, soil type, or boundary conditions (Małoszewski et al., 2006; Stumpp et al., 2009; Timbe et al., 2014; Sprenger et al., 2015b). In artificial labeling experiments, deuterated water has been used to identify plant–soil interactions (Meinzer et al., 2006; Schwendenmann et al., 2010) or hydraulic lift (Hafner et al., 2017; Meunier et al., 2018).

For the analysis of stable water isotopes in the unsaturated zone, a number of different methods are available and were summarized in detail by Sprenger et al. (2015a). In particular, methods for the analysis of stable isotopes in the vapor phase using water-vapor equilibration techniques (Wassenaar et al., 2008) have enabled a broader application of this approach in the unsaturated zone by obviating the need for laboratory soil water extraction methods that are currently highly debated because of the lack of common laboratory extraction protocols (Orłowski et al., 2018). Making use of water-vapor equilibration techniques, water isotopes can be directly and even continuously measured in lysimeter discharge (Pangle et al., 2013), column outlets (Herbstritt et al., 2012), at different column depths (Rothfuss et al., 2013, 2015; Gangi et al., 2015), or even in situ in soils (Soderberg et al., 2012; Volkmann and Weiler, 2014; Gaj et al., 2016). In a similar context, rapid CO^{18}O –water equilibration techniques measured with laser spectrometers can also provide dynamic information on changes in the water isotope composition of soils in the laboratory and in the field (Wingate et al., 2009, 2010a; Gangi et al., 2015), and methodological progress on this topic is now indicating that it may not be necessary in the future to destructively sample soils to obtain information on soil water isotope composition (Jones et al., 2017). However, further studies are still required to test this approach on different soil types. In contrast, destructive sampling methods are still necessary to enable the analysis of stable water isotopes in sediment cores (Wassenaar et al., 2008; Hendry et al., 2011; Stumpp and Hendry, 2012) and thus are particularly suited to the study of flow processes and transit times in deep unsaturated zones. Nonetheless, many of these new applications based on water-vapor equilibration require improvement, as no common protocols are available and analytical uncertainties are still not well understood (Koehler et al., 2013; Hendry et al., 2015; Pratt et al., 2016; Gralher et al., 2016, 2018).

Nutrient Cycling and Source Identification

The early seminal work on the stable C and O isotope composition of soil carbonates in both modern soils and paleosols revealed a relationship between climatic conditions and the stable isotope composition of soil carbonates (Cerling, 1984) and provided understanding of C_4 plant expansion in the late Miocene (Cerling et al., 1993). In addition, our understanding of changes in the size of terrestrial ecosystem C pools and the factors affecting C and water fluxes between ecosystems and the atmosphere has benefited from detailed stable isotope studies (as reviewed by, e.g., Bowling et al., 2008; Paterson et al., 2009; Brüggemann et al., 2011; Wehr et al., 2016). In particular, the process information derived from

the C isotope composition of plant assimilates and metabolites was advanced to a level that enabled detection of diel variations in various plant respiratory C sources, explaining short-term variability in the $\delta^{13}\text{C}$ of respired CO_2 (Wingate et al., 2010b; Werner and Gessler, 2011; Wehr et al., 2016). The successful combination of $^{13}\text{CO}_2$ pulse labeling and online tracing of the $\delta^{13}\text{C}$ of plant- and soil-respired CO_2 with isotope-specific laser spectrometers further advanced the field, facilitating the tracing of C flow from the aboveground part of the plant to the root and finally to the soil with high temporal resolution (Bahn et al., 2009; Epron et al., 2012). The increasing use of isotope-specific laser analyzers in the field has opened up a whole new route to ecosystem research in real time (Griffis, 2013) and will provide the means for long-term monitoring of isotope fluxes between different ecosystems and the atmosphere (Wehr et al., 2016). Great advances have also been made in the tracing and compound-specific isotopic fingerprinting of characteristic organic compounds, such as organic contaminants for identifying sources or transformation processes (Moshkovich et al., 2018) or fatty acids in soils and sediments, allowing source apportioning of different land uses and land covers to soil translocation and sediment formation (Reiffarth et al., 2016; Wang et al., 2016; Rach et al., 2017).

Biogeochemical N cycling is as complex as C cycling in both terrestrial and aquatic ecosystems. Already more than 50 yr ago, Cheng et al. (1964) found variations in natural ^{15}N abundance in different soils and in different forms of N. This was later attributed to fractionation processes during microbial turnover and physical transport of N species in the soil (Delwiche and Steyn, 1970; Mariotti et al., 1981). Since then, the potential of tracing N through ecosystem compartments and whole landscapes using ^{15}N isotopic information has been recognized, but certain limitations have also been identified (Bedard-Haughn et al., 2003). The combined use of N and O isotopic information in oxidized N species has recently enhanced the degree of information on source, sink, and transport processes in soils, sediments, and water, allowing, for example, tracing sources and pathways of NO_3^- through forested catchments (Ohte, 2013), reconstructing ancient agricultural management practices (Szpak, 2014), and quantifying of turnover and fluxes in the marine N cycle (Casciotti, 2016). However, despite these advances, a great deal of information still needs to be gathered on isotopic fractionation factors of the various microbial N turnover processes (Denk et al., 2017; Nikolenko et al., 2018) before a reliable apportionment of N sources and sinks in landscapes can be made, e.g., in and under agricultural areas. A great discovery in this respect was the process-specific intramolecular site preference of ^{15}N in the non-symmetric N_2O molecule, where N_2O with no or only a weak ^{15}N site preference was attributed to bacterial denitrification, and a strong ^{15}N site preference in favor of the central position in the N_2O molecule was attributed to nitrification (Toyoda et al., 2017). However, unfortunately this bipolar picture turned out to be too simple, as it is complicated by almost indistinguishable additional contributions of fungal denitrification and nitrifier denitrification, N_2O reduction, and abiotic N_2O

formation, rendering the N_2O isotopomer analysis insufficient when trying to identify unambiguously sources and sinks of N_2O in the landscape (Wei et al., 2017). One possible way out of the dilemma of ambiguous source identification might be the analysis of clumped isotopes, i.e., the combination of two or more rare isotopes in one molecule (e.g., $^{15}\text{N}^{15}\text{N}^{16}\text{O}$), which is very specific for a certain reaction (Yeung, 2016). However, the analysis of clumped isotopes is technically very demanding and costly because of their extremely low natural abundance, and further testing is required before it can be recommended more generally for biogeochemical studies. Another promising approach for more reliable process identification might be triple isotope analysis (e.g., combining ^{13}C or ^{15}N with ^{17}O and ^{18}O information), as already used in certain studies on atmospheric CO_2 (Hofmann et al., 2012) or the fate of atmospheric NO_3^- in ecosystems (Ohte, 2013).

Ecohydrological Processes

Our understanding of how, where, and when plants use soil water and groundwater has recently undergone a paradigm shift. The increased use of less expensive laser spectrometers to measure the isotope composition of ecosystem water pools enabled major advances in existing concepts about where in the soil a plant accesses water for transpiration during the growing season and how this might be affected in the future with global changes such as increased drought. For many decades, theory maintained that the isotope composition of water taken up from soils by plant roots did not undergo any isotopic fractionation (Washburn and Smith, 1934; Ehleringer and Dawson, 1992), except in the restricted cases of halophytes and certain xerophytes (Ellsworth and Williams, 2007). This was an important assumption for studies that tried to attribute the source of transpiration water to different locations in the soil profile or to a switch in water uptake to groundwater during drought periods (Dawson and Ehleringer, 1991). The assumption that root water uptake is a non-fractionating process was often used to help understand ecological processes such as competition in soils for water and nutrients between the roots of different plant species (Dawson and Pate, 1996) and furthermore could contribute to understanding the variability of transpiration vs. evapotranspiration across large scales (Jasechko et al., 2013; Evaristo et al., 2015; Barbeta and Peñuelas, 2017; Evaristo and McDonnell, 2017). However, more and more studies are now showing that the isotopic composition of soil water and xylem water is not always the same, and the isotopic differences can vary with soil type, plant species, and moisture status (Martín-Gómez et al., 2017; Newberry et al., 2017; Vargas et al., 2017). Consequently, this has led to much debate about the existence (or not) of “two water worlds,” with a soil micropore-bound water pool only accessible to plants and a mobile water pool that does not exchange isotopically with the soil-bound pool (Brooks et al., 2010; McDonnell, 2014; Evaristo et al., 2015). However, a number of studies have shown that these two pools can exchange (Araguás-Araguás et al., 1995; Oshun et al., 2016; Sprenger et al., 2018) and that, during water uptake, fractionation of water isotopes can take

place under certain soil moisture conditions and on different soil types. In addition, a number of studies have also indicated that it is now time to revisit the equilibrium isotope fractionation factors between soil water and water vapor that have been shown to be different from those of liquid and the vapor of bulk water (Lin and Horita, 2016; Lin et al., 2018). In the very near future, it is likely that a number of new processes will need to be accounted for and revised in isotope-enabled land surface models that will be born out of the continued investigation of stable isotope variations in vadose zone water pools.

This Special Section Analytical Developments

Water-vapor equilibration techniques for measuring water stable isotopes in the unsaturated zone have been applied for a decade now. However, no common protocols are available, and uncertainties in using this approach are still not well understood. To this end, Gralher et al. (2018) developed a post-correction scheme that accounts for biogenic gas matrix effects for pore water isotope analysis when combining laser-based isotope analyzers and water-vapor isotope equilibration using evaporation-proof metalized sample bags and air inflation. Such a correction scheme was necessary because of biogenic CO₂ accumulation in the headspace of the bag immediately after soil sample preparation, which caused biases in the analysis of the vapor, exceeding accepted measurement uncertainties. For reliable post-correction, it was further recommended to inflate the bags with air rather than N₂ due to differences in the line broadening of the spectral absorption lines caused by the two different gas matrices.

Water Flow and Transport Modeling

Groundwater recharge rates can be estimated from vertical profiles of water content and water stable isotope composition in pore water. However, existing approaches either need additional information about soil hydraulic parameters or assume simplified flow and transport processes in the unsaturated zone. The latter was improved by coupling a surface water and isotope budget model to a lumped parameter model (Barbecot et al., 2018). This enabled estimating groundwater recharge rates by measuring water stable isotopes in the pore water at two field sites with contrasting hydrologic and climatic conditions. Considering the enrichment of isotopes due to evaporation, a water budget approach resulted in similar recharge rates as a modified lumped dispersion model approach. Even without having detailed information about soil hydrological parameters of these soils, average groundwater recharge rates and average apparent transport parameters were quantified.

When information about soil hydraulic parameters is available, more complex numerical model approaches can be used to simulate water flow and transport in the unsaturated zone. However, it still remains to be systematically tested whether additional information from stable water isotope measurements can help improve

the calibration of water flow and transport models. To this end, Groh et al. (2018) used different optimization strategies to investigate which types of observations are necessary to simultaneously estimate soil hydraulic and solute transport parameters in layered soils. They found that the best optimization strategy was to use all measured data (water content, matrix potential, and isotopes) at the same time to inversely fit the system's flow and transport parameters. Furthermore, the analysis of water stable isotopes confirmed that Br⁻ behaved non-conservatively because of adsorption on amorphous oxides (Al and Fe) and clay minerals in the tested soils.

As mentioned above, it was found recently that the isotopic composition of mobile water can be different from the isotopic composition of bulk water in soils. How this influences water flow and the isotopic exchange between these two different water pools has not been simulated before. Therefore, Sprenger et al. (2018) improved simulations of soil water isotope dynamics in soils of northern environments considering fast and slow flow domains and accounting for isotope fractionation and water vapor exchange between the two flow domains. The modeling results accounting for such processes confirmed the experimental results. In particular, the isotope ratios of mobile water sampled in suction cups plotted close to the local meteoric water line in contrast to isotopically enriched bulk water sampled and analyzed with a direct-equilibration method.

Contaminant Fate

Compound-specific isotope analysis has been often used to assess the fate of organic contaminants in the subsurface and the suitability of related remediation strategies. However, transport processes of organic contaminants in the unsaturated zone can additionally be impacted by volatilization and diffusion, challenging the use of isotopes for identifying biodegradation by analyzing water samples only. Therefore, compound-specific isotope analysis of nonaqueous-phase liquids in the aqueous and vapor phases was used to assess the effect of enhanced biostimulation when infiltrating nutrient- and oxygen-amended water in the contaminated vadose zone (Moshkovich et al., 2018). Enrichment of δ¹³C between initial values and values during biostimulation confirmed the biodegradation of contaminants. However, fractionation processes due to abiotic processes were also observed. Real-time observations using a vadose zone monitoring system allowed adjustment of the remediation strategy with time.

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