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Andrea L. Popp and Harsh Beria
contributed equally to this work.

Key Points:

- Tracer-aided mixing models are uniquely capable of identifying water flow paths and sources within the Critical Zone
- Recent advances offer novel tracers and models for deeper and more accurate insights into the Critical Zone
- Tracer and model-related uncertainties should be accounted for in model assessment

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

A. L. Popp and H. Beria,
andrea.popp@smhi.se;
hberia@ethz.ch

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Author Contributions:

Conceptualization: Andrea L. Popp, Harsh Beria, Matthias Sprenger, Pertti Ala-Aho, Miriam Coenders-Gerrits, Jannis Groh, Julian Klaus, Julia L. A. Knapp, Gerbrand Koren, Christine Stumpp, Giulia Zuecco, James W. Kirchner

Funding acquisition: Andrea L. Popp, Ilja van Meerveld, Daniele Penna

Methodology: Andrea L. Popp, Harsh Beria, Matthias Sprenger, Pertti Ala-Aho, Christophe Hissler, Ghulam Jeelani, Petra Žvab Rožič, Tricia Stadnyk, Christine Stumpp, Jana von Freyberg,

Recent Advances in Tracer-Aided Mixing Modeling of Water in the Critical Zone

Andrea L. Popp^{1,2,3} , Harsh Beria^{4,5} , Matthias Sprenger^{6,7} , Pertti Ala-Aho⁸ , Miriam Coenders-Gerrits⁹, Jannis Groh^{10,11,12} , Julian Klaus¹³ , Julia L. A. Knapp¹⁴ , Gerbrand Koren¹⁵ , Iris Bakiri¹⁶ , Esther Xu Fei¹⁷, Marina Gillon¹⁸ , Ciaran Harman^{17,19} , Christophe Hissler²⁰ , Tegan Holmes²¹, Ghulam Jeelani²² , Andis Kalvans²³ , Alessandro Montemagno²⁰, Emel Zeray Öztürk²⁴ , Petra Žvab Rožič²⁵, Tricia Stadnyk²¹ , Christine Stumpp²⁶, Nicolas Valiente²⁷ , Jana von Freyberg^{28,29} , Polona Vreča³⁰ , Giulia Zuecco^{31,32} , Ilja van Meerveld³³ , Daniele Penna^{34,35} , and James W. Kirchner^{4,29,36} 

¹Department of Geosciences, University of Oslo, Oslo, Norway, ²Hydrological Research Unit, Swedish Meteorological and Hydrological Institute (SMHI), Norrköping, Sweden, ³Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden, ⁴Department of Environmental Systems Science, ETH Zurich, Zurich, Switzerland, ⁵WSL Institute for Snow and Avalanche Research SLF, Davos, Switzerland, ⁶Lawrence Berkeley National Laboratory, Earth and Environmental Sciences Area, Berkeley, CA, USA, ⁷Department of Forestry and Environmental Resources, North Carolina State University, Raleigh, NC, USA, ⁸Water, Energy and Environmental Engineering, University of Oulu, Oulu, Finland, ⁹Department of Water Management, Delft University of Technology, Delft, The Netherlands, ¹⁰Department Soil Science and Soil Ecology, Institute of Crop Science and Resource Conservation, University of Bonn, Bonn, Germany, ¹¹Agrosphere Institute (IBG-3), Forschungszentrum Jülich (FZJ), Jülich, Germany, ¹²Isotope Biogeochemistry and Gas Fluxes, Leibniz Centre for Agricultural Landscape Research (ZALF), Müncheberg, Germany, ¹³Department of Geography, University of Bonn, Bonn, Germany, ¹⁴Department of Earth Sciences, Durham University, Durham, UK, ¹⁵Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, The Netherlands, ¹⁶Department of Instrumental Analytical Methods, University of Tirana, Tirana, Albania, ¹⁷Department of Environmental Health and Engineering, Johns Hopkins University, Baltimore, MD, USA, ¹⁸Mediterranean Environment and Agrohydrosystems Modelling, Avignon University, Avignon, France, ¹⁹Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD, USA, ²⁰Catchment and Ecohydrology Research Group, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg, ²¹Department of Civil Engineering, University of Calgary, Calgary, AB, Canada, ²²Department of Earth Sciences, University of Kashmir, Srinagar, India, ²³Faculty of Geography and Earth Sciences, University of Latvia, Riga, Latvia, ²⁴Department of Geomatics Engineering, Konya Technical University, Konya, Turkey, ²⁵Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, Ljubljana, Slovenia, ²⁶Department of Landscape, Water and Infrastructure, BOKU University, Institute of Soil Physics and Rural Water Management, Vienna, Austria, ²⁷Department of Science and Agroforestry Technology and Genetics, University of Castilla-La Mancha, Albacete, Spain, ²⁸School of Architecture, Civil and Environmental Engineering, EPFL, Lausanne, Switzerland, ²⁹Swiss Federal Institute for Forest, Snow and Landscape Research (WSL), Birmensdorf, Switzerland, ³⁰Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia, ³¹Department of Land, Environment, Agriculture and Forestry, University of Padova, Padova, Italy, ³²Department of Chemical Sciences, University of Padova, Padova, Italy, ³³Department of Geography, University of Zurich, Zurich, Switzerland, ³⁴Department of Agriculture, Food, Environment and Forestry, University of Florence, Florence-Firenze, Italy, ³⁵Forest Engineering Resources and Management Department, Oregon State University, Corvallis, OR, USA, ³⁶Department of Earth and Planetary Science, University of California, Berkeley, CA, USA

Abstract Safeguarding water resources for society and ecosystems requires a comprehensive understanding of hydrological fluxes within the Critical Zone, Earth's living skin where the atmosphere, hydrosphere, biosphere, and lithosphere meet. For decades, tracer-aided mixing models have been used to track water flow paths through the Critical Zone, mapping the journey of water particles from atmospheric moisture to groundwater. Recent advances in novel tracer measurements and modeling methodologies offer new insights into hydrological partitioning within the Critical Zone, enabling improved quantification of water fluxes across scales ranging from microscopic to macroscopic. Advanced tracer-aided modeling approaches enable more rigorous testing of assumptions and improved quantification of uncertainties. In this review, we (a) summarize state-of-the-art tracer and modeling techniques, with an emphasis on stable water isotope tracers, (b) synthesize insights emerging from new approaches, and (c) highlight opportunities to apply these methods in interdisciplinary Critical Zone research.

Plain Language Summary The Critical Zone is a dynamic interface where air, water, soil, plants, and rocks interact. Ensuring sustainable water resources and healthy ecosystems requires understanding how water

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Ilja van Meerveld, Daniele Penna, James W. Kirchner

Project administration: Andrea L. Popp, Harsh Beria, Miriam Coenders-Gerrits, Christine Stumpp, Ilja van Meerveld, Daniele Penna, James W. Kirchner

Resources: Andrea L. Popp, Harsh Beria, Ilja van Meerveld, Daniele Penna

Supervision: Andrea L. Popp, Harsh Beria, James W. Kirchner

Visualization: Andrea L. Popp, Harsh Beria, James W. Kirchner

Writing – original draft: Andrea L. Popp, Harsh Beria, Matthias Sprenger, Pertti Ala-Aho, Miriam Coenders-Gerrits, Jannis Groh, Julia L. A. Knapp, Gerbrand Koren, Iris Bakiri, Esther Xu Fei, Ciaran Harman, Tegan Holmes, Andis Kalvans, Alessandro Montemagno, Petra Žvab Rožić, Tricia Stadnyk, Nicolas Valiente, Giulia Zuecco, James W. Kirchner

Writing – review & editing: Andrea L. Popp, Harsh Beria, Matthias Sprenger, Pertti Ala-Aho, Miriam Coenders-Gerrits, Jannis Groh, Julian Klaus, Julia L. A. Knapp, Gerbrand Koren, Iris Bakiri, Esther Xu Fei, Marina Gillon, Ciaran Harman, Christophe Hissler, Emel Zeray Öztürk, Jana von Freyberg, Polona Vreča, Ilja van Meerveld, Daniele Penna, James W. Kirchner

moves within the Critical Zone and how this may change in the future. To model water partitioning within the Critical Zone, researchers often use tracer-aided mixing models that allow us to track the movement of water using naturally occurring markers or “tracers.” This approach quantifies the sources and flowpaths of water in the water cycle, from raindrops to aquifers deep below the ground. In this Review, we summarize the latest advancements in tracer-aided mixing models and how they help us to gain a clearer and more precise understanding of water pathways in the Critical Zone. In addition, we propose future research directions in this evolving field.

1. Introduction

Hydrological measurements and their subsequent modeling applications are widely used to quantify hydrological storages and fluxes. Tracers can provide additional insights into the path a water molecule takes through the Critical Zone (CZ) (e.g., Jasechko, 2019; Penna et al., 2018; Tetzlaff et al., 2015). “Conservative” (also called “passive”) tracers interact minimally with their surrounding environment, and thus follow the water parcel that carries them. Conservative tracers thereby provide important constraints on flow paths and residence times within the CZ. Using tracer measurements combined with mass balance equations, mixing models can quantify the contributions of different water sources (typically called “end-members”) to a water flux or compartment (typically called “mixture”) (e.g., Barthold et al., 2011; Carrera et al., 2004; Cook & Dogramaci, 2019).

Tracer-aided mixing models (here also referred to as “mixing models”) have been instrumental in advancing hydrology and related disciplines because they allow us to quantify the contribution of different water sources (e.g., snowmelt) to various hydrological compartments or fluxes (e.g., streamwater and groundwater). For example, mixing models can answer questions such as what proportion of streamflow originates from recent precipitation (vs. from groundwater stored within the catchment), and how this proportion changes as catchment wetness varies. Given the anticipated changes in the water cycle due to global warming and other environmental changes, answering such questions is crucial for protecting ecosystem functioning and sustainable water resource management.

Using naturally occurring tracers (so-called “environmental tracers”) to infer hydrological processes through mixing models dates back to the 1950s (Begemann & Libby, 1957). This approach has revealed several previously unknown phenomena, such as that stormflow peaks are often dominated by water released from catchment storage, rather than recent rainwater that has rapidly reached the stream (e.g., Bishop et al., 2004; Kirchner, 2003). Another important discovery from the use of tracers is that, in certain landscapes, summer transpiration is predominantly supplied by winter precipitation, even when the bulk of annual rainfall occurs during summer (Allen, Kirchner, et al., 2019; Floriancic et al., 2024; Goldsmith et al., 2022). Environmental tracers have also been instrumental in quantifying fluxes to and through the CZ. For example, stable water isotopes have shown that groundwater recharge is often dominated by winter precipitation in temperate climates, and by intense rainfall in (semi-)arid climates (Jasechko et al., 2014; Jasechko & Taylor, 2015). Stable water isotopes have also suggested that in many landscapes, streamflow and tree water uptake originate from different water storages in the CZ (Brooks et al., 2010; Dawson & Ehleringer, 1991; Sprenger & Allen, 2020).

Mixing models have evolved from simple two- or three-component models (e.g., Johnson et al., 1969; Pinder & Jones, 1969; Sklash & Farvolden, 1979) (Figure 1), including the widely used “end-member mixing analysis” (EMMA) introduced by Christophersen et al. (1990) and Christophersen and Hooper (1992). These models are now advancing toward ensemble hydrograph separation (Kirchner, 2019) and Bayesian approaches, which allow for better characterization of uncertainties (e.g., Beria et al., 2020; Popp et al., 2019). Most modeling approaches require identifying all potential end-members, regardless of the number of tracers used. Typically, end-members are identified based on a conceptual understanding of the study site, aided by quantitative methods such as Principal Component Analysis, which assesses the minimum set of end-members required to explain the variability in the tracer signals of the water mixture (Christophersen & Hooper, 1992). In the next step, a mass-balance equation is used to estimate the mixing ratios for n end-members:

$$f_1 C_{1,k} + f_2 C_{2,k} + \dots + f_n C_{n,k} = \sum_{i=1}^n f_i C_{i,k} = C_{m,k} \quad (1)$$

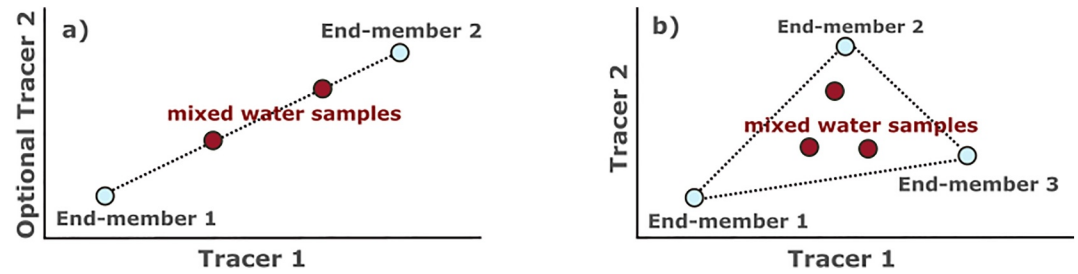


Figure 1. Simple example (with synthetic data) of end-member mixing with two (a) and three (b) end-members and two tracers (1 and 2). Blue circles denote tracer signatures of end-members, red circles denote signatures of mixtures. Note that example “a” could also be resolved with only one tracer.

where end-member i with tracer concentration $C_{i,k}$ of tracer k contributes a fraction $f_i \in [0, 1]$ to the mixture concentration $C_{m,k}$. The fractional contribution of all end-members should sum to one:

$$f_1 + f_2 + \dots + f_n = \sum_{i=1}^n f_i = 1 \quad (2)$$

Most traditional mixing models rely on several assumptions including: (a) the tracer signature of the mixture can be explained as a linear combination of the end-member signatures, (b) the tracers are conservative, meaning that any reactions that might alter the tracer concentrations in a mixture are much slower than the mixing process, (c) the tracer signatures of end-members are constant in time and space, (d) the end-members are sufficiently distinct from each other, and (e) all end-members are correctly identified. However, these assumptions are often violated in real-world applications, leading to substantial uncertainties in mixing model results (Carrera et al., 2004; Delsman et al., 2013; Hooper, 2003; Popp et al., 2019). Many of these assumptions can now be relaxed using novel mixing model approaches, as highlighted in this review.

Uncertainty in mixing ratios arising from space-time variability in tracer measurements is usually estimated using either linear error propagation (Genereux, 1998; Hooper et al., 1990; Uhlenbrook & Hoeg, 2003) or Monte Carlo methods (e.g., Bazemore et al., 1994; Durand & Torres, 1996). The temporal variability of a tracer at a specific location is often less than its spatial variability at a field site (Penna & van Meerveld, 2019), so spatial variability is often considered a more important source of uncertainty in mixing models (Iorgulescu et al., 2007; Joerin et al., 2002; Soulsby et al., 2003). The ability to constrain the mixing ratio depends on the size and composition of the tracer data set (Barthold et al., 2011; Popp et al., 2019), as well as uncertainties arising from field sampling, measurement procedures, and subsequent data analyses (see Box 1).

Box 1 Uncertainty Box

Tracer-aided mixing modeling requires a rigorous consideration of the associated uncertainties that arise from various sources, including the following:

- **Spatial and temporal variability in hydrologic processes:** Hydrological processes within the CZ are variable in space and time. Consequently, the scales at which studies are conducted will influence the outcomes. Spatial and temporal heterogeneity (e.g., caused by differences in subsurface properties or weather) combined with an insufficient sampling resolution can introduce scaling issues, making it challenging to generalize findings to larger scales or understand temporal patterns.
- **Model uncertainty:** The assumptions underlying a mixing model (e.g., concerning the number of end-members and linearity of mixing processes) will dictate its scope and limitations (Section 3).
- **Laboratory uncertainties:** Different instruments have different precision levels. Like field measurements, human or technical errors can distort the results, for instance, during calibration or post-processing of data. Accounting for such potential variations is important, particularly when working with data from other laboratories or when merging data from different sources.
- **Non-unique source characterization:** Different end-members can have similar tracer signatures (depending on the tracer used), which can result in difficulties distinguishing their contributions to a mixture. Some end-members may also be unmeasured, which complicates the interpretation of mixing model results.
- **Tracer uncertainty:** Each tracer's characteristics make it more suitable for some research questions than others (Section 2). The processes that control some tracer signals are still not fully understood. Resource constraints can also limit the scope of the available tracer data.
- **Inconsistencies with data collection:** Differing field sampling procedures, equipment calibration, or weather conditions, as well as human mistakes (e.g., accidental sample contamination) can introduce considerable uncertainties. The timing of sampling can also impact the results of mixing model analyses, particularly if samples are sporadic and infrequent.

Despite these limitations, tracers and mixing models remain essential tools for understanding water movement through the CZ, providing integrated signals over large areas that aid in inferring water mixing dynamics. This review has two main objectives. Firstly, we review recent advances in environmental tracers and mixing models. Secondly, we present improvements in process understanding arising from applications of mixing models to CZ research. The structure of this Review is as follows: Section 2 summarizes both conventional and novel tracers and tracer techniques; Section 3 outlines long-standing and recently developed mixing model approaches; Section 4 shows how recent advances in tracer and modeling techniques have led to new insights into transport, storage, and fate of waters in the CZ (Figure 2).

Due to the many advances in tracers and mixing models in recent years, it is necessary to limit the scope of this review. For example, we only include environmental tracers and exclude reactive tracers, and tracers that are not widely used (yet) or accessible, such as vanadium or eDNA. Similarly, we do not discuss reactive transport of solutes within the CZ, or transport and mixing in urban landscapes. We also do not address the integration of tracers into process-based hydrological and biogeochemical models, instead, we refer readers to the recent review by Jung et al. (2025) for a detailed discussion on this topic. Lastly, although transit-time modeling is equivalent to end-member mixing over continuous time, we exclude transit-time modeling from our review and refer to two recent reviews on this topic (Benettin et al., 2022; Sprenger, Stumpp, et al., 2019). Given the widespread use of stable water isotopes in CZ research, much of this review focuses on their application.

To enhance the readability of this review, Table S1 in Supporting Information S1 provides a glossary of specific terms as they are commonly understood in the field of hydrology.

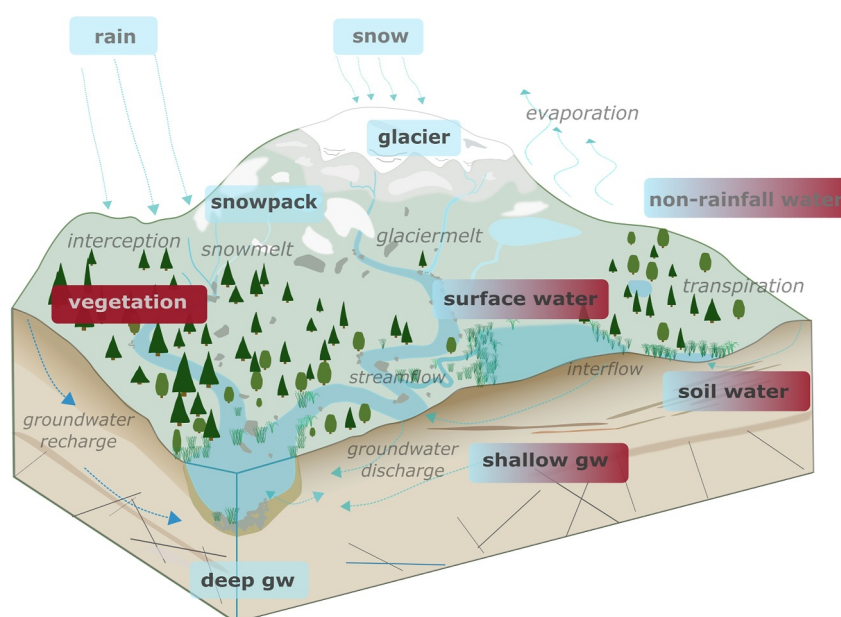


Figure 2. Conceptual model of the water compartments (boxes) and water fluxes (*italic text*) within the Critical Zone that are typically studied using tracer-aided mixing models. Light blue boxes indicate compartments that are considered to be end-members. Red boxes indicate compartments that are considered as mixtures. Boxes with both colors represent compartments that are either end-members or mixtures. “Gw” stands for groundwater.

2. Advances in Tracer Techniques

Here, we summarize tracers commonly used with mixing models for water source partitioning applications in the CZ (Table 1). Furthermore, we identify the typical temporal and spatial scales at which tracer aided mixing models are applied (Supplement Information of Table 1) and highlight novel tracers and tracer techniques that allow us to gain a better understanding of water exchange in the CZ (Table 1). Table 1 highlights relatively novel tracers in bold, while tracers that can be analyzed using recently developed techniques are shown in italics. We chose not to include tracers that have only been demonstrated in one or very few studies, as their usability has yet to be validated across a range of hydrological contexts. Therefore their broader applicability remains uncertain. In addition, analytical methods for these tracers are often not standardized or widely accessible to the broader research community.

Note that we only cover environmental tracers, which are substances that originate from the natural environment. Artificially added tracers, such as dye tracers (e.g., rhodamine, fluorescein, or uranine), salt tracers, or added gases (e.g., SF_6), are typically used to study water residence/travel times or biogeochemical turnover (e.g., Abbott et al., 2016; Sprenger, Stumpp, et al., 2019)—processes we do not cover in this review.

To enhance readability and comprehension, we have subdivided the various environmental tracers into groups. Tracers within one group share similarities, for example, the instruments or laboratory techniques that are needed for their measurement or the processes that they can help quantify (Supporting Information for Table 1). The tracer groups consist of (a) major elements, (b) trace elements, (c) noble gases, (d) radionuclides, (e) stable isotopes of water (also referred to as stable water isotopes), (f) derived isotopic signatures, (g) stable isotopes of major elements, (h) stable isotopes of trace elements, and (i) radiogenic isotopes of trace elements (Table 1).

Table 1 also contains the most common tracer species within these tracer groups and their main use within water compartments. Finally, we highlight advances, advantages and disadvantages of the different tracers, which are typically application-dependent. Mostly, advances and advantages are related to reduced costs, on-site analysis (vs. grab sampling and subsequent lab analysis), and smaller sample volume—all of which help to reduce uncertainty and facilitate high-resolution measurements to better understand the mixing dynamics within the CZ (e.g., Popp, Manning, & Knapp, 2021). Another factor is how conservative the tracers are. Some tracers, such as stable isotopes of water or noble gases, behave particularly conservatively in the saturated zone, which is key for

Table 1
Overview of the Types of Tracers That Are Typically Used in Tracer-Aided Mixing Modeling, Including Their Primary Applications, Advantages, and Disadvantages

Tracer group	Most common tracer species	Primary application	Advantages	Disadvantages
Major elements	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , HCO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , Si	Atmospheric water, soil water, surface water, groundwater	Distinct signatures in many water sources, widely available, low-cost analytical methods	Non-conservative behavior
Trace elements	Sr, Ba, Mn, Zn, Cu, B, Li, Cr, Mo	Atmospheric water, soil water, surface water, groundwater	Widely available, low-cost analytical methods	Non-conservative behavior, low concentrations in natural waters
Noble gases	⁴ Helium, ²²² Radon, ³ H/ ³ He, ⁸⁵ Krypton, ⁸¹ Krypton, ³⁹ Argon	Groundwater	Very conservative behavior, new analytical tools allow for (in situ) high-resolution measurements	Difficult to sample, expensive with traditional analytical tools, limited analytical accessibility, potential for contamination
Radionuclides	Tritium (³ H)	Atmospheric water, surface water, groundwater	Part of the water molecule	High-uncertainties if used alone, costly
Stable isotopes of water	$\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$	Atmospheric water, plant water, soil water, surface water, groundwater	Ideal tracer for most water compartments, new analytical tools allow for (in situ) high-resolution measurements	Non-unique tracer signal among potential end-members
Derived isotopic signatures	Deuterium-excess , $\delta^{17}\text{O-excess}$	Atmospheric water, soil water, surface water, groundwater	Provides constraints in addition to isotope measurements from which they are derived	Require measurement of multiple isotopic signatures, higher costs; no international standards available
Stable isotopes of other major elements	$\delta^{13}\text{C}$, $\delta^{34}\text{S}$, $\delta^{15}\text{N}$, $\delta^{44}\text{Ca}$, $\delta^{26}\text{Mg}$, $\delta^{30}\text{Si}$	Atmospheric water, soil water, surface water, groundwater	Process specific	High-costs
Stable isotopes of trace elements	$\delta^7\text{Li}$, $\delta^{11}\text{B}$, $\delta^{138}\text{Ba}$	Atmospheric water, soil water, surface water, groundwater	Distinctive among end-members	High analytical costs, often large sampling volume needed; potential for contamination
Radiogenic isotopes of trace elements	⁸⁷ Sr/ ⁸⁶ Sr, ²⁰⁶ Pb/ ²⁰⁷ Pb, ²³⁴ U/ ²³⁸ U, ¹⁴³ Nd/ ¹⁴⁴ Nd	Surface water, soil water, groundwater	No fractionation at any typically studied temporal scale	High costs, no widely available analytical technique

Note. Primary applications refers to the use of tracers both in characterizing end-members and in analyzing mixtures, as reflected in the literature. Novel tracers (i.e., tracers that recently became more widely available) are highlighted in bold; tracers that can be analyzed with techniques that have been recently developed are highlighted in italics. Tracers are assigned to groups based on their typical applications and analysis method.

reducing uncertainties in water source partitioning (e.g., Popp et al., 2019). Similarly, the most common disadvantages are related to high costs of labor and/or equipment, the lack of distinct signatures of end-members, and the fact that some tracers can currently only be analyzed by a few laboratories worldwide. The advantages and disadvantages summarized in Table 1 thus broadly govern the spatial and temporal applicability for each particular tracer. Note that when using “high/low” concentrations or costs, we speak in relative terms. The Table S1 in Supporting Information S1 further contains information on common analysis techniques for different tracer species as well as references including application examples.

Previous research studies (Barthold et al., 2011; Delsman et al., 2013; Popp et al., 2019) have shown that the number of different tracers, as well as the correct identification of end-members substantially influence the derived mixing ratios. Barthold et al. (2011) showed that including trace elements in addition to major elements can considerably reduce uncertainties and thereby lead to an improved understanding of water source partitioning in catchments. Popp et al. (2019) showed that a diverse set of conservative tracers exhibits the lowest uncertainties, while including non-conservative tracers such as nitrate and sulfate (which are still commonly used for mixing analyses) can considerably increase uncertainty (see Box 1 about uncertainties). These examples show that employing unsuitable tracers and disregarding underlying uncertainties can lead to a flawed interpretation of results and, thus, a potentially faulty understanding of hydrological processes. Generally, for a more robust approach, we advise using a combination of diverse tracers that exhibit different geochemical behavior while accounting for tracer-related uncertainties (Abbott et al., 2016; Popp et al., 2019; Tetzlaff et al., 2015). We refrain from providing general guidelines on which tracers to use for a specific research question, as this largely depends on the particular problem one aims to solve and available resources. For more detailed information on each particular tracer application, we refer to the respective references in Table S1 in Supporting Information S1 (see link provided in the Data Availability Statement section).

3. Advances in Tracer-Aided Mixing Models

The previous section summarized tracers that are commonly used in mixing models. This section focuses on recent advances in mixing models that employ these tracers to quantify water source partitioning within the CZ.

3.1. Hydrograph Separation Using EMMA

End-member mixing analysis (EMMA) is widely used to estimate the contributions of end-members to mixtures (Christophersen et al., 1990). In EMMA, the mixture combines the chemical and isotopic signatures of the end-members, which are assumed to mix conservatively, that is, without reacting with each other or with the media through which they travel (Hooper, 2003). Applications of EMMA typically (a) use Principal Component Analysis to reduce the dimensionality of the tracer data, (b) identify end-members that span the compositions of the mixture in principal component space, and (c) estimate the fractional contributions of the end-members to the mixture using matrix methods as described in Christophersen and Hooper (1992) and Barthold et al. (2011).

3.2. A GLUE-Based Approach to End-Member Mixing Analysis (G-EMMA)

EMMA explains tracer concentrations in a mixture in terms of tracer concentrations of end-members, and typically assumes that these end-member concentrations are invariant in space and time. Delsman et al. (2013), however, argue that observed tracer concentrations may not represent all potential end-members and that end-member concentrations may vary. Thus, they developed an approach that quantifies uncertainties in end-member identification, while allowing for overdetermined mixing models. Their approach is based on the generalized likelihood uncertainty estimation (GLUE) methodology (Beven & Binley, 1992) and is thus named G-EMMA. GLUE acknowledges equifinality (Beven, 2006), the often-observed phenomenon that the available observational data may be adequately explained by multiple sets of model parameters.

3.3. Convex Hull End-Member Mixing Analysis (CHEMMA)

In contrast to EMMA which requires the independent identification and sampling of end-members, Convex Hull End-Member Mixing Analysis (CHEMMA) infers the end-members (and their associated uncertainties) solely from the samples of the mixture (Xu Fei & Harman, 2022). Essentially, this “blind” decomposition of tracer data is achieved by fitting a simplex around the tracer data, where the corners of the simplex represent the tracer profiles of potential end-members. CHEMMA combines two machine learning methods, convex hull non-

negative matrix factorization (CH-NMF) and constrained K-means clustering (COP-KMEANS). Tight clusters indicate that the end-members can be robustly identified, while diffuse clusters suggest that the end-members cannot be adequately separated with the available data. Xu Fei and Harman (2022) tested this approach using streamflow isotope samples from the Panola data set and successfully identified the three end-members originally reported by Hooper et al. (1990). CHEMMA performed best when the mixture had contributions from all end-members, even if individual contributions were small, effectively exploring the boundaries of the mixing space.

3.4. Ensemble End-Member Mixing Analysis (EEMMA)

Conventional end-member mixing approaches require that all end-members have been sampled and that their mean tracer signatures are sufficiently distinct. The number of end-members also must not exceed the number of independent tracers, plus one. Where multiple sets of tracer measurements are available, however, these constraints can be relaxed by exploiting the information contained in correlations between fluctuations in the end-members and the mixture. This approach, termed Ensemble End-Member Mixing Analysis (EEMMA) (Kirchner, 2023) re-casts conventional end-member mixing problems as linear regressions, making several types of previously unsolvable problems mathematically tractable. For example, a single tracer can be sufficient to estimate the average mixing fractions of any number of end-members, even if their means overlap, as long as their fluctuations are sufficiently uncorrelated. One can also estimate mixing fractions for an incomplete set of end-members (or even just a single end-member), as long as their fluctuations are not too strongly correlated with any unmeasured end-members. It is even possible to estimate the time series of the weighted average of those missing end-member(s), if they are sufficiently uncorrelated with the measured end-members. To date, the potential of this new method has been demonstrated with synthetic benchmark data (Kirchner, 2023).

3.5. Bayesian End-Member Mixing Approaches

Bayesian mixing models (Parnell et al., 2010) have recently been applied in hydrology to estimate components of groundwater recharge (Beria et al., 2020; Popp, Pardo-Alvarez, et al., 2021; Popp et al., 2019), streamflow (Birkel et al., 2021; He et al., 2020; Miller et al., 2021) and root water uptake (Couvreur et al., 2020; Evaristo & McDonnell, 2017), among others. Bayesian mixing methods estimate the probability density function (pdf) of the mixing ratio, thereby offering a robust way to estimate uncertainty in water partitioning studies.

Broadly, two approaches are prevalent in Bayesian mixing analysis. In the first approach, pdfs are fitted to the tracer concentrations in different end-members (e.g., rainfall, snowfall) and the mixture (e.g., groundwater, streamwater). The pdf of the mixing ratio is estimated using standard Bayesian inference principles. If the pdfs that are fitted to the end-member and mixture tracers follow standard statistical distributions (e.g., Gaussians), the mixing ratio pdf can be inferred analytically (Stock et al., 2018). In other cases, the mixing ratio pdf is estimated by an optimization routine that seeks the best fit between the observed and simulated mixture tracers, through an iterative improvement of an initial guess of the mixing ratio distribution (Birkel et al., 2021; He et al., 2020; Popp et al., 2019). Recent advances in probabilistic programming languages have greatly simplified these optimization tasks (e.g., Carpenter et al., 2017).

Bayesian approaches typically require a large tracer data set to robustly fit the pdf. Tracer measurements are often scarce, particularly for potential end-members (Penna & van Meerveld, 2019). In such cases, a bootstrap approach can be used employing all possible combinations of end-member tracer measurements and a given distribution of mixing ratios to simulate mixture tracer concentrations. In this case, a likelihood function is formulated based on an assumed pdf of the underlying error function, which is the difference between simulated and observed target mixture concentrations (Beria et al., 2020). Therefore, this approach does not require fitting pdfs to the tracer compositions of different end-members. By using all available combinations of end-member concentrations, the method builds an empirical pdf while optimizing the likelihood function. This approach has been shown to work both theoretically and in real-case scenarios (Figure 3). In addition, this Bayesian approach can be combined with other EMMA-based methods that provide potential end-member suggestions. For example, CHEMMA's output of potential end-members can be used as a prior distribution of potential end-members.

3.6. Ensemble Hydrograph Separation

In contrast to conventional end-member mixing analyses, which are based on mass balances, ensemble hydrograph separation (Kirchner, 2019) is based on correlations between fluctuations in input and output tracer time

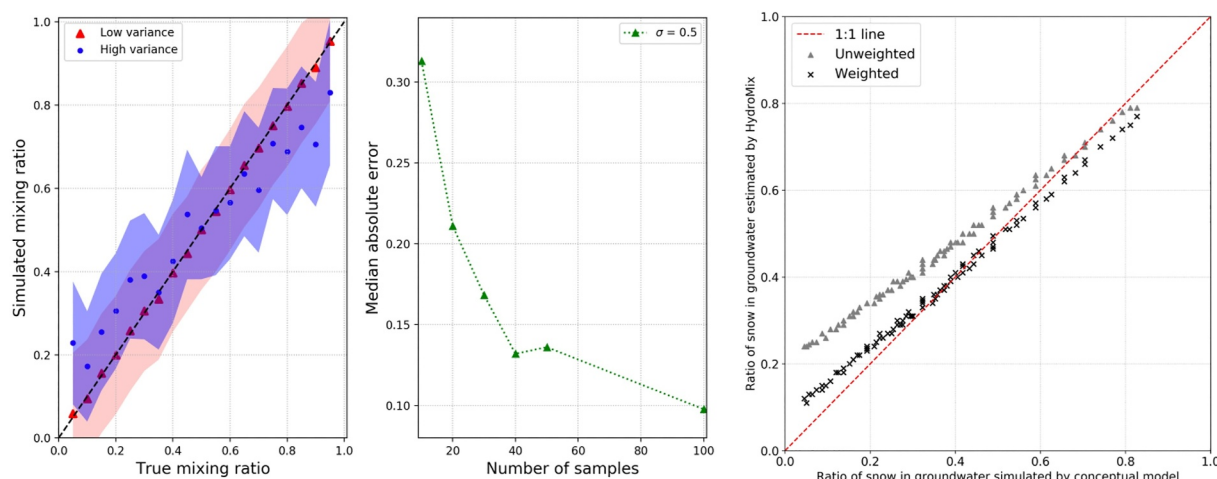


Figure 3. Figure benchmarking a Bayesian mixing model (HydroMix) using a synthetic data set and a conceptual hydrological model. (a) HydroMix-inferred mixing ratios closely match theoretical mixing ratios in low-variance data sets, while higher variance leads to greater deviations. The uncertainty band represents one standard deviation around inferred mixing ratio values. (b) Median absolute errors reduce with increasing sample size. (c) Ratios of snow in groundwater estimated using HydroMix are plotted against theoretical values of snow in groundwater obtained from a conceptual hydrological model, showing that flux-weighted mixing results in more accurate mixing. Figure adapted from Beria et al. (2020).

series. These correlations yield estimates of the new water fraction F_{new} , averaged over ensembles of either precipitation or discharge time steps. The method does not require continuous time series, so subsets of the data can be selected to reflect conditions of particular interest, such as wet versus dry antecedent conditions or high-intensity versus low-intensity precipitation. Thus catchment response to precipitation can be mapped out, directly from data, as a function of ambient conditions and external forcing. The “new” in F_{new} refers to precipitation that has fallen since the previous streamflow tracer sample. Thus, weekly sampling yields weekly new water fractions, daily sampling yields daily new water fractions, and so forth. This approach has successfully been applied by others (e.g., Burt et al., 2023; Floriancic et al., 2024; Knapp et al., 2019), and scripts are available to implement the approach (Kirchner & Knapp, 2020).

Because ensemble hydrograph separation is based on correlations rather than mass balances, it does not need to assume that end-member tracer signatures are constant (instead, it exploits their fluctuations). For the same reason (and in contrast to conventional end-member mixing methods), ensemble hydrograph separation does not need to assume that all potential end-members have been identified and measured; it must only assume that tracer fluctuations in any unmeasured end-members are not strongly correlated with those in the measured end-members. Ensemble hydrograph separation can also easily accommodate cases in which the end-member tracer concentrations overlap with each other; these cases simply have little leverage on the solution, whereas they lead to mathematical blowups in conventional end-member mixing. The ensemble hydrograph separation approach can be extended to multiple time lags, yielding estimates of transit time distributions (Kirchner, 2019), but these are beyond the scope of this review. This approach can potentially be extended beyond catchments to quantify the coupling between inputs and outputs in other systems as well.

3.7. End-Member Splitting Approach

Most of this review is concerned with interpreting CZ compartments (e.g., soil water, groundwater, xylem water, or streamwater) as mixtures of end-members (i.e., end-member mixing analysis; Figure 2). Often, it would be useful to know not only how end-members are combined in mixtures, but also how individual end-members are partitioned among their possible fates. This latter question is the domain of end-member splitting analysis (Kirchner & Allen, 2020), which combines isotope tracers and water flux measurements to estimate how isotopically distinct end-members (such as summer vs. winter precipitation) are partitioned among their different ultimate outputs (such as evapotranspiration or streamflow).

End-member splitting is derived from combining end-member mixing and isotope mass balance methods. Thus, all of the conventional assumptions of end-member mixing apply here, including (a) that the measured mixtures

are derived entirely from only two end-members (or $n + 1$ end-members if we have n non-redundant tracers), (b) that the end-member tracer measurements are unbiased, and (c) that the tracer signatures of the mixtures are not affected by any fractionation that was not also present in the end-members. In addition, end-member splitting also requires that the sampled mixture(s) comprise all the outputs from the system except one, and that the water fluxes in these sampled mixtures, and the end-members, can be quantified with sufficient accuracy. Scripts are publicly available that perform all the necessary calculations, including error propagation (Kirchner, 2020).

4. Application: Insights on Temporal and Spatial Variability of Water Fluxes Within Different Critical Zone Compartments

This section highlights recent applications of tracer-aided mixing modeling approaches within specific compartments of the Critical Zone. The compartments we address are (a) atmospheric and frozen water (Section 4.1), (b) surface water (Section 4.2), (c) soil water (Section 4.3), (d) plant water (Section 4.4), and (e) groundwater (Section 4.5). For each of these compartments, we first identify the major end-members (except in the case of atmospheric water and frozen water, which are primarily considered as end-members themselves). We then describe how each compartment is typically sampled in time and space, and outline how its relevant hydrological processes have been elucidated through the application of mixing models.

4.1. Atmospheric and Frozen Water

4.1.1. Precipitation: Rainfall and Snowfall

Rainfall and snowfall collectively constitute the majority of global precipitation. Several naturally occurring tracers have been used to characterize rainfall and snowfall as end-members in mixing analyses. Among these, stable isotopes of water are the most commonly used (Table 1). Stable water isotopes have also been used to quantify the contribution of recycled moisture to precipitation (Froehlich et al., 2008). For example, in the semi-arid Heihe River Basin in China, a three-component isotopic mixing model revealed that 25%–50% of growing-season precipitation originated from local moisture recycling, primarily driven from transpiration (Zhao et al., 2019).

Mixing studies frequently require estimating average tracer signatures in both rainfall and snowfall, ideally accounting for their spatial and temporal variability. Capturing this variability necessitates extensive sampling to obtain representative end-member tracer signatures (Fischer et al., 2017).

Rainfall and snowfall samples are usually collected at fixed time intervals or as time-integrated samples after precipitation events. The sampling frequency varies depending on the research objectives and site accessibility. It can be relatively high, based on fixed time intervals, for example, 30-min collection intervals (von Freyberg et al., 2017) or fixed volumes, for example, 5 mm collection intervals (Cayuela et al., 2018), to study streamflow dynamics during storm events. Alternatively, for studies focusing on seasonal catchment dynamics, biweekly or monthly sampling campaigns may be sufficient (Michelon et al., 2023). Although data requirements regarding the length and frequency of measurements are rarely specified in the literature, Putman et al. (2019) suggests that at least 48 months of monthly precipitation isotope measurements are necessary to adequately characterize the long-term distribution of stable isotopes of water at a given site. Precipitation sampling networks should ideally be designed to be spatially representative (Hatvani et al., 2021). However, they are typically based on existing meteorological stations within larger international data collection networks (Stumpp et al., 2014; Vreča et al., 2022). In mountainous terrain, valleys and lowlands are often over-sampled relative to higher-elevation locations due to logistical constraints. When sampling is not feasible, precipitation tracers can sometimes be inferred from publicly available monitoring programs and databases, such as the Global Network of Isotopes in Precipitation (GNIP), or estimated using models such as isoscape interpolations (e.g., Allen et al., 2018; Nelson et al., 2021).

4.1.2. Non-Rainfall Water (NRW)

Non-rainfall water (NRW, comprising all water inputs in addition to rain or snow) can account for 5%–40% of annual precipitation in some regions (Aguirre-Gutiérrez et al., 2019; Groh et al., 2019; Lekouch et al., 2012).

NRW includes dew (e.g., Forstner et al., 2021; Kaseke, Mills, Brown, et al., 2012), fog (e.g., Breuer et al., 2021), frost (e.g., Feher et al., 2021; Groh et al., 2018), rime ice (e.g., Meissner et al., 2007), and water vapor adsorption to soils (e.g., Agam & Berliner, 2006; Saaltink et al., 2020). The composition of the NRW tracer varies temporally and spatially, depending on meteorological factors (Groh et al., 2018; Ritter et al., 2019), moisture sources (Kaseke et al., 2017), soil properties (Kaseke, Mills, Esler, et al., 2012), landscape position (e.g., Uclés et al., 2015), and vegetation characteristics (e.g., Malik et al., 2015). Inputs from NRW are frequently overlooked in end-member mixing studies, potentially amplifying uncertainties in mixing estimates. Although NRW generally accounts for a small proportion of daily precipitation (Zhuang et al., 2021), it can play a significant role in specific hydrological processes (Chung et al., 2017; Runyan et al., 2019), such as vegetation water uptake ((Zhuang et al., 2021), see Section 4.4) and soil recharge (see Section 4.3).

Only a few applications of mixing models have been made to understand the impact of NRW on ecohydrological processes. Dawson (1998) was one of the first to use water isotopes to show the significant role of fog in tree water uptake, demonstrating that fog water inputs to several California redwood trees accounted for 13%–45% of their annual transpiration. X.-F. Wen et al. (2012) showed that the stable isotopic composition of the dew water is significantly correlated with leaf water in a Chinese grassland site, indicating significant leaf water uptake at night. Li et al. (2021) used water isotopes to estimate the contribution of dew and fog to plant water uptake in a Swiss grassland and highlighted the importance of plant water uptake through soil distillation. Tian et al. (2021) showed that nighttime evaporation during heavy dew events was primarily driven by changes in relative humidity in three different climates: the arid central Namib Desert, Mediterranean Nice (France), and humid Indianapolis (USA). Using ^{17}O -excess alongside ^2H and ^{18}O , the study detected evaporation during dew formation in the Namib Desert and in Indianapolis when temperatures exceeded 14.7°C; however, dew in the Mediterranean climate of Nice showed minimal evaporation.

4.1.3. Snowpack and Glaciers

Precipitation can be stored above the ground surface for time scales varying from a few hours in forest canopies to several months in snowpacks, and even decades to millennia in glaciers and ice sheets. During above-ground storage, tracer concentrations can change considerably. For example, changes in the water isotopes have been documented in seasonal snowpacks (e.g., Noor et al., 2023; Rücker et al., 2019; Taylor et al., 2001) and during canopy interception (Allen et al., 2016; von Freyberg et al., 2019; Cayuela et al., 2018). In the following, we summarize how tracers can quantify the contributions of snow and glacier melt to hydrological processes in cold regions.

4.1.3.1. Seasonal Snow

In snow-dominated regions, water input to the CZ includes rainfall, snowmelt, and potentially glacial melt. The tracer composition of the snowmelt end-member can be estimated from samples of snowfall, snowpacks, or snowmelt, or numerical snowmelt models based on snowfall and snowpack measurements (Beria et al., 2018).

The variability in tracer composition generally decreases from snowfall to snowpack and snowmelt (Beria et al., 2018). However, due to the heterogeneity in snow accumulation and melt processes, tracer measurements in snow can exhibit high spatial variability, even over short distances (R. W. H. Carroll, Deems, Sprenger, et al., 2022; Hürkamp et al., 2018). Characterizing the tracer variability in seasonal snowpacks thus requires extensive sampling across the landscape. Snowmelt varies over time, and it is unclear which phase of melt (e.g., early, peak, or late) best characterizes the snowmelt end-member. Recently, Noor et al. (2023) revealed potential sublimation biases in tracer signals during early snowmelt in the Finnish Laplands, and recommended more frequent sampling during peak melt periods.

Snowpack sampling typically involves coring or excavating snow pits. In some cases, the entire snowpack, from top to bottom, is integrated into one sample (e.g., Ceperley et al., 2020; Penna et al., 2017; Rodhe, 1981). Alternatively, individual layers within the snowpack can be separately sampled (e.g., Ala-aho et al., 2021; R. W. H. Carroll, Deems, Sprenger, et al., 2022; Taylor et al., 2001). Snowpack tracers typically vary both vertically and laterally. Vertical variations often reflect the accumulated sequence of snowstorms and their tracer signatures, as modified by canopy interception, wind-driven snow redistribution, sublimation, snow metamorphism, and vapor

exchange with ambient air (e.g., Feng et al., 2002; von Freyberg et al., 2019; Koeniger et al., 2008; Taylor et al., 2001). Lateral variations in snowpack reflect topographic influences (e.g., Beria et al., 2018; R. W. H. Carroll, Deems, Maxwell, et al., 2022; Dietermann & Weiler, 2013), in addition to the factors mentioned above. Snowmelt is often collected at regular intervals using lysimeters or passive capillary samplers (e.g., Laudon et al., 2002; Nehemy et al., 2022; Penna et al., 2014; Thaw et al., 2021), or sampled on an ad-hoc “grab sample” basis, directly from the base of a melting snowpack (e.g., Beria et al., 2018; Miller et al., 2021; Penna et al., 2016). Fractionation during melting and subsequent refreezing within the snowpack results in meltwaters being isotopically lighter than the bulk snowpack early in the melt season, becoming isotopically heavier than the bulk snow as the melt season progresses (Taylor et al., 2001). This underscores the importance of timing in snowmelt sampling and highlights the need for guidelines to sample snowmelt.

The snowmelt tracer composition can also be estimated via numerical modeling. There are currently two prominent modeling paradigms. The first approach simulates changes in snowpack tracer composition resulting from snow metamorphism and liquid-ice interaction along a vertical snowpack column. These models can also account for changes in tracers induced by atmospheric exchanges, such as the deposition of water vapor on the snowpack or snow mass loss via sublimation (e.g., Feng et al., 2002; Pu et al., 2020). The second approach uses mass balance models and assumes a uniform snowpack tracer composition, thereby simplifying tracer changes due to snow metamorphism (Ceperley et al., 2020; Stadnyk et al., 2013). This approach can simulate the spatial variability in snowmelt tracer compositions over large regions, without the exhaustive input data required by vertically-resolved snowmelt tracer models (Ala-aho et al., 2017; R. W. H. Carroll, Deems, Sprenger, et al., 2022). Modeling studies have revealed significant uncertainty in estimated snowpack contributions to streamflow, arising from the highly variable and dynamic nature of the melt.

4.1.3.2. *Glaciers*

Glaciers accumulate precipitation over periods ranging from years to millennia. Glacial ice preserves the tracer composition of precipitation at the time of its initial formation, serving as a valuable proxy record of past climates. However, post-depositional snow processes can modify the original precipitation water isotope signal, complicating the interpretation of ice core climate records (Dietrich et al., 2023). Glacial meltwater streams contain a mixture of ice melt from the glacier itself, rain falling on the ice surface, and snowmelt from snowpacks atop the glacier. From the onset of the snow ablation season, the tracer composition of glacial meltwater streams will change as melting progresses toward higher elevations, reflecting shifting contributions of snowmelt, rainfall, and ice melt, as well as altitude gradients in precipitation tracers preserved in the snow and ice. Capturing these seasonal dynamics requires frequent sampling campaigns, especially during the ablation season (Engel et al., 2015; Zuecco et al., 2019).

Water isotopes are frequently used to quantify runoff contributions from the melting of glacier ice (Liu et al., 2015; Ohlanders et al., 2013; Pu et al., 2017) due to the distinct signature of glacial melt compared to summer rainfall and groundwater. To distinguish tracer signatures of snowmelt from glacier melt in glacial meltwater streams, researchers have separately sampled snowmelt from glacier-free areas (Dietermann & Weiler, 2013; Schmieder et al., 2018) and sampled meltwater after seasonal snowpacks have melted out (Müller et al., 2022). There can be isotopic differences between glaciers and the snow from which they originate, due to isotopic fractionation during snow-firn metamorphism (Beria et al., 2018). However, stable isotopes of water often cannot be used to distinguish between glacial melt and snowmelt, because they frequently exhibit similar isotopic compositions (Zuecco et al., 2019). Differentiating glacial melt from snowmelt may therefore require multiple tracers, potentially including dissolved iron (Bhatia et al., 2013) or electrical conductivity (Penna et al., 2017; Rai et al., 2019).

As glaciers are often located in remote areas, they pose considerable logistical constraints, making it challenging to collect long-term tracer data at high spatio-temporal resolutions. Consequently, accurate characterization of the glacier end-member, a critical aspect for mixing models in glacierized catchments, is often compromised (He et al., 2021; Schmieder et al., 2018; Zuecco et al., 2019). These limitations highlight the need for new data collection approaches for remote glacial environments, to facilitate more robust and comprehensive assessments of runoff dynamics in cold regions.

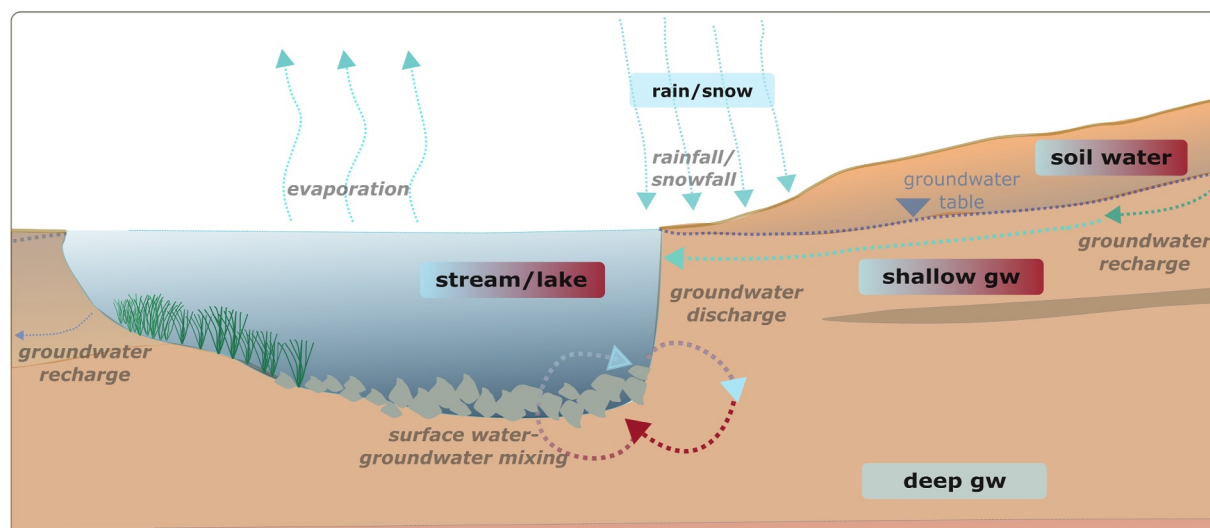


Figure 4. Water mixing processes in surface waters and groundwaters (gw) are typically studied using tracer-aided mixing approaches. Typical end-members are illustrated in blue. Water compartments that are considered as end-members or mixtures, depending on the study, are shown in blue (end-member) and red (mixtures).

4.2. Surface Water

4.2.1. Streamwater

4.2.1.1. Streamwater and Its End-Members in Time and Space

Quantifying the contributions of different end-members to streamflow is a common task in hydrology. Streamflow is generally a mixture of precipitation, soil water and groundwater, and depending on the specific catchment, can also include other fluxes such as snow and glacier meltwater, irrigation water, and leakage from water supply infrastructure. Since the 1960s, hydrologists have used tracer measurements and mixing models to determine the contributions of different end-members to streamflow and their variations through time (Gat & Tzur, 1967) (Figure 4).

The contributions of individual end-members can be quantified if their tracer concentrations are sufficiently distinct (Burns et al., 2001; James & Roulet, 2006; Soulsby et al., 2003). Depending on the available tracer measurements, it may also be possible to further differentiate individual end-members, for example, by distinguishing individual soil layers based on their geochemical tracer signatures (Hooper et al., 1990). In addition to quantifying the contributions of spatially distinct end-members, tracers are also widely used to distinguish contributions from waters of different ages, such as recent precipitation, snowmelt or glacier melt, as distinct from older soil waters or groundwaters (Sprenger, Stumpp, et al., 2019). Typical hydrograph separation studies use conservative tracers such as stable water isotopes to separate stormflow following precipitation events into “event water” (from the recent precipitation itself) and “pre-event water” stored within the catchment from previous precipitation inputs (Buttle, 1994; Klaus & McDonnell, 2013; Leibundgut et al., 2009).

Over time, approaches have emerged that blur the distinction between temporal and spatial hydrograph separation. Earlier studies contrasted the contributions of groundwater and direct runoff to streamflow (e.g., Pinder & Jones, 1969; Sklash & Farvolden, 1979). More recent studies have separated pre-event water into groundwater and soil water (McHale et al., 2002) or assessed contributions from different landscape units (e.g., riparian vs. hillslope zones) (McGlynn & McDonnell, 2003).

4.2.1.2. Sampling Streamwater and Its End-Members in Time and Space

Surface water sampled at the outlet of a catchment integrates hydrological processes within the catchment, making tracer signals useful for understanding spatially integrated water storage and release dynamics at the catchment scale. Characterizing and identifying potential end-members often requires comprehensive spatial sampling of both isotopic and geochemical tracers (see Table 1) in distinct catchment areas, such as riparian zones and hillslopes (e.g., James & Roulet, 2006).

The number of end-members required to explain streamflow tracer variability can depend on the timeframe of the research question. For instance, in a study of nested forested catchments in Canada, James and Roulet (2006) found that two distinct groundwater end-members, each with different average residence times, were essential to capture streamflow tracer variability at a seasonal scale. However, for the timescale of a single storm event, a single well-mixed groundwater end-member was sufficient. Hydrograph separation studies typically estimate the composition of pre-event water by sampling streamflow during baseflow conditions before the storm event (Sklash & Farvolden, 1979), and the composition of event water by sampling rainfall at one or several locations during the storm (McDonnell et al., 1991). However, the unequivocal identification of potential end-members is challenging due to their substantial spatial and temporal variability (Burns & McDonnell, 1998; Fischer et al., 2017; Kiewiet et al., 2019; Uhlenbrook et al., 2002). Quantifying how end-member contributions change within individual storm events often requires high-frequency streamflow sampling (Michel et al., 2020; von Freyberg et al., 2017), particularly in small and flashy headwater streams. Furthermore, spatial variations in precipitation, such as altitude effects in isotopic tracers, pose further challenges (Section 4.1).

4.2.1.3. Streamwater: Mixing Model Applications

Mixing models have been instrumental in advancing our understanding of water storage and release processes in diverse landscapes (Ceperley et al., 2020; Klaus & McDonnell, 2013). For instance, it has been widely observed that pre-event waters stored within a catchment are the primary contributors to streamflow during storm events, rather than the event precipitation itself. This phenomenon has been reported across diverse environments, including croplands, forests, and peatlands (Bishop et al., 2004; Burns et al., 2001; Gracz et al., 2015; Kirchner, 2003; Sklash et al., 1976). Mixing models have also been used to identify dominant water flow pathways in different landscapes (Durand & Torres, 1996). For example, in an agricultural catchment in Scotland, Soulsby et al. (2003) used tracers to show that overland flow predominantly occurs only during the peak of a storm, and subsurface flow pathways contribute the majority of streamwater recharge. While most mixing model studies quantify streamflow contributions from predefined end-members, Kirchner (2023) recently demonstrated that this approach can also be used to identify missing, unknown, or unsampled end-members.

Mixing models have also been proven to be useful in diverse environments including peatlands: Gracz et al. (2015) have shown that pore waters stored in the near-surface of Alaskan peatlands sustain streamflow during dry periods. This ability to regulate streamflow has been attributed to the buffering capacity of peatlands, which helps maintain stable water tables even under varying snowmelt conditions in Banff National Park, where groundwater contributes up to 53% of the water budget (Mercer, 2018). Interestingly, a semi-arid peatland in Chile has even exhibited a reverse water flow, where water moves from streams into the peatland, contrary to the more typical flow from peat-bearing soils to streams (Valois et al., 2021). These insights have significantly improved our understanding of peatland hydrology and its complex interactions with streamflow dynamics.

Mixing analyses have also been used to identify the seasonal sources of streamflow. For example, in the Willamette Basin in Oregon, during winters, river water is primarily recharged by precipitation falling in low mountains and valley bottoms, whereas during summers, the majority (60%–80%) of river flows are derived from snowmelt at higher elevations (Brooks et al., 2012). Similarly, in the headwater catchments of the Colorado River, high-elevation snowmelt contributes disproportionately (up to 70%) to streamflow during peak snowmelt periods, with greater high-elevation snowmelt contributions in years with lower snowpack and warmer spring temperatures (Sprenger et al., 2024). Numerous studies (Van Tiel et al., 2024) in cold regions have shown that seasonal snowmelt and glacial melt often account for the majority of streamflow during the melt season, such as in the European Alps (Engel et al., 2015; Penna et al., 2014; Schmieder et al., 2019), the Andes (Gribbin et al., 2024; Ohlanders et al., 2013), Svalbard (Blaen et al., 2014), the Wind River Range in Wyoming (Cable et al., 2011), the Tibetan plateau (Zongxing et al., 2015), and the Himalayas (Maurya et al., 2010; A. Lone et al., 2021; Dar et al., 2024). However, snow is not always over-represented in streams relative to its proportion in annual precipitation, as evidenced in the Swiss Alps (Allen, von Freyberg, et al., 2019).

As a complement to end-member mixing, an “end-member splitting” approach has been proposed to move beyond only identifying the sources of streamflow, to exploring where precipitation ultimately goes. Kirchner and Allen (2020) illustrated this approach using isotope time series to infer the fates of summer and winter precipitation at Hubbard Brook, New Hampshire, USA (Figure 5). Their results show that end-member splitting can lead to different insights than end-member mixing. For example, at Hubbard Brook, about one-sixth of

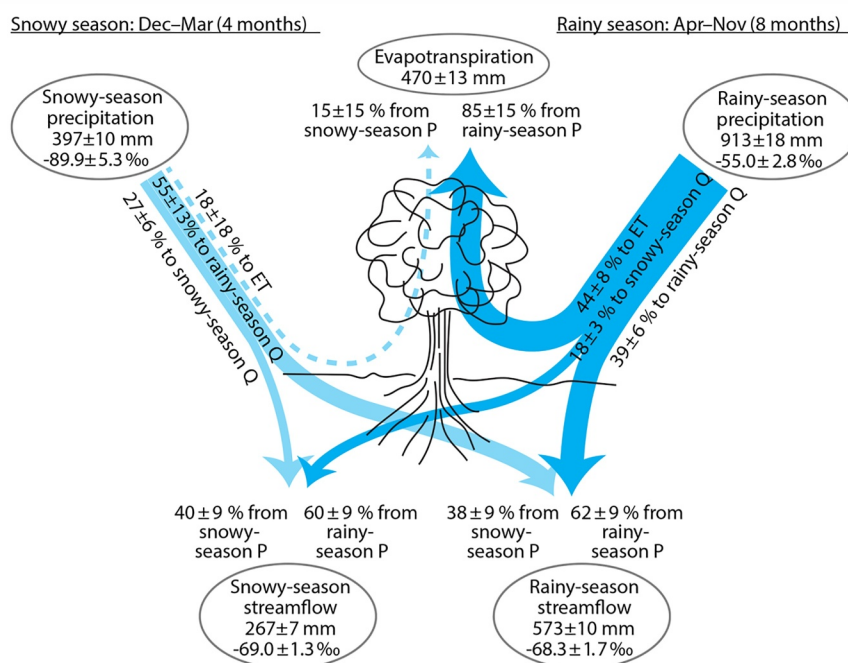


Figure 5. End-member splitting results illustrating how precipitation (P) is partitioned into streamflow (Q) and evapotranspiration (ET) during the snow-dominated season and the rain-dominated season at Hubbard Brook, US (analysis by Kirchner and Allen (2020) based on 4 years of fortnightly ^2H measurements by Campbell and Green (2019)). Wider lines indicate larger water fluxes; dashed lines show fluxes that differ from zero by less than one standard error.

rainy-season precipitation is discharged during the snowy season (end-member splitting), but this accounts for over half of snowy-season streamflow (end-member mixing). Conversely, roughly half of snowy-season precipitation is discharged during the rainy season, accounting for nearly 40% of rainy-season streamflow. Each season's precipitation contributes significantly to the following season's streamflow, implying substantial inter-seasonal storage in snowpacks and groundwaters. Marttila et al. (2021) used end-member splitting to show that rainfall at the Lompolonjärgänoja catchment in Finland is partitioned roughly equally between streamflow and evapotranspiration, but snowfall predominantly leaves the catchment via evapotranspiration. Sprenger et al. (2022) applied the end-member splitting approach to nine headwater catchments in the Rocky Mountains and found that in catchments with higher tree cover, more snow becomes evapotranspiration, leaving less snowmelt available to sustain summer flows. These examples illustrate the contrasting insights that emerge from asking not only where streamflow or evapotranspiration comes from, but also where precipitation goes.

4.2.2. Lake Water

4.2.2.1. Lake Water and Its End-Members in Time and Space

End-member sources of lake waters include direct precipitation, groundwater, stream/river water, and soil water (Figure 4). Groundwater contributions are particularly important in karstic areas and humid regions (Hayashi et al., 2016; Valiente et al., 2020), but quantifying groundwater inflows into lakes remains challenging due to the heterogeneous spatiotemporal distributions of groundwater flow (Isokangas et al., 2015; Rosenberry et al., 2015) (Section 4.5). The temporal delineation of end-members ranges from single precipitation events to seasonal (e.g., spring snowmelt) and even multi-year periods (Shaw et al., 2014).

4.2.2.2. Sampling Lake Water and Its End-Members in Time and Space

Estimates of long-term water balances in lakes typically assume isotopic steady state and complete mixing of lake water (J. Gibson et al., 2016). However, verifying this assumption requires water sampling both horizontally across the lake and vertically along the water column (Rozanski et al., 2001). Vertical profiling of stratified lakes is essential to accurately quantify end-members (Ross et al., 2015), and to document variations in tracer

composition with depth, given the influence of seasonal temperature fluctuations on water quality, oxygen levels, and nutrient dynamics (Deeds et al., 2021; Perga et al., 2023; S. Wang et al., 2022). Horizontal sampling across the lake is equally important to capture lateral heterogeneity driven by factors such as wind direction, stream inflows, and groundwater discharge patterns (Lewandowski et al., 2015). To quantify temporal variability, sampling at regular intervals, ranging from sub-daily to yearly periods, is often necessary (e.g., Valiente et al., 2018).

4.2.2.3. Lake Water: Mixing Model Applications

Mixing models have been used to quantify components of the water balance that are challenging to measure directly, such as groundwater inflows (Pierchala et al., 2022), lake evaporation (Dinçer, 1968; J. J. Gibson et al., 1996; Welch et al., 2017; Brooks et al., 2014), and catchment-scale evaporation-transpiration partitioning (J. J. Gibson & Edwards, 2002; Jasechko et al., 2013). Tracer characterization in lakes provides insights into processes such as river intrusion (Cotte & Vennemann, 2020), transient flood contributions to the lake water balance (Masse-Dufresne et al., 2021) and biogeochemical cycling in lakes and reservoirs (Dong et al., 2022; Valiente et al., 2022).

Lake evaporation and its isotopic composition are key components in mixing model analysis, particularly in (semi-)arid regions (Sanz et al., 2022), yet their direct measurement remains difficult. Stable isotopes of lake water are the primary tracers used in lake water balance studies since evaporation preferentially enriches the heavier isotopes in the lake water that is left behind (Brooks et al., 2014; Voigt et al., 2021). Incorporating additional tracers, such as ^{17}O in a “triple mass balance” approach, have been shown to complement traditional ^2H and ^{18}O analyses of lake evaporation (Pierchala et al., 2022). The isotopic composition of evaporating water is commonly estimated from temperature, humidity, and the isotopic composition of the surface water and ambient air using the Craig-Gordon model (Craig & Gordon, 1965). However, the isotopic composition of local atmospheric water vapor, a crucial input in the model, is rarely measured directly, and inferring it from precipitation can be problematic (J. Gibson et al., 2016). Crawford et al. (2019) showed that precipitation-equilibrium isotope ratios were poor predictors of the isotopic composition of atmospheric water vapor between precipitation events, and proposed an evaporation pan method as an alternative.

Recent advances in in situ measurement technologies have led to direct measurements of isotopes in water vapor around lakes (Chazette et al., 2021). These instruments support the development of both discrete and continuous monitoring systems, which are essential to capture short-term variations driven by weather events (e.g., rainfall, windstorms), and longer-term trends influenced by seasonal changes or anthropogenic activities. Such advances have the potential to considerably improve our understanding of the hydrological functioning of lentic ecosystems.

4.3. Soil Water

4.3.1. Soil Water and Its End-Members in Time and Space

Soil water is sourced from end-members such as precipitation, snowmelt, or groundwater. In turn, soil water is a potential source for plant water uptake, streamflow and groundwater (Figure 6).

Geochemical tracer concentrations in soil water can change over time, not only via interactions with other end-members, but also through biogeochemical reactions and evapoconcentration. Evaporation also enriches stable isotopes of soil water, with the result that the relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in soil waters often deviates from the local meteoric water line (LMWL) that characterizes local precipitation. Soil water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values usually plot along a trendline that is less steep than the LMWL (see green dashed line in Figure 7), representing precipitation that has evaporated by different amounts in different seasons. Individual $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in soil waters can be projected back onto the LMWL using evaporation lines inferred from ambient temperature and humidity data (Benettin et al., 2018; Bowen et al., 2018), thus estimating the isotopic signature of the soil's precipitation source water and facilitating mixing analyses (Figure 7).

In soil water, isotope fractionation signals from evaporation usually decrease with soil depth due to mixing with precipitation that has infiltrated rapidly, with little evaporative fractionation (Sprenger et al., 2016). Analogous to the event-based hydrograph separation later described in Section 4.2, contributions of recent precipitation to soil

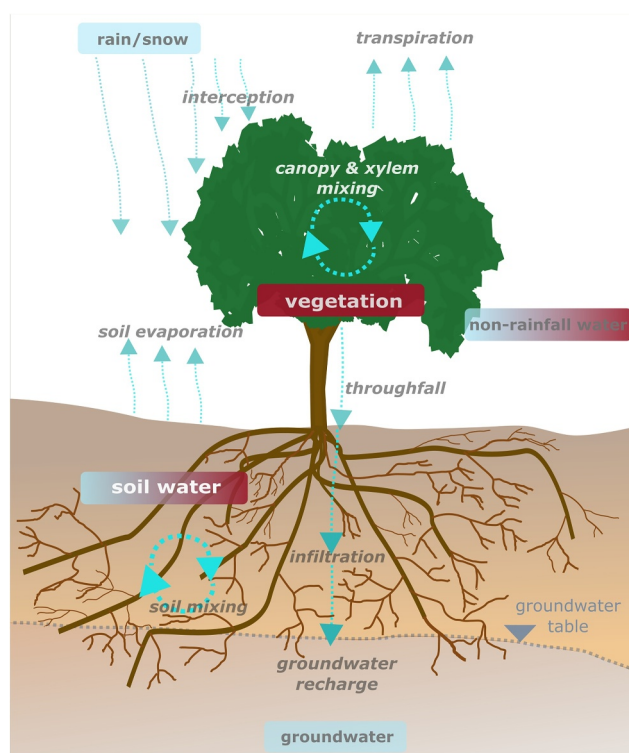


Figure 6. Water exchange and mixing in the atmosphere-vegetation-soil continuum. Blue boxes represent end-members, red boxes represent mixtures, and the blue-red box represents both end-members and mixtures.

water can be estimated by two-component end-member mixing (Equation 1), using the pre-event soil water and the precipitation input as end-members, and the post-event soil water as the mixture.

Instead of sampling the soil water itself, one can also infer soil water composition by sampling plant xylem water, assuming that it represents an integrated sample across the plant's rooting zone (Luo et al., 2019). However, where root water uptake is not equally distributed across the rooting zone, the results will be biased toward depths of higher root density and water availability (Kulmatiski et al., 2017).

4.3.2. Sampling Soil Water and Its End-Members in Time and Space

The optimal sampling frequency of soil water will depend on the research question and the site conditions. For example, monthly sampling intervals are sufficient for mixing models to determine how winter and summer precipitation contribute to soil water storage (e.g., Sprenger, Llorens, et al., 2019). By contrast, daily or weekly sampling would be required to study snowmelt infiltration and mixing with previously stored soil water (e.g., Hürkamp et al., 2018; Muhic et al., 2023).

Spatial sampling strategies must take account of both the vertical and horizontal variability in soil water tracers. For example, investigations of groundwater recharge might focus on sampling deeper soil layers (Koeniger et al., 2016), whereas understanding rainfall infiltration and its mixing with pre-event water would require also sampling the shallow soil layers (e.g., Sprenger et al., 2017). Seepage outflows at trenches or from weighing lysimeters provide integrated signals from the contributing flow paths, and thus cannot identify depth-specific mixing across the soil profile (Imig et al., 2023). However, soil water sampling across the soil profile can reveal the mixing processes behind the tracer signals observed at the outlet of lysimeters or trenches (Benettin, Nehemy, Asadollahi, et al., 2021).

Volumetric soil water content and the corresponding tracer concentrations also exhibit very high lateral heterogeneity, which is difficult to capture with practically feasible sampling schemes (Beyer & Penna, 2021). Initial screening of this variability with a manageable number of samples can potentially facilitate estimates of the number of parallel samples (i.e., samples taken at the same time from different locations) that would be needed to

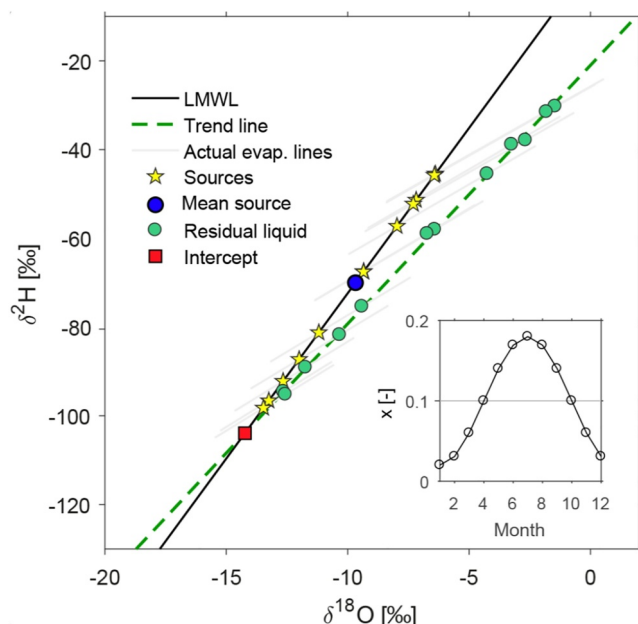


Figure 7. Example from Benettin et al. (2018) showing the kinetic effect of evaporation on residual water isotopes from seasonally varying precipitation using a synthetic data set. The evaporatively fractionated residual water samples (green dots) cluster around a trend line (dashed green line), with considerably steeper slopes than the individual evaporation lines (gray lines). Inset depicts the assumed annual cycle in evaporated fractions x .

achieve the desired precision in the average tracer signature. However, the relevance of such an average will often be unclear because water flow in soils is often strongly preferential (i.e., a large fraction of the flow passes through a small fraction of the volume).

When soil water is used as an end-member, knowledge about its spatial and temporal variability is crucial for interpreting its contributions relative to other end-members like precipitation or groundwater. For example, Correa et al. (2017) showed that Andosols and Histosols in their study catchment had significantly different soil water ion concentrations, and based on these differences, they showed that during the dry season, soil water from Andosols was contributing less to the catchment runoff than Histosols.

4.3.3. Soil Water: Mixing Model Applications

Mixing models have been applied to the unsaturated zone much less often than to streamflow, owing to the difficulties in obtaining soil water tracer data. Nevertheless, mixing analyses using soil water tracers have revealed important insights into water mixing along heterogeneous preferential flow paths (Radolinski et al., 2021). A mixing model study of soil water in a Mediterranean climate (Spain) showed that the contribution of event water to soil pores in monthly sampling intervals was strongly correlated with the soil moisture content prior to the events because precipitation was more likely to refill empty pore spaces in drier soils (Sprenger, Llorens, et al., 2019). The rewetting of the soil water storage driven by newly infiltrating water was further investigated in a Mediterranean region in South Australia, revealing that the portion of newly infiltrated water was highest in the first storms following the end of the dry season (Xu et al., 2019).

Event water will infiltrate the fastest and deepest when preferential flow paths exist. Recent laboratory experiments used isotope-based mixing analyses to assess the impact of preferential flow paths on event water infiltration and mixing (Radolinski et al., 2021; Williams et al., 2023). In addition, field experiments using isotopically-labeled water coupled with mixing models could be applied to map the infiltration of stemflow and its contribution to soil water at different depths and distances from individual trees (Zuecco et al., 2025). With sufficiently dense sampling, it is possible to estimate the stemflow infiltration area (Pinos et al., 2023; Van Stan & Allen, 2020; Zuecco et al., 2025). In situ measurements of stable isotopes of water on the plot scale also open up new opportunities for short-term mixing investigations. For example, Volkmann et al. (2016) measured ^2H breakthrough at soil depths of 5–60 cm in response to a pulse of ^2H -labeled precipitation, applying a Bayesian mixing model (Erhardt & Bedrick, 2012) to quantify how infiltration lag times varied with soil depth.

End-member mixing studies at agricultural sites in temperate regions have shown that subsurface stormflow sampled at tile drains consists of about 20%–30% event water (Granger et al., 2010; Zajíček et al., 2016), consistent with the mobilization of previously stored water to comprise the remaining 70%–80% of soil water drainage (Smith et al., 2021).

Soil water contributions to streamflow are highly relevant as a source of nutrients and contaminants. An end-member mixing study of a small Arizona catchment estimated that soil water contributions varied seasonally from 21% to 62% of streamflow (Dwivedi et al., 2019). Soil water also represents a critical link controlling surface-atmosphere exchange by acting as a reservoir for potential evapotranspiration loss, and an important regulator of runoff generation processes.

4.4. Plant Water

4.4.1. Plant Water and Its End-Members in Time and Space

Plants function as conduits between the atmosphere and the soil: plants absorb water from the soil through their roots, transport it to the leaves via the xylem, and release it into the atmosphere through the stomata. Plants also

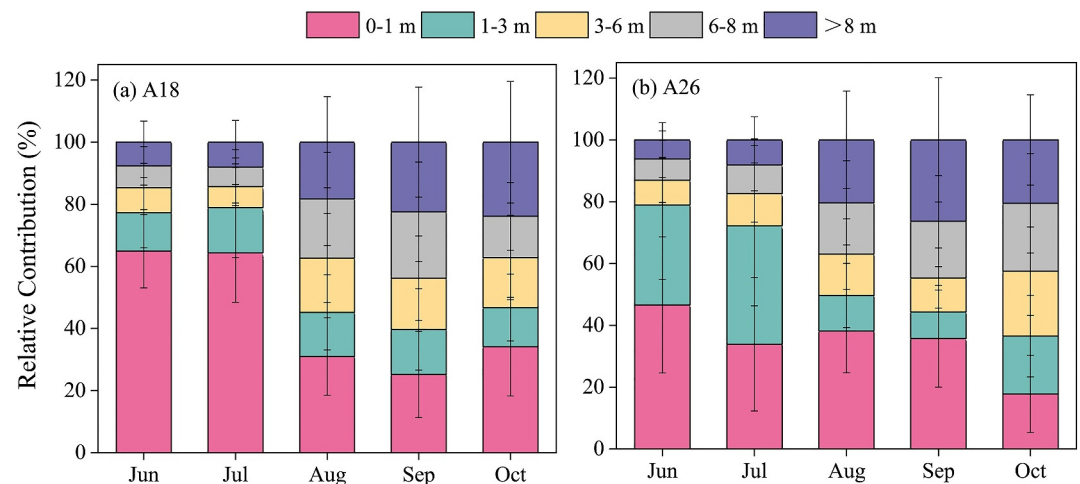


Figure 8. The relative contributions of water from different soil layers to xylem water of apple trees of different ages (a=18 years and b=26 years), using stable water isotopes and a Bayesian mixing model (MixSIAR). Figure and data from Gai et al. (2023).

function as atmosphere-soil interfaces in the opposite direction, intercepting precipitation and modifying its tracer composition before it infiltrates the soil (Allen et al., 2013; Xia et al., 2023) (Figure 6).

Plants primarily source water from different soil depths and groundwater via their root systems. Taking representative samples of these potential sources is challenging, because plant root distributions are often unknown. Plants also absorb water through their leaves, a process known as foliar water uptake (e.g., Berry et al., 2018). Estimating the extent of foliar water uptake is difficult because it involves sampling leaf water, which undergoes significant changes in its tracer composition due to evaporation through stomatal openings.

End-member mixing models are used to estimate the different sources of plant water uptake (Figure 8), mostly using stable water isotopes (e.g., Gai et al., 2023; Rothfuss & Javaux, 2017; Sutanto et al., 2012). However, waters in the different compartments, including leaves and near-surface soils, can be significantly evaporated or mixed with atmospheric water vapor (Section 4.1; Benettin et al., 2018; Bowen et al., 2018; Holloway-Phillips et al., 2016; Jiménez-Rodríguez et al., 2020; Li et al., 2021). These effects need to be corrected before conducting the mixing analysis. Tracer measurements in other end-members such as precipitation and groundwater are relatively straightforward, however their spatial and temporal variability should be taken into account (Sections 4.1 and 4.5).

4.4.2. Sampling Plant Water in Time and Space

In tracer-aided mixing modeling studies, plant water is typically sampled from the xylem, most often by extracting water from mature stems or branches. Sampling is usually conducted less frequently than for soil or surface waters due to the labor-intensive nature of collection and analysis, but is strategically timed to capture key hydrological or phenological transitions. Sampling commonly focuses on different stages of the growing season, periods before and after rainfall events, or periods of water stress such as droughts. Sampling locations are generally co-located with soil and groundwater sampling sites to allow direct comparisons with potential water sources. Studies often target dominant or functionally diverse plant species to capture variability in water uptake strategies (Ceperley et al., 2024).

4.4.3. Plant Water: Mixing Model Applications

Isotopic mixing models have been crucial in elucidating water mixing dynamics across the soil-plant-atmosphere interface (Orlowski et al., 2023). An important focus of mixing models in plant water uptake studies is to partition evapotranspiration into soil and canopy evaporation and plant transpiration (Dubbert et al., 2013; Good, Soderberg, et al., 2014; L. Wang et al., 2010). This is particularly relevant in agricultural applications, where minimizing evaporative losses is crucial for ensuring adequate plant water availability during times of water

scarcity. Numerous studies have used stable water isotopes to show that different irrigation schemes, tillage methods, and crop rotation practices influence evapotranspiration partitioning (e.g., Liebhard, Klik, Stumpp, Morales Santos, et al., 2022; Liebhard, Klik, Stumpp, & Nolz, 2022).

Isotope-based mixing models are often used to quantify where plants take their water from, which improves our understanding of their rooting systems, water flow in the unsaturated subsurface, and plants' adaptation strategies to different environmental conditions (Carrière et al., 2020; Gessler et al., 2021). For example, Allen, Kirchner, et al. (2019) showed that alpine trees predominantly rely on winter precipitation, challenging the common assumption that their primary water source is growing-season precipitation. The dominant role of winter precipitation in tree water uptake has been shown in regions with dry growing seasons (Brooks et al., 2010) as well as in regions with year-round precipitation (Floriancic et al., 2024; Goldsmith et al., 2022). However, studies in the tropical cloud forest in Peru have also shown that plant-water uptake can be in sync with the seasons, with plants accessing wet-season precipitation during the wet season and dry-season precipitation during the dry season (Burt et al., 2023). Floriancic et al. (2024) showed that plant water uptake is constrained by available soil moisture within the rooting zone, a factor that varies among tree species and seasons. During periods of ample soil water availability, plant water uptake is maintained at normal levels, but it declines during soil drying, as observed in beech trees during the 2018 drought in Switzerland, where increased relative uptake from deeper soil depth could not compensate for the lack of available water at shallow soil depths (Gessler et al., 2021). In the Northern Rockies, Douglas fir trees in lower-elevation, water-limited environments rely on winter precipitation sourced from deeper soils, whereas Douglas fir trees in higher-elevation, water-excess environments primarily use summer precipitation from near-surface soil layers (Martin et al., 2018). Mixing analyses using tree ring cellulose ^{18}O in the Rocky Mountains indicate that conifer trees primarily use snowmelt water, but may also use summer rainfall during high-growth years in response to higher precipitation during periods of maximum plant water demand (Berkelhammer et al., 2020).

While many studies have focused on plant water uptake from different soil depths, few have investigated the use of stemflow by trees. One exception is Snyder et al. (2024)'s use of labeling experiments to detect a small but significant fraction of stemflow used by piñon and juniper trees, which was not associated with detectable changes in sap flow rates or plant water potentials. Further studies are needed to investigate the role of stemflow in plant water uptake, particularly compared to throughfall, and under different soil wetness conditions and precipitation intensities.

4.5. Groundwater

4.5.1. Groundwater and Its End-Members in Time and Space

Groundwater can be sourced from all compartments of the water cycle (e.g., Jasechko, 2019) (Figure 4): rainfall, snowmelt (e.g., R. W. Carroll et al., 2019; Penna et al., 2014; Schilling et al., 2021), glacial melt (Miller et al., 2021), infiltration from lakes and streams (e.g., Engel et al., 2022; Isiorho & Matisof, 1990; Popp, Pardo-Alvarez, et al., 2021), inter-aquifer flow (e.g., Popp et al., 2019; Thiros et al., 2023) and permafrost thaw (e.g., Lamontagne-Hallé et al., 2018). In turn, groundwater can also be a source for plant water uptake (e.g., Bertrand et al., 2012; Knighton et al., 2021), soil moisture (e.g., Martínez-de la Torre & Miguez-Macho, 2019) and surface waters (e.g., streams, rivers, lakes and wetlands) (e.g., Winter et al., 1998) (Figure 4).

The tracer composition of groundwater is variable in space and time, reflecting subsurface heterogeneity (e.g., Kiewiet et al., 2019) and seasonally varying contributions from different end-members (e.g., rain or snow) (Jasechko, 2019). However, it is not well understood how the variability in the end-members contributes to variability in groundwater composition. While most tracer studies map out the different sources recharging groundwater, few have considered the time lag between tracers entering the CZ and their appearance in groundwater (Beria et al., 2020; Popp, Pardo-Alvarez, et al., 2021). This consideration is crucial as these delays can vary with the hydrological state of the catchment (see Figure 9). For instance, precipitation can be expected to recharge underlying aquifers faster when it falls on wet landscapes than on dry ones. This is particularly relevant in snowy regions, where snowmelt has a disproportionately high impact on groundwater recharge since the catchment is wet during the snowmelt period (Beria et al., 2018).

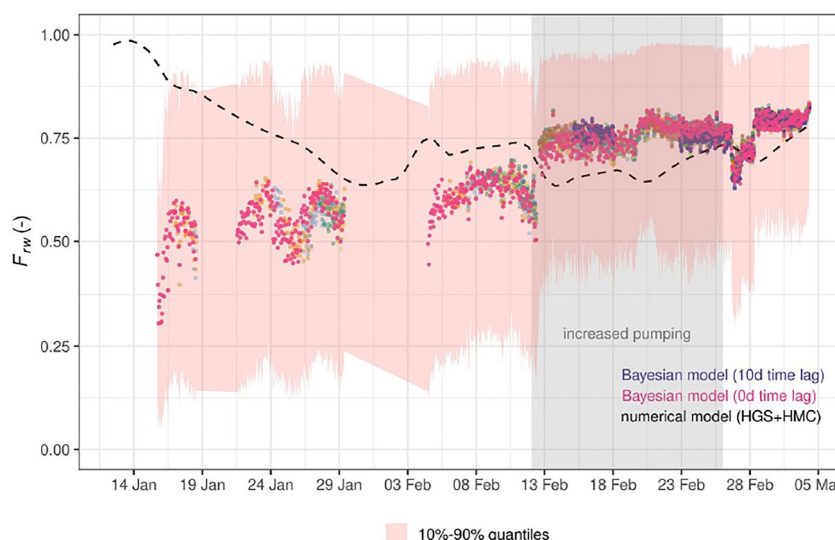


Figure 9. Estimated fraction of river water (F_{rw}) in groundwater derived from a Bayesian mixing model where one end-member is river water and the other is regional groundwater. Colors indicate different time lags between 0 and 10 days that the river water potentially took to travel from the river to the groundwater well where the mixture was analysed (for simplicity, the legend only shows 0 and 10 days; the black dashed line shows results from a physically-based model; HydroGeoSphere). Figure from Popp, Pardo-Alvarez, et al. (2021).

4.5.2. Sampling Groundwater in Time and Space

Groundwater is sampled either through groundwater wells, or through springs which discharge water from underlying aquifers. As springs are not widely available, most groundwater measurements involve sampling existing wells or installing new ones, which typically entails high costs for drilling. Consequently, groundwater studies are often more data-limited than surface water studies. The financial, logistic, and technical challenges of sampling groundwater are even more pronounced in mountainous and arctic environments. As a result, groundwater systems in these regions are under-studied, even though they have been experiencing rapid changes due to global warming (Van Tiel et al., 2024).

Keeping in mind these limitations, it is helpful to have a preliminary conceptual model that provides insights into potential end-members and their variability before starting a detailed field campaign (Enemark et al., 2019). A preliminary field study using easily measurable tracers, such as water temperature, electrical conductivity (EC), and pH, which can readily be assessed with a handheld field probe, can provide a broad overview of groundwater composition and help define an initial conceptual model. Such preliminary studies, in combination with available hydrometric measurements (e.g., water table data), can help to define a sampling scheme that fits the research question and the resources at hand. When designing a sampling scheme, it is important to account for groundwater depth: shallow groundwater shows significant spatial and temporal variability in tracer signals, while deeper groundwater, often isolated from surface waters, typically has less tracer variability (e.g., Jasechko, 2019). Finally, sampling should capture the variability of hydrological conditions over time. Depending on the research question and site-specific dynamics, it may be necessary to sample across different hydrologic regimes to gain deeper insights. The sampling frequency should be tailored to the objectives of the study and the response characteristics of the aquifer.

4.5.3. Groundwater: Mixing Model Applications

Globally, groundwater systems are changing rapidly due to excessive groundwater pumping, land-use changes and warming-induced alterations in precipitation patterns (e.g., Famiglietti, 2014; Jasechko et al., 2024). Moreover, in cold regions increased glacial melt, earlier snowmelt and increasing prevalence of ephemeral snowpacks are altering the timing and magnitude of groundwater recharge (Van Tiel et al., 2024). Several mixing model studies have shown that in snow-impacted regions, snowmelt has a larger impact than summer rainfall on groundwater recharge (Beria et al., 2018). This has been observed in diverse geographic settings, ranging from

California's Sierra Nevada (Winograd et al., 1998) to the European Alps (Penna et al., 2014, 2017), the Andes (Herrera et al., 2016) and the Himalayas (Jeelani et al., 2017; S. A. Lone et al., 2021). A few studies in mountainous landscapes have also estimated the average altitude at which snowmelt recharges aquifers using the isotopic lapse rate (i.e., the change in average isotopic composition of precipitation with elevation) (Arellano et al., 2020; Kohfahl et al., 2008). More recently, recharge temperatures inferred from noble gases have been used to assess the impact of snowmelt dynamics on groundwater recharge (Schilling et al., 2021). Schilling et al. (2021) found that mixing models using dissolved gases provide better-constrained estimates of groundwater recharge from snowmelt than mixing models based on stable isotopes of water. In glacierized landscapes, glacial meltwater streams and subglacial flows are both derived from glacier melt water, and thus cannot be readily distinguished based on their stable isotope signatures. However they can be distinguished based on electrical conductivity, because subglacial flow has higher ion concentrations and thus higher EC (Zuecco et al., 2019). These examples illustrate how using multiple (and novel) tracers can lead to more robust assessments of dominant hydrological processes, especially if relevant water sources are not clearly identifiable using one tracer alone.

Tracers have also been used to quantify the relative contribution of older groundwater that is stored within deeper aquifers, at timescales of 1000s of years. Tracers such as ^{14}C , ^4He , and $^{234}\text{U}/^{238}\text{U}$ are typically used to assess mixing with very old groundwater (Table 1). Azevedo da Silva et al. (2020), for instance, document a case in which a geologically older (and deeper) aquifer has a shorter mean groundwater residence time than the geologically younger (and shallower, but less permeable) aquifer that overlies it. Santoni et al. (2021) used a combination of tracers to show that a Mediterranean peatland was dependent on deep groundwater in spring and summer, and on surface water and shallow groundwater in fall and winter. Similarly, Petersen et al. (2018) used a combination of tracers to show that the Algerian Atlas Mountains are the primary contributor to groundwater recharge of the Continental Intercalaire aquifer—a continental-scale aquifer of major importance in North-Western Africa. Mixing models using stable isotopes and geochemical tracers have also shown that groundwater originating from Pleistocene ice sheets is preserved in several North American and European aquifers, and is used for public water supply (Clark et al., 2000; Pärn et al., 2016). Mixing models have also been used to identify how different aquifers are connected to surface water bodies. For example, Popp et al. (2019) detected the contribution of an old groundwater component to regional and very young groundwater by using high-resolution *in situ* analyses of ^4He and other tracers, in combination with a Bayesian end-member mixing model. In Cambodia's Kandal Province, mixing models using stable water isotopes were used to estimate the relative extent of evaporation of the different groundwater recharge sources in arsenic-affected aquifer (Richards et al., 2018). Groundwater recharge from surface waters has also been quantified using mixing models in Southeastern France, where Poulain et al. (2021) quantified groundwater recharge from three different river water end-members that differ in residence times. Their study showed that end-member contributions differ at pumping wells even though they are very closely located to each other (within 70 m) and have similar depths. Comparing isotopic tracers and geochemistry allowed the authors to quantify the groundwater contributions from different hydrological compartments. In a pre-alpine Swiss valley, Popp, Pardo-Alvarez, et al. (2021) used quasi-continuously analyzed ^4He concentrations to estimate the fraction of groundwater recharged by recently infiltrated river water. Only high-resolution time-series data allowed the authors to properly assess the system response to forcing such as increased river discharge. Moreover, they showed that the common assumption of constant end-members can be inaccurate. They found that, on average, the majority (~70%) of the groundwater mixture originated from recently infiltrated river water. In a site near the Colorado River Christensen et al. (2018) found using strontium isotopes that vadose zone pore water contributed up to 38% of aquifer recharge, with the exact contribution depending on the site's microtopography. In summary, these studies underscore the critical role of mixing models in advancing our understanding of groundwater recharge and discharge dynamics.

5. Outlook

This outlook highlights research directions that have the potential to advance the understanding of Critical Zone processes by enhancing or complementing more traditional tracer-aided mixing modeling approaches covered so far in this review.

5.1. Advances in Tracer Measurement and Data Collection Techniques

Advances in measurement technologies are making tracer measurements more affordable and accessible, thereby enhancing their spatial coverage, while emerging *in situ* measurement capabilities are enhancing their temporal

resolution. Both developments are expanding the availability of tracer data for hydrological analyses (e.g., Popp, Manning, & Knapp, 2021). There is much to be learned by expanding tracer data collection in regions with coarse spatial coverage (e.g., the Arctic, Africa, South America, etc.), synthesizing published data, and collating existing data sets from regional and national networks (Massoud et al., 2023).

Recent developments in novel tracers, such as fluorescence proxies for particulate organic matter (Derrien et al., 2020), noble gas temperatures for groundwater dynamics in snow-dominated landscapes (Schilling et al., 2021), and in situ portable mass spectrometers measuring noble gas tracers (Popp, Manning, & Knapp, 2021) can offer additional insights into water flow pathways. Recent studies highlight the value of incorporating ^{17}O -excess into hydrological analyses alongside $\delta^2\text{H}$ and $\delta^{18}\text{O}$. Because ^{17}O -excess is relatively insensitive to temperature but sensitive to humidity (Angert et al., 2004), it offers a unique constraint on kinetic processes such as evaporation. For example, ^{17}O -excess has been used to detect non-steady-state evaporation during dew formation (Tian et al., 2021), improve lake evaporation estimates (Pierchala et al., 2022), and differentiate drought mechanisms in Southern Africa (Kaseke et al., 2018). These findings underscore the potential of ^{17}O -based tracers to advance our understanding of evaporation and moisture source dynamics. However, some of these tracers remain costly and labor-intensive, limiting their widespread usage. As long as certain tracers can only be analyzed by a few specialized laboratories, their applications will be limited.

Citizen science—also termed community science—initiatives present an opportunity to considerably expand the scope and scale of tracer data collection for water research. Citizen/community science projects have generated extensive data on stream water quality and the isotopic composition of rainfall events, groundwater, surface water, and tap water (Bowen et al., 2007; Cole & Boutt, 2021; de Wet et al., 2020; Good, Mallia, et al., 2014; Njue et al., 2019; Ramírez et al., 2023). By collecting water samples, reporting local hydrologic conditions, and participating in data analyses, citizen/community scientists can help generate higher-resolution data sets. This approach not only enhances hydrological research, but also promotes public engagement, trust in scientific findings, and awareness of water-related issues.

5.2. New Data Sources and Interdisciplinary Research

The use of satellite-based remote sensing data has increasingly gained traction in hydrological research in recent years (Beria et al., 2017; Dembélé et al., 2020; Jiang & Wang, 2019). These data sets provide broad spatial coverage of numerous hydrometeorological variables (e.g., precipitation, temperature, snow coverage, etc.), which when combined with tracers, can help map water flow pathways and elucidate hydrological processes at larger spatial scales, which are otherwise inaccessible to tracer-based studies (He et al., 2021). Remote sensing data sets can also validate and refine the outputs of mixing models. One such application was in the western Himalayas, where S. A. Lone et al. (2017) used LiDAR data in conjunction with glacial meltwater isotopes to reveal divergent glacial melt patterns at different altitudes through the year. Similarly, Sprenger et al. (2024) combined streamflow d-excess values with snowmelt estimates using Airborne Snow Observatory (ASO) flights to quantify the contributions of high- and low-elevation snowmelt to streamflow in three Colorado river basins. New satellite data sets enable the monitoring of water vapor isotopes globally at a daily resolution (Schneider et al., 2022). These data sets are becoming important inputs for large-scale hydrological models that incorporate isotope data, although their applications at the catchment scale are still emerging.

Beyond the integration of tracer and satellite data, the inclusion of other data types, such as groundwater levels, meteorological data, and ecological indicators (e.g., vegetation cover, microbial communities, and biodiversity indicators), can enhance our understanding of water flow dynamics within the Critical Zone. For instance, changes in vegetation cover can directly influence evaporation rates, thereby impacting the overall catchment water balance. Similarly, land use changes resulting from forest fires can dramatically alter streamflow dynamics.

5.3. Machine Learning Techniques

The advent of machine learning (ML) has revolutionized data analysis across various disciplines by uncovering patterns and relationships within large complex data sets. In hydrology, ML holds significant promise for enhancing our understanding of non-linear water flow dynamics within the Critical Zone. To date, the applications of ML in tracer hydrology have primarily been limited to predicting isotopic ratios in hydrological fluxes. For example, Sahraei et al. (2021) used a Long Short-Term Memory (LSTM) model to predict streamflow and groundwater isotopes at a 3-hr resolution, indicating the potential for gap-filling high-frequency streamflow

isotope records. ML has also been employed to estimate precipitation isoscapes across Europe (Nelson et al., 2021), thereby extending the applicability of mixing models to regions where direct sampling of precipitation isotopes may not be feasible.

ML models are emerging as an alternative that can out-perform traditional water quality models, given sufficient training data (Zhi et al., 2024). However, the “enormous” data sets needed to train ML models (Zhi et al., 2024) are usually unavailable in tracer hydrology. A further challenge is that ML models often perform poorly when predicting beyond the range of their training data—precisely where models are most urgently needed to supplement observations. Physics-informed ML has potential to integrate prior physical knowledge into neural networks, thereby constraining the parameter space (Shen et al., 2023). However, ML applications in tracer-aided hydrological modeling remain largely unexplored.

5.4. Tracers in Earth System Models (ESMs) and Other Large-Scale Modeling Approaches

ESMs are essential tools for addressing modern environmental challenges, including the UN's six transformation goals, which highlight linkages between the Sustainable Development Goals (SDGs) (Sachs et al., 2019). However, inadequate knowledge, data, and models constrain our understanding of cause-effect dependencies that are crucial for informing global climate adaptation practices. Although ESMs can theoretically predict complex environmental and human interactions, their computational demands limit coupled simulations of Earth's systems. Resolving the multitude of CZ processes requires many model parameters, and determining realistic parameter values is crucial to improve the reliability of ESMs for their subsequent use in climate change impact assessments (Holmes et al., 2023). However, many regions lack sufficient hydrological data for robust parameter estimation of ESMs, restricting their use and accuracy (Stadnyk & Holmes, 2023).

Tracer-aided ESM modeling, integrating tracer observations with hydrometric data, can improve parameter identifiability and the representation of CZ processes in large-scale models (Holmes et al., 2023; Jung et al., 2025; Stadnyk & Holmes, 2020, 2023). Currently, only a few ESMs simulate tracers directly (IAEA, 2023), highlighting opportunities to expand their capabilities. Tracer integration can be performed either offline by using mixing modeling results to constrain specific ESM parameters, or by implementing particle tracer routines within ESMs and then using tracer data directly during ESM calibration (similar to the approaches that have been used to integrate particle-tracking in hydrological models, e.g., Dennedy-Frank et al. (2024); Kuppel et al. (2018)). Tracer modules that can directly plug into existing ESMs hold promise for rapid progress in tracer-aided ESM modeling.

Advancing tracer-aided modeling requires a concerted effort to establish common practices with shared standards and model evaluation benchmarks (IAEA, 2023). Despite numerous tracer-aided modeling studies, inconsistencies remain in the metrics used for model evaluation and in the standards for what constitutes “acceptable” performance (Holmes et al., 2023). Open sharing of data, code, and workflows within the community (Hall et al., 2022; Knoben et al., 2022) is essential for advancing Critical Zone research.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data were not used, nor created for this research. The Supporting Information for Table 1 can be accessed via Popp et al. (2025).

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