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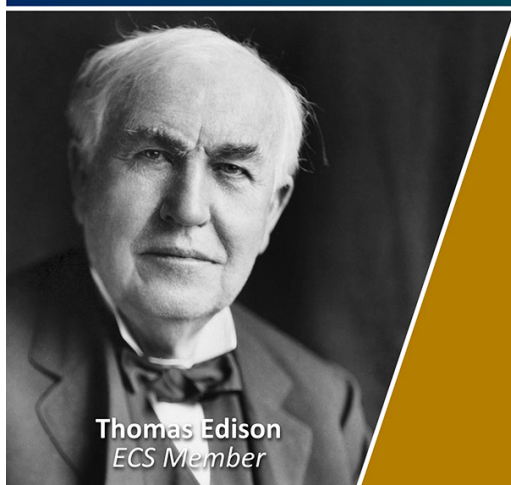
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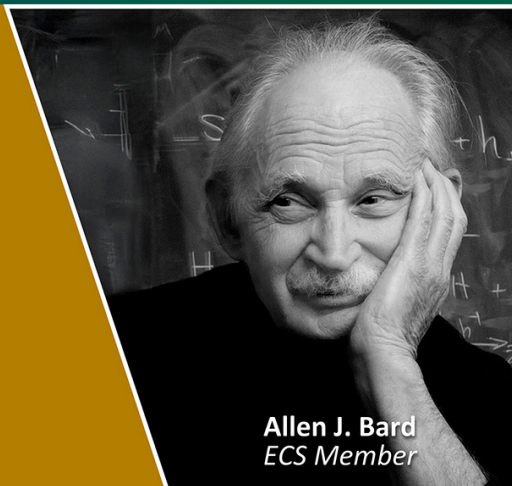
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Toward a process-oriented understanding of water in the climate system: recent insights from stable isotopes

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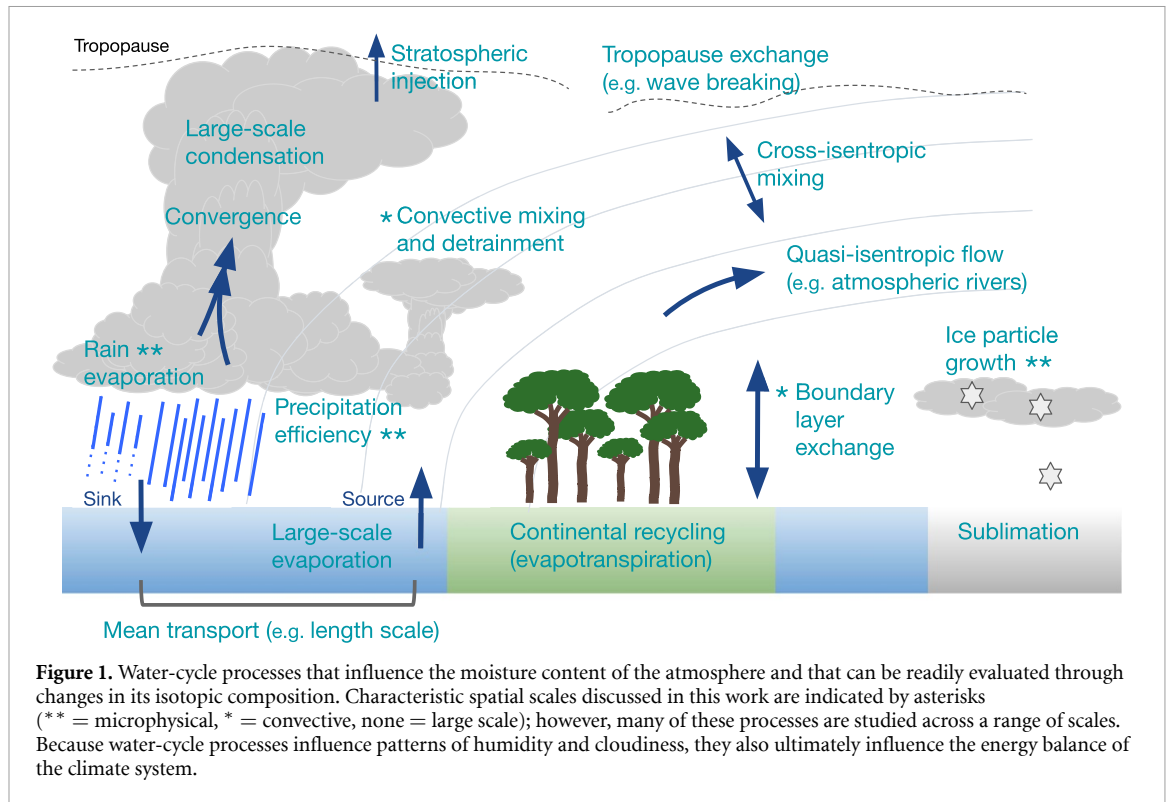
Abstract

Describing the processes that regulate the flows and exchanges of water within the atmosphere and between the atmosphere and Earth's surface is critical for understanding environmental change and predicting Earth's future accurately. The heavy-to-light hydrogen and oxygen isotope ratios of water provide a useful lens through which to evaluate these processes due to their innate sensitivity to evaporation, condensation, and mixing. In this review, we examine how isotopic information advances our understanding about the origin and transport history of moisture in the atmosphere and about convective processes—including cloud mixing and detrainment, precipitation formation, and rain evaporation. Moreover, we discuss how isotopic data can be used to benchmark numerical simulations across a range of scales and improve predictive skill through data assimilation techniques. This synthesis of work illustrates that, when paired with air mass thermodynamic properties that are commonly measured and modeled (such as specific humidity and temperature), water's isotope ratios help shed light on moist processes that help set the climate state.

1. Introduction

Processes controlling the flows and exchanges of water within the atmosphere and between the atmosphere and Earth's surface are intrinsic features of the climate system that define its sensitivity to external forcing. Even processes acting on the smallest scales, such as the conversion of cloud droplets to rain, have large impacts on macrophysical properties critical for climate, such as cloud cover and the bulk efficiency with which moisture returns to Earth's surface as precipitation (Mülmenstädt *et al* 2021, Lutsko *et al* 2023). Yet many of the details surrounding these processes are highly uncertain.

In part, this is due to the fact that while observations that describe the state of water in the climate system abound, few innately reveal the underlying processes that shape it. Consider, for example, that radiosondes launched twice daily from locations worldwide provide vertical humidity profiles that are used to initialize and validate numerical simulations and forecasts. But these measurements cannot tell us whether simulations reproduce humidity patterns for the right reasons. Similarly, satellite observations provide snapshots of cloudiness around the globe but are limited in what they can tell us about the controls on cloud amount and lifetime, both of which are important for climate sensitivity (Sherwood *et al* 2020, Zelinka *et al*



2020). To bolster our knowledge of the climate system and our confidence in future projections of climate risks, greater progress toward understanding the details of water-cycle processes is needed.

The isotope ratios of water, and in particular their spatial and temporal variation, facilitate identification of the moist processes that help set the hydroclimate state (figure 1) due to the fact that distinct water isotopologues change phase and diffuse at different yet predictable rates (Urey 1947, Dansgaard 1953, 1964, Craig 1961a, Craig and Gordon 1965, Merlivat 1978, Gat 1996, Noone 2012, Bolot *et al* 2013). Moreover, in the absence of phase changes, the isotope ratio of an isolated air parcel is conserved, providing a way to evaluate mixing associated with air mass exchange (Gedzelman 1988, Gat 2005, Noone *et al* 2011). Since characteristic moisture transport pathways are defined by patterns of evaporation, precipitation, and mixing, isotope ratios—when paired with additional thermodynamic information—can provide a useful way to track how moisture moves through the atmosphere (e.g. Yoshimura *et al* 2004, Noone 2008, Bailey *et al* 2017, 2018, Dee *et al* 2018, Nusbaumer and Noone 2018, Hu *et al* 2019, Chiang *et al* 2020, Siler *et al* 2021). They provide similar insight for the oceans, elucidating large-scale circulations, riverine input, heat and mass exchange with the atmosphere, and temporal variations in continental ice sheet volume over glacial–interglacial periods and longer (Craig and Gordon 1965, Imbrie *et al* 1984, Jacobs *et al* 1985, Strain and Tan 1993, Frew *et al* 2000, Benway and Mix 2004, Lisiecki and Raymo 2005, Biddle *et al* 2019, Akhoudas *et al* 2021; and see the companion review by, Dee *et al* 2023). Such process-level analyses are increasingly facilitated by the integration of water isotopic tracers in numerical simulations ranging from local to global scales (e.g. Noone and Simmonds 2002b, Schmidt *et al* 2007, Bony *et al* 2008, Lee and Fung 2008, Yoshimura *et al* 2008, Blossey *et al* 2010, Kurita *et al* 2011, Werner *et al* 2011, Risi *et al* 2012, 2020, 2021, Field *et al* 2014, Dee *et al* 2015, Nusbaumer *et al* 2017, Wei *et al* 2018, Brady *et al* 2019, Cauquoin *et al* 2019, Fiorella *et al* 2021, Tada *et al* 2021, Bong *et al* 2024) and by recent advances in measurement capabilities, which include new *in-situ* measurement techniques and strategies (e.g. Gupta *et al* 2009, Finkenbiner *et al* 2022, Henze *et al* 2022) and the development of global data products from a variety of remote sensors (e.g. Worden *et al* 2019, Diekmann *et al* 2021, Schneider *et al* 2022b, 2020, 2022a).

Despite these developments, use of water isotope ratios as essential process-oriented climate variables remains fairly limited to small pockets within the broader climate community. Here, we make the case for advancing efforts to measure and model water isotope ratios to yield new insights in hydroclimate research. In this topical review—which complements others focusing on connected water cycles (e.g. Beria *et al* 2018, Bowen *et al* 2019), climate variability (Dee *et al* 2023), and isotope observing and modeling (Sturm *et al* 2010, Xi 2014, Galewsky *et al* 2016, Sánchez-Murillo *et al* 2020, Stadnyk and Holmes 2023)—we highlight examples of new efforts that are leveraging water isotopic information to study moisture provenance, transport, and exchange (section 3), to investigate cloud and precipitation processes (section 4), and to

perform process-oriented model evaluations and improve model predictive skill (section 5). We conclude with recommendations for how to facilitate continued integration of water isotopic information in hydroclimate studies as a means to better understand, predict, and prepare for water-cycle changes in a warmer world.

2. Background: isotopes of water

2.1. Understanding the isotope ratio

In the atmosphere, distinct isotopologues of water (H_2^{16}O , H_2^{18}O , HDO being the most commonly modeled and observed) change phase and diffuse at different rates (Majoube 1971). Consequently, oxygen and hydrogen isotope ratios (e.g. $^{18}\text{O}/^{16}\text{O}$, D/H, with $\text{D} = ^2\text{H}$) are set by processes at the moisture source—typically evaporation from an ocean or land surface—and also by mass removal during precipitation (Dansgaard 1964, Gat 1996, Noone 2008, 2012). Over time, atmospheric mixing also dilutes, or resets, the isotopic composition (Hendricks *et al* 2000, Noone 2012). The isotope ratio is thus not just a tracer of atmospheric motion but also an integrated record of the moist processes that define hydrological flows. For an appropriately defined problem, they can therefore provide unique insight into how exchanges of water influence the time scales and length scales of moisture transport.

Isotope ratios, denoted R , are typically expressed as the molar ratio of the heavy (rare) isotope to the light (abundant) isotope in a substance relative to a standard:

$$\delta = \frac{R_{\text{observation}}}{R_{\text{VSMOW}}} - 1.$$

In the case of water isotopes, the standard is VSMOW, or Vienna Standard Mean Ocean Water, and the delta value is typically reported in parts per thousand or permil (with $\delta^{18}\text{O}$ and δD expressing the standardized forms of $^{18}\text{O}/^{16}\text{O}$ and D/H, respectively; e.g. Craig 1961b, Sharp 2007). Heavier water isotopologues are characterized by lower equilibrium vapor pressures than light isotopologues (Urey 1947). They also diffuse more slowly (Merlivat 1978), as predicted by a larger effective cross-sectional area that influences the mean free path for Brownian motion (Einstein 1905, <https://einsteinpapers.press.princeton.edu/vol2-trans/137>). As a consequence of these two physical characteristics, lighter isotopologues evaporate more readily than their heavier counterparts, while heavier isotopologues are more likely to condense and deposit. This preferential partitioning—or fractionation—lowers the isotope ratio of water vapor with respect to the liquid and solid reservoirs with which it exchanges—including reservoirs such as seawater, plant water, lakes, rivers, oceans, rainwater, snow, and ice—and is reflected in the negative delta values that typify atmospheric moisture. Sublimation is the one phase change often modeled as non-fractionating at the microphysical level since the diffusive time scale in ice is long (Kuhn and Thürkauf 1958; Bolot *et al* 2013). However, recent work suggests that deposition continues under conditions of net sublimation, creating a net exchange of molecules that effectively partitions hydrogen and oxygen isotopes between the solid and vapor states (Wahl *et al* 2024). It has been hypothesized that this exchange may explain observations of fractionation in surface snow in polar regions during periods when net sublimation occurs (see Casado *et al* 2021, Wahl *et al* 2021, 2022).

2.2. Relating isotopic physics to atmospheric processes

Early work on understanding the distribution of $\delta^{18}\text{O}$ and δD in the atmosphere utilized the simple idea that air masses were isolated. This led to the pervasive conceptual use of a Rayleigh distillation (Dansgaard 1964, Galewsky *et al* 2016), which, while qualitatively satisfying, rarely provides quantitative usefulness beyond acting as a null hypothesis (e.g. Lee *et al* 2007, Worden *et al* 2007, Noone 2008): that is that there is only one moisture source, and the isotope ratio changes in one direction, decreasing with continual mass removal by rainout.

In reality, both fine-scale and macro-scale turbulence in the atmosphere drive a continual stream of water from multiple sources to eventual precipitation sinks (e.g. Koster *et al* 1986, Sodemann *et al* 2008a, Singh *et al* 2016a). Consequently, atmospheric mixing emerges as a fundamental characteristic of the system, and stable isotope abundance—combined with the thermodynamic properties of air masses (including temperature, entropy, and water content)—can be used to track the mixing state of the atmosphere and characterize the dominant transport paths that influence it (Noone 2008, Noone *et al* 2011, Hurley *et al* 2012).

Simple models that represent the atmosphere in the zonal mean can capture the effect of this mixing state on the distribution of water isotope ratios so long as they account for both the removal of moisture by precipitation and the recharge of moisture by evaporation (Hendricks *et al* 2000, Noone 2008, Bailey *et al* 2018). These models have also provided an intuitive means to study how the energetic state of the climate system influences polar isotope ratios, refining our use of isotopic information as a paleoclimate indicator

(Kavanaugh and Cuffey 2002, Noone 2008, Siler *et al* 2021). For example, Noone (2008) used a simple depiction of the overturning circulation to demonstrate that isotope ratios in Antarctic snowfall are closely tied to the strength of the mid-latitude circulation, with a weaker circulation in a warmer climate resulting in a shift toward more poleward moisture sources and higher isotope ratios at the pole.

Of course, comprehensive models, equipped with detailed physics, provide the most complete depiction of water isotope ratios in the climate system (albeit with a host of assumptions that are accompanied by error). These models—which include atmosphere-ocean General Circulation Models (GCMs), Earth System Models (ESMs), regional models, Cloud-Resolving Models (CRMs), and Large-Eddy Simulations (LES)—are able to capture mixing at multiple scales (e.g. Blossey *et al* 2010, Risi *et al* 2012, 2020, Nusbaumer *et al* 2017, Dee *et al* 2018). Some also treat water exchange processes in a more nuanced manner, representing the complex details of microphysical transitions and simulating bulk variations in the efficiency with which precipitation forms and falls to the surface and with which moisture evaporates from a variety of land types (including ice) across a spectrum of relative humidities. (For a recent list of isotopically enabled models, readers are referred to Dee *et al* 2023).

2.3. Measurement and model advances in support of process-oriented studies

Although, historically, the integration of water isotope tracers in comprehensive models was motivated by the desire to elucidate water isotope signals in modern and paleoclimate records (e.g. Joussaume *et al* 1984, Jouzel *et al* 1987, Hoffmann *et al* 2000, Noone and Simmonds 2002b, Bony *et al* 2008, Risi *et al* 2008, Tindall *et al* 2009, Moore *et al* 2014, Cauquoin *et al* 2019), recent work has shifted toward leveraging isotopic information as a tool for conducting process-oriented model evaluations (e.g. Risi *et al* 2012, Nusbaumer *et al* 2017, Fiorella *et al* 2021). Indeed, it is because comprehensive models can be designed to treat all isotopologues with the same level of specificity that they create opportunities to use isotopic information to evaluate the numerical depiction of the physics and dynamics governing the flows and exchange of bulk water within a complex environment. Figure 2 provides an example of such an application by showing tiered experiments in the Community Atmosphere Model (CAM), in which cloud and microphysical changes are introduced sequentially. Here, the isotope ratio captures the weakening of the zonal circulation during El Niño periods (see Dee *et al* 2018) and shows that changes in the microphysical representation of precipitation (though not necessarily precipitation amount, figures 2(c) and (g)) are important for explaining differences in Walker cell dynamics between versions 5 (figure 2(a)) and 6 (figure 2(d)) of CAM.

Continued growth in the temporal and spatial coverage of isotopic observations, especially those in water vapor, has also played an important role in facilitating process-oriented analyses by providing critical benchmarks for model output (figure 3). Indeed, while discrete sampling efforts have produced records of isotope ratios in precipitation, river, lake, and ocean water for decades (e.g. Global Network of Isotopes in Precipitation, Rozanski *et al* 1993; US National Atmospheric Deposition Program, Welker 2012, Scholl *et al* 2023a, 2023b; Global Network of Isotopes in Rivers, Halder *et al* 2015; US National Water Information System, US Geological Survey 2022; US National Aquatic Resource Surveys, US Environmental Protection Agency 2024; CoralHydro2k, DeLong *et al* 2022; CISE-LOCEAN, Reverdin *et al* 2022), measurements of isotope ratios in water vapor have only recently become commonplace (e.g. Galewsky *et al* 2016, Wei *et al* 2019). Today, commercial sensors can measure water vapor isotope ratios *in situ* at better than 1 s temporal resolution and can be deployed on flux towers (Berkelhammer *et al* 2013, Finkenbinder *et al* 2022), ships (Kurita *et al* 2011, Klein and Welker 2016, Benetti *et al* 2017, Bonne *et al* 2019, Thurnherr and Aemisegger 2022, Bailey *et al* 2023, Brunello *et al* 2023), aircraft (Sodemann *et al* 2017, Salmon *et al* 2019, Henze *et al* 2022, Bailey *et al* 2023), and other mobile platforms (Bailey *et al* 2013, Noone *et al* 2013, Wang *et al* 2023). Simultaneous improvements in calibration methods have allowed these measurement systems to achieve precisions of better than 0.1 permil in both $\delta^{18}\text{O}$ and δD with only one minute averaging (Steen-Larsen and Zannoni 2024). These real-time sensors thus contrast starkly with previous offline sampling techniques, in which a handful of vapor samples were collected by flask, later cold-trapped, and finally analyzed in the lab (e.g. Ehhalt 1974, He and Smith 1999, Ehhalt *et al* 2005).

Several large-scale field campaigns have taken advantage of these developments in water isotopic measurement technology to study fast processes such as cloud microphysics (e.g. ORACLES, Henze *et al* 2022) and turbulent mixing (e.g. EUREC⁴A, Bailey *et al* 2023). The recent proliferation of commercial sensors has also facilitated the development of long-term measurement programs, such as that of the US National Ecological Observatory Network (NEON; Finkenbinder *et al* 2022, Li *et al* 2023a). This formal, geographically expansive measurement network follows in the footsteps of grassroots efforts that have measured isotope ratios in water vapor at selected sites for weeks, months, and years (e.g. Noone *et al* 2011, Welp *et al* 2012, Tremoy *et al* 2012, 2014, Steen-Larsen *et al* 2013, 2014, 2015, Bonne *et al* 2014, Berkelhammer *et al* 2016, González *et al* 2016, Casado *et al* 2016, Fiorella *et al* 2019, Akers *et al* 2020, Leroy-Dos Santos *et al* 2020, Bailey *et al* 2021, Landais *et al* 2024). It also expands opportunities to conduct

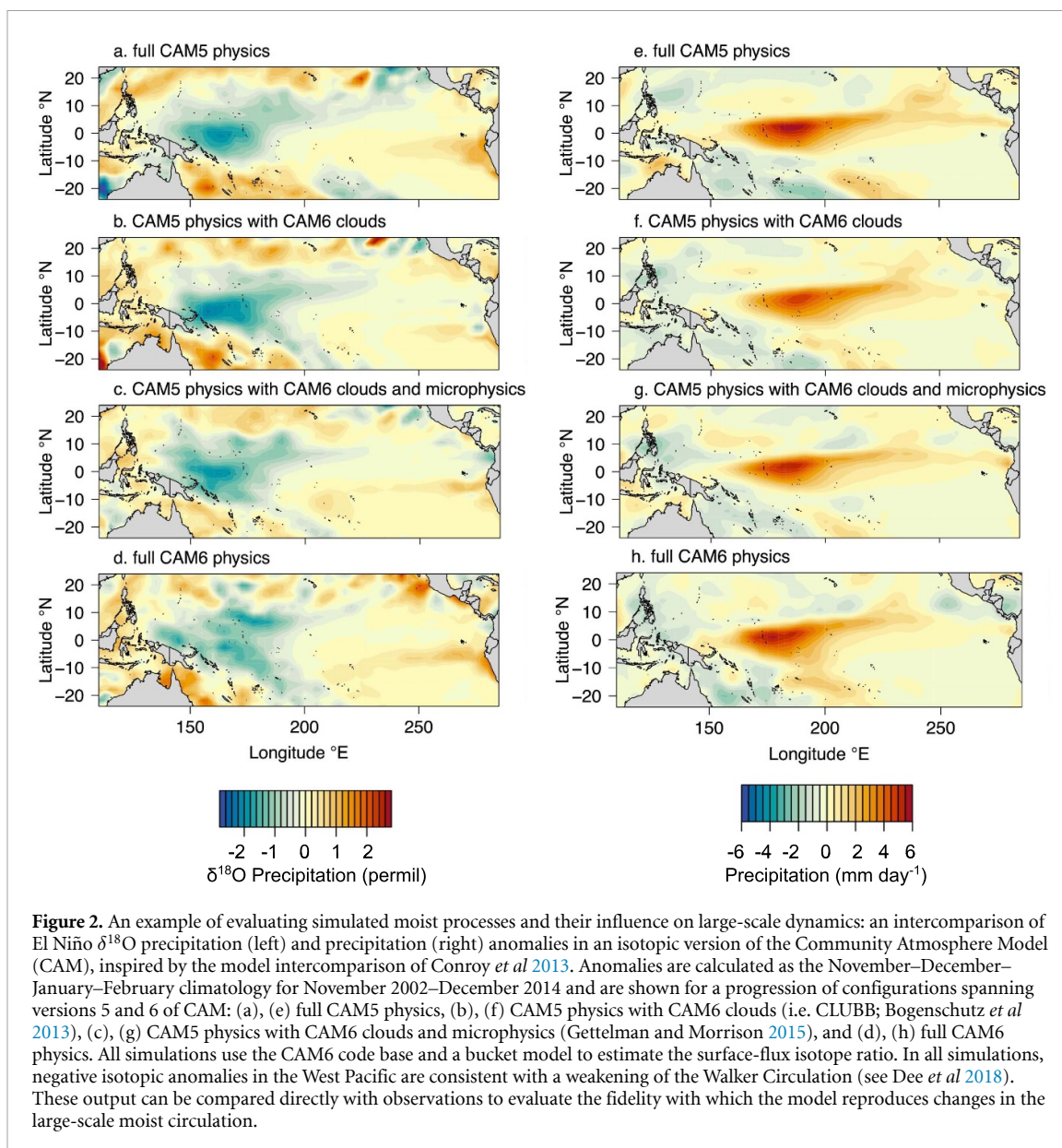
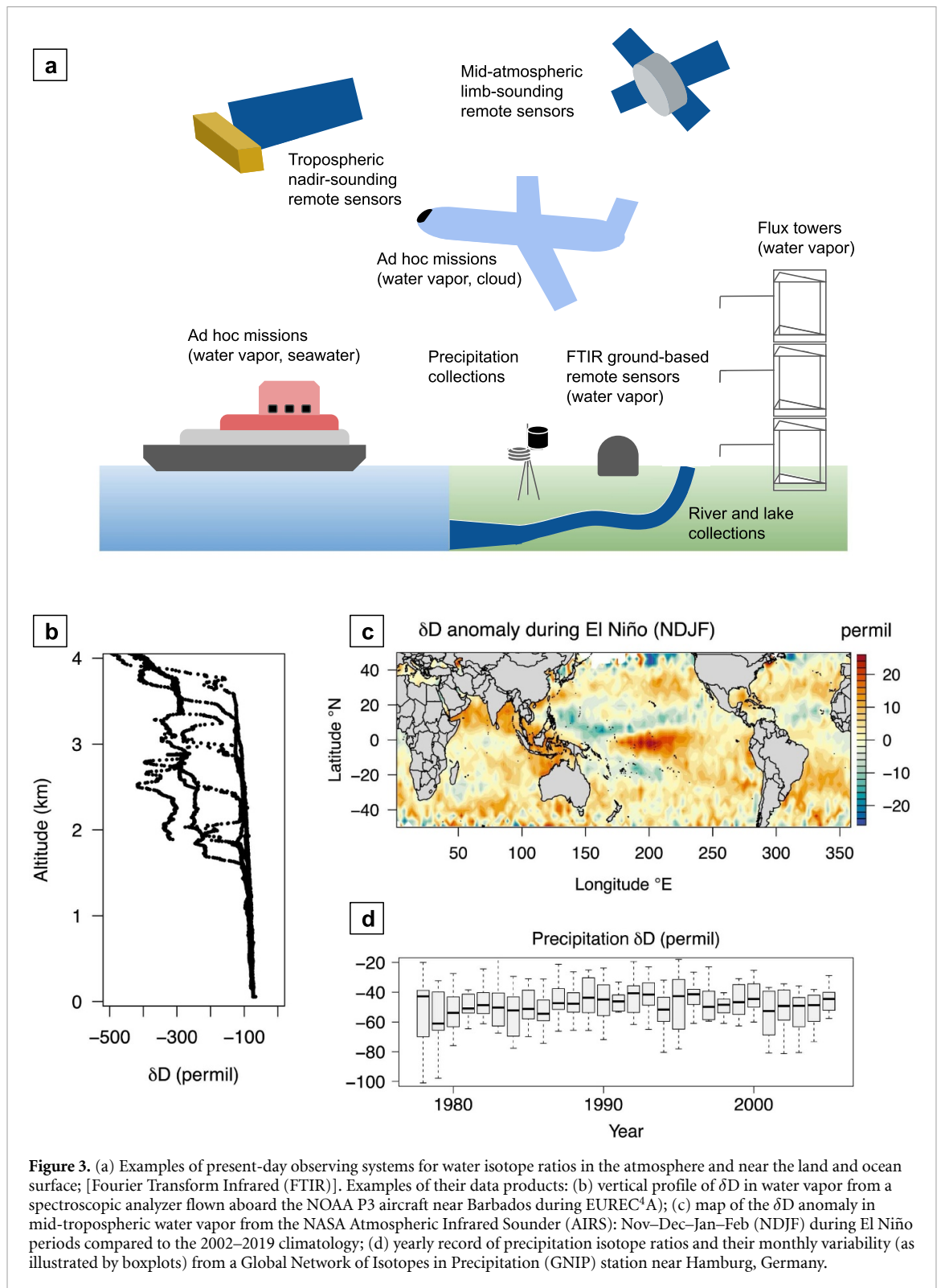


Figure 2. An example of evaluating simulated moist processes and their influence on large-scale dynamics: an intercomparison of El Niño $\delta^{18}\text{O}$ precipitation (left) and precipitation (right) anomalies in an isotopic version of the Community Atmosphere Model (CAM), inspired by the model intercomparison of Conroy *et al* 2013. Anomalies are calculated as the November–December–January–February climatology for November 2002–December 2014 and are shown for a progression of configurations spanning versions 5 and 6 of CAM: (a), (e) full CAM5 physics, (b), (f) CAM5 physics with CAM6 clouds (i.e. CLUBB; Bogenschutz *et al* 2013), (c), (g) CAM5 physics with CAM6 clouds and microphysics (Gettelman and Morrison 2015), and (d), (h) full CAM6 physics. All simulations use the CAM6 code base and a bucket model to estimate the surface-flux isotope ratio. In all simulations, negative isotopic anomalies in the West Pacific are consistent with a weakening of the Walker Circulation (see Dee *et al* 2018). These output can be compared directly with observations to evaluate the fidelity with which the model reproduces changes in the large-scale moist circulation.

model-observation comparisons on regional-to-continental scales, which have otherwise relied on the pioneering efforts of independent archival projects (e.g. Wei *et al* 2019, Waterisotopes Database 2024, <http://waterisotopesDB.org>).

At the same time that *in situ* measurements have become more widespread, isotopic information is becoming increasingly available from remote sensors. Today there is near-global daily coverage of δD in atmospheric water vapor. For the troposphere, isotope ratios in water vapor are publicly archived from GOSAT (Boesch *et al* 2013, Frankenberg *et al* 2013), TROPOMI (Schneider *et al* 2020, 2022a), SCIAMACHY (Frankenberg *et al* 2009, Schneider *et al* 2018), TES (Worden *et al* 2006, 2012), AIRS (Worden *et al* 2019), IASI (Diekmann *et al* 2021, Schneider *et al* 2022b), and CrIS. Meantime, ACE-FTS (Nassar *et al* 2007, Randel *et al* 2012), MIPAS (Payne *et al* 2007, Steinwagner *et al* 2007) and ODIN/SMR (Urban *et al* 2007) provide isotope ratios for stratospheric and middle-atmosphere water vapor. These space-based instruments are complemented by ground-based atmospheric profilers at selected sites (Schneider *et al* 2010, 2012, Galewsky *et al* 2016).

Remotely sensed isotopic measurements are typically characterized by larger biases than *in-situ* measurements (e.g. 8 permil δD for a single AIRS observation, Worden *et al* 2019). They also often provide just one or two levels of independent information in the vertical—with greatest coverage in the tropics and lower mid-latitudes. Yet the volume of isotopic data they provide is creating unique possibilities to evaluate meteorological knowledge and predictive skill through data assimilation techniques (Tada *et al* 2021, Toride *et al* 2021). Opportunities to increase the number of remotely sensed data products and obtain near real-time



measurements of ‘isotopic weather’ are only hindered by the pace of retrieval algorithm development, or, for those instruments where HDO is already retrieved as part of obtaining the most accurate H₂O profile (e.g. CRiS, IASI), by gaps in operational procedures. Furthermore, high-spectral-resolution infrared sounders, planned for launch on the next generation of polar-orbiting and geostationary operational weather satellites, will create new data collection opportunities in the coming decade.

Collectively, the substantial expansion of isotopic observations and increasing availability of isotope-enabled comprehensive models is facilitating a new wave of process-based studies—one that is focused on evaluating how the hydrological cycle is shifting in response to anthropogenic forcing. In the

sections that follow, we describe recent contributions of isotopic information to climate science and present emerging opportunities to use isotope ratios to address today's grand challenges for understanding tomorrow's climate future.

3. The moist circulation and moisture provenance

Identifying moisture sources can help us understand the processes that set distributions of humidity, cloudiness, and precipitation and ultimately influence weather, water resources, and climate feedbacks. This is because, on average, the delivery of moisture from a particular source is associated with a characteristic moisture transport pathway and mechanism. For example, low-latitude source regions supply much of the moisture to higher latitudes via episodic atmospheric river-like events (Zhu and Newell 1994). Similarly, as monsoons develop seasonally, moisture source changes contribute to precipitation intensification (Cai *et al* 2018, Hu *et al* 2019, Tulley-Cordova *et al* 2021, Hassenruck-Gudipati *et al* 2023).

Traditionally, efforts to evaluate regional moisture sources and transport pathways have relied on one of several approaches, including back trajectories (e.g. Sodemann *et al* 2008a, Tulley-Cordova *et al* 2021, Landais *et al* 2024), water tags (e.g. Singh *et al* 2016a, 2016b, Hu *et al* 2019), and vapor source distribution tracers (e.g. Lewis *et al* 2013, Nusbaumer *et al* 2019), with the first two being more common. Lagrangian back trajectory analyses use wind fields from simulations to estimate the transport paths supplying moisture to a particular site. Some analyses specifically track where the air parcel last came into contact with the boundary layer and/or where increases in parcel moisture content occurred (Sodemann *et al* 2008a, Sodemann and Stohl 2009, Bonne *et al* 2015, Steen-Larsen *et al* 2015, Putman *et al* 2017, Akers *et al* 2020, Bailey *et al* 2021, Brunello *et al* 2023, Landais *et al* 2024). The resulting moisture source designations can be somewhat sensitive to choices about the location, height, and time at which back trajectories are initiated.

In comparison, water tags in GCMs keep track of water that has evaporated from distinct regions, allowing one to calculate the fractional contributions of various sources to a particular gridbox (Koster *et al* 1986, Delaygue *et al* 2000, Bosilovich and Schubert 2002, Werner *et al* 2001, Jouzel *et al* 2013, Singh *et al* 2016a, 2016b, Nusbaumer and Noone 2018, Hu *et al* 2019). Fiorella *et al* (2021) generalized the approach to directly track moisture source and transport properties, such as time in transit, within the Eulerian GCM framework. Tagging has the advantage of using full GCM physics to predict the flows of moisture; however, it is computationally intense, which limits the number of source regions that can be defined. For global studies, it is thus often best suited for evaluating hydrological processes on the large scales of continents or ocean basins, rather than over smaller domains. In the case of either method, verifying the simulated pathways of transport is challenging.

Because water isotope ratios integrate signals of moist processes along characteristic moisture transport routes, they provide an observable metric that shares similarities with a GCM water tag diagnostic. Isotope ratios can also be simulated alongside tags to provide an even more exact comparison with observations, permitting a more robust assessment of how moisture is transported and mixed in the model environment (Delaygue *et al* 2000, Noone and Simmonds 2002a, Jouzel *et al* 2013, Bonne *et al* 2015, Nusbaumer and Noone 2018, Bailey *et al* 2019, Hu *et al* 2019, Fiorella *et al* 2021, Arnault *et al* 2022). Furthermore, because isotopic information is preserved in paleoclimate proxy records, it creates opportunities to benchmark variations in simulated global moisture transport paths between different climate states (e.g. Schmidt *et al* 2007, Tabor *et al* 2018, Hu *et al* 2019). In this way, isotope ratios provide a rare common unit linking climates of the past (via paleoclimate proxy records), present (via observations), and future (via simulations). This makes them useful for probing how changes in moisture sources respond to and impact climate change.

3.1. Geographic source and transport distance

In the simplest framework, if an isolated air mass travels away from its moistening source(s), its isotopic evolution will be shaped by water mass loss through precipitation, making it possible to relate isotopic depletion to moisture transport distance, at least in an approximate sense. Early work first identified a dependence of rainfall $\delta^{18}\text{O}$ isotope ratios on wind direction and temperature (Dansgaard 1954) and later framed the isotope dependence on distance in terms of 'latitude,' 'continentality,' and 'altitude' effects, with evidence of lower isotope ratios in rainwater at sites farther poleward, inland, and at higher elevations (Dansgaard 1964). Geostatistical interpolation methods applied to land-based measurements of precipitation isotope ratios have since provided an illustration of how these effects jointly influence isotopic gradients on regional-to-continental scales (Bowen 2010, Terzer-Wassmuth *et al* 2021), while water-tagging simulations have provided a more direct means to verify the imprint of source distance on isotope ratios quantitatively (Delaygue *et al* 2000, Jouzel *et al* 2013). More recent studies have worked to evaluate the effects of specific transport characteristics on precipitation isotopes, including the direction and magnitude of advective and convergent fluxes (Konecky *et al* 2019). Other studies, working in the zonal mean, have shown

that precipitation isotope ratios vary with the seasonal migration of the subtropical highs—which supply a large portion of the evaporated water around the globe (Feng *et al* 2009)—and have identified linear scaling terms that relate meridional moisture transport distance to the climatological distribution of water isotope ratios (Bailey *et al* 2018, Siler *et al* 2021).

One important implication of these spatial tendencies is that one can use isotopic information to assess the relative contributions of local and distant moisture supplies to a region. Indeed, many studies have used isotopic variations in polar regions as indicators of shifts between local and lower-latitude moisture sources (e.g. Sodemann *et al* 2008b, Jouzel *et al* 2013, Bonne *et al* 2015, Akers *et al* 2020, Leroy-Dos Santos *et al* 2020). Isotope ratios can also be used to distinguish between remote sources whose transport routes are characterized by different amounts of distillation. Regional studies focusing on California and the inner continental Great Basin of the United States, for example, have used isotopic information as part of a suite of meteorological tools to distinguish between moisture transported zonally and moisture transported from southern sources (Friedman *et al* 1992, 2002, Berkelhammer *et al* 2012b). They have leveraged the fact that zonal transport in these regions typically experiences greater rainout upon crossing the western mountain ranges and thus delivers moisture with lower isotope ratios. Similar studies in Central and South America have shown that isotope ratios become lower as more distal sources become more important (Jouzel *et al* 2013, Sánchez-Murillo *et al* 2020). Such analyses help reveal the seasonality of weather patterns that regulate humidity and precipitation. They also create the possibility of benchmarking changes in moisture sources on longer, climate timescales (see Berkelhammer and Stott 2008, Tabor *et al* 2018).

Like δD and $\delta^{18}O$, second-order isotopic parameters, including deuterium excess ($d\text{-excess} = \delta D - 8 \times \delta^{18}O$; Dansgaard 1964), are also useful for distinguishing moisture source regions⁹ (Jouzel *et al* 2013, Steen-Larsen *et al* 2015, Kopec *et al* 2019, Akers *et al* 2020, Leroy-Dos Santos *et al* 2020, Bailey *et al* 2021, Ala-aho *et al* 2021, Brunello *et al* 2023). When phase changes occur under equilibrium (e.g. condensation at saturation), the preferential partitioning of heavy isotopes towards the condensed phase (i.e. fractionation) produces a δD vs. $\delta^{18}O$ slope of roughly 8. (In actuality, this slope varies from about 7.3 at 30 °C to about 12.1 at –80 °C (Majoube 1971, Bolot *et al* 2013, Dütsch *et al* 2017, Kopec *et al* 2019)—a variation that is nontrivial in cold environments such as the Antarctic inland or the upper troposphere). In contrast, when phase changes occur outside of equilibrium (e.g. evaporation at subsaturation; condensation at supersaturation), exchange is limited by diffusion. And, since HDO and $H_2^{18}O$ diffuse at approximately the same rate, the result is a δD vs. $\delta^{18}O$ slope closer to one. This produces an apparent excess of deuterium in the direction of the bulk flow (e.g. in the gas phase during evaporation; in the solid phase during ice deposition).

If condensation occurs close to equilibrium, as has often been assumed, the d-excess should provide a first-order indicator of temperature and/or relative humidity conditions at the evaporative source (Merlivat and Jouzel 1979, Jouzel *et al* 1982, Johnsen *et al* 1989, Vimeux *et al* 2001, Pfahl and Wernli 2008, Pfahl and Sodemann 2014, Steen-Larsen *et al* 2014), with higher d-excess indicating that the moisture has originated from warmer and drier regions. Working from this supposition, measurements of d-excess in polar regions have been used to show that most of the moisture supplying Earth's ice sheets originates from the midlatitudes (e.g. Johnsen *et al* 1989, Ciais *et al* 1995, Stenni *et al* 2010). More recent studies are using d-excess to reveal the effects of changing sea ice conditions on local source dependencies in the Arctic and their implications for extreme mid-latitude weather (Bailey *et al* 2021)—an area of inquiry that is likely to become increasingly critical as global temperatures continue to rise. For example, Kopec *et al* (2016) argued that Arctic-sourced water increases 20% with a 100 000 km² decline in sea ice coverage. These results support water tag simulations by Singh *et al* (2016b) that suggest that polar regions are some of the few places on Earth where moisture sources become more local as the planet warms—an outcome that, importantly, also appears to explain the positive isotope-temperature relationship from ice cores used to infer past climate (Sime *et al* 2019, Siler *et al* 2021).

3.2. Identifying moisture type

While often useful for identifying moisture's *geographic* provenance, isotopic information can also help differentiate moisture from distinct sources within the same region—an attribute that may be just as important for evaluating the fate of water resources in a warmer future. Although isotopic differences between air masses are often set by the characteristic condensation histories associated with transport, they are also influenced by the way in which water exchanges between the ocean or land and the air at the moisture source. A classic example is the isotopic difference that occurs when water is transpired by vegetation (often non-fractionating) versus evaporated from freshwater bodies and soils (often

⁹ Note. ¹⁷O-excess ($\Delta^{17}O = \ln(\delta^{17}O + 1) - 0.528 \times \ln(\delta^{18}O + 1)$; Barkan and Luz 2007) can also be used as an indicator of source but is thought to be more strictly sensitive to variations in relative humidity compared to d-excess.

fractionating). Here, we describe how isotopic measurement and modeling techniques allow such knowledge to further refine our understanding of moisture source.

3.2.1. Land sources

Moisture fluxes from the land and ocean are often distinguishable because of differences in the conditions controlling evaporation and transpiration. On the one hand, evaporative fluxes from the ocean occur over an abundant reservoir that is relatively uniform in terms of its isotopic composition. Consequently, it is not uncommon for the overlying air mass to be close to isotopic equilibrium with the seawater, unless acted upon by significant exchange with the free troposphere above (Benetti *et al* 2018) or by intense evaporative fluxes during periods, such as cold air outbreaks, when humidity and temperature gradients between air and sea are strong (Aemisegger and Sjolte 2018). On the other hand, water evaporated from the land contains an isotopic record of prior precipitation and water storage in the heterogeneous subsurface (Brooks *et al* 2010, Stahl *et al* 2020, Bowen *et al* 2022). Repeated evaporation of surface and soil waters—which is especially common in arid landscapes—will nudge the slope of δD vs. $\delta^{18}O$ in these liquid reservoirs below 8 (e.g. Brooks *et al* 2010) and produce high d -excess in the water vapor content of the overlying air (Gat *et al* 1994, Aemisegger *et al* 2014).

Of course, in most vegetated landscapes, the land-atmosphere flux comprises both an evaporation component and a transpiration component—the latter being the direct exchange of water between plants and air. Isotopic measurements help differentiate between these two components of the evapotranspiration (ET) flux, since net fractionation during transpiration is often much smaller, or even trivial, compared to evaporation from moist soil. The result is that isotope ratios of transpired water are often higher than isotope ratios of evaporated water at the same location (Gat 1996, Worden *et al* 2007, Bowen *et al* 2019).

Many studies have taken advantage of these characteristics to evaluate the critical contributions plants make to atmospheric moisture. For example, Worden *et al* 2007 used satellite observations to demonstrate that transpired water's fingerprint is evident in atmospheric humidity at continental scales. Later work using remote-sensing isotopic measurements over the Amazon and Congo has shown that transpiration pre-conditions the atmosphere for deep convection, initiating rainfall and helping trigger the development of the wet season (Wright *et al* 2017, Worden *et al* 2021). These findings suggest that even qualitative estimates of transpiration's moistening role are valuable for characterizing land-atmosphere exchange, its seasonal variability, and its likely response to climate forcings.

Meanwhile, several methods exist to derive quantitative estimates of transpiration from isotopic information. One method, frequently used in early studies, involves injecting strongly tritiated or deuterated water into the trunks of trees and then measuring the so-called labeled water in the leaf tissue or surrounding air (e.g. Kline *et al* 1970, Calder *et al* 1986). Another method uses a Keeling—or mixing—plot to determine the isotopic composition of the ET flux from observations of water vapor content and its isotopic composition (e.g. Yakir and Sternberg 2000, Williams *et al* 2004). If the isotope ratios of evaporation and transpiration are known, or can be modeled, the Keeling approach provides the fractional contribution of transpiration to the total land-air flux. Still other work has estimated regional-to-global scale transpiration fluxes by using isotopic moisture budget models (e.g. Gat and Matsui 1991, Jasechko *et al* 2013, Good *et al* 2015).

When transpiration estimates from isotope-based methods are compared with estimates from non-isotope methods for the same location and conditions, the results are in reasonable agreement (Williams *et al* 2004, Good *et al* 2014, Sutanto *et al* 2014). However, on average, isotope-based studies suggest transpiration comprises a larger portion—some $\frac{2}{3}$ or higher—of the total ET flux (Sutanto *et al* 2014). This discrepancy may result from a number of assumptions made in isotopic techniques—one being the assumption that transpiration is in steady state (and therefore that net fractionation is zero; see Zhang *et al* 2010, Welp *et al* 2012, Noone *et al* 2013).

One way that new research is avoiding these types of assumptions is by incorporating isotopic tracers into high-resolution models that resolve turbulent fluxes and simulate their time evolution (Lee *et al* 2012, Wei *et al* 2018). Another direction of new work has emerged with the launch of isotopic measurements at eddy flux towers managed by the US NEON (Finkenbiner *et al* 2022). These measurements make it possible to carry out systematic intercomparisons of transpiration-estimation techniques and to derive unique insight into water exchange (Li *et al* 2023a) across a range of ecosystem types. Given the important role of the land surface in climate and the large uncertainties in the response of its water fluxes to warming, leveraging isotopic information as an extra degree of freedom in evaluating land-atmosphere exchange presents a vast opportunity.

3.2.2. Cryospheric sources

Snow on land or sea ice provides another source of moisture to the atmosphere in polar and other cold environments (e.g. Casado *et al* 2016, Pang *et al* 2019, Wahl *et al* 2021). Sublimation of snow from the surface increases the d -excess of the overlying vapor (Bonne *et al* 2019, Kopec *et al* 2019) due to the contrast between the d -excess of preexisting vapor and that of the snowpack. There is also evidence that the sublimation process itself can lower the d -excess of the remaining snowpack, possibly due to variations in the isotope ratio of the snow at different depths or evaporation of thin liquid layers within the snow (Noone *et al* 2013, Hughes *et al* 2021; and see review by, Beria *et al* 2018). The steepness of the δD vs. $\delta^{18}O$ slope in surface snow, ice, or precipitation can thus serve as a gauge for evaluating the relative importance of local sublimation fluxes (Stichler *et al* 2001, Pang *et al* 2019). Kopec *et al* (2022) used this strategy in Greenland to identify periods with a higher contribution of moisture to the atmosphere from the ice sheet and a shift away from Arctic Ocean sources. They suggested that the sublimated moisture directly influences low (rather than high-level) clouds—which illustrates opportunities to evaluate the role that locally sourced moisture plays in altering radiative energy balance in the Arctic.

3.3. The mixing paradigm

Because water isotope ratios help distinguish between air masses influenced by different moisture source types and distinct transport histories, they can also provide a way to evaluate how air mass mixing sets the mean hydroclimate state—an important feature given that water vapor observed at any one place and time rarely originates from a single source. Several studies have used isotopic information in this manner to evaluate the role mixing plays in the subtropics (Galewsky *et al* 2007, Lee *et al* 2011, Hurley *et al* 2012, Brown *et al* 2013, González *et al* 2016, Guilpart *et al* 2017). As a case in point, Hurley *et al* (2012) showed that the humidity values of the subtropical free troposphere are seldom set by a single deep convective source. Instead, shallow convective mixing adds a small but significant amount of moistening that, if ignored, results in detectable biases in simulated humidity patterns. Paleoclimate studies have also substantiated the importance of mixing by demonstrating that zonal models replicate isotopic observational records more accurately when they account for diffusive transport—the movement of water across gradients, as opposed to with the bulk flow (Hendricks *et al* 2000, Noone 2008).

The ability to evaluate how cumulative distributions of moisture sources set the atmospheric state also creates opportunities to investigate how distinct patterns of evaporation and transport contribute to spatiotemporal anomalies, such as intense rainfall events. For instance, Nusbaumer and Noone (2018) used a combination of isotopic tracers and numerical tags in the Community Earth System Model (CESM) to study the balance of local and remote moisture contributions to atmospheric river (AR) events affecting the US West Coast. They showed that while 71% of AR moisture originates from the northeast Pacific, some 16% originates from the deep tropics, south of 20° N. They also proposed that a larger portion of the land-falling precipitation originates from more remote sources in a warmer world—a prediction that future isotopic measurements in precipitation are well suited to test.

3.4. The energetics of moisture transport

The fact that water isotope ratios provide insight into cumulative distributions of moisture sources suggests that they can also be used to investigate the average distance moisture travels between a mixture of sources and an eventual precipitation sink. This so-called ‘moisture length scale’ is dictated by the balance of atmospheric moistening and drying across a network of moisture transport routes, tying it closely to the efficiency with which water cycles through the atmosphere and thus the energetics of the climate system (Singh *et al* 2016a, 2016b, Gimeno *et al* 2020). Fisher (1990) was the first to suggest that water isotope ratios could be used as an indicator of moisture length scale by contextualizing meridional isotopic gradients in terms of moisture’s ‘survival distance.’ More recent work hints at an approximate correlation between local precipitation isotope ratios and coarse estimates of atmospheric residence time (Aggarwal *et al* 2012)—a related quantity that summarizes transport efficiencies in terms of time rather than the more complex convolution of the moisture history across space. Meanwhile, advanced modeling techniques with numerical tags have created ways to capture the integrated length and timescales of upstream processes to compare isotope ratios to explicit measures of water cycling directly and expose the (geographic) limits of using isotopic information in this manner (Fiorella *et al* 2021).

Basic thermodynamic theory suggests that as the atmosphere warms, precipitation, evaporation, and the moisture content of the atmosphere will all increase (Held and Soden 2006). However, since the pace of atmospheric moistening is expected to exceed the rates of precipitation and evaporation change, moisture residence times should lengthen—except where modified strongly by dynamical adjustments (Trenberth 1998, Held and Soden 2006, Seager *et al* 2010). In turn, these changes should increase the average distance moisture travels between source and sink, except in regions, such as the Arctic, where evaporative sources

become ‘more local’ (Singh *et al* 2016b). New research is focused on investigating the regional details of these changes (e.g. Singh *et al* 2016b, Nusbaumer *et al* 2019, Gimeno *et al* 2020) and presents opportunities to probe whether signals of length-scale change are already starting to emerge in isotopic observations, providing a means to elucidate how the atmosphere’s underlying Lagrangian transport characteristics are adjusting to warming.

4. Convective processes

Many of the characteristics that make water isotope ratios useful for evaluating the movement of moisture on large spatial (e.g. global) scales also make them valuable for evaluating moisture fluxes on relatively small spatial scales, including those that are parameterized in numerical simulations. Studies have leveraged isotope ratios, for instance, to study convective updrafts and the importance of rain evaporation in recycling moisture back into the atmosphere (Bony *et al* 2008, Risi *et al* 2008, Nusbaumer *et al* 2017, Sarkar *et al* 2023), to evaluate precipitation formation in winter orographic clouds (Moore *et al* 2016), to investigate the microphysics that characterize mesoscale convective systems (MCS) and distinguish stratiform from convective precipitation (Kurita 2013, Aggarwal *et al* 2016, Maupin *et al* 2021), and to assess the role of distinct convective phases in modulating larger scale variability, such as that associated with the Madden Julian Oscillation (MJO; Kurita *et al* 2011, Berkelhammer *et al* 2012a, Tuinenburg *et al* 2015, Hurley *et al* 2019). In this section, we discuss how isotope ratios have been used to evaluate the climate impacts of deep and shallow convection, to quantify precipitation efficiency—a determinant of climate sensitivity, and to identify the fingerprint of organized convection in order to characterize the development of storm systems under different environmental conditions and climate states.

4.1. Deep convective detrainment

While the tropospheric water vapor feedback is the strongest climate feedback, stratospheric water vapor also exerts a significant radiative effect (Dessler *et al* 2013). Indeed, variations in stratospheric moisture content are believed to have altered 21st century global warming trends by as much as 25% (Solomon *et al* 2010). Understanding the processes that set the moisture content of the upper troposphere and lower stratosphere (UTLS) is thus of considerable importance.

Isotopic information has been instrumental in evaluating the role that deep convection plays in moistening the UTLS due to the fact that detrained condensate is a source of water enriched in heavy isotopes (Dessler *et al* 2007, Hanisco *et al* 2007, Blossey *et al* 2010, de Vries *et al* 2022). Enrichment is particularly acute when ice dominates the total water mass because ice particles record the isotope ratio of the altitude at which they form, allowing them to transfer a relatively high proportion of heavy-to-light isotopes upon sublimation at higher altitudes. Isotopic observations have thus been used to show that the UTLS humidity is higher than what one would expect in the absence of a significant convective lofting process (Moyer *et al* 1996, Kuang *et al* 2003, Webster and Heymsfield 2003).

Interestingly, although stronger convection can lift larger masses of ice, isotopic enrichment of the UTLS does not always co-vary with the strength of convection. Satellite studies have shown, for example, that isotopic enrichment over the North American monsoon is higher than over the Asian monsoon, despite the latter exhibiting climatologically stronger upward transport (Randel *et al* 2012). One possible explanation for these findings is that UTLS enrichment—and thus moistening—depends not just on the energetics of convection (e.g. CAPE, the convective available potential energy) but also on the upper level relative humidity. This argument is consistent with idealized simulations that require a continual source of convectively lofted dry air to promote ice sublimation and reproduce observed isotope ratios (Dessler and Sherwood 2003). Since the radiative effects of moistening are strongest where relative humidity is low, isotopic data could help identify regions where upper atmospheric moistening has particularly important climate effects. Furthermore, the development of isotopically enabled convection-permitting simulations is creating new opportunities to explicitly test the upper tropospheric water vapor response to variations in convective updrafts and downdrafts and their associated microphysical processes (de Vries *et al* 2022).

4.2. Shallow convective detrainment

Just as isotopic measurements provide a way to study moistening of the UTLS, they also provide a lens through which to examine moistening of the lower troposphere through the detrainment and evaporation of cloud droplets associated with shallow convection. Moistening by shallow convection plays an important role in destabilizing the atmosphere and creating conditions that favor deeper convection (e.g. Yano and Plant 2012). It is also hypothesized to affect low-level cloudiness, though the exact impact on cloud cover is unclear. Some studies suggest that shallow convective moistening enhances low-to-mid level cloud cover (Zhao *et al*

2016), while others suggest that it exports moisture away from the boundary layer, reducing low-level relative humidity sufficiently to limit new low-cloud development (Sherwood *et al* 2014, Vial *et al* 2017).

Isotopic measurements during the 2020 EUREC⁴A field campaign were part of a larger measurement strategy to evaluate whether upward moisture transport by shallow convection—also known as lower tropospheric or shallow convective mixing—effectively desiccates low-level clouds, reducing cloudiness in trade cumulus regions and allowing more sunlight to reach and warm Earth's surface (Stevens *et al* 2021, Bailey *et al* 2023). Early results from the campaign's non-isotopic measurements suggest that, contrary to many GCM predictions, low-level cloudiness increases as shallow convective mixing strengthens (Vogel *et al* 2022). The isotopic measurements provide an independent means to verify this finding by allowing one to quantify the strength of mixing according to the amount of moisture that has been exported from the sub-cloud layer (see Berkelhammer *et al* 2012a).

Meanwhile, satellite retrievals of the water vapor isotopic lapse rate provide another, albeit qualitative, measure of mixing strength in trade cumulus regions that can help bridge the spatiotemporal gaps between field campaigns such as EUREC⁴A and climate simulations. Recent analyses of these data suggest that relationships between mixing and cloudiness are actually weak on 100 km scales (Hu *et al* 2022). Isotopic evidence of increased shallow convective mixing with convective aggregation (Galewsky *et al* 2023) provides a possible explanation: aggregated clouds can be surrounded by large areas of cloud-free air, thus weakening the relationship between mixing and cloudiness over large spatial domains. These kinds of studies can help support existing efforts to place upper bounds on the likely range of climate sensitivity by identifying models whose low-level cloud response to mixing in the tropics is likely too strong (Vogel *et al* 2022). Additional opportunities abound to use water isotopic information to evaluate processes influencing low-level clouds in numerical simulations and to evaluate modifications to GCM physics broadly (e.g. figure 2).

4.3. Precipitation processes

As important as convective mass fluxes are to water vapor and cloud feedbacks on climate, so too are the rates at which condensate precipitates and the efficiency with which precipitation reaches the surface (e.g. Lutsko *et al* 2023, Li *et al* 2023b). These efficiencies redistribute moisture vertically in the air column and influence the tendency for clouds to dissipate, ultimately altering the long and shortwave radiative properties of the atmosphere. While the detail with which models represent these processes is continually improving, observations that can evaluate the parameterizations and variable tuning parameter choices used to simulate them are few (Morrison *et al* 2020). Given how difficult it is to infer microphysical processes based on most observations of state, process-oriented variables like water isotope ratios provide an important path forward for advancing our understanding of precipitation and its role in climate.

4.3.1. Precipitation conversion efficiency

The microphysical precipitation efficiency (ε)—defined in Lutsko *et al* (2023) as the ratio of surface precipitation to condensation rates—is actually the product of two efficiencies. The first—the conversion efficiency—describes the rate with which cloud condensate converts to precipitation; it has been referred to as precipitation efficiency in its own right (e.g. Sui *et al* 2007, Noone 2012, Bailey *et al* 2015). The second—the sedimentation efficiency—describes the rate with which precipitation reaches the surface; it is more commonly evaluated in terms of its linear inverse: the rain evaporation rate. Lower precipitation efficiency means that more moisture detrains into the surrounding environment, while higher precipitation efficiency implies that moisture is returned back to the surface. Given the influence of these factors on the lifetime of clouds and the distribution of moisture in the atmospheric column, studies suggest ε plays an important role in governing model climate sensitivity (Lutsko *et al* 2023).

In warm liquid clouds, water isotope ratios provide a rare quantitative constraint on both the conversion efficiency and the rain evaporation rate. For instance, when the conversion efficiency is 1, and all condensate precipitates immediately, theory suggests that the isotopic evolution of an isolated rising parcel should be well described by a Rayleigh distillation. However, as the conversion efficiency decreases and condensate is retained within the convective plume, the vapor will equilibrate with this suspended liquid reservoir, causing the isotope ratio to decrease more slowly with height. Thus, if the isotopic lapse rate and vertical humidity and temperature profiles are known, the conversion efficiency can be estimated theoretically and compared with observations (Noone 2012).

Studies using extensions of such simple parcel models have characterized high and low conversion efficiency environments (e.g. Brown *et al* 2013) and identified the weather systems responsible for modulating the likelihood of precipitation formation within a given region (Bailey *et al* 2015). They have even related the conversion efficiency to aerosol number concentration, indicating a direct link to the efficiency with which precipitation scavenges pollutants and cloud-nucleating particles from the atmosphere (Bailey *et al* 2015, Stopelli *et al* 2015, Henze *et al* 2023).

Opportunities exist to expand on these efforts and derive more accurate estimates of rain formation rates. For example, pairing isotopic observations with full-physics weather and climate models creates the possibility of accounting for the confounding effects of dilution by entrainment-mixing on cloud and raindrop populations. Measurements of isotope ratios in condensate—made with specialized airborne inlets known as Counterflow Virtual Impactors (e.g. Redemann *et al* 2021, Henze *et al* 2022)—can also provide further constraints on the conversion efficiency when paired with concurrent measurements of isotope ratios in water vapor.

4.3.2. Rain evaporation

Just as detrained cloud droplets influence the surrounding environment isotopically (see section 4.2), moisture evaporated from falling rain leaves a detectable isotopic fingerprint in many regions (Worden *et al* 2007, Wright *et al* 2009, Field *et al* 2010, Lee *et al* 2011, Brown *et al* 2013, Tremoy *et al* 2014). Whether it enriches or depletes the water vapor of the surrounding environment is a good indicator of the efficiency of the rain evaporation process. While near-complete or complete evaporation transfers most or all of the isotopic signature of the drops, enriching the surrounding vapor, incomplete evaporation preferentially transfers the lighter isotopologues to the vapor phase, lowering the isotope ratio of the environment (Worden *et al* 2007, Noone 2012, Galewsky *et al* 2016, Risi *et al* 2021). By some isotopic estimates 5%–25% of the moisture in the atmosphere can, on average, be attributed to such post-condensational exchange (Worden *et al* 2007, Wright *et al* 2009); and as much as 20%–50% of the rain near tropical convective clouds is thought to evaporate before reaching the surface (Worden *et al* 2007).

One of the simplest ways to characterize the rain evaporation isotopically is to examine the isotopic composition of the rain drops themselves (Stewart 1975). Raindrops become enriched in heavy isotopes as they evaporate, but their δD decreases *relative* to $\delta^{18}O$ due to the kinetic effects described in section 2. As a result, the d-excess of the precipitation decreases. This causes the slope of precipitation δD vs. $\delta^{18}O$ —also known as the slope of the local meteoric water line (LMWL)—to become lower. Low LMWL slopes are common in arid regions and in regions with a dry warm season (Putman *et al* 2019), as well as during periods when rainfall amount and relative humidity are low (Peng *et al* 2007, Chen *et al* 2015). However, they have also been identified in association with typhoon rains (Xu *et al* 2019), which suggests that rain evaporation is significant in tropical cyclones—a result now backed by cloud-resolving simulations (Risi *et al* 2023). Putman *et al* (2019) argued that LMWL slopes tend to be lower in observations than in GCMs, indicating a general deficiency in the parameterization of cloud and precipitation processes.

Differences in d-excess between precipitation and water vapor ‘upstream’ can also be used to estimate the fraction of rain evaporation. Using this semi-quantitative approach, Peng *et al* (2010) calculated a rain evaporation rate between 7% and 15% for Taiwan Island in winter. Chen *et al* (2015) estimated rain evaporation rates to be between 6% and 10% for the summer monsoon in the Gansu Province of Northwest China, near Lanzhou. Graf *et al* (2019) proposed a similar, though independent approach that considers differences in both the d-excess and the isotope ratio between precipitation and near-surface water vapor.

More quantitative approaches can simulate the isotopic evolution of the falling raindrops using one-dimensional batch-distillation or bin-resolved microphysical models (Stewart 1975, Salamalikis *et al* 2016, Graf 2017, Sarkar *et al* 2023). These models create opportunities to evaluate both the fraction of rain evaporated and the rain evaporation flux, or its linear inverse: the sedimentation efficiency. For example, Sarkar *et al* (2023) used airborne microphysical and water isotopic measurements, compared with surface precipitation samples, to estimate a rain evaporation flux of 15–352 $W m^{-2}$ in the trade cumulus environment of the western tropical Atlantic. Even though mean precipitation intensity in the trade cumulus regime is weak, the large fraction of rain evaporation appears to be energetically significant, contributing the equivalent of 2–50 $K d^{-1}$ in evaporative cooling in the regions of the rain shafts. Given that raindrops can be sampled via large aircraft and analyzed isotopically offline (Lawrence *et al* 2002), new field missions offer the possibility of constraining one-dimensional isotopic models directly, leading the way for improved parameterizations of atmospheric moistening by condensate evaporation and refined estimates of climate sensitivity in GCMs.

4.3.3. Ice particle growth

In mixed-phase clouds, the efficiency of precipitation is strongly influenced by the joint presence of water in both liquid and solid form. Because the saturation vapor pressure is lower with respect to ice than with respect to liquid, ice crystals grow rapidly at the expense of supercooled liquid drops, with mass transfer occurring via the vapor phase (i.e. Wegener–Bergeron–Findeisen process). Ice particles can also grow by the direct accretion of droplet material through a process commonly known as riming. Riming tends to produce very heavy ice particles, which facilitates precipitation formation and enhances the total precipitation flux. These effects modify the location and intensity of weather (Hou *et al* 2016, Moisseev *et al* 2017) and,

ultimately, can influence climate if they alter precipitation patterns in a way that reduces cloud lifetime (see Lohmann 2004, Seinfeld *et al* 2016). Aiming to improve the skill of our weather and climate forecasts, model development efforts are now working to predict the rime mass fraction (RMF) in new microphysical schemes; however, obtaining observations that are capable of verifying the simulated RMF remains challenging (e.g. Morrison *et al* 2020).

Isotopic measurements offer the possibility to help fill this gap, since riming and vapor deposition impart distinct isotopic signatures on precipitation. While riming transfers the complete isotopic signature of the drops to the ice, the diffusional transfer of mass associated with deposition under supersaturation increases the precipitation d-excess substantially. This strong kinetic effect has long been incorporated into simple models used to describe the poleward transport of moisture (Ciais and Jouzel 1994) but has only recently been considered a possible benchmark for understanding particle growth in mixed-phase clouds (e.g. Moore *et al* 2016). Interestingly, simulations and observations from mountain environments suggest that most of the isotopic signal of precipitating snow reflects the height—and thus temperature—at which ice particle formation occurs (Lowenthal *et al* 2011, 2016, Moore *et al* 2016). New in-cloud isotopic measurements combined with particle imaging over the Norwegian Sea and Fram Strait as part of the 2024 Cold Air Outbreak Experiment in the Sub-Arctic Region (CAESAR; <https://catalog.eol.ucar.edu/caesar>) will provide a novel test of the ability of isotopic information to differentiate ice particle growth pathways in a non-orographic environment.

Meanwhile, the strong fractionation associated with depositional growth has lent itself to other forms of model evaluation, namely an assessment of how supersaturation is represented in GCMs (Werner *et al* 2011, Dütsch *et al* 2019, Putman *et al* 2019). Putman *et al* (2019), for example, showed that GCMs produce LMWL slopes and intercepts that are too high in cold continental regions. The cause appears to be high sensitivity of the supersaturation function to temperature, which drives excessive diffusion of heavy hydrogen relative to heavy oxygen onto simulated ice. Given the sensitivity of d-excess to diffusive processes, this second-order parameter provides a useful lens through which to evaluate the microphysics that couple with larger-scale circulations to set the atmospheric moist state. Continued focus on high-accuracy water vapor isotopic measurements in extreme cold environments (e.g. Casado *et al* 2016, Steen-Larsen *et al* 2017, Leroy-Dos Santos *et al* 2020, Brunello *et al* 2023), as well as improved calibration techniques (e.g. Steen-Larsen and Zannoni 2024), are critical for expanding opportunities to leverage d-excess toward such process-oriented efforts.

4.4. Convective development and organization

Because water isotope ratios record cloud processes and precipitation microphysics, they also create opportunities to investigate the development of convection and its upscale growth into organized mesoscale convective systems, or MCS. MCS activity is often associated with more severe storms in the mid-latitudes and is a defining feature of the MJO—the dominant source of intraseasonal variability in the tropics. Several studies have used isotopic information to elucidate the moist processes that characterize distinct stages of the MJO. These include large-scale vertical mixing, shallow convective moistening, rain evaporation, and large-scale drying and depletion associated with subsidence and stratiform cloud formation (Kurita *et al* 2011, Berkelhammer *et al* 2012a, Tuinenburg *et al* 2015, Conroy *et al* 2016, Hurley *et al* 2019). Other studies have focused more broadly on the tendency for mature and organized convection to carry lower isotopic signatures relative to isolated convective cells (e.g. Kurita 2013, Moerman *et al* 2013, Tremoy *et al* 2014, Risi *et al* 2023). Maupin *et al* (2021), for example, used isotope ratios in cave stalactites to determine that MCS activity in the US Southern Great Plains has consistently increased an order of magnitude during global warm periods (i.e. interstadials). There is also a long history of using isotopic information to study the high precipitation efficiency and complex moisture exchange specific to tropical cyclones (Lawrence *et al* 1998, 2002, Ohsawa and Yusa 2000, Gedzelman *et al* 2003, Fudeyasu *et al* 2008, Munksgaard *et al* 2015, Sánchez-Murillo *et al* 2019, Xu *et al* 2019, Jackisch *et al* 2022, Sun *et al* 2022, 2024, Risi *et al* 2023). These studies have shown that intense convective activity is sustained by water vapor that becomes increasingly depleted of heavy isotopologues, indicating that atmospheric moisture is ‘recycled’ both toward the center of the storm and from one rain band to the next. A similar phenomenon occurs within the convective envelope of the MJO, where developing storm cells feed off moisture already depleted of heavy isotopologues by past precipitation events (Kurita *et al* 2011, Hurley *et al* 2019).

In addition to being defined by a highly efficient precipitation process, mature and organized convection likely carries a low isotopic signature for several other reasons. Because water vapor in an air parcel becomes more distilled as the parcel rises pseudoadiabatically to greater altitudes, and because isotopic fractionation becomes stronger as temperature decreases, deeper convection effectively removes heavy isotopologues from the atmospheric column (Scholl *et al* 2009, Lacour *et al* 2018, Yu *et al* 2024). MCS are also characterized by broad regions of stratiform rain, which first forms as ice at high altitudes (Houze 2004). Ice growth by vapor

deposition favors the diffusion of lighter isotopologues from the vapor to the particles, producing relatively low isotope ratios in the resultant precipitation; this signal can then be transferred to low-level vapor by rain evaporation and exchange processes (Kurita 2013, Risi *et al* 2023). Indeed, several studies have shown a strong relationship between a region's stratiform rain fraction and its precipitation isotope ratios (Aggarwal *et al* 2016, Konecky *et al* 2019, Sun *et al* 2019, Sánchez-Murillo *et al* 2020). Mesoscale downdrafts from the stratiform region can also act as a source of low-isotope ratio vapor (Risi *et al* 2008, Kurita 2013, Tremoy *et al* 2014).

Mid-level convergence associated with deep convection can also lower isotope ratios by drawing on moisture that has experienced mass loss through condensation prior to horizontal transport—a signal that is analogous to a distant moisture source (Lee *et al* 2007, Moore *et al* 2014, Bailey *et al* 2017). Observations have substantiated this idea by showing that for a given amount of convergence, isotopic depletion is strongest when the vertical velocity profile is top-heavy and moisture convergence occurs at higher altitudes, where upstream condensation is more likely to have had a significant effect (Lacour *et al* 2018, Torri *et al* 2017, see Galewsky *et al* 2023). Interestingly, boundary layer isotope ratios also tend to decrease when moisture convergence is present, though for a slightly different reason. Recent LES experiments reveal that low-level convergence helps moisten the boundary layer, causing the vertical isotopic gradient to steepen (Risi *et al* 2020). As a result, vertical convective motions preferentially export isotopically heavier water from the boundary layer, lowering the boundary-layer water vapor isotope ratio.

Several opportunities emerge from our ability to examine convective development through the lens of isotopic measures. On weather timescales, isotopic information can help provide insight into the moist processes that influence convective intensity and precipitation extremes (Kurita *et al* 2011, Berkelhammer *et al* 2012a, Kurita 2013, Bailey *et al* 2015, Hurley *et al* 2019, Risi *et al* 2023). On long timescales, it can help differentiate the roles of convergent transport (dynamics) versus temperature (thermodynamics) in regulating tropical humidity and water vapor feedbacks on climate (see Dee *et al* 2018). Yet another emerging application stems from the principle of conservation of mass, which requires that moisture convergence balance precipitation minus evaporation (P-E) over long averages. Working over the Amazon, Shi *et al* (2022) showed that satellite retrievals of isotope ratios readily capture the seasonal variability in P-E. Their proof-of-concept work suggests that while precipitation drives variability in P-E over most of the rainforest, ET is particularly important for atmospheric water balance along the 'arc of deforestation,' where large swaths of vegetation—a critical source of moisture to the atmosphere—are being removed for agriculture and grazing.

5. Process-oriented model evaluation

Comprehensive models with the capacity to simulate water-cycle processes (e.g. GCMs, CRMs, LES, etc) greatly expand opportunities to understand the Earth system's complex behavior. However, many simulated features of hydroclimate are not well constrained observationally, raising uncertainties about conclusions drawn from numerical experiments. For models equipped with isotopic tracers, benchmarking simulations against isotopic data offers unique benefits for guiding hydrologically focused improvements in model dynamics and physics and for enhancing model predictive skill (e.g. Risi *et al* 2012, Dee *et al* 2015, Nusbaumer *et al* 2017, Hu *et al* 2018).

Indeed, as described in the previous sections, when paired with other thermodynamic data, isotopic information facilitates evaluation of moisture flows on—and across—a variety of scales, spanning cloud microphysics, convective mixing, and large-scale advection. It can be especially helpful for identifying the balance of processes that shapes a particular hydroclimate state, or, for that matter, contributes to deficiencies in its simulation. As a case in point, Nusbaumer *et al* (2017) used isotopic information in the Community Atmosphere Model version 5 (CAM5) to show that, even though the model replicated observed patterns of humidity, the moisture climatology of the mid-latitudes was improperly modeled. They found that a low-threshold convective trigger—which also contributed to positive precipitation biases in the tropics—increased the contribution of local moisture relative to long-range transport in the extratropics, leaving a fingerprint detectable only in the isotope ratio of free tropospheric water vapor. The isotopic information thus uniquely demonstrated that the macro-scale balance between the parameterized vertical transport and the resolved, quasi-horizontal poleward flow was incorrect.

5.1. Evaluating microphysical processes

Isotopic information can also help reveal problems in the tuning of microphysics schemes that may not be obvious, or even observable, through other variables. This is because cloud microphysical processes are fundamentally governed by diffusion and equilibrium thermodynamics, whose isotopic fractionation can be expressed, and therefore simulated, using first principles. Consider, for instance, that isotope ratios allow one

to distinguish whether the bulk flux of precipitation at the grid scale accumulates as many small drops over a long duration or as few large drops over a short period (e.g. Lee and Fung 2008, Kurita 2013, Sarkar *et al* 2023)—the latter possibly favoring precipitation extremes. Models without isotopic tracers lack the diagnostics necessary to distinguish between these possibilities. Given the tendency for most GCMs to produce precipitation that is too frequent and too drizzle-like (Stephens *et al* 2010), isotopic information can provide a valuable lens through which to address model biases that ultimately affect simulated cloud lifetime and cover.

Another microphysical process to which isotope ratios are particularly sensitive is the rain evaporation flux (e.g. Worden *et al* 2007, Bony *et al* 2008, Tremoy *et al* 2014, Dee *et al* 2015, Risi *et al* 2021, 2023; see also section 4). Isotope ratios respond both to the efficiency of exchange between the falling drops and their environment and to the ‘effective relative humidity,’ which accounts for the fact that evaporating raindrops hydrate their immediate surroundings (e.g. Bony *et al* 2008, Risi *et al* 2010). Tuning these two parameters to isotopic data has improved the simulation of rain evaporation (e.g. Dee *et al* 2015)—a parameter with broader climate implications (Lutsko *et al* 2023).

Paleo records based on water isotopic data have also been used to identify problems with the representation of microphysical processes that commonly influence mixed-phase clouds. For instance, simulations with CESM2 have shown that artificial limits on the number of cloud ice particles exaggerate cooling during the Last Glacial Maximum by over-strengthening the shortwave cloud feedback (Zhu *et al* 2022). Interestingly, the problem of too little cloud ice in CESM2 contrasts starkly with the problem of too much cloud ice in its predecessor. CESM1 was characterized by too many active ice-nucleating aerosols and an overly efficient timescale for ice crystal growth by vapor deposition—shortcomings that a comparison with observed d -excess and δD in snow measurements helped discover (Dütsch *et al* 2019). Expanding efforts to observe isotope ratios in conjunction with key microphysical parameters, including particle size distributions, would diversify opportunities to further benchmark microphysics in simulations.

5.2. Evaluating advection and diffusion

In addition to benchmarking simulated water cycle processes explicitly, water isotope ratios are also valuable for evaluating model performance broadly. For instance, because GCM dynamical cores need to avoid model instabilities produced by discretization of the equations governing transport, they employ artificial smoothing techniques, which do not conserve correlations between atmospheric trace constituents. Being a quotient, the isotope ratio is especially sensitive to this so-called ‘numerical’ mixing (see Noone and Sturm 2010). Risi *et al* (2012) leveraged the sensitivity of isotopes to mixing processes to show that excessive numerical diffusion during vertical transport is largely responsible for creating free tropospheric moist biases common across most GCMs.

Other isotopic work has similarly demonstrated that errors in the advection of water tracers are particularly evident near the poles, where the atmosphere is dry and meridional humidity gradients are strong (Jouzel *et al* 1987, Noone and Simmonds 2002b, Yoshimura *et al* 2008, Noone and Sturm 2010). These findings point to the need for numerical schemes that favor conservative transport of trace constituents—as well as conservation of tracer-tracer relationships—a need not exclusive to stable isotopes (e.g. Hall *et al* 2016). The ratio-preserving finite volume transport scheme by Lin and Rood (1996) is an example of a scheme that provides robust characteristics for isotope ratios (Noone and Sturm 2010). However, as with any model decision, care must be taken to consider tradeoffs to the simulation as a whole, including effects on mass conservation and phase errors in wave propagation speed. Coupling isotope ratios with other tracers of transit (see Orbe *et al* 2016, Fiorella *et al* 2019) might create additional opportunities to probe biases in GCM transport across a range of scales. Meanwhile, evaluating the transport features associated with specific synoptic events—including cold-front passages, warm-conveyor belts, and extratropical cyclones (Aemisegger *et al* 2015, Bonne *et al* 2015, Dütsch *et al* 2016, Nusbaumer and Noone 2018, Landais *et al* 2024)—will continue to create additional opportunities to verify simulation realism both in GCMs and in higher resolution models.

5.3. Evaluating forecast skill through data assimilation

In addition to representing global climate through free-running model simulations, GCMs are also commonly used in data assimilation applications to create hindcast and forecast products. Recent work has shown that the assimilation of water isotopic data can improve model simulations and forecast skill in these contexts. For example, Tada *et al* (2021) showed that assimilating isotope ratios alone can improve 6 d forecasts not just of moisture variables but also of temperature, geopotential height, and wind. Meanwhile, observing system simulation experiments have shown that including synthetic isotopic observations in conventional data assimilation efforts can produce an additional 3%–4% improvement in simulated meteorological fields above what conventional observational constraints and water vapor measurements

provide (Toride *et al* 2021). Moreover, isotopic data have been shown to improve the simulation of regional structures in the atmosphere, such as low-pressure systems (Tada *et al* 2021).

Whether through parameter evaluation and tuning or more holistic evaluations of model performance, water isotopic tracers create an extra degree of freedom that can help ensure simulation accuracy and bolster predictive skill. Furthermore, as process-oriented variables, they help identify the balance of contributing processes, rather than just the resulting mean state—a diagnostic capacity that is especially effective in guiding model improvement. Gearing isotopic observations toward processes suspected of contributing most strongly to model deficiencies and creating isotopic data archives that can be easily assimilated in simulations will no doubt help facilitate the use of isotopic information in improving numerical forecast skill.

6. Conclusions and outlook

This topical review highlights avenues for improving climate science by leveraging water isotopes as process-oriented variables. While traditional measurements of humidity, cloudiness, and precipitation help us describe the state of the climate system, pairing these measurements with their associated water isotope ratios elucidates the underlying physics that govern the response of the climate system to natural variability and anthropogenic forcing. Isotope ratios are sensitive to patterns of condensation and evaporation, as well as to the thermodynamic conditions governing these fluxes. They thus serve as a fingerprint for air masses that have experienced distinct water-cycle histories, creating opportunities, when contextualized with appropriate theoretical assumptions, to identify moisture provenance and study the characteristic transport pathways that connect moisture sources to precipitation sinks. These pathways can be studied on scales as local as an isolated convective plume to scales as broad as the global circulation.

Moreover, because of the well known physical principles that control the fractionation associated with condensation and evaporation, water isotope ratios are a useful lens through which to investigate detailed microphysical mechanisms that determine how cloud particles grow, how efficiently they form precipitation, and how effectively precipitation reaches Earth's surface—particularly when incorporated in comprehensive models that represent aspects of these processes. Given the large uncertainties associated with microphysics and their role in shaping climate feedbacks, isotope ratios are an important tool for verifying our understanding of the processes governing the climate system's sensitivity.

Isotope ratios also house great potential to advance the predictive capabilities of comprehensive models. Indeed, recent work has used water isotopic information to finetune parameterized processes, such as rain evaporation, to evaluate the fidelity of tracer advection by model dynamical cores, and to improve meteorological forecast skill through data assimilation efforts. In addition, model experiments have capitalized on isotopic information in climate proxy records that predate the instrumental period, creating a more comprehensive backdrop against which to evaluate the climate response to anthropogenic forcing (see Sherwood *et al* 2020, Zhu *et al* 2022, Dee *et al* 2023). These studies suggest that integrating isotopic information across the past and present creates unique possibilities for reducing uncertainties in projections of Earth's future.

Although there has been significant recent progress in leveraging isotopic information to elucidate how moisture flows and exchanges in the climate system, still more can be done to maximize the usefulness of water isotope ratios as process-oriented climate variables. Despite the recent uptick in both *in situ* and remotely sensed water vapor isotopic measurements and their compilation in open-access archives (e.g. Wei *et al* 2019), regular inclusion of isotopic sampling in large-scale observational campaigns and delivery of remotely sensed isotopic 'byproducts' as part of standard processing is extremely limited. Enhancing these observational capacities would expand the density of high-temporal resolution data and increase opportunities to obtain vertically resolved information in the atmosphere and ocean, which are critical for data-model comparisons.

Regular integration of water isotopic information into climate modeling efforts is also needed. Maintaining isotopic tracers in model code bases will increase their availability for evaluating water-cycle processes and fine-tuning parameters related to clouds and precipitation. Moreover, by coupling isotopic tracers with numerical water tags (see section 2), model experiments should be able to link simulations of key moisture properties, including moisture convergence, residence time, and length scale, to observable quantities more directly.

The water cycle plays a critical role in determining both the degree to which the climate system will change and how these changes will alter the availability and quality of water resources for society. Water isotope ratios provide a natural way to track this cycling of moisture—a fact that has long been leveraged to evaluate climate changes of the past (Dee *et al* 2023). Now, with the continued expansion of water isotopic measurement capabilities and the development of isotopic tracers in models ranging in scale from large eddies to the globe, we have an opportunity to incorporate water isotopic information more fully into the

investigation and prediction of Earth's future. Given that today's grand hydroclimate challenges require new measurement and modeling approaches that are oriented toward evaluating processes rather than simply describing the state of the climate system, isotope ratios are an essential climate variable—one that can help us better track and predict Earth's climate, its variability, and its response to forcing.

Data availability statement

CESM output in figure 2 are archived at doi: [10.5281/zenodo.12812239](https://doi.org/10.5281/zenodo.12812239). No new data were otherwise created or analysed in this study.

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