Isotopes in the Water Cycle: Regional to Global Scale Patterns and Applications

Gabriel J. Bowen, Zhongyin Cai, Richard Fiorella, Annie Putman

Department of Geology & Geophysics and Global Change and Sustainability Center

University of Utah, Salt Lake City, UT 84108, USA

gabe.bowen@utah.edu, zyc@itpcas.ac.cn, rich.fiorella@utah.edu, putmanannie@gmail.com

Keywords

stable isotopes, water cycle, water resources, atmospheric dynamics, hydrology, climate

Summary Phrases

Isotope ratios of water integrate information on hydrological processes over scale from cities to the globe

Tracing water with isotopes helps reveal the processes that govern variability in the water cycle and may govern future global changes

Advances in instrumentation, data sharing, and quantitative analysis have advanced isotopic water cycle science over the past 20 years

Abstract

Stable isotope ratios of hydrogen and oxygen have been applied to water cycle research for over 60 years. Over the past two decades, however, new data, data compilations, and quantitative methods have supported the application of isotopic data to address large-scale water cycle problems. Recent results have demonstrated the impact of climate variation on atmospheric water cycling, provided constraints on continental- to global-scale land-atmosphere water vapor fluxes, revealed biases in the sources of runoff in hydrological models, and illustrated regional patterns of water use and management by people. In the past decade, global isotopic observations have spurred new debate over the role of soils in the water cycle, with potential to impact both ecological and hydrological theory. Many components of the water cycle remain underrepresented in isotopic databases. Increasing accessibility of analyses and improved platforms for data sharing will refine and grow the breadth of these contributions in the future.

Introduction

Earth's water cycle links solid earth, biological and atmospheric systems, and is both pivotal to our fundamental understanding of our planet and critical to our practical well-being. Several lines of evidence point to ongoing water cycle changes (Dai 2006, Gedney et al 2006, Zhang et al 2007, Syed et al 2008) that may have far-reaching significance for the planet and point to a need for robust, quantitative prediction of future change. More than a century of water cycle research has led to a detailed understanding of fundamental processes controlling the distribution and flows of water within and between many of the subsystems of the global hydrological cycle (Vörösmarty & Sahagian 2000, Trenberth et al 2007). Understanding how these processes interact in time and space remains a classic scaling challenge, however, and the predictability of future water cycle changes remains relatively poor (e.g., Hattermann et al 2017, Myhre et al 2017).

Investigation of the hydrological cycle represents one of the earliest applications of stable isotope chemistry (Dansgaard 1954, Craig 1961, Dansgaard 1964, Craig & Gordon 1965). This early work produced local and global data syntheses, identified fundamental processes controlling isotope distributions in the water cycle, and spawned a wealth of work gathering (Rozanski et al 1993) and applying (Gat 1996, Kendall & McDonnell 1998) information on water isotopes to a diverse spectrum of water cycle research. Sixty-five years after the publication of Willi Dansgaard's first water isotope observations (Dansgaard 1954), the research community has amassed a substantial body of theory and data with which to probe water cycle processes at a range of scales and levels of detail. In recent years, as the volume and accessibility of data has grown and quantitative tools supporting analysis of large spatial datasets have matured, meta-analyses of water isotope data have produced important and provocative new ideas about the fundamental structure of and ongoing changes in the hydrosphere.

The power of isotopic data in these applications is threefold. First, the isotopic composition of water can be a powerful tracer of water source. Atmospheric processes produce natural variation in isotope ratios of rainfall among storms and throughout the seasonal cycle, and isotope ratios of soil or groundwater reflect sources of water to that system (O'Driscoll et al 2005, Oerter & Bowen 2017). Second, isotope ratios and their variation can be diagnostic for important water cycle processes that may be transparent to other methods. Evaporation produces a diagnostic isotopic effect that can be detected either in dual hydrogen/oxygen or triple oxygen isotope (^{18}O-^{17}O-^{16}O) datasets, and can be observed in the covariance of atmospheric humidity and water vapor isotope ratios; such signals have been used to quantify the importance of re-evaporation of falling raindrops on atmospheric water balance (Worden et al 2007). Third, isotope ratios can integrate information on the history of water as it moves through the hydrological cycle. Isotope ratios of a single sample of public supply tap water might preserve information on the timing of precipitation input and magnitude of land surface evaporation across an entire watershed. Many such samples collected at different times and locations might be used to develop a spatially and temporally resolved understanding of these effects over a basin, continent, or the globe (Jameel et al 2016).

Here we review and synthesize a broad swath of multidisciplinary research that has leveraged water isotope data and theory to advance our understanding of the water cycle at spatial scales from cities to the globe. We focus on work conducted over the past 20 years, a period that has seen significant, technology- and investigator-driven growth in isotope data documenting the water cycle and advances in data analysis tools and techniques. After some preliminaries, we discuss a few areas where large-scale thinking has advanced our understanding of water isotope systematics. We then look at contributions using large-scale isotope data to understanding water cycling within the atmosphere, between the land surface and atmosphere, within land-surface hydrological systems, and in human-managed water distribution systems.

We close by summarizing overarching themes uniting these contributions and highlighting future directions that we believe will support continued progress.

Preliminaries

Water Isotope Fundamentals

The stable isotopes of hydrogen and oxygen, ^{1}H, ^{2}H, ^{16}O, ^{17}O, and ^{18}O are here referred to as "water isotopes" and comprise the focus of this review. Each of these isotopes occurs naturally at abundances suitable for measurement with contemporary mass spectrometers, laser spectroscopy instruments, and in some cases, spectrometric imaging methods. The relatively rare ^{17}O isotope has received less attention, and much of the information recorded in its variation is redundant with that recorded by ^{18}O. Recent work focusing on subtle deviations from this equivalency due to kinetic effects and O input from stratospheric ozone, however, is spurring new interest in many fields including hydrology and paleoclimate science (Schoenemann et al 2014, Li et al 2015).

Each isotope varies in its relative abundance throughout the hydrological cycle. With rare exception, this variation is driven by mass-dependent isotope fractionation resulting from differences in bond energy, reaction rate, or diffusivity of isotopologues containing the "light" common (^{1}H, ^{16}O) or "heavy" rare (^{2}H, ^{17}O, ^{18}O) isotopes. The primary driver of fractionation is the phase change between vapor and liquid or solid phase water (Fig. 1). During equilibrium exchange, the higher-energy vapor phase preferentially accumulates the light isotopes. As a result, water vapor formed from evaporation of ocean, lake or soil water is lighter (contains relatively more of the light isotopes) than the water from which it was derived. Conversely, as precipitation condenses from the atmosphere, it preferentially removes the heavy isotopes, leading to condensate that is heavier than the source vapor and, by mass balance, progressively depleting the remaining atmospheric vapor of the heavy isotopes. This process is thought to govern much of the natural variation in precipitation isotope ratios worldwide, and can be represented using a Rayleigh distillation model (Gat 1996). Precipitation formed from vapor that has experienced greater rainout (e.g., generally drier, cooler airmasses) has lower water isotope ratios.

Phase changes can also be recorded in the dual-isotope ($\delta^{2}H$ and $\delta^{18}O$) composition of water if they involve non-equilibrium diffusive transport of vapor to/from the sites of condensation/evaporation. This effect results from a difference in the relative fractionation factors for the equilibrium exchange of isotopes between phases (which affect H isotope ratios ~8 times as strongly as O isotope ratios) and diffusion (producing a sub-equal shift in H and O isotope compositions). The effect is frequently documented in terms of the "deuterium excess" parameter, $d = \delta^{2}H - 8 \times \delta^{18}O$ (Dansgaard 1964). Most ocean water has a d value near zero, and most meteoric waters have a value close to +10‰ due to the effect of diffusion on isotope ratios of vapor derived from evaporation of ocean water (Craig & Gordon 1965). Freshwaters values that deviate significantly from d = 10‰ are often taken as evidence for additional diffusive effects, such as contributions of land-surface evaporation to atmospheric vapor or partial evapoconcentration of lake waters.

Water isotopes have also found extensive use in the hydrological sciences as conservative tracers. The processes described above give rise to natural variation among hydrologic pools and within pools over space and time. For example, soil water isotope ratios can be distinct from those of collocated groundwater due to the effects of evaporation from the soil, and summer precipitation falling within a temperate catchment is often isotopically heavier than winter precipitation. Where these isotopic 'signatures' are unmodified within a study system, or where changes in the source water signatures can be accounted for and corrected (Bowen et al 2018), isotope data can be used to identify the source(s) contributing to water sampled at a given place and time.

Water Isotope Data at Large Scales

Global-scale data from the International Atomic Energy Agency's Global Network for Isotopes in Precipitation (GNIP; Rozanski et al 1993) has long been a cornerstone of isotope hydrology research, and supported development of much of the theory described above. Although such efforts continue to be critical to large-scale water isotope research, recent years have seen a growth in meta-analyses which tap data collected by many researchers over decades of site-based research. How many data are available, and are they representative of the water cycle at regional to global scales (Fig. 1)? Our group has developed a community repository storing isotope data for all parts of the water cycle, the Waterisotopes Database (wiDB). Early in its development, wiDB already contains data for more than 184,000 precipitation samples (dominated by GNIP but supplemented by many local and national network records), 27,000 surface water samples, 10,000 tap waters, and 4,800 groundwaters. Although spatial and temporal coverage is uneven, and some hydrological pools such as soil water remain seriously undersampled, these numbers are adequate to begin to characterize many key hydrological processes, as illustrated by many of the studies described in this review. Other coordinated efforts to develop and widely share water 'modern' isotope data are limited at this point, but include a collection of ground-based vapor isotope data and web portals associated with various satellite-based vapor measurement platforms (Table 1).

At the same time, technological advances have opened up new opportunities for large-scale water isotope data generation. Perhaps most remarkable has been the deployment and use of satellite-based sensors with the ability to quantify the H isotope ratio of water vapor at different levels within Earth's atmosphere (e.g., Worden et al 2007, Frankenberg et al 2009). Although issues related to calibration and data coverage remain, these data streams offer a completely novel scale of observation for isotope hydrology, providing 'continuous', spatially extensive measurements of a key component of the global water cycle. Ground-based water isotope data production has also been revolutionized with the advent of laser spectroscopic analyzers (Lis et al 2007), which have greatly reduced the cost and complexity of routine water isotope analyses and allowed adoption of this technique in a growing number of labs worldwide. The result will likely be a continued growth in the volume of data available to support large-scale hydrological research in the future.

Complimenting advances in isotope data, analysis techniques facilitating inference from large, often heterogeneous isotope datasets have expanded in recent years. "Isoscapes," data products representing the predictions of spatial models trained on stable isotope data (Bowen 2010), have been developed for many water isotope systems. By using geostatistical modeling to develop gridded estimates of isotope distributions from irregularly distributed observational data, isoscapes facilitate the integration of different datasets and are widely used in large-scale studies that involve comparison of isotope distributions for different hydrological pools. Bayesian and simulation-based statistical analysis are also becoming more widely used in such work, and facilitate the development of robust uncertainty estimates in complex meta-analyses that often involve many poorly constrained components. Lastly, though water isotope tracers were first added to climate system models more than 40 years ago, recent years have seen a growth in the development and use of isotope tracers within many components of Earth system models. By coupling the representation of isotope-discriminating processes directly with the model physics, these isotope-enabled models provide an ideal approach to benchmarking model physics against observational data. The development of model ensembles supporting isotope-based intercomparisons has supported refinements in our understanding of climate system controls on observed water isotope distributions and allowed testing of different model structures against isotope databases (e.g., Henderson-Sellers et al 2006, Risi et al 2012a, Risi et al 2012b).

Atmospheric Water Isotope Systematics

Many of the fundamental ideas underpinning our mechanistic understanding of isotopic variation in the water cycle stem from synthesis of observations across large-scale isotopic observing networks (Rozanski et al 1993). Since the last seminal review on this topic (Gat 1996), however, there has been a shift in thinking toward the recognition that many patterns observed in monitoring data arise from large-scale atmospheric phenomena, rather than variation in the local or regional climate state. This thinking emphasizes the role of isotope ratios as integrators of atmospheric water cycling, giving rise to new opportunities for understanding and reconstructing variation in the climate system. It has also, however, required re-thinking many 'classical' approaches to the interpretation of paleo-water isotope archive data in which emphasis was placed on quantitative reconstruction of local climate conditions.

Understanding the "amount effect"

The classical amount effect refers to an empirically observed negative correlation between local monthly precipitation amount and precipitation isotope ratios in the tropics (Dansgaard 1964, Rozanski et al 1993). When describing the amount effect, Dansgaard (1964) proposed several possible explanations. First, large precipitation events are associated with stronger rainout or cooling effects, and thus produce isotopically lighter precipitation. Second, both raindrop evaporation and isotopic exchange between droplets and ambient vapor tend to enrich raindrops in the heavy isotopes; larger raindrop sizes and higher humidity in heavy rainfall events reduce these effects. Although the mechanisms underlying the observed relationship were never fully resolved, the amount effect became a cornerstone of many paleoclimate studies, wherein it was inverted to estimate past rainfall in tropical and monsoonal regions.

Although observations from many low-latitude monitoring sites express the amount effect at seasonal timescales, it is not a universal relationship in space and time. In general, the rainfall-isotope correlation is most pronounced over the tropical oceans, but less significant and much more variable over land (Rozanski et al 1993, Kurita 2013). With the accumulation of more data, precipitation-independent variation in isotope ratios has been demonstrated within many classical amount effect regions (e.g., Tan 2014, Fiorella et al 2015, Cai & Tian 2016a, Conroy et al 2016). These results raise questions about the utility of paleo-water isotope archives as indicators of local precipitation intensity in the past. What are the mechanisms that really govern isotopic variation in these regions, and are they coupled with precipitation intensity in such a way that the traditional link between precipitation amount and isotope value still make sense as a framework for interpreting isotopic proxy data?

Perhaps the most fundamental shift in thinking about the amount effect has come from combining isotope monitoring with large-scale meteorological data and airmass back-trajectories. This work has led to the recognition that rainfall isotope ratio variation in areas commonly associated with the amount effect more strongly reflects rainfall and convective activity in upwind regions than it does local precipitation rates (Risi et al 2008b, Kurita et al 2009, Samuels-Crow et al 2014, Fiorella et al 2015, He et al 2015, Zwart et al 2016). According to this model, variation in rainfall and convective intensity at the site of precipitation collection plays a secondary role in governing isotopic values; rather the integrated effects of rainout, rain-vapor exchange, and vertical redistribution of moisture associated with convection over larger regions produce atmospheric vapor that is lower when convection is more widespread or intense, and as a result precipitation values within and downwind of these regions of convective activity are low.

The importance of various mechanisms by which convection may decrease the isotope ratios of vapor remain a subject of debate. Deep convection can lower the isotope ratios of lower tropospheric vapor through rain re-evaporation when the portion of re-evaporation is small (Worden et al 2007, Lee & Fung 2008, Risi et al 2010, Galewsky et al 2016). Downdrafts associated with convection also reduce the isotope ratios of lower troposphere vapor by transporting light vapor from higher levels in the atmosphere (Risi et al 2008a, Kurita 2013), and the intensity of these effects may vary with convective intensity (Samuels-Crow et al 2014, Cai & Tian 2016b). Despite continued uncertainty regarding the relative importance of these mechanisms, the now generally-accepted link between isotope ratios and regional convective activity presents several new opportunities for hydroclimatic research. For instance, precipitation isotopes have been used to discriminate stratiform from convective precipitation (Kurita 2013, Aggarwal et al 2016), characterize vertical profiles of convective heating (Moore et al 2014, Torri et al 2017), and constrain convective parameterizations in model simulations (Risi et al 2012a, Tharammal et al 2017).

Moreover, this work sheds light on the classical amount effect as a tool for tropical and subtropical paleoclimate reconstruction. If the goal is truly to quantitatively reconstruct local precipitation change, such interpretations are likely to be robust only where and when variation in local precipitation amount is closely and consistently coupled with variation in large-scale convection over the timescales of interest. In many cases, however, the goal of these reconstructions is actually to estimate past changes in the larger-scale system itself (e.g., past mosoon varaibility; Wang et al 2008). Here, the traditional amount effect approach may remain useful in essence, if not in detail, and may be bolstered by drawing on networks of proxy observations to extract coherent signals linked to large-scale variability and limiting the sensitivity or reconstructions to changes in the coupling between single sites and the large-scale system. Cai et al. (2017), for example, demonstrated that recent variation in Asian Summer Monsoon strength was better reflected in an index based on data from sites across southeast Asia than in individual records from this region.

Dynamical modes

A second advance in understanding atmospheric isotope systematics involves recognition of the influence of large-scale modes of climate variability on water isotope ratios. Analogous to work on the amount effect, this has stemmed from the integration of large-scale isotope datasets with meteorological data using methods such as spatial correlation analysis, atmospheric back trajectories, and isotope-enabled climate modeling. The result is a growing understanding of how large-scale atmospheric conditions control vapor and precipitation isotope ratios, and along with this potential to leverage isotopic paleo-archives to reconstruct the past state of climatic systems at regional to hemispheric scales.

The El Niño/Southern Oscillation (ENSO) is a naturally occurring large-scale oceanic warming (El Niño) or cooling (La Niña) in the tropical Pacific Ocean, accompanied by a tropical sea level pressure seesaw between the western and eastern Pacific (Southern Oscillation), that varies over interannual timescales. ENSO has global impacts through atmospheric teleconnections (Cai et al 2015, Wang et al 2017). Given its reach, it is not surprising that precipitation isotope effects of ENSO have now been observed in many regions, including southeast Asia (Ishizaki et al 2012, Tan 2014, Yang et al 2016, Cai et al 2017, Kurita et al 2018), the tropical Pacific (Conroy et al 2013, Martin et al 2018), tropical South America (Vuille & Werner 2005, Thompson et al 2017), and some parts of North America (Liu et al 2011, Liu et al 2014b). A comprehensive theory explaining water isotope patterns associated ENSO across these regions has not yet been developed, and considerable debate remains even over the causes of some regional effects (e.g., Tan 2014, Cai et al 2017). Despite this, the discovery of significant relationships between modern ENSO and paleo-precipitation archive records such as ice cores (Wang et al 2003, Thompson et al 2013) and tree rings (Liu et al 2017) has generated enthusiasm for the potential to improve reconstructions of past ENSO variability using paleo-water archives.

Another isotopic opportunity in paleo-ENSO research involves the question of whether recently observed variation in the characteristics of El Niño has analogues in the past. A distinctive “central Pacific” (CP) El Niño, with ocean temperature and weather impacts different from those of the classically defined events, appears to have become more common within the past few decades (Larkin & Harrison 2005, Kug et al 2009). There are currently only a few CP El Niño events in observational records, however, limiting our understanding of this ENSO state and its occurrence in the past (Wang et al 2017). The isotopic ‘fingerprint’ of CP El Niño has not yet been characterized, but given the distinctive weather impacts of this ENSO state a diagnostic fingerprint may exist and offer potential to search for past evidence of CP El Niño and extend our knowledge of the history and impacts of these events.

Precipitation isotopes have also been applied in the study of other climate modes, such as the North Atlantic Oscillation (NAO) and the Pacific North America (PNA) pattern (Fig. 2). NAO and PNA are two prominent climate modes in the Northern Hemisphere that have significant impacts on the climate of Europe and North America, respectively. These modes have received recent attention for their potential contribution to extreme winter weather in these regions and possible changes in their mean state in the future. Correlation analysis across a network of precipitation isotope monitoring stations in Europe has suggested that NAO impacts are most pronounced in the central continent (Baldini et al 2008), likely due to the effect of amplified temperature changes on vapor distillation from airmasses sourcing these continental interior sites. Early work on the expression of PNA variability in precipitation isotope records identified a regional correlation in northwestern North America that was linked with variation in circulation and moisture transport (Birks & Edwards 2009). Paleo-archive records from regions sensitive to these modes have been used to reconstruct past NAO and PNA-linked variation (e.g., Vinther et al 2003, Anderson et al 2005), but uncertainty regarding the uniqueness and stationarity of the climate-isotope correlation has limited confidence in these findings. For example, subsequent work has revealed that central European NAO-isotope response is modulated by variation in the East Atlantic pattern, a secondary mode of variability in the North Atlantic domain (Comas-Bru et al 2016).

In both cases, more recent work has identified new approaches that leverage spatial information to produce more diagnostic isotopic signatures of these climate modes. Liu et al. (2011) extended the analysis of PNA signals to precipitation isotope data across the United States and western Canada, and documented a strong dipole response consistent with the circulation and climate impacts of this mode. The authors proposed that an isotopic index based on correlated changes in values from the two poles could provide a more diagnostic record of PNA state than would values from any single location, and demonstrated the performance of this index using historical precipitation isotope data. The concept, which is analogous to pressure- and temperature-based indices that are widely used to characterize the state of climate modes, has since been applied to generate a 8,000-year reconstruction, based on pared isotope archive records, that suggests a prominent shift in the mean PNA state during the mid- to late-Holocene transition (Liu et al 2014a). Deininger et al (2016) has similarly examined the spatial structure of isotope effects associated with NAO and proposed that the longitudinal gradient in European winter precipitation isotope ratios may be a robust recorder of NAO states.

Atmospheric Water Balance

Spatial and temporal variation in the atmospheric water cycle reflects the balance between evaporation, precipitation, and lateral vapor transport. Water isotope signatures associated with each of these processes, as well as 'recycling' of water vapor within the atmosphere via rain re-evaporation, can be distinctive. These signals provide unique opportunities to identify processes that are obscure to many traditional observational methods and test estimates of the atmospheric water budget derived from reanalysis or other non-isotopic methods. This work capitalizes on both the long-standing legacy of global rainfall isotope monitoring from the GNIP program and novel data and techniques, including satellite-based atmospheric vapor isotope ratio data, atmospheric back-trajectory analysis, and isotope-enabled climate and Earth system modeling.

One such application is in the identification of water vapor source regions and their change in response to seasonal or climatic variability. Both variation in evaporation conditions over different land or ocean regions and differences in isotopic rainout and mixing effects along circulation trajectories can produce contrasting isotope values for airmasses transporting water from different sources. In fact, recent theoretical estimates suggest that poleward of ~40° latitude atmospheric vapor and precipitation isotope values are more sensitive to up-stream, than to local, conditions, and thus these values represent strong tracers of atmospheric water sources (2018). In regional studies using site-specific data, isotope signatures associated with source variability are commonly evaluated using back trajectory modeling (e.g., Pfahl & Wernli 2008, Kaseke et al 2018). For example, Putman et al. (2017) linked variability in vapor source region and transport trajectory with precipitation isotope ratios at Barrow, AK, USA, supporting the importance of vapor source region characteristics as a control on isotope ratios.

Perhaps the best developed application of vapor sourcing has been within the Asian summer monsoon region. There a sharp shift in precipitation and vapor isotope values during the monsoon onset, reflecting advection of moisture from convectively active regions, has been used to establish dates of monsoon onset across southeast Tibetan Plateau (TP) and southeast China (e.g., Yang et al 2017) and for the southern and northern slopes of Himalayas (Yu et al 2015). Contrasting seasonal precipitation isotope patterns have further been used to delineate areas of the TP dominated by moisture sourced from the monsoon versus those receiving vapor predominantly from westerly flow (Tian et al 2007, Yao et al 2013). Precipitation isotope values have similarly been used to identify different sub-monsoon systems, such as the Bay of Bengal branch and the Arabian Sea branch of the Asian summer monsoon (Midhun et al 2018). Elsewhere, this approach has been applied to identify water sources to synoptic-scale events. Good et al. (2014b) used precipitation isotope sampling across an extratropical cyclone ("Superstorm Sandy") to infer vapor source contributions to different parts and stages of the storm. D-excess values provided evidence for a period of substantial vapor influx to the land-falling storm from ocean evaporation in areas of dry, off-shore flow; this supply of vapor waned as storm weakened, the center of circulation moved further inland and the organized circulation became removed from the ocean.

Rainfall re-evaporation is an important process affecting the vertical distribution of energy and water vapor in the atmosphere, but has been challenging to quantify with traditional meteorological methods. Isotope ratios of both surface precipitation and tropospheric water vapor have been shown to reflect this process (Dansgaard 1964, Wright et al 2009), however, and may provide information on significance of re-evaporation to the atmospheric vapor budget. Worden et al. (2007) demonstrated theoretically that contributions of vapor derived from rain re-evaporation could be identified in tropospheric water vapor isotope data: this vapor source is isotopically light relative to others and thus drives atmospheric vapor to lower isotope ratios than otherwise expected for a given specific humidity. This isotopic signature was widely observed in satellite-based water vapor isotope data collected in the vicinity of tropical convective systems, suggesting significant, widespread moistening of the lower atmosphere due to rain re-evaporation in these environments (Worden et al 2007). Quantitative interpretation of the data suggested that re-evaporation of 20% of rainfall was common, and up to 50% was observed in some cases.

Land-Atmosphere Fluxes

Continental recycling

Continental precipitation is approximately three times greater than the atmospheric transport of water from the oceans to the continents (Trenberth et al 2007). These elevated precipitation amounts are supported by the recycling of water over continents by evapotranspiration (ET), with recycling broadly defined as the amount of continental precipitation arising from continental ET. ET and its influence on water availability links land water fluxes to a wide array of other biogeochemical cycles and influences atmospheric processes and boundary layer conditions. Yet despite its broad significance, spatial patterns of continental recycling and the ET processes underpinning these patterns remain difficult to constrain at regional to continental scales (Wang & Dickinson 2012, Long et al 2014). Water isotopes can provide useful constraints.

Isotopic evidence for continental recycling has been derived from precipitation, groundwater, and water vapor isotope ratios. Two patterns are commonly used. First, recycling effectively reduces the degree of rainout along atmospheric circulation trajectories by returning recently fallen precipitation to the atmosphere, and this produces $\delta^{18}O$ or $\delta^{2}H$ gradients along trajectories that are smaller than predicted for Rayleigh distillation. Spatially distributed precipitation isotope data have thus been interpreted as evidence for recycling in the western USA (Ingraham & Taylor 1991) and used to quantify recycling over the Amazon (Salati et al 1979). This phenomenon has also been invoked in the interpretation of paleo-climate data to argue for past changes in continental recycling associated with ecological changes such as grassland expansion (Chamberlain et al 2014). Second, partial evaporation of meteoric waters, particularly under conditions of low relative humidity, produces vapor with high values of d-excess, and both water vapor isotope data and values from down-wind precipitation may reflect the contribution of recycled meteoric water in their d-excess values (Gat et al 1994). For example, isotopic measurements of water downwind of Lake Michigan indicate that nearly a third of groundwater recharge and 10-18% of precipitation in western Michigan arises from vapor evaporated from Lake Michigan (Bowen et al 2012).

Direct observations of water vapor provide an additional dimension for such work, in that that continental recycling and other processes produce contrasting pathways of coupling between humidity and vapor isotope changes (Worden et al 2007, Aemisegger et al 2014). Despite this, quantitative constraints on recycling intensity from vapor isotope ratios alone remain difficult to obtain, largely due to data limitations. Satellite records of vapor isotope ratios tend to be short and infrequent, and surface measurement campaigns have generally lacked sufficient spatial density to quantify air parcel changes along trajectories between stations. Several studies have been able to use back-trajectory models to demonstrate links between ground-based vapor isotope measurements and upwind land-atmosphere exchange (Sodemann et al 2008, Aemisegger et al 2014, Fiorella et al 2018b), but quantitative inversion of isotope data in this context to produce new information on recycling fluxes is still in its infancy.

On larger scales, continental recycling estimates suffer from high uncertainty in the isotopic composition of fluxes, including isotope ratios of vapor on the windward and leeward sides of continents and of runoff (Gat 2000). Long-term estimates of vapor isotope ratios from satellite observations, calibrated by surface observations (e.g., Good et al 2015b), may help reduce uncertainty in the vapor inputs to and outputs from continents, though substantial uncertainty remains on interannual and shorter timescales.

Evapotranspiration partitioning

In addition to providing constraints on the bulk land surface contribution to atmospheric moisture, water isotope measurements can be used to partition ET into its evaporation (E) and transpiration (T) components. In most cases the isotopic compositions of the E and T fluxes, δE and δT respectively, are distinct. Vapor evaporated from soils will be fractionated with respect to soil water, generating vapor isotope ratios that are lower than the soil water (Allison et al 1983). In contrast, most plants do not fractionate soil water during root uptake (e.g., Ehleringer & Dawson 1992, though see Ellsworth & Williams 2007 for fractionation in xerophytes). Although leaf water is commonly enriched in the heavy isotopes relative to water taken in by the roots (Cernusak et al 2016), mass balance dictates that the isotope ratios of transpiration must closely match the isotope ratios of the plant's water source on timescales longer than the residence time of water in plants (e.g., days). Therefore, δT will be enriched in heavy isotopologues relative to δE, the isotopic composition of the total ET flux (δET) will be intermediate to these two end-member compositions, and the ratio of T/ET can be estimated with a mixing model equation (Wang & Yakir 2000; see sidebar):

$$T/ET=(\delta ET-\delta E)/(\delta T-\delta E).$$

In applications of this method isotope ratios of transpiration are typically estimated from measurements of plant water sources or stem water, whereas evaporation isotope ratios are usually calculated using a version of the Craig-Gordon model adapted for soils (Craig & Gordon 1965, Allison et al 1983, Soderberg et al 2012). The isotope ratio of transpiration, δET, is estimated from measured water vapor isotope values, typically using Keeling plots or flux-gradient methods (Wang & Yakir 2000, Good et al 2012). When combined with estimates of the net ET flux from eddy covariance or similar methods, direct estimates of E and T flux magnitudes can be obtained.

Isotope-based methods can provide useful constraints on ET partitioning, even in circumstances where other methods are difficult to apply. For example, isotopic methods can be applied in grassland ecosystems, where methods such as sap flux measurement, which can provide direct estimates of transpiration from trees, are not possible. Additionally, water isotope ratios vary overnight, which provides insights into nocturnal water cycling (Welp et al 2012, Berkelhammer et al 2013, Fiorella et al 2018b) that cannot otherwise be obtained. However, several challenges complicate regional-to-global syntheses of ET partitioning using isotopic methods. First, plants within the same ecosystem may use a range of water sources with different isotopic values (Ehleringer & Dawson 1992, Evaristo & McDonnell 2017), complicating estimates of δT. Second, estimating isotope ratios of transpiration is significantly more challenging under conditions or over time scales where the plant's water balance is not at steady state (Dongmann et al 1974, Cernusak et al 2002, Farquhar & Cernusak 2005, Lai et al 2006, Simonin et al 2013, Dubbert et al 2014), limiting the method's utility in the study of short-term (e.g., sub-daily) processes. Third, soil heterogeneity imparts significant uncertainty to estimates of δE. Recent advances in measurement techniques may help resolve each of these issues. The use of field-portable laser spectrometers coupled with in-situ soil probes can resolve high-frequency dynamics governing soil water isotope distributions and δE (Volkmann & Weiler 2014, Oerter & Bowen 2017). Likewise, in situ measurement techniques for isotope ratios of δT (Wang et al 2012) and stem water (Volkmann et al 2016) may improve estimates of ecosystem-level δT.

There have been several recent attempts to use isotopes to constrain T/ET at global scales (Fig. 3). An initial effort using a compilation of lake isotope ratios suggested a global T/ET ratio of >80% of total ET (Jasechko et al 2013), a value significantly higher than estimated by non-isotopic methods and land surface models (Wei et al 2017). This estimate may have been biased high due to some methodological assumptions (Schlesinger & Jasechko 2014), and moreover estimates of T/ET ratios from surface waters likely discount soil evaporation where soils are not well connected to surface waters (Good et al 2015a;

see subsequent section). A revised analysis accounting for these factors yields a global T/ET estimate of 64±13% (Good et al 2015a), which agrees well with plot-scale and non-isotopic partitioning methods. Land surface models, however, tend to predict even lower T/ET ratios; for example, the mean value for models included in the 5th Climate Model Intercomparison Project is 43% (Wei et al 2017). Recent land surface model releases have begun to incorporate water isotope physics (e.g., Wong et al 2017), which when coupled with observations of water isotopes across the soil-plant-atmosphere continuum may guide improvements in the representation of land-atmosphere water fluxes in these models.

Through the Critical Zone and Catchments

Two water worlds?

Water isotopes can be used to trace water during infiltration within soils and recharge or flow of groundwaters, leveraging natural seasonal and event-scale variation in precipitation water isotope ratios (Kendall & McDonnell 1998). This approach has been extended by plant ecophysiologists to trace the source of water used by vegetation based on the isotopic composition of xylem water. In addition to signals associated with precipitation isotope variation, these studies also capitalize on soil water evaporation, which allows diagnosis of plant water uptake from shallow soil where evaporation isotope effects are strongest (e.g., Ehleringer et al 1991).

In the past decade, the integration of plant xylem, soil, groundwater and stream datasets has led to the development of a conceptual model of water partitioning within the critical zone termed ‘two water worlds’ (TWW) (McDonnell 2014). First described at the HJ Andrews experimental forest (Oregon, USA), TWW stems from the observation that plant and soil waters exhibit similar isotope ratios, and show evidence for strong evaporative effects, whereas groundwater and streamflow do not (Brooks et al 2010). The authors argued that within this specific ecosystem soil waters were largely emplaced at the start of the winter wet season, and that water from additional precipitation events passed through the soil, recharging groundwater and generating streamflow. Over the summer growing season, residual soil water evaporated. Trees using this soil water thus also reflected the isotope effects of soil water evaporation.

Although the original elaboration of the TWW model emerged from a specific set of observations and hydroclimatic conditions, much follow-on work has tested and generally supported ubiquity of the model (e.g., Goldsmith et al 2012, Geris et al 2015, Oerter & Bowen 2017). A large number of site-specific isotope studies replicating the fundamental TWW observations were summarized in a global meta-analysis by Evaristo et al. (2015). These authors concluded that significant support for the TWW hypothesis could be found at approximately 80% of sites. Uncertainties in the representativeness of soil and plant water isotope measurements made using different methods (Orlowski et al 2016) underlie one common critique of this assessment. However, the first-order result that isotopic separation between soil/plant and runoff water is widespread was also supported by the global water isotope mass-balance analysis of Good et al. (2015a), who estimated that 62% of global runoff carried no isotopic imprint of soil water evaporation. This analysis relied only on the impact of TWW separation on the isotopic composition of global river runoff and evapotranspiration fluxes, and not on direct measurements of soil or plant waters.

Two aspects of the TWW model have attracted broad attention because, if widely applicable, they would have significant implications for our fundamental ecohydrological understanding and practical ability to make hydrological predictions. First, TWW constitutes a mechanism by which evapotranspiration and runoff may be derived from precipitation falling at different times or under different conditions. For example, in some environments infiltration and recharge of groundwater may be biased toward water derived from winter season snowpack or toward water falling in short-lived, intense events, whereas transpiration might be dominantly sourced by less intense summer-season storms (Bowen et al 2012, Jasechko et al 2014, Bowen et al 2018). Second, and more controversial, plants may rely predominantly on the relatively small fraction of total annual precipitation that is retained as 'immobile', tightly-bound soil water. Whether such a tendency is physically plausible and how it can be reconciled with evolutionarily pressure favoring diverse water acquisition strategies in many ecosystems remains an open question (Berry et al 2018). A subsequent meta-analysis of plant xylem water isotope data by Evaristo & McDonnell (2017) assessed the contention that groundwater use by plants, in particular, is widespread, in contrast to the TWW concept. The authors concluded that detectable groundwater use was limited to 37% of available samples, and constituted only 23% of xylem water volumetrically across 12 biomes, but with large uncertainty. Given reasonably strong support for the generality of TWW-type separation of transpiration and recharge/runoff water sources, understanding both the physical dynamics of soil water compartmentalization and the evolutionary context of water use strategies whereby plants seemingly exploit a volumetrically small component of total precipitation represents an intriguing challenge for future research (Bowen 2015, Bowling et al 2017, Berry et al 2018).

Runoff and recharge processes

The TWW hypothesis invokes physical and/or temporal segregation between water that leaves the soil environment via land-atmosphere (evapotranspiration) and lateral or subsurface flow. The concept that some fraction of precipitation moves rapidly through soils along preferential flow paths is deep-rooted in the hydrological sciences (Beven & Germann 1982). The degree to which such segregation of water fluxes in the critical zone controls sources of recharge and runoff at regional to global scales, however, has been less apparent. Recent work capitalizing on the potential of water isotopes to integrate water source information has begun to address this question.

Seasonal variation in precipitation water isotope ratios offers one powerful source signature for such work. Data from a water sample can be compared with measured or modeled isotope ratios for precipitation during seasons of interest, commonly cold/warm or wet/dry seasons depending on the local climate regime. Differences between the measured sample value and a precipitation-amount weighted mixture for the two seasons can then be interpreted to reflect a disproportionate contribution of precipitation from one season, termed recharge or runoff bias. This approach has been applied to Holocene-aged groundwater isotope data from a global-scale compilation, and has provided strong support for cool-season recharge bias in temperate and arid climate regions and wet-season bias in the tropics (Jasechko et al 2014).

Recharge bias has also been assessed at the regional to national scale for streams and lakes. Henderson and Shuman (2010) suggested an intriguing dichotomy between streams and lakes, whereby the former exhibited cool season runoff bias across much of the USA but the latter did not. Bowen et al. (2018) revisited this conclusion using new Bayesian data analysis approaches that addressed potential biases related to the correction for isotope effects of lake water evapoconcentration and supported more explicit hypothesis testing than previous approaches. They applied this method to data from a network of lakes across the contiguous USA, and compared the isotopic data directly with seasonal runoff estimates from climate reanalysis products. Their results suggested that cool season bias was common for lakes in most snow-prone regions, but indicated warm season bias in the Great Plains (Fig. 4). This work highlights the pronounced seasonality of recharge and runoff, beyond what is predicted from current-generation models used in reanalysis, and suggests the need to further improve the representation of processes governing the storage and routing of water through the critical zone in land surface models.

People in the Water Cycle

The application of isotope tracers to study human water use and management is relatively recent. Human impacts on the water cycle are unequivocal, and many of the processes already discussed here feature a strong human imprint. However, much remains to be learned about the processes by which human water use alters regional and global water budgets. Recent work on transport and management of drinking water has used stable isotopes to document links between water in built infrastructure and the environment over a range of scales. Such research has potential both to inform our understanding of patterns of water use that may impact other components of the water cycle and to provide new information to water managers that could advance and support sustainable water use.

Systematic sampling of tap water has now been conducted at the national scale for several countries and at regional and city scales in a limited number of cases (e.g., Bowen et al 2007b, Good et al 2014a, West et al 2014, Jameel et al 2016, Tipple et al 2017, Zhao et al 2017). Among the most fundamental observations across these studies is widespread evidence for use of non-locally sourced water. Tap water across much of the western United States, for example, has water isotope ratios significantly lower than those of annually averaged local precipitation, providing evidence for use of water derived from isotopically lighter precipitation sources (Bowen et al 2007b). Although multiple factors may contribute to this effect, the widespread use of water from high-elevation mountain sources is clearly the dominant factor in many, if not most, such examples (Kennedy et al 2011).

Redistribution of high-elevation water can occur at local scales, where, for example, reservoirs and aquifers sourced from high-elevation snowmelt in the US Western Interior provide water to cities in adjacent basins. Across water-stressed regions, however, redistribution often is associated with significant lateral transport. Tap waters in cities and towns situated along the Colorado and Missouri Rivers provide an example of natural lateral redistribution. Water used in these towns commonly has isotope ratios characteristic of precipitation sources more than 1,000 km away (Bowen et al 2007a). In other cases lateral transfers occur via man-made diversions that can completely circumvent the boundaries of natural hydrological basins. Good et al. (2014a) analyzed tap water data from across the western USA in the context of modeled estimates of within-basin precipitation and surface water sources, and found evidence for use of out-of-basin waters at more than 30% of the study sites (Fig. 5). These studies provide a method for characterizing risk exposure associated with current water use practices: by highlighting the climatological sources of tap water (where and when did the precipitation fall), uncharacterized or obscure for most water supply systems, they allow assessment of potential supply impacts of future climate, land use, or management changes in these areas.

One risk factor of concern for many arid region water supply systems is evaporative loss, and water isotope data provide one of the most direct methods for quantifying this flux. Classical water flux data (e.g., reservoir inflow and outflow) give very accurate estimates of net losses from surface water storage systems, but provide no basis for separating loss by evaporation from seepage losses. Adapting theory widely applied to estimate evaporation from lakes (e.g., Jasechko et al 2013), Jameel et al. (2016) and Tipple et al. (2017) used extensive tap water isotope sampling in two urban centers of the western USA (Salt Lake City, UT and the San Francisco Bay Area, CA) to quantify the extent and variability of the evaporative losses from municipal supply systems. In both cases significant evaporative losses, constituting up to 6% of the total water use, were inferred, and changes in evaporation through the study period could be linked to climate variation. Given the widespread importance of surface storage in many parts of the world, the ability to identify, quantify, and characterize water supply system sensitivity to change in evaporation loss using water isotopes could be critical in informing discussions about optimal management of storage systems (e.g., Kraft et al 2016).

An additional area where tap water isotope ratios have shown some promise is in monitoring and interrogating the operation of water distribution systems. Applications involving inter-basin transfers were introduced above, but in addition to providing site-specific information the integration of data from across the western USA allowed Good et al. (2014a) to assess hydroclimatic and demographic correlates of imported water use across this region. The results, which highlighted both water availability and financial factors as drivers of water importation, were used to project the site-based results and generate estimates of total water transfers across the study region (Fig. 5). This result, and also recent findings by Jameel et al. (2016) linking the allocation of water from different sources to socioeconomic status across the Salt Lake City metropolitan area (Utah, USA), provide an empirical alternative to survey and management data that may be useful to researchers interested in water rights and environmental equity issues.

Finally, water vapor isotope ratios have recently been used to understand how urban environments influence atmospheric land-water exchange. Urban areas influence near-surface humidity in a variety of ways, though perhaps the largest imprint in water vapor isotope ratios arises from fossil fuel combustion. Vapor released during fossil fuel combustion has a low d-excess value otherwise not observed in the hydrologic cycle, and therefore can be used to estimate the humidity subsidy to near-surface humidity (Gorski et al 2015). Pilot studies in Salt Lake City, UT indicate that up to 16% of winter urban humidity may be attributable to fossil fuel combustion during periods of strong atmospheric stability (Fiorella et al 2018a). Such influences are likely to be localized within areas of high emissions, but vapor isotope measurements offer the potential to assess combustion-derived subsidies to atmospheric vapor and their impact on atmospheric processes across a range of scales and systems (Salmon et al 2017).

Summary and perspective

The examples reviewed here demonstrate how fundamental understanding of isotope-discriminating processes has been integrated with large-scale data and data analysis methods to inform our understanding of water cycle processes at scales from cities to the globe. At least three different types of contributions can be identified. First, water isotope data has been used to gain quantitative information on a specific hydrological process across many locations in order to understand or characterize its variability. For example, estimates of rainfall re-evaporation under different meteorological conditions and locations demonstrated the magnitude of this flux and its association with tropical convection (Worden et al 2007), and estimates of inter-basin water transfers from cities and towns across the western US revealed the scope and patterns of variation in this process (Good et al 2014a). In both cases, information gained from analyzing the isotopic data across many locations provides a basis for developing and calibrating models describing these processes and for up-scaling to assess their importance to regional or global water budgets.

Second, many of these examples capitalize on the process-integrating power of isotopes to obtain direct information on the large-scale significance of specific water cycle process. Global water isotope budgets constrained by precipitation isoscapes, global satellite-derived vapor isotope estimates, and isotope fractionation theory, for example, provided global-scale constraints on evapotranspiration partitioning and connectivity between soil water and runoff (Good et al 2015a). Analyses of stream and lake water data gave catchment-integrated estimates of ET partitioning and runoff bias (Bowen et al 2011, Jasechko et al 2013, Bowen et al 2018). These quantities can be interesting in and of themselves, revealing information about processes and properties of the regional to global scale water cycle that are not otherwise obvious, but also provide excellent benchmarks against which hydrological, atmospheric, and Earth system models can be tested.

Third, in some cases these analyses have revealed surprises, casting light on novel processes or phenomena that require re-thinking or adding to existing paradigms. The basic concept that two water worlds may exist within the critical zone was not itself novel, but the widespread support for this phenomenon across a broad range of ecosystems and the suggestion that vegetation in most environments is coupled primarily to the soil immobile water fraction has significant implications for models of land surface hydrology, ecophysiology, and water quality (Evaristo et al 2015). The demonstration that water vapor derived from combustion was a significant and quantifiable source to the atmosphere in an arid-region urban center was somewhat unexpected (Gorski et al 2015); recent work suggesting this may be true in areas of more humid climate (Salmon et al 2017) requires additional attention but may motivate revisions to our thinking about the water budget of urban atmospheres.

The past 20 years have seen major advances in the application of large and large-scale isotope datasets in water cycle research. Looking forward, the potential for continued advances from such work is strong, and we see at least three drivers for this progress. First, technological advances such as membrane-inlet laser spectroscopy (Volkmann & Weiler 2014) are fueling growth in the production of water isotope data for key hydrological pools such as soil water and atmospheric vapor that represent key gaps in our current data coverage. As these data grow they will provide improved constraints for many of the types of analyses discussed here and create opportunities for novel analyses.

Some of this new data resource development will be accomplished through coordinated networks, but given the increasing accessibility and growing uptake of water isotope measurements we think that much of the growth in potentially useful data will be driven by individual investigators and small groups. This underlies our second driver for future large-scale water isotope science: the development and adoption of community-driven, community-supported data infrastructure. A vast number of water isotope data generated around the world are either inaccessible or published in venues and formats where reuse by other scientists represents a major challenge. These data, were they accessible, would not only be of use in large-scale analyses but could also provide baseline data for many local-scale studies. Researchers conducting meta-analyses have begun to compile many historic data in more useful formats, but the effort invested in these studies would be leveraged to greater effect if these data compilations became part of a larger community data resource that made the data easily discoverable and reusable. Community buy-in to such a resource as a storehouse for newly generated data, along with programmatic interfaces that made it easy for labs and investigators to contribute new data as they were produced, would allow it to grow efficiently into the future. A community effort to compile paleo-water isotope data for the common era is underway (Konecky et al 2018). The wiDB, introduced above, now includes records from dozens of contributors. Recent support from the US National Science Foundation is launching a series of community activities to develop IsoBank (Pauli et al 2017), a multidisciplinary isotope data archive that will assimilate the wiDB and hopefully provide a framework for increasing community data sharing.

Finally, we see additional opportunities for isotope-based water cycle research as novel and widely-applicable data analysis and modeling frameworks are developed and shared. Much of the work described here was facilitated by the development of simple metrics or data analysis approaches that allowed process information to be extracted from heterogeneous and/or incomplete isotope datasets. Statistical techniques that support robust error assessment are critical to such efforts and have and should continue to increase confidence in their results. Moreover, the integration of isotope tracers in process-based physical models promises the ultimate potential to benchmark our understanding against isotope metrics, and as more isotope-enabled model components (e.g., land surface models) are developed and their output becomes more accessible, we anticipate many opportunities to use large-scale water isotope datasets in the testing, validation, and refinement of such models.

Acknowledgements

We thank numerous colleagues and collaborators for discussions that are reflected in the content of this article; special thanks in this respect go to the instructors and students of the SPATIAL summer course. Support for this work was provided by US National Science Foundation Grants EF-1241286, DBI-1565128, DBI-1759730, and EF-1802880. AP was supported by the University of Utah Graduate Research Fellowship program and ZC by the China Scholarship Council.

Literature Cited

Aemisegger F, Pfahl S, Sodemann H, Lehner I, Seneviratne SI, Wernli H. 2014. Deuterium excess as a proxy for continental moisture recycling and plant transpiration. *Atmos. Chem. Phys.* 14: 4029-54

Aggarwal PK, Romatschke U, Araguas-Araguas L, Belachew D, Longstaffe FJ, et al. 2016. Proportions of convective and stratiform precipitation revealed in water isotope ratios. *Nature Geoscience* 9: 624-9

Allison G, Barnes C, Hughes M. 1983. The distribution of deuterium and ^{18}O in dry soils 2. Experimental. *Journal of Hydrology* 64: 377-97

Alton P, Fisher R, Los S, Williams M. 2009. Simulations of global evapotranspiration using semiempirical and mechanistic schemes of plant hydrology. *Global Biogeochemical Cycles* 23: GB4023

Anderson L, Abbott MB, Finney BP, Burns SJ. 2005. Regional atmospheric circulation change in the North Pacific during the Holocene inferred from lacustrine carbonate oxygen isotopes, Yukon Territory, Canada. *Quaternary Research* 64: 21-35

Bailey A, Posmentier E, Feng X. 2018. Patterns of evaporation and precipitation drive global isotopic changes in atmospheric moisture. *Geophysical Research Letters* 45: 7093-101

Baldini LM, McDermott F, Foley AM, Baldini JUL. 2008. Spatial variability in the European winter precipitation δ18O-NAO relationship: Implications for reconstructing NAO-mode climate variability in the Holocene. *Geophysical Research Letters* 35

Berkelhammer M, Hu J, Bailey A, Noone D, Still C, et al. 2013. The nocturnal water cycle in an open-canopy forest. *Journal of Geophysical Research: Atmospheres* 118

Berry ZC, Evaristo J, Moore G, Poca M, Steppe K, et al. 2018. The two water worlds hypothesis: Addressing multiple working hypotheses and proposing a way forward. *Ecohydrology* 11: e1843

Beven K, Germann P. 1982. Macropores and water flow in soils. *Water Resources Research* 18: 1311-25

Birks SJ, Edwards TWD. 2009. Atmospheric circulation controls on precipitation isotope-climate relations in western Canada. *Tellus* 61B: 566-76

Bowen GJ. 2010. Isoscapes: Spatial pattern in isotopic biogeochemistry. *Annual Review of Earth & Planetary Sciences* 38: 161-87

Bowen GJ. 2015. The diversified economics of soil water. *Nature* 525: 43-4

Bowen GJ, Cerling TE, Ehleringer JR. 2007a. Stable isotopes and human water resources: Signals of change. In *Stable Isotopes as Indicators of Ecological Change*, ed. TE Dawson, R Siegwolf, pp. 285-300. Amsterdam: Elsevier

Bowen GJ, Ehleringer JR, Chesson LA, Stange E, Cerling TE. 2007b. Stable isotope ratios of tap water in the contiguous USA. *Water Resources Research* 43, W03419

Bowen GJ, Kennedy CD, Henne PD, Zhang T. 2012. Footprint of recycled water subsidies downwind of Lake Michigan. *Ecosphere* 3(6): 53

Bowen GJ, Kennedy CD, Liu Z, Stalker J. 2011. Water Balance Model for Mean Annual Hydrogen and Oxygen Isotope Distributions in Surface Waters of the Contiguous USA. *Journal of Geophysical Research* 116, G04011

Bowen GJ, Putman A, Brooks JR, Bowling DR, Oerter EJ, Good SP. 2018. Inferring the source of evaporated waters using stable H and O isotopes. *Oecologia* 187: 1025-39

Bowling DR, Schulze ES, Hall SJ. 2017. Revisiting streamside trees that do not use stream water: can the two water worlds hypothesis and snowpack isotopic effects explain a missing water source? *Ecohydrology* 10: e1771

Brooks JR, Barnard HR, Coulombe R, McDonnell JJ. 2010. Ecohydrologic separation of water between trees and streams in a Mediterranean climate. *Nature Geoscience* 3: 100-4

Cai W, Santoso A, Wang G, Yeh S-W, An S-I, et al. 2015. ENSO and greenhouse warming. *Nature Climate Change* 5: 849

Cai Z, Tian L. 2016a. Atmospheric controls on seasonal and interannual variations in the precipitation isotope in the East Asian Monsoon region. *Journal of Climate* 29: 1339-52

Cai Z, Tian L. 2016b. Processes Governing Water Vapor Isotope Composition in the Indo-Pacific Region: Convection and Water Vapor Transport. *Journal of Climate* 29: 8535-46

Cai Z, Tian L, Bowen GJ. 2017. ENSO variability reflected in precipitation oxygen isotopes across the Asian Summer Monsoon region. *Earth and Planetary Science Letters* 475: 25-33

Cernusak LA, Barbour MM, Arndt SK, Cheesman AW, English NB, et al. 2016. Stable isotopes in leaf water of terrestrial plants. *Plant Cell Environ* 39: 1087-102

Cernusak LA, Pate JS, Farquhar GD. 2002. Diurnal variation in the stable isotope composition of water and dry matter in fruiting *Lupinus angustifolius* under field conditions. *Plant, Cell & Environment* 25: 893-907

Chamberlain CP, Winnick MJ, Mix HT, Chamberlain SD, Maher K. 2014. The impact of Neogene grassland expansion and aridification on the isotopic composition of continental precipitation. *Global Biogeochemical Cycles*: 2014GB004822

Comas-Bru L, McDermott F, Werner M. 2016. The effect of the East Atlantic pattern on the precipitation δ^{18}O-NAO relationship in Europe. *Climate Dynamics*: 1-11

Conroy JL, Cobb KM, Noone D. 2013. Comparison of precipitation isotope variability across the tropical Pacific in observations and SWING2 model simulations. *Journal of Geophysical Research: Atmospheres* 118: 5867-92

Conroy JL, Noone D, Cobb KM, Moerman JW, Konecky BL. 2016. Paired stable isotopologues in precipitation and vapor: A case study of the amount effect within western tropical Pacific storms. *Journal of Geophysical Research: Atmospheres* 121: 3290-303

Craig H. 1961. Isotopic variations in meteoric waters. *Science* 133: 1702-3

Craig H, Gordon LI. 1965. Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In *Proceedings of a Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures*, ed. E Tongiorgi. Spoleto, Italy

Dai A. 2006. Recent climatology, variability, and trends in global surface humidity. *Journal of Climate* 19: 3589-606

Dansgaard W. 1954. The O^{18}-abundance in fresh water. *Geochimica et Cosmochimica Acta* 6: 241-60

Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* 16: 436-68

Deininger M, Werner M, McDermott F. 2016. North Atlantic Oscillation controls on oxygen and hydrogen isotope gradients in winter precipitation across Europe; implications for palaeoclimate studies. *Climate of the Past* 12: 2127-43

Dongmann G, Nurnberg HW, Forstel H, Wagener K. 1974. On the enrichment of H2O18 in the leaves of transpiring plants. 11: 41-52

Dubbert M, Cuntz M, Piayda A, Werner C. 2014. Oxygen isotope signatures of transpired water vapor: the role of isotopic non-steady-state transpiration under natural conditions. *New Phytologist* 203: 1242-52

Ehleringer JR, Dawson TE. 1992. Water uptake by plants: perspectives from stable isotope composition. *Plant, Cell & Environment* 15: 1073-82

Ehleringer JR, Phillips SL, Schuster WSF, Sandquist DR. 1991. Differential utilization of summer rains by desert plants. *Oecologia* 88: 430-4

Ellsworth PZ, Williams DG. 2007. Hydrogen isotope fractionation during water uptake by woody xerophytes. *Plant and Soil* 291: 93-107

Evaristo J, Jasechko S, McDonnell JJ. 2015. Global separation of plant transpiration from groundwater and streamflow. *Nature* 525: 91-4

Evaristo J, McDonnell JJ. 2017. Prevalence and magnitude of groundwater use by vegetation: a global stable isotope meta-analysis. *Scientific Reports* 7: 44110

Farquhar GD, Cernusak LA. 2005. On the isotopic composition of leaf water in the non-steady state. *Functional Plant Biology* 32: 293-303

Fiorella RP, Bares R, Lin JC, Ehleringer JR, Bowen GJ. 2018a. Detection and variability of combustion-derived vapor in an urban basin. *Atmospheric Chemistry and Physics* 18: 8529-47

Fiorella RP, Poulsen CJ, Matheny AM. 2018b. Seasonal Patterns of Water Cycling in a Deep, Continental Mountain Valley Inferred From Stable Water Vapor Isotopes. *Journal of Geophysical Research* 123: 7271-91

Fiorella RP, Poulsen CJ, Zolá RSP, Barnes JB, Tabor CR, Ehlers TA. 2015. Spatiotemporal variability of modern precipitation $\delta^{18}O$ in the central Andes and implications for paleoclimate and paleoaltimetry estimates. *Journal of Geophysical Research* 120: 4630-56

Frankenberg C, Yoshimura K, Warneke T, Aben I, Butz A, et al. 2009. Dynamic processes governing lower-tropospheric HDO/H_2O ratios as observed from space and ground. *Science* 325: 1374-7

Galewsky J, Steen-Larsen HC, Field RD, Worden J, Risi C, Schneider M. 2016. Stable isotopes in atmospheric water vapor and applications to the hydrologic cycle. *Reviews of Geophysics*: n/a-n/a

Gat JR. 1996. Oxygen and Hydrogen Isotopes in the Hydrologic Cycle. *Annual Review of Earth and Planetary Sciences* 24: 225-62

Gat JR. 2000. Atmospheric water balance-the isotopic prespective. *Hydrological Processes* 14: 1357-69

Gat JR, Bowser CJ, Kendall C. 1994. The contribution of evaporation from the Great Lakes to the continental atmosphere; estimate based on stable isotope data. *Geophysical Research Letters* 21: 557-60

Gedney N, Cox PM, Betts RA, Boucher O, Huntingford C, Stott PA. 2006. Detection of a direct carbon dioxide effect in continental river runoff records. *Nature* 439: 835-8

Geris J, Tetzlaff D, McDonnell J, Anderson J, Paton G, Soulsby C. 2015. Ecohydrological separation in wet, low energy northern environments? A preliminary assessment using different soil water extraction techniques. *Hydrologic Processes* 29: 5139-52

Gerten D, Hoff H, Bondeau A, Lucht W, Smith P, Zaehle S. 2005. Contemporary "green" water flows: Simulations with a dynamic global vegetation and water balance model. *Physics and Chemistry of the Earth, Parts A/B/C* 30: 334-8

Goldsmith GR, Muñoz-Villers LE, Holwerda F, McDonnell JJ, Asbjornsen H, Dawson TE. 2012. Stable isotopes reveal linkages among ecohydrological processes in a seasonally dry tropical montane cloud forest. *Ecohydrology* 5: 779-90

Good SP, Kennedy CD, Stalker JC, Chesson LA, Valenzuela LO, et al. 2014a. Patterns of local and non-local water resource use across the western United States determined via stable isotope intercomparisons. *Water Resources Research* 50

Good SP, Mallia DV, Lin JC, Bowen GJ. 2014b. Stable Isotope Analysis of Precipitation Samples Obtained via Crowdsourcing Reveals the Spatiotemporal Evolution of Superstorm Sandy. *PLoS ONE* 9: e91117

Good SP, Noone D, Bowen GJ. 2015a. Hydrologic connectivity constrains partitioning of global terrestrial water fluxes. *Science* 349: 175-7

Good SP, Noone D, Kurita N, Benetti M, Bowen GJ. 2015b. D/H Isotope Ratios In the Global Hydrologic Cycle. *Geophysical Research Letters* 42

Good SP, Soderberg K, Wang L, Caylor KK. 2012. Uncertainties in the assessment of the isotopic composition of surface fluxes: A direct comparison of techniques using laser-based water vapor isotope analyzers. *Journal of Geophysical Research: Atmospheres* 117: D15301

Gorski G, Strong C, Good SP, Bares R, Ehleringer JR, Bowen GJ. 2015. Vapor hydrogen and oxygen isotopes reflect water of combustion in the urban atmosphere. *Proceedings of the National Academy of Sciences* 112: 3247-52

Hattermann FF, Krysanova V, Gosling SN, Dankers R, Daggupati P, et al. 2017. Cross-scale intercomparison of climate change impacts simulated by regional and global hydrological models in eleven large river basins. *Climatic Change* 141: 561-76

He Y, Risi C, Gao J, Masson-Delmotte V, Yao T, et al. 2015. Impact of atmospheric convection on south Tibet summer precipitation isotopologue composition using a combination of in situ measurements, satellite data and atmospheric general circulation modeling. *Journal of Geophysical Research: Atmospheres* 120: 3852-71

Henderson-Sellers A, Fischer M, Aleinov I, McGuffie K, Riley WJ, et al. 2006. Stable water isotope simulation by current land-surface schemes: Results of iPILPS Phase 1. *Global and Planetary Change* 51: 34-58

Henderson AK, Shuman BN. 2010. Differing controls on river- and lake-water hydrogen and oxygen isotopic values in the western United States. In *Hydrological Processes*: Wiley Online Library

Ingraham NL, Taylor BE. 1991. Light stable isotope systematics of large-scale hydrologic regimes in California and Nevada. *Water Resources Research* 27: 77-90

Ishizaki Y, Yoshimura K, Kanae S, Kimoto M, Kurita N, Oki T. 2012. Interannual variability of $H_2^{18}O$ in precipitation over the Asian monsoon region. *Journal of Geophysical Research: Atmospheres* 117: D16308

Jameel Y, Brewer S, Good SP, Tipple BJ, Ehleringer JR, Bowen GJ. 2016. Tap water isotope ratios reflect urban water system structure and dynamics across a semiarid metropolitan area. *Water Resources Research*

Jasechko S, Birks SJ, Gleeson T, Wada Y, Fawcett PJ, et al. 2014. The pronounced seasonality of global groundwater recharge. *Water Resources Research* 50: 8845-67

Jasechko S, Sharp ZD, Gibson JJ, Birks SJ, Yi Y, Fawcett PJ. 2013. Terrestrial water fluxes dominated by transpiration. *Nature*

Kaseke KF, Wang L, Wanke H, Tian C, Lanning M, Jiao W. 2018. Precipitation Origins and Key Drivers of Precipitation Isotope (^{18}O, ^{2}H, and ^{17}O) Compositions Over Windhoek. *Journal of Geophysical Research* 123: 7311-30

Kendall C, McDonnell JJ, eds. 1998. *Isotope Tracers in Catchment Hydrology*. Amsterdam: Elsevier. 839 pp.

Kennedy CD, Bowen GJ, Ehleringer JR. 2011. Temporal variation of oxygen isotope ratios ($\delta^{18}O$) in drinking water: Implications for specifying location of origin with human scalp hair. *Forensic Science International* 208: 156-66

Konecky B, Comas-Bru L, Dassié E, DeLong K, Partin J. 2018. Piecing Together the Big Picture on Water and Climate. *Eos* 99

Kraft JC, Tuzlak D, Walker A. 2016. *Fill Mead First: A technical assessment*, Utah State University Quinney College of Natural Resrouces, Logan, Utah

Kug J-S, Jin F-F, An S-I. 2009. Two Types of El Niño Events: Cold Tongue El Niño and Warm Pool El Niño. *Journal of Climate* 22: 1499-515

Kurita N. 2013. Water isotopic variability in response to mesoscale convective system over the tropical ocean. *Journal of Geophysical Research: Atmospheres* 118: 10,376-10,90

Kurita N, Horikawa M, Kanamori H, Fujinami H, Kumagai To, et al. 2018. Interpretation of El Niño–Southern Oscillation-related precipitation anomalies in north-western Borneo using isotopic tracers. *Hydrological Processes* 32: 2176-86

Kurita N, Ichiyanagi K, Matsumoto J, Yamanaka MD, Ohata T. 2009. The relationship between the isotopic content of precipitation and the precipitation amount in tropical regions. *Journal of Geochemical Exploration* 102: 113-22

Lai CT, Ehleringer JR, Bond BJ, U KTP. 2006. Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the $\delta^{18}O$ of water vapour in Pacific Northwest coniferous forests. *Plant, Cell & Environment*

Larkin NK, Harrison DE. 2005. Global seasonal temperature and precipitation anomalies during El Niño autumn and winter. *Geophysical Research Letters* 32

Lawrence DM, Thornton PE, Oleson KW, Bonan GB. 2007. The Partitioning of Evapotranspiration into Transpiration, Soil Evaporation, and Canopy Evaporation in a GCM: Impacts on Land–Atmosphere Interaction. *Journal of Hydrometeorology* 8: 862-80

Lee J-E, Fung I. 2008. "Amount effect" of water isotopes and quantitative analysis of post-condensation processes. *Hydrological Processes* 22: 1-8

Li S, Levin NE, Chesson LA. 2015. Continental scale variation in ^{17}O-excess of meteoric waters in the United States. *Geochimica et Cosmochimica Acta* 164: 110-26

Lian X, Piao S, Huntingford C, Li Y, Zeng Z, et al. 2018. Partitioning global land evapotranspiration using CMIP5 models constrained by observations. *Nature Climate Change* 8: 640-6

Lis G, Wassenaar LI, Hendry MJ. 2007. High-precision laser spectroscopy D/H and $^{18}O/^{16}O$ measurements of microliter natural water samples. *Analytical Chemistry* 80: 287-93

Liu Y, Cobb KM, Song H, Li Q, Li CY, et al. 2017. Recent enhancement of central Pacific El Nino variability relative to last eight centuries. *Nature Communications* 8: 15386

Liu Z, Kennedy CD, Bowen GJ. 2011. Pacific/North American teleconnection controls on precipitation isotope ratios across the contiguous United States. *Earth & Planetary Science Letters* 310: 319-26

Liu Z, Yoshimura K, Bowen GJ, Buenning NH, Risi C, et al. 2014a. Paired oxygen isotope records reveal modern North American atmospheric dynamics during the Holocene. *Nature Communications* 5: 3701

Liu Z, Yoshimura K, Bowen GJ, Welker JM. 2014b. Pacific North American teleconnection controls on precipitation isotopes (δ18O) across the contiguous United States and adjacent regions: A GCM-based analysis. *Journal of Climate* 27: 1046-61

Long D, Longuevergne L, Scanlon BR. 2014. Uncertainty in evapotranspiration from land surface modeling, remote sensing, and GRACE satellites. *Water Resources Research* 50: 1131-51

Martens B, Miralles DG, Lievens H, van der Schalie R, de Jeu RAM, et al. 2017. GLEAM v3: satellite-based land evaporation and root-zone soil moisture. *Geosci. Model Dev.* 10: 1903-25

Martin NJ, Conroy JL, Noone D, Cobb KM, Konecky BL, Rea S. 2018. Seasonal and ENSO Influences on the Stable Isotopic Composition of Galápagos Precipitation. *Journal of Geophysical Research: Atmospheres* 123: 261-75

Maxwell RM, Condon LE. 2016. Connections between groundwater flow and transpiration partitioning. *Science* 353: 377-80

McDonnell JJ. 2014. The two water worlds hypothesis: ecohydrological separation of water between streams and trees? *WIREs Water* 1: 323-9

Midhun M, Lekshmy PR, Ramesh R, Yoshimura K, Sandeep KK, et al. 2018. The Effect of Monsoon Circulation on the Stable Isotopic Composition of Rainfall. *Journal of Geophysical Research: Atmospheres* 123: 5205-21

Miralles DG, Jiménez C, Jung M, Michel D, Ershadi A, et al. 2016. The WACMOS-ET project – Part 2: Evaluation of global terrestrial evaporation data sets. *Hydrol. Earth Syst. Sci.* 20: 823-42

Moore M, Kuang Z, Blossey PN. 2014. A moisture budget perspective of the amount effect. *Geophysical Research Letters* 41: 1329-35

Myhre G, Forster PM, Samset BH, Hodnebrog Ø, Sillmann J, et al. 2017. PDRMIP: A Precipitation Driver and Response Model Intercomparison Project—Protocol and Preliminary Results. *Bulletin of the American Meteorological Society* 98: 1185-98

O'Driscoll MA, DeWalle DR, McGuire KJ, Gburek WJ. 2005. Seasonal ^{18}O variations and groundwater recharge for three landscape types in central Pennsylvania, USA. *Journal of Hydrology* 303: 108-24

Oerter EJ, Bowen G. 2017. In situ monitoring of H and O stable isotopes in soil water reveals ecohydrologic dynamics in managed soil systems. *Ecohydrology* 10

Orlowski N, Pratt DL, McDonnell JJ. 2016. Intercomparison of soil pore water extraction methods for stable isotope analysis. *Hydrologic Processes* 30: 3434-49

Pauli JN, Newsome SD, Cook JA, Harrod C, Steffan SA, et al. 2017. Opinion: Why we need a centralized repository for isotopic data. *Proceedings of the National Academy of Sciences* 114: 2997-3001

Pfahl S, Wernli H. 2008. Air parcel trajectory analysis of stable isotopes in water vapor in the eastern Mediterranean. *Journal of Geophysical Research* 113: D20104

Putman AL, Feng X, Sonder LJ, Posmentier ES. 2017. Annual variation in event-scale precipitation δ^2H at Barrow, AK, reflects vapor source region. *Atmospheric Chemistry and Physics* 17: 4627-39

Risi C, Bony S, Vimeux F. 2008a. Influence of convective processes on the isotopic composition ($\delta^{18}O$ and δD) of precipitation and water vapor in the tropics: 2. Physical interpretation of the amount effect. *Journal of Geophysical Research: Atmospheres* 113: D19306

Risi C, Bony S, Vimeux F, Descroix L, Ibrahim B, et al. 2008b. What controls the isotopic composition of the African monsoon precipitation? Insights from event-based precipitation collected during the 2006 AMMA field campaign. *Geophysical Research Letters* 35: L24808

Risi C, Bony S, Vimeux F, Jouzel J. 2010. Water-stable isotopes in the LMDZ4 general circulation model: Model evaluation for present-day and past climates and applications to climatic interpretations of tropical isotopic records. *Journal of Geophysical Research* 115

Risi C, Noone D, Worden J, Frankenberg C, Stiller G, et al. 2012a. Process-evaluation of tropospheric humidity simulated by general circulation models using water vapor isotopic observations: 2. Using isotopic diagnostics to understand the mid and upper tropospheric moist bias in the tropics and subtropics. *Journal of Geophysical Research: Atmospheres* 117: n/a-n/a

Risi C, Noone D, Worden J, Frankenberg C, Stiller G, et al. 2012b. Process-evaluation of tropospheric humidity simulated by general circulation models using water vapor isotopologues: 1. Comparison between models and observations. *Journal of Geophysical Research: Atmospheres* 117: n/a-n/a

Rozanski K, Araguas-Araguas L, Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. In *Climate Change in Continental Isotopic Records*, ed. PK Swart, KC Lohmann, J McKenzie, S Savin, pp. 1-36. Washington, D.C.: American Geophysical Union

Salati E, Dall'Olio A, Matsui E, Gat JR. 1979. Recycling of water in the Amazon Basin: An isotopic study. *Water Resources Research* 15: 1250-8

Salmon OE, Shepson PB, Ren X, Collow M, Allison B, et al. 2017. Urban emissions of water vapor in winter. *Journal of Geophysical Research* 122: 9467-84

Samuels-Crow KE, Galewsky J, Hardy DR, Sharp ZD, Worden J, Braun C. 2014. Upwind convective influences on the isotopic composition of atmospheric water vapor over the tropical Andes. *Journal of Geophysical Research* 119: 7051-63

Schlesinger WH, Jasechko S. 2014. Transpiration in the global water cycle. *Agricultural and Forest Meteorology* 189: 115-7

Schoenemann SW, Steig EJ, Ding Q, Markle BR, Schauer AJ. 2014. Triple water-isotopologue record from WAIS Divide, Antarctica: Controls on glacial-interglacial changes in 17Oexcess of precipitation. *Journal of Geophysical Research* 119: 8741-63

Simonin KA, Roddy AB, Link P, Apodaca R, Tu KP, et al. 2013. Isotopic composition of transpiration and rates of change in leaf water isotopologue storage in response to environmental variables. *Plant, Cell & Environment* 36: 2190-206

Sodemann H, Schwierz C, Wernli H. 2008. Interannual variability of Greenland winter precipitation sources: Lagrangian moisture diagnostic and North Atlantic Oscillation influence. *Journal of Geophysical Research* 113

Soderberg K, Good SP, Wang L, Caylor K. 2012. Stable isotopes of water vapor in the vadose zone: A review of measurement and modeling techniques. *Vadose Zone Journal* 11

Syed TH, Famiglietti JS, Rodell M, Chen J, Wilson CR. 2008. Analysis of terrestrial water storage changes from GRACE and GLDAS. *Water Resources Research* 44: W02433

Tan M. 2014. Circulation effect: response of precipitation δ^{18}O to the ENSO cycle in monsoon regions of China. *Climate Dynamics* 42: 1067-77

Tharammal T, Bala G, Noone D. 2017. Impact of Deep Convection on the Isotopic Amount Effect in Tropical Precipitation. *Journal of Geophysical Research: Atmospheres* 122: 1505-23

Thompson LG, Davis ME, Mosley-Thompson E, Beaudon E, Porter SE, et al. 2017. Impacts of Recent Warming and the 2015/2016 El Niño on Tropical Peruvian Ice Fields. *Journal of Geophysical Research: Atmospheres* 122: 12688-701

Thompson LG, Mosley-Thompson E, Davis ME, Zagorodnov VS, Howat IM, et al. 2013. Annually Resolved Ice Core Records of Tropical Climate Variability over the Past ~1800 Years. *Science* 340: 945-50

Tian L, Yao T, MacClune K, White JWC, Schilla A, et al. 2007. Stable isotopic variations in west China: A consideration of moisture sources. *Journal of Geophysical Research* 112

Tipple BJ, Jameel Y, Chau TH, Mancuso CJ, Bowen GJ, et al. 2017. Stable hydrogen and oxygen isotopes of tap water reveal structure of the San Francisco Bay Area's water system and adjustments during a major drought. *Water Research* 119: 212-24

Torri G, Ma D, Kuang Z. 2017. Stable Water Isotopes and Large-Scale Vertical Motions in the Tropics. *Journal of Geophysical Research: Atmospheres* 122: 3703-17

Trenberth KE, Smith L, Qian T, Dai A, Fasullo J. 2007. Estimates of the global water budget and its annual cycle using observational and model data. *Journal of Hydrometeorology - Special Section* 8: 758-69

Vinther BM, Johnsen SJ, Andersen KK, Clausen HB, Hansen AW. 2003. NAO signal recorded in the stable isotopes of Greenland ice cores. *Geophysical Research Letters* 30

Volkmann T, Weiler M. 2014. Continual in situ monitoring of pore water stable isotopes in the subsurface. *Hydrology and Earth System Sciences* 18: 1819

Volkmann TH, Haberer K, Gessler A, Weiler M. 2016. High-resolution isotope measurements resolve rapid ecohydrological dynamics at the soil–plant interface. *New Phytologist* 210: 839-49

Vörösmarty CJ, Sahagian D. 2000. Anthropogenic disturbance of the terrestrial water cycle. *AIBS Bulletin* 50: 753-65

Vuille M, Werner M. 2005. Stable isotopes in precipitation recording South American summer monsoon and ENSO variability: observations and model results. *Climate Dynamics* 25: 401-13

Wang-Erlandsson L, van der Ent RJ, Gordon LJ, Savenije HHG. 2014. Contrasting roles of interception and transpiration in the hydrological cycle – Part 1: Temporal characteristics over land. *Earth System Dynamics* 5: 441-69

Wang C, Deser C, Yu J-Y, DiNezio P, Clement A. 2017. El Niño and Southern Oscillation (ENSO): A Review. In *Coral Reefs of the Eastern Tropical Pacific: Persistence and Loss in a Dynamic Environment*, ed. PW Glynn, DP Manzello, IC Enochs, pp. 85-106. Dordrecht: Springer Netherlands

Wang K, Dickinson RE. 2012. A review of global terrestrial evapotranspiration: Observation, modeling, climatology, and climatic variability. *Reviews of Geophysics* 50: RG2005

Wang L, Good SP, Caylor KK, Cernusak LA. 2012. Direct quantification of leaf transpiration isotopic composition. *Agricultural & Forest Meteorology* 154: 127-35

Wang N, Thompson LG, Davis ME, Mosley-Thompson E, Tandong Y, Jianchen P. 2003. Influence of variations in NAO and SO on air temperature over the northern Tibetan Plateau as recorded by $\delta^{18}O$ in the Malan ice core. *Geophysical Research Letters* 30: 2167

Wang XF, Yakir D. 2000. Using stable isotopes of water in evapotranspiration studies. *Hydrological Processes* 14: 1407-21

Wang Y, Cheng H, Edwards RL, Kong X, Shao X, et al. 2008. Millennial- and orbital-scale changes in the East Asian monsoon over the past 224,000 years. *Nature* 451: 1090-3

Wei Z, Yoshimura K, Wang L, Miralles DG, Jasechko S, Lee X. 2017. Revisiting the contribution of transpiration to global terrestrial evapotranspiration. *Geophysical Research Letters* 44: 2792-801

Welp LR, Lee X, Griffis TJ, Wen X-F, Xiao W, et al. 2012. A meta-analysis of water vapor deuterium-excess in the midlatitude atmospheric surface layer. *Global Biogeochemical Cycles* 26: GB3021

West AG, February EC, Bowen GJ. 2014. Spatial analysis of hydrogen and oxygen stable isotopes ("isoscapes") in ground water and tap water across South Africa. *Journal of Geochemical Exploration* 145: 213-22

Wong TE, Nusbaumer J, Noone DC. 2017. Evaluation of modeled land-atmosphere exchanges with a comprehensive water isotope fractionation scheme in version 4 of the Community Land Model. *Journal of Advances in Modeling Earth Systems* 9: 978-1001

Worden J, Noone D, Bowman K, Beer R, Eldering A, et al. 2007. Importance of rain evaporation and continental convection in the tropical water cycle. *Nature* 445: 528-32

Wright JS, Sobel AH, Schmidt GA. 2009. Influence of condensate evaporation on water vapor and its stable isotopes in a GCM. *Geophysical Research Letters* 36: L12804

Yang H, Johnson KR, Griffiths ML, Yoshimura K. 2016. Interannual controls on oxygen isotope variability in Asian monsoon precipitation and implications for paleoclimate reconstructions. *Journal of Geophysical Research: Atmospheres* 121: 8410-28

Yang X, Davis ME, Acharya S, Yao T. 2017. Asian monsoon variations revealed from stable isotopes in precipitation. *Climate Dynamics*

Yao T, Masson-Delmotte V, Gao J, Yu W, Yang X, et al. 2013. A review of climatic controls on $\delta^{18}O$ in precipitation over the Tibetan Plateau: Observations and simulations. *Reviews of Geophysics*: 2012RG000427

Yu W, Yao T, Tian L, Ma Y, Wen R, et al. 2015. Short-term variability in the dates of the Indian monsoon onset and retreat on the southern and northern slopes of the central Himalayas as determined by precipitation stable isotopes. *Climate Dynamics*: 1-14

Zhang X, Zwiers FW, Hegerl GC. 2007. Detection of human influence on twentieth-century precipitation trends. *Nature* 448: 461-6

Zhang Y, Peña-Arancibia JL, McVicar TR, Chiew FHS, Vaze J, et al. 2016. Multi-decadal trends in global terrestrial evapotranspiration and its components. *Scientific Reports* 6: 19124

Zhao S, Hu H, Tian F, Tie Q, Wang L, et al. 2017. Divergence of stable isotopes in tap water across China. *Scientific Reports* 7: 43653

Zwart C, Munksgaard NC, Kurita N, Bird MI. 2016. Stable isotopic signature of Australian monsoon controlled by regional convection. *Quaternary Science Reviews* 151: 228-35

Terms and Definitions

isotope – an atom of an element having a given number of neutrons in its nucleus, and thus a specific atomic mass

fractionation – change in isotope ratio due to mass selectivity of a chemical reaction or physical process

isotopologue – a molecule of a given compound having a given distribution of isotopes, and thus a specific molecular mass

δ – notation for reporting isotope ratios, equal to Rsample/Rstandard – 1; R the rare to common isotope ratio, Rstandard a reference value

Rayleigh distillation – model describing the evolution of a 2-component mixture (e.g., of water isotopes) as material is lost with fractionation

evapoconcentration – reduction in the volume of a water body due to evaporation

geostatistics – the study of the statistical properties and prediction of values associated with spatial phenomena

amount effect – an empirically observed correlation between precipitation amount and isotopic composition, often observed in monthly-average data from tropical and subtropical sites

Troposphere – the lowest layer of Earth's atmosphere, in which most weather phenomena occur, containing ~99% of all atmospheric water vapor

Convection – three-dimensional motion of a fluid (e.g., the atmosphere) due to (often thermall-driven) density contrasts

NAO – North Atlantic Oscillation, a mode of climate variability defined by sea level pressure patterns over the North Atlantic

ENSO – El Niño-Southern Oscillation, a mode of climate variability defined by sea surface temperature gradients across the tropical Pacific Ocean

PNA – Pacific North American pattern, a mode of climate variability defined by atmospheric pressure patterns over the Pacific and North America

Evapotranspiration – the land-atmosphere flux of water vapor comprised of plant transpiration and direct evaporation from soils and surface water bodies

Transpiration – loss of water vapor from plant leaves to the atmosphere by diffusion through pores in the leaf surface (stomata)

Recycling – the return of meteoric water to the atmosphere via evapotranspiration

Sidebar

Flux partitioning using water isotopes

Stable isotopes are used in many fields for flux partitioning: estimating the fraction of a net flux, often measured using traditional methods, that is associated with each of two or more specific processes. This application is possible wherever the processes result in component fluxes with different isotopic compositions. In this case the isotope composition of the net flux can is equal to the weighted average of the compositions for the component fluxes, and the relative magnitudes of each component can be calculated by solving a mixing equation, as in Eq. (1). The crux of any such application is obtaining estimates of the isotope values for each flux component (and the net flux) that are precisely resolved relative to the difference between components: the quality of the partitioning estimate increases with greater isotope separation between components and more precise estimates of the isotopic values. In ET partitioning, the transpiration and evaporation fluxes are usually well separated, isotopically (i.e. by many 10’s of ‰ for δ^2H). Obtaining precise estimates of transpiration and evaporation isotope compositions remains challenging, however, since these values may vary significantly over space and time, even for small-scale (e.g., plot-based) studies.

Table 1: Major web-accessible water isotope data collections

Name	URL	Access	Water types	Time covered	Notes
National Center for Atmospheric Research Climate Data Guide	https://climatedataguide.ucar.edu/climate-data/water-isotopes-satellites	N/A	Vapor	21st century	Summary of several major satellite-based vapor isotope data products; data must be downloaded from individual providers
National Ecological Observatory Network (NEON)	http://data.neonscience.org/home	Open	Precipitation, groundwater, surface water, vapor	2015 - present	Records from coordinated network of ~30 sites across the USA
Stable Water Vapor Isotopes Database (SWVID)	https://vapor-isotope.yale.edu/	Open	Vapor	21st century	Time series for ~40 globally distributed sites
Waterisotopes Database (wiDB)	http://waterisotopes.org	Open	All	~1960 - present	Metadata and contact info provided for records that cannot be downloaded directly
Water Isotope System for Data Analysis, Visualization and Electronic Retrieval (WISER)	https://nucleus.iaea.org/wiser/index.aspx	Account-based	Precipitation, river	~1960 - present	Long-term records from GNIP program; shorter time series from river monitoring network; visualization tools; # records per download limited

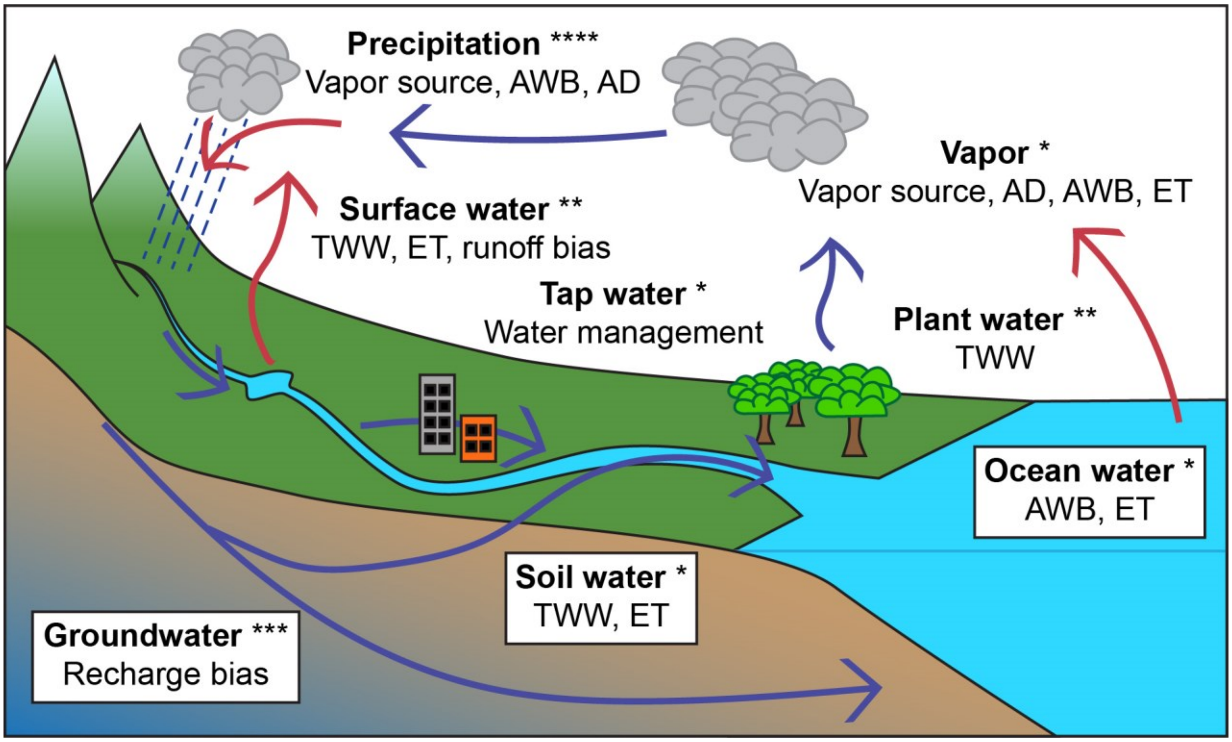

Figure 1: Schematic depiction of the global water cycle, showing major pools and fluxes (bold text) relevant to the applications discussed here. Asterisks indicate the adequacy of isotopic data, as compiled in databases and/or available in literature, for large-scale water cycle research, based on the authors' judgement and considering the inherent variability of each component (five would reflect full adequacy). Normal font gives applications, discussed herein, informed by each type of data (AD = atmospheric dynamics, AWB = atmospheric water balance, ET = evapotranspiration partitioning and/or continental recycling, TWW = two water worlds). Arrows show major isotope-fractionating (red) and non-fractionating (blue) fluxes.

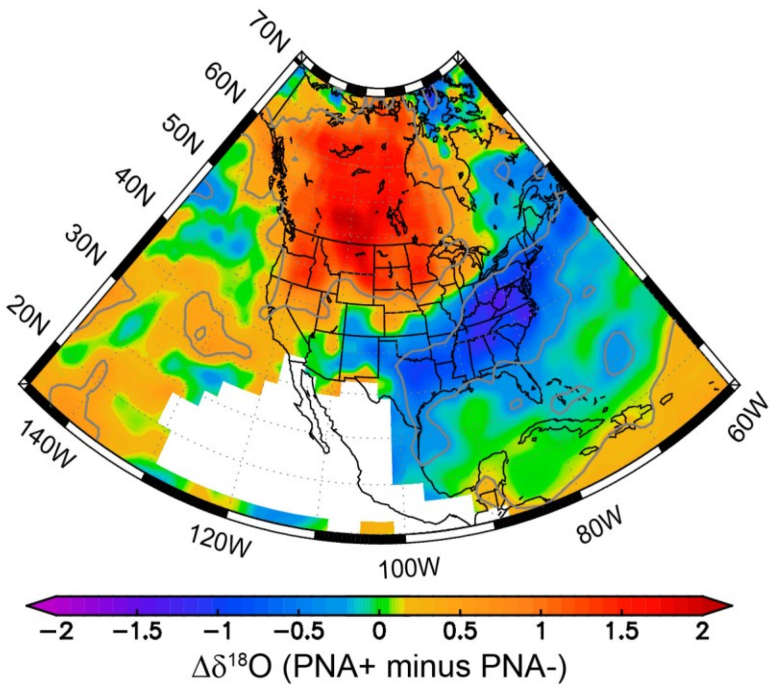

Figure 2: Spatial expression of the Pacific North American climate mode (PNA) in North American winter precipitation. Data from an isotope-enabled general circulation model were used to calculate differences between years of high (greater than 1, PNA+) and low (less than -1, PNA-) PNA index values. Grey outlines show areas of significant difference ($p < 0.1$). Modified from Liu et al. (2014a), reused with permission under a CC-BY license.

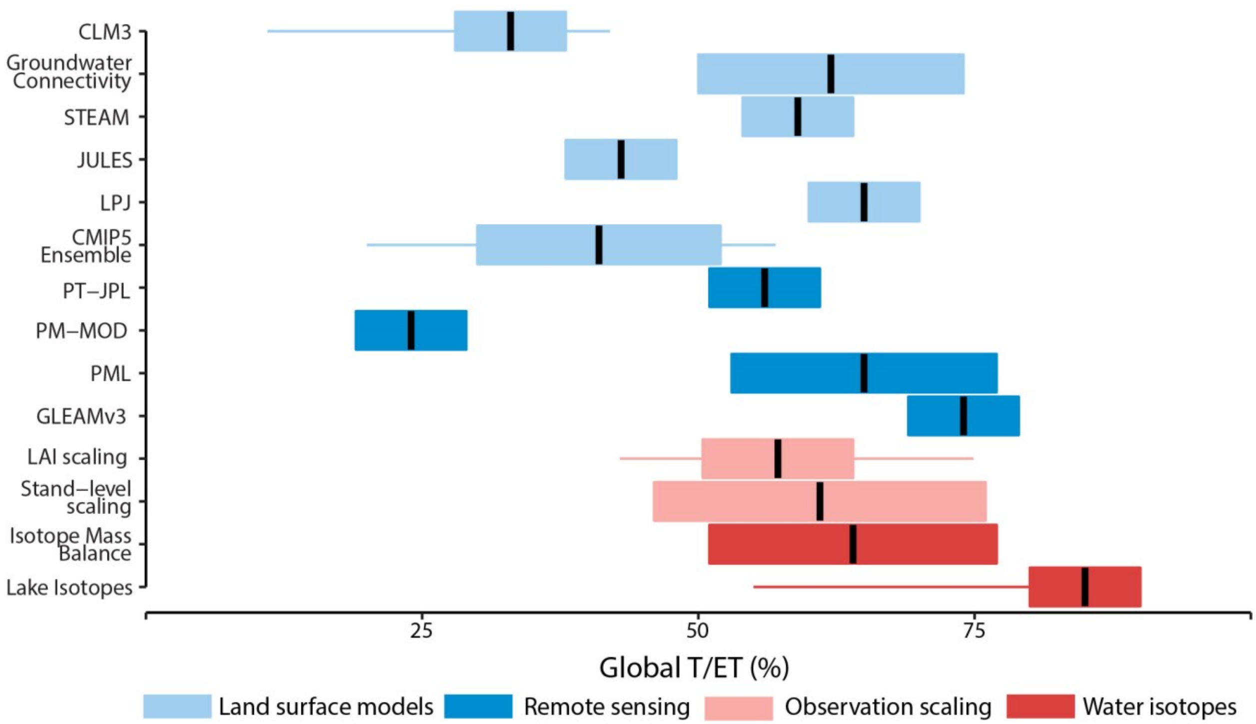

Figure 3: Global evapotranspiration partitioning estimates from a range of sources. All symbols show mean +/- 1 standard deviation, with whiskers giving minimum and maximum values if reported. If no measurer of variance was given a value of 5% was used. Original sources: CLM3 (Lawrence et al 2007); Groundwater Connectivity (Maxwell & Condon 2016); STEAM (Wang-Erlandsson et al 2014); JULES (Alton et al 2009); LPJ (Gerten et al 2005); CMIP5 ensemble (Lian et al 2018); PT-JPL and PM-MOD (Miralles et al 2016); PML (Zhang et al 2016); GLEAMv3 (Martens et al 2017); LAI scaling (Wei et al 2017); Stand-level scaling and Lake Isotopes (Schlesinger & Jasechko 2014); Isotope Mass Balance (Good et al 2015a).

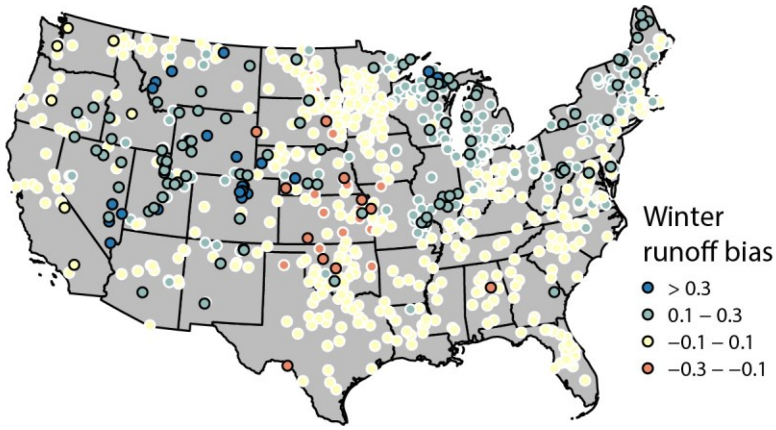

Figure 4: Runoff bias estimated using water isotope data from lakes. Results show difference between mean estimated fraction of winter water in the lake minus that estimated from regional climate model reanalysis data products. Symbols with black outlines show sites where the reanalysis-estimated mixtures had conditional probabilities less than 0.1 given the isotopic observations. Reprinted with modification by permission from Springer Nature: Springer Oecologia, Bowen et al. (2018).

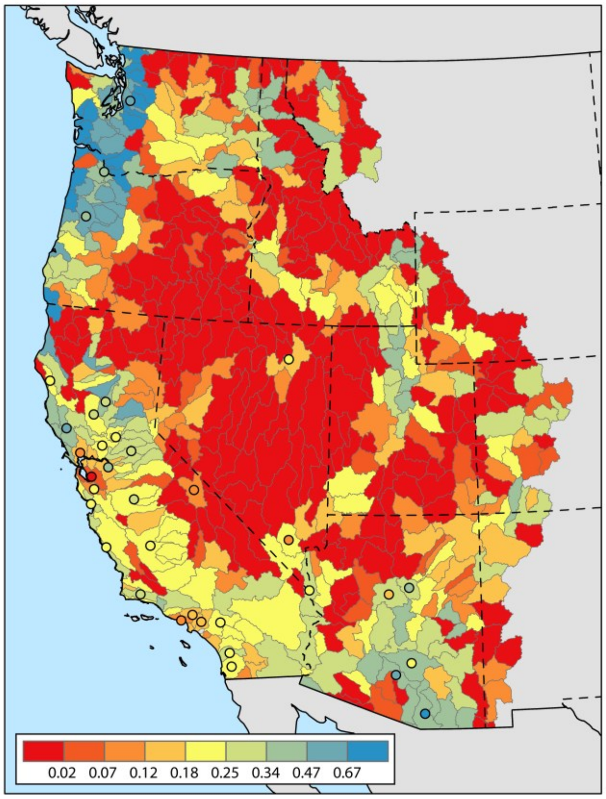

Figure 5: Estimated (points) and modeled (polygons) likelihood that western USA cities and towns use water resources from within their local drainage basin. Point values show average likelihoods estimated from tap water isotope data collected at 5 or more locations within a given basin. Model predictions are based on calibrated relationships between the isotope estimates and environmental and socioeconomic variables. Modified with permission from Good et al. (2014a). Copyright 2014, American Geophysical Union.