

Chapter 8

Approaches to Plant Hydrogen and Oxygen Isoscapes Generation

Jason B. West, Helen W. Kreuzer, and James R. Ehleringer

8.1 Introduction

The hydrogen and oxygen stable isotope ratios ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of plant water, the organic molecules that make up plant tissues and the gases produced during plant metabolism all record important aspects of a plant's growth environment and physiological activity at various spatial and temporal scales. These environmental signals are also modulated by morphological and other differences between species, including their responses to environmental variation. As such, stable isotope ratios are important tools for improved understanding in plant ecology and beyond (West et al. 2006). The connections between these isotopic records in plants and spatially-varying processes have been evident for decades. Recent efforts are expanding our mechanistic understanding (e.g., Barbour et al. 2007; Cuntz et al. 2007; Ripullone et al. 2008; Shu et al. 2008) and significant technological developments continue to provide the potential to significantly accelerate advances in understanding (e.g., Lis et al. 2008; Peters and Yakir 2008; Vendramini and Sternberg 2007). Among others, these advances will stimulate a significant increase in sampling intensity and model sophistication, allowing the generation of highly useful and data rich plant hydrogen and oxygen isoscapes and insights in a wide variety of fields (Helleriker and Richter 2008; Kahmen et al. 2008).

J.B. West(✉)

Texas AgriLife Research and Department of Ecosystem Science and Management, Texas A&M University System, College Station, TX
e-mail: jbwest@tamu.edu

H.W. Kreuzer

Pacific Northwest National Laboratory, Richland, Washington
e-mail: helen.kreuzer@pnl.gov

J.R. Ehleringer

Department of Biology, University of Utah, Salt Lake City Utah,
e-mail: ehleringer@biology.utah.edu

The focus for this chapter is on spatial variation in plant hydrogen and oxygen isotopes, with an emphasis on continental to global scales and the utility of isoscapes to improving understanding of a variety of processes. The central research areas in which plant $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isoscapes are likely to continue to yield significant insights are: (1) biosphere–atmosphere interactions, (2) past continental climate, and (3) forensic applications. The role of plant $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isoscapes in these three central research areas will form the focus of this chapter, with an attempt to identify common themes and approaches across disciplines rather than to treat these comprehensively. It should also be noted that many aspects of the use of plant $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in primarily non-spatial contexts have been reviewed elsewhere (e.g., Barbour 2007; Dawson et al. 2002; Ehleringer et al. 2002; Pataki et al. 2003; Yakir and Sternberg 2000).

In order to provide a mechanistic context for the generation and application of isoscapes to spatial problems, the major models of leaf water and cellulose $\delta^2\text{H}$ and $\delta^{18}\text{O}$ will be outlined first and existing efforts to utilize these models to make spatially explicit predictions will be described.

8.2 Leaf Water Isoscapes

Attempts to model large-scale spatial variability in leaf water $\delta^{18}\text{O}$ were first motivated by a desire to understand its effect on the isotopic composition of atmospheric gases, specifically atmospheric oxygen $\delta^{18}\text{O}$ (Farquhar et al. 1993; Gillon and Yakir 2001) and the $\delta^{18}\text{O}$ of CO_2 (Peylin et al. 1999). Leaf water may also be thought of as the fundamental starting point for plant H & O isoscapes, linking plant H & O isoscapes to meteoric, surface, and sub-surface waters, as well as plant organic compounds and their connection to the rest of the biosphere. In general, the isotopic composition of xylem water prior to entering the leaf will be very similar to the isotopic composition of plant source water, as there is generally no fractionation with root uptake (White et al. 1985), with this source water being derived ultimately from precipitation. This is true also only in the case that there is not evaporation from the stems being sampled (Dawson and Ehleringer 1993). There are two primary classes of models that describe the isotopic composition of leaf water: steady-state and non-steady-state and a range of approaches to modeling both, including a set of approaches to understanding within-leaf heterogeneity (e.g., Gan et al. 2003; Helliker and Ehleringer 2000; Ogee et al. 2007; Yakir et al. 1994). In this section, we discuss briefly the primary models that form the basis for describing leaf water isotope ratios and the current state of leaf water H & O isoscapes.

Leaf water isotope ratios have been modeled using modified open water body analogs (the Craig–Gordon model, Flanagan et al. 1991; Roden and Ehleringer 1999). A formulation of the steady-state leaf water isotope ratio, which includes diffusion through the leaf boundary layer, is:

$$R_e = \alpha^* \left[\alpha_k R_S \left(\frac{e_i - e_s}{e_i} \right) + \alpha_{kb} R_S \left(\frac{e_s - e_a}{e_i} \right) + R_A \left(\frac{e_a}{e_i} \right) \right] \quad (8.1)$$

where R_e is the isotope ratio of evaporatively-enriched leaf water (at the site of evaporation), R_S is the isotope ratio of the source water, R_A is the isotope ratio of the atmospheric water vapor, e_i is internal leaf vapor pressure, e_s is the leaf surface vapor pressure, and e_a is atmospheric vapor pressure. The equilibrium fractionation (α^*) is described as:

$$\alpha^* = \frac{R_L}{R_V} = e^{\left(\frac{a}{T^2} \frac{b}{T} - c \right)} \quad (8.2)$$

where e here is Euler's number, R_L is the liquid water isotope ratio ($^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$), R_V is the water vapor isotope ratio, and T is temperature in degrees Kelvin, and a & b are constants (Majoube 1971). Values for the constants are: $a = 1,137$, $b = 0.4156$, $c = 0.0020667$ for oxygen and $a = 24,844$, $b = 76.248$, and $c = 0.052612$ for hydrogen. The effect of diffusion is described by α_k and is estimated as 1.032 for oxygen and 1.0164 for hydrogen, with boundary layer diffusion estimated by $\alpha_k^{2/3}$ (Cappa et al. 2003). Observed leaf water isotope ratios are often less enriched than those predicted by C-G formulations, although monocot leaves yield a special case of greater enrichment not treated here (Helliker and Ehleringer 2000; Ogee et al. 2007). Modifications to account for this discrepancy recognize multiple pools within the leaf (Gan et al. 2002), as well as the incorporation of a Péclet effect (opposing effects of convection of water towards the site of evaporation and diffusion of the heavier isotopologues away from the site of evaporation; Barbour et al. 2000):

$$\rho = \frac{LE}{CD} \quad (8.3)$$

where L is the effective path length between the site of evaporation and the un-enriched source water, E is the evaporation rate ($\text{mol m}^{-2} \text{s}^{-1}$), C is the molar density of water ($55.5 \times 10^3 \text{ mol m}^{-3}$), and D is the diffusivity of the H_2^{18}O in water ($2.66 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

Non-steady state models of leaf water oxygen isotope ratios explicitly include the dynamic nature of changing leaf water isotope ratios as conditions change (Dongmann et al. 1974; Lai et al. 2006). A formulation that describes the non-steady leaf water $\delta^{18}\text{O}$ is:

$$\delta_{en}(t) = \delta_e(t) - [\delta_e(t) - \delta_{en}(t-1)] \exp\left(\frac{-\delta t}{\tau_\zeta}\right) \quad (8.4)$$

where $\delta_{\text{en}}(t)$ and $\delta_{\text{en}}(t - 1)$ represent non-steady state oxygen isotope ratios of leaf water at the sites of evaporation at time t and $t - 1$, respectively, and $\delta_{\text{e}}(t)$ is the leaf water $\delta^{18}\text{O}$ at steady state, predicted by Eq. 8.3. τ and ζ describe the turnover times and fractionations, which are dependent on leaf water volume, transpiration and relative humidity (Bariac et al. 1994; Cuntz et al. 2003). Further developments and improvements in modeling the isotopic composition of leaf water continue in this active area of research (Cuntz et al. 2007) and as our understanding of the controls on leaf water isotopic composition grows so will the sophistication of leaf water H & O isoscapes and their potential utility to a range of questions.

Global leaf water oxygen isoscapes have been produced based primarily on these models and with the goal of understanding the isotopic composition of atmospheric gases, (e.g., Ciais et al. 1997; Farquhar et al. 1993). Although clearly useful for specific research questions, these model outputs are not readily accessible across the scientific disciplines that could benefit from them. This is in spite of their potential utility to a number of researchers in diverse fields. Following the development of high resolution climate and precipitation isotope data layers, an approach that takes advantage of Geographic Information System tools was developed to generate global, continuous leaf water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isoscapes (West et al. 2008). These isoscapes were generated using a steady-state modeling approach similar to that described above, with input drivers that included global precipitation isoscapes (<http://waterisotopes.org>, also see Bowen this volume) and continuous climate grids from, in this case, the Climate Research Unit (<http://www.cru.uea.ac.uk>). The annual average (unweighted) leaf water isoscapes for the sites of evaporation from this work are shown in Fig. 8.1. These annual average isoscapes as well as the monthly isoscapes generated directly by the models are available now as GIS raster data layers (<http://isoscapes.org>), along with the model code and data layers used as inputs from the author, and will soon be available through a web-based modeling interface called “IsoMAP.” In addition to the steady-state Craig–Gordon output, other leaf water isoscapes were generated using a two-pool model for bulk leaf water and an additional output incorporating a Péclet effect. Clearly a large range of model structures and parameters could be envisioned and potentially appropriate for a specific question, making the GIS platform a productive avenue for streamlining modeling efforts and sharing among researchers. Certain assumptions were necessary for the generation of these isoscapes and should be noted. Among the most important were: (1) the model(s) accurately described the controls on long-term, average leaf water enrichment (across species), (2) long-term, average plant source water was approximated well by the annual average precipitation isoscapes, (3) long-term, average environmental conditions affecting leaf water isotope enrichment were approximated well by the long-term average climate grids, and (4) vapor was in isotopic equilibrium with plant source water (average precipitation). Adjustments of stomatal conductance and leaf temperature were also made (see West et al. 2008 for more information). Although these assumptions are difficult to test at global scales and

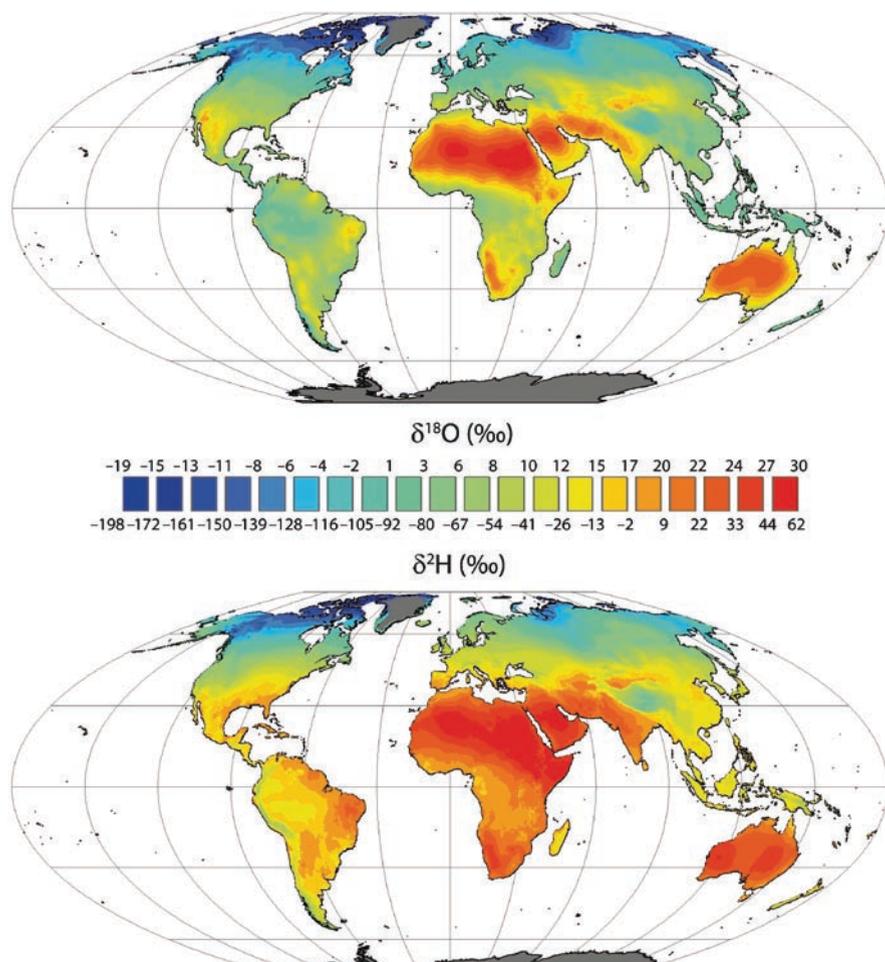


Fig. 8.1 Global mean annual average leaf water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isoscapes for the sites of evaporation within leaves (Eq. 8.1; reproduced with permission from West et al. 2008; see Appendix 1, Color Section)

are certainly incorrect at small scales in particular cases, the long-term average leaf water $\delta^{18}\text{O}$ isoscape produced values were quite comparable to measured average values and prior modeled latitudinal variation (West et al. 2008), suggesting that at a global scale, the modeling approach yielded leaf water isoscapes that approximated reasonably well the true long term average values. The advantage of the GIS approach using mechanistic models is that it is scalable to the objective and available data layers and can be interfaced with other spatially explicit data that could be relevant.

8.3 Modern Biosphere–Atmosphere Interactions

The integration of plant hydrogen and oxygen isoscapes into biosphere–atmosphere modeling and research is in its infancy. This is due in part to significant uncertainties in key variables and data limitations imposed by the labor and time intensive nature of stable isotope analysis of relevant components. However, we know that terrestrial vegetation has a significant impact on the hydrogen and oxygen isotopic composition of atmospheric gases, varies across space and time (Vaughn et al. this volume), and this impact is the result of a range of biological and biophysical processes (Cuntz et al. 2003; Farquhar et al. 1993; Hoffmann et al. 2004; Lee et al. 2007). In addition to the dominant role of soils and anthropogenic influences, biomass burning also has important consequences for the stable isotope ratios of CH₄ and H₂ globally, but with this component likely dominated by the fractionations associated with combustion, rather than spatial variation in the vegetation $\delta^2\text{H}$ (Gerst and Quay 2001; Yamada et al. 2006). Improved interpretation of the observed spatiotemporal variation in atmospheric gas $\delta^2\text{H}$ and $\delta^{18}\text{O}$ will develop in part through better understanding of the spatiotemporal variation in vegetation. That is, better vegetation H & O isoscapes will yield better understanding of coupled carbon and water cycle processes, especially at regional to global scales. The development of improved isoscapes follows in part improved mechanistic understanding of the relationships between vegetation, incoming radiation and climate. Exciting advances in this area are being made, for example in understanding the complex influences of clouds on plant physiology and therefore on the exchange of CO¹⁸O and CO₂ between vegetation and the atmosphere through intensive measurement and modeling efforts (Still et al. *in press*). New approaches to partitioning the transpiration and evaporation fluxes from the biosphere to the atmosphere based on the isotopic composition of precipitation and river stable isotopes in closed hydrologic basins are also being pursued (Ferguson and Veizer 2007). Here, if spatially explicit direct estimates of transpiration fluxes across these watersheds could be developed, this would provide an independent test of these indirect estimates. Although several unknowns remain, plant hydrogen and oxygen isoscapes hold significant promise in this area by contributing to improved understanding of the coupled carbon–water dynamics of the biosphere.

8.4 Inferring Past Environments

Understanding the controls on spatiotemporal variation in plant $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values is also critical to interpreting a wide range of proxies for past environments (Feng and Epstein 1996; Feng et al. 2007; Hou et al. 2008; Loader and Hemming 2004; Miller et al. 2006, also see Leavitt et al. this volume). Because the isotopic composition of plant compounds have the potential to record climate (e.g., the

oxygen isotope ratios of cellulose extracted from tree rings (Epstein et al. 1977; Gray and Thompson 1977), significant experimentation and modeling has been done to address fractionation associated with photosynthesis and post-photosynthesis biochemical reactions. Interest in spatial variation of the $\delta^2\text{H}$ & $\delta^{18}\text{O}$ of the organic components of plants has been focused primarily on bulk cellulose as a potential recorder of temperature (Gray and Thompson 1977), but has since expanded to other exciting potential proxies such as n-alkanoic acids from leaf waxes and compounds derived from cellulose that might be better recorders (phenylglucosazone; Hou et al. 2008; Sternberg et al. 2007). The fractionations associated with cellulose synthesis have been modeled as an essentially two-step process: photosynthetic formation of sucrose in isotopically-enriched leaf water followed by cellulose formation, either in the leaf or in the stem where the water environment is assumed to be similar to that of the plant source water. Fractionation factors for hydrogen and oxygen have been estimated as $\epsilon = -171\text{‰}$ and $+27\text{‰}$ (Yakir and Deniro 1990) for the effects of photosynthesis (note that Estep and Hoering 1981 estimated a range from -120‰ to -100‰ for hydrogen). The subsequent formation of cellulose (so-called heterotrophic fractionation) has been estimated as $\epsilon = +158\text{‰}$ for hydrogen and $+27\text{‰}$ for oxygen (Roden and Ehleringer 2000), again with other observations being similar (e.g., Luo and Sternberg 1992 estimated it to range from ranging from $+144\text{‰}$ to $+166\text{‰}$). These models group or “black box” a number of biochemical processes and make implicit or explicit assumptions that, if incorrect, could have significant consequences for interpretations of the isotopic composition of cellulose. For example, recent work on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of cellulose argues that, contrary to one of these assumptions, there are position-specific effects, calling into question efforts to interpret bulk cellulose $\delta^{18}\text{O}$ in terms of source water and climate influences only (Augusti et al. 2008; Sternberg et al. 2006). An additional, central assumption used to interpret cellulose $\delta^{18}\text{O}$ records in tree rings is that leaf temperature is coupled to atmospheric temperature. A recent paper reports striking constancy of leaf temperature across a wide range of environments, suggesting homeostasis in leaf temperature and only weak coupling with ambient temperatures (Helliker and Richter 2008). Continued efforts here promise to improve and refine models of isotopic fractionations in plants during metabolism, thus yielding greater accuracy in developing plant organic matter isoscapes. The isotopic compositions of several other plant compounds have recently been analyzed and described (e.g., leaf waxes, Sachse et al. 2004; Smith and Freeman 2006) and hold promise as additional proxies as our understanding of these plant-based archives improves.

A recent report provides an excellent example of the utility of spatially explicit sampling and analysis of modern wood cellulose $\delta^{18}\text{O}$ to improve the interpretation of cellulose $\delta^{18}\text{O}$ in the context of reconstructing paleoenvironmental conditions (Richter et al. 2008). Samples here were collected both across a wide range of environments and from several species in one area. Comparisons were made between the cellulose $\delta^{18}\text{O}$ and climate variables (temperature and relative humidity) and precipitation $\delta^{18}\text{O}$. As expected, strong correlations between precipitation and climate variables were observed. However, variation was observed across species

and the significant correlation with relative humidity limits the potential to interpret cellulose $\delta^{18}\text{O}$ simply in terms of temperature. Clearly large, distributed sampling networks and the development of improved cellulose isoscapes that reflect the drivers of spatiotemporal variability in cellulose or other plant compound $\delta^2\text{H}$ and $\delta^{18}\text{O}$ would significantly improve our ability to interpret these proxies (Hemming et al. 2007; Williams et al. 2007).

In addition to archives preserved in organic plant material, atmospheric gases trapped in ice cores have been studied for decades as rich stores of past atmospheric and environmental conditions. Much of the isotopic information in these cores is related to the activities of the biosphere, including that of vegetation. As discussed above, a significant effect of vegetation on the isotopic composition of atmospheric gases is the effect of leaf water $\delta^{18}\text{O}$ on atmospheric oxygen $\delta^{18}\text{O}$, which is enriched above ocean water and therefore results in a significant enrichment of atmospheric O_2 . This effect remains relatively poorly constrained because of the incomplete understanding of the spatiotemporal variation in leaf water $\delta^{18}\text{O}$, thus limiting inferences that can be drawn from atmospheric O_2 $\delta^{18}\text{O}$ trapped in ice cores. The difference between ocean water $\delta^{18}\text{O}$ and atmospheric oxygen is +23.8‰ and largely reflects photosynthesis and respiration in the marine and terrestrial biospheres, as well as other more minor influences. The magnitude of this “Dole effect” has remained surprisingly constant over approximately 130,000 years (Bender et al. 1994), with some more rapid variations reported recently from ice cores (Landais et al. 2007). Understanding these variations depends on an understanding of the primary controls on atmospheric oxygen $\delta^{18}\text{O}$, and leaf water $\delta^{18}\text{O}$ is an important factor here. Although great strides are being made in improving our understanding of the controls on leaf water $\delta^{18}\text{O}$, this remains an important area of research, especially as it relates to what controls variation in leaf water $\delta^{18}\text{O}$ at a range of spatiotemporal scales. Again, large sampling networks, continued efforts to understand and model the mechanistic controls, and further work on generating leaf water isoscapes and integrating them into larger modeling efforts promise to significantly improve the interpretability of these archives.

8.5 Forensic Applications

Hydrogen and oxygen isotope ratios of plant organic materials have shown significant utility for a wide array of research and applications related to human activities. These include archaeological trade routes and social interactions, modern criminal forensic reconstructions and investigations, and food and trade security and verification (Aramendia et al. 2007; DeNiro et al. 1988; Kelly et al. 2005; Keppler et al. 2007; Stern et al. 2006, 2008). Across all three categories, the utility of hydrogen and oxygen isotope ratios have been recognized as potential recorders of geographic origin and initial efforts at generating isoscapes for use in these fields are

ongoing. Two examples are described here demonstrating both the potential utility of plant H and O isoscapes and two different approaches to their generation with the intention that future work will further enhance the accuracy and utility of the models and isoscapes generated. We describe the methodological aspects in some detail to illustrate the range of questions, data, and decisions related to the generation of these isoscapes.

8.5.1 Cellulose Isoscapes – Counterfeit Money Tracking

As part of an effort to develop a tool for tracking sources of counterfeit money (the paper of which is composed largely of cotton cellulose) global cellulose isoscapes have been developed (Ehleringer 2009 unpublished). These cellulose isoscapes could also be utilized for forming expectations about spatial variability of cellulose isotope ratios, or in an inverse fashion to infer climate from cellulose isotopic compositions of spatial gradients. Just as in the leaf water example above, a GIS approach was taken. Monthly climate normal grids (WMO normal period of 1961–1990) produced at 10' resolution over the Earth's land surface for air temperature and relative humidity (CRU CL 2.0; <http://www.cru.uea.ac.uk>) were used. In order to produce a "cotton growing season" climate grid, each month's grid was masked with a "binary grid" produced from the monthly temperature grids. These binary grids were produced by replacing each grid cell with a "1" if the monthly average temperature was at least 16°C, or a "0" if that grid cell value was less than 16°C (null values remained null). Both the temperature and relative humidity monthly grids were then multiplied by their respective "binary grids" and then divided by the annual sum of binary grids. This produced an estimate of cotton growing season climate for each grid cell. This method results in some grid cells that have non-zero climate values based on as little as 1 month of climate. Clearly cotton is not grown in regions where the average monthly temperature rises above 16°C for only 1 or 2 months. These cells are eliminated from the final prediction map based on a raster of cotton growing regions described below.

Amount-weighted growing season precipitation isotope grids were also produced in a similar fashion. We began with monthly precipitation isoscapes estimated using modified published methods and at 10' resolution (Bowen this volume). Each monthly isotope grid was then multiplied by its respective binary 16°C grid described above. In addition, average monthly total precipitation grids were multiplied by their respective binary 16°C grids to produce approximate cotton growing season grids. Each month's growing season isotope grid ($\delta_{gs,i}$, where i = month number) was then multiplied by its respective growing season precipitation amount grid ($P_{gs,i}$). These 12 monthly grids were then summed and divided by the sum of the 12 monthly precipitation amount grids to give an amount-weighted growing season precipitation isotope grid (δ_{gs-wtd}). These input layers were then used to calculate cotton boll cellulose $\delta^{18}\text{O}$ at each raster grid cell using the

model described by Roden et al. (2000). Note that, as described previously, several of the characteristics of this model are the subject of active, current investigation and debate. As such, the predictions from the model should be taken as an initial attempt at a global cellulose isoscape, limited by available data and model uncertainties. In order to make cotton boll $\delta^{18}\text{O}$ predictions only for locations in which it is likely that cotton is grown, an additional raster layer was used to mask these “raw” predictions of cotton boll cellulose. Leff et al. (2004) employed satellite, agricultural census, and other data to produce global datasets of major crop producing regions. These datasets are available as 5' resolution global grids where each grid cell has a value that represents the fraction of that area covered by a given crop. The 5' grids made available by the authors were averaged to our 10' resolution using nearest neighbor re-sampling. Non-zero cells were assigned a value of one, and the cells with a value of zero retained that value. This resulted in a binary raster where each grid cell with a 1 represented a non-zero probability of having cotton growing within that cell. This binary grid was then multiplied by the above cotton boll cellulose $\delta^{18}\text{O}$ grids. This eliminated predictions for regions that are unlikely to produce cotton, but it may be thought of as a conservative elimination since it includes all cells that Leff et al. estimated contained any cotton production.

The resulting global $\delta^{18}\text{O}$ range covers approximately 36‰ (see Fig. 8.2). The highest predicted values in the world were for areas of Africa and the Middle East, whereas some of the lowest values predicted were for areas such as the eastern region of China and North Korea. Values predicted for the United States exhibited a mean of 29‰, with a low of 25‰, and a few isolated values reaching as high as 39‰. Comparisons with a small, poorly-constrained global collection of cotton fiber and currencies revealed reasonable overlap between data and model predictions. Of the 11 fiber samples obtained from nine countries, ten of the $\delta^{18}\text{O}$ values fell within the predicted ranges for those countries (Ehleringer 2009 unpublished). Although evaluation of the cotton isoscape is currently limited by comparison with “authentic,” the reasonable agreement at a large scale was encouraging. It is possible that isoscapes targeted at perhaps phenylglucosazone or other compounds along with a greater intensity of data for authentic could yield better predictive isoscapes. At present these cellulose isoscapes are useful for general targeting of efforts, in conjunction with additional information.

8.5.2 Plant Lipid Isoscapes – Ricin Source Tracking

Although leaf water and cellulose have been the most extensively modeled, other plant components, such as lipids, have the potential to yield important information about plant environments (Jia et al. 2008; Jones et al. 2008; Smith and Freeman 2006; Sternberg 1988; Xia et al. 2008). Motivation for understanding the drivers of geographic variation in plant lipids also includes their potential use in forensic reconstruction or intelligence. An example is provided by the oil derived from

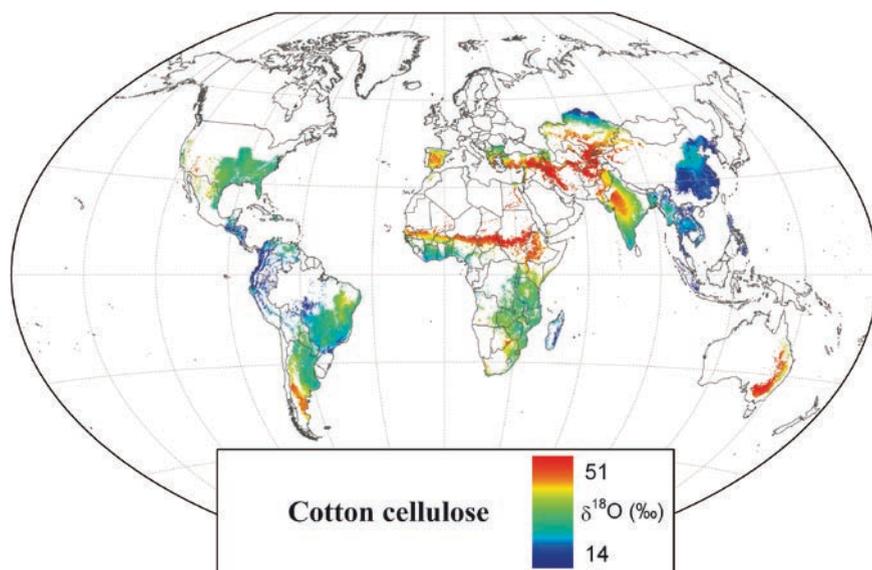


Fig. 8.2 Cotton $\delta^{18}\text{O}$ isoscape produced using a steady-state leaf water model (see Fig. 7.1), published fractionation factors for cellulose and masked for climate limitations and mapped agricultural production of cotton (see text for details; see Appendix 1, Color Section)

Castor Bean (*Ricinus communis*) seeds. From a forensics standpoint, the growth location of castor bean seeds used to make ricin (a deadly poison) is important. The simplest component of the castor bean seed is arguably castor oil. It is primarily ricinoleate (McKeon et al. 2000) and therefore from a compositional standpoint, should be relatively simple to model its isotopic composition, relative to the ricin itself, for example. In addition, the $\delta^2\text{H}$ of plant lipids is well correlated with plant source water isotopic composition. From a controlled experiment with known source water isotopic composition, a castor oil fractionation factor of $\alpha = 0.875$ was estimated (Ehleringer 2009 unpublished), a value that compares well to a previous model of lipid fractionation of $\alpha = 0.870$ (Sternberg 1988). With this experimentally derived model of castor oil, global castor oil hydrogen isoscape could be constructed, assuming that the source water is accurately estimated, the model is complete and there is no retention of the leaf water $\delta^2\text{H}$ in the castor oil (i.e., all, or nearly all of the hydrogen atoms exchange with the seed water that is close to the source water $\delta^2\text{H}$). Part of the outcome of this exercise is to determine the potential magnitudes of the effect of these uncertainties on global-scale modeling of plant lipids. The model shown above was executed using annual average precipitation values from the Bowen precipitation $\delta^2\text{H}$ isoscape to yield the castor oil $\delta^2\text{H}$ isoscape (Fig. 8.3). Individual predictions from the isoscape were then compared with measured values from plants grown at many locations around the world.

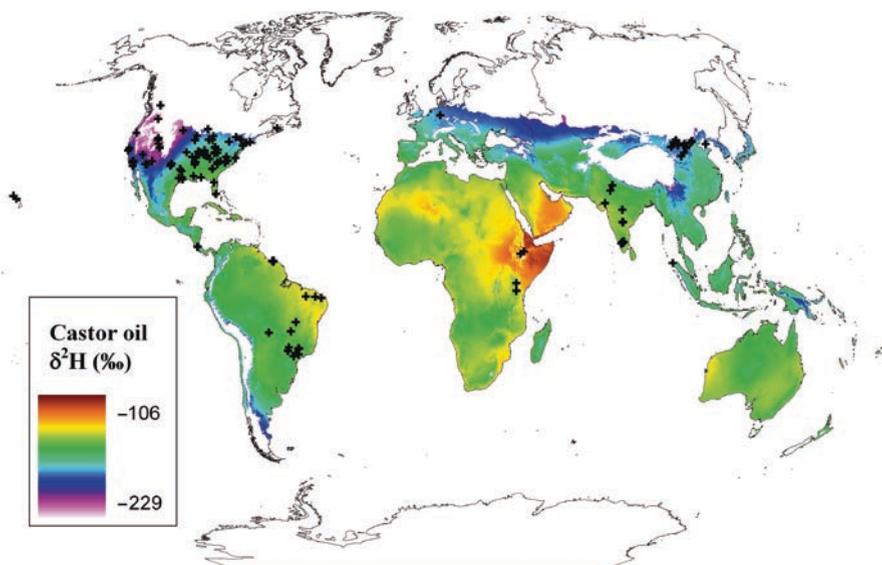


Fig. 8.3 Source water $\delta^2\text{H}$ and predicted castor oil $\delta^2\text{H}$ (‰) based on an experimentally-derived fractionation factor (see text). Land areas in *white* have mean annual temperatures below 7°C and are therefore unlikely to be regions where castor beans are grown. Continents are outlined in *black*. Locations of plants sampled and for which the $\delta^2\text{H}$ of extracted castor oil was determined are shown as *black crosses* (see Appendix 1, Color Section)

All measured values fell close to the 1:1 line suggesting that the very simplistic model predicts the observed castor oil $\delta^2\text{H}$ reasonably well, but does not capture the local and perhaps regional variability (Fig. 8.4). In evaluating the scatter around the 1:1 line of the model, it is important to understand the potential sources of variation. For the locations of the castor oil samples, the average 95% confidence interval for the modeled precipitation $\delta^2\text{H}$ was 6‰ (Bowen this volume), with a minimum of 1‰ and a maximum of 11‰. This suggests that some of the variation observed in Fig. 8.4 is likely due to precipitation model inaccuracies. Also, plant source water can vary from long term average annual precipitation and this potential source of variation is not well constrained here. Further, even under controlled conditions castor oil $\delta^2\text{H}$ exhibits substantial variability (potentially as much as $\pm 10\%$), contributing to uncertainty about the model itself (Ehleringer 2009 unpublished). In addition, no mechanisms for physiological effects were incorporated into the model.

Although modeled castor oil $\delta^2\text{H}$ values occur above and below the 1:1 line, a greater proportion of them fall above the line, suggesting a general over-prediction of castor oil $\delta^2\text{H}$ by this simple model. In addition, a large part of this group is composed entirely of tropical samples. This suggests that either the model does not perform well in the tropics, or that the map predictions for tropical precipitation consistently overestimate the actual castor bean source water $\delta^2\text{H}$. Although Bowen & Revenaugh point out that their model does generally account for the tropical

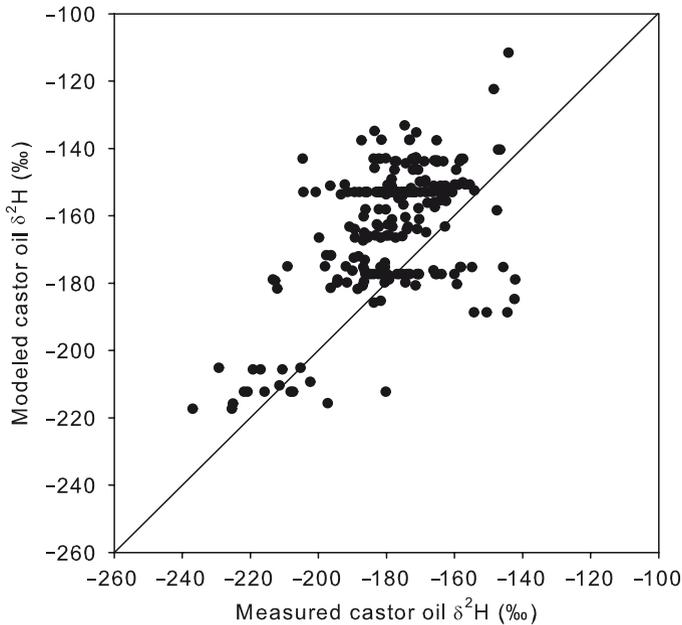


Fig. 8.4 Measured versus predicted castor oil $\delta^2\text{H}$ (‰). *Open circles* are samples from the temperate zone and the *closed triangles* are tropical samples (within 23.5° of the equator). The diagonal line is the 1:1 line

“rainout effect,” due to the somewhat poor data sampling density in the tropics, there might remain some consistent inaccuracies in the model predictions for that part of the globe. In addition, there was no provision for the effects of either evaporative enrichment of seed water or retention of the leaf water signal in the castor oil, both of which could increase its $\delta^2\text{H}$ value. Since the fractionation factor was estimated in a relatively dry environment (Salt Lake City, Utah), this might also have resulted in enrichment bias in the model.

This example demonstrates the promise and current challenges associated with plant isoscapes. Clearly there is a record of global spatial variation in this plant organic material and a simple model captures this variation reasonably well. However, there are also obviously important effects not incorporated in this particular model, including accounting for potential effects of evaporative enrichment.

8.6 Frontiers

Networks of observations of plant H & O isotope ratios are only recently being assembled (Hemming et al. 2007, Agarwaal et al. this volume) and are not yet able to supply the distributed data necessary to directly test large-scale spatial

predictions of plant stable isotope ratios. However, individual efforts at data collection and model application are improving our understanding and ability to test and develop models and descriptions of spatial variability in plant H & O isotope ratios. These efforts should be encouraged and supported. In addition, there are a number of large-scale enterprises underway that include distributed sampling and stable isotope analysis, including the National Ecological Observatory Network (NEON) in the USA and more commerce or forensics oriented initiatives (e.g., TRACE, <http://www.trace.eu.org/>; Kelly et al. 2005; Rossmann et al. 1999). Nascent efforts such as the IAEA-sponsored Moisture Isotopes in the Biosphere and Atmosphere (MIBA) should be encouraged and expanded to begin to describe the large-scale variability in plant stable isotopes and to include where possible measurements of the isotope ratios of atmospheric water vapor. These large, spatially explicit databases of plant or plant-derived materials continue to be populated and expanded to more species or products and are of obvious utility for geo-sourcing these materials.

Efforts to improve underlying models are also ongoing and should be enhanced and expanded, given the significant potential insights to be gained by improving our understanding of the spatio-temporal variability of plant hydrogen and oxygen isotope ratios. The technological capacity to collect and efficiently analyze large, spatially explicit databases is now available and should also be actively exploited. It will be critical that workers across disciplines share data, models, and model products, including isoscapes using available and forthcoming cyberinfrastructure. In addition to ongoing model improvements and distributed data collection, cross-disciplinary interaction will be critical to rapid advancements in the utilization of the information recorded in the spatiotemporal variation of plant hydrogen and oxygen stable isotopes. It is likely that efforts targeted at specific objectives (e.g., wine provenancing; West et al. 2007) can yield insights into other areas (e.g., wines as climate archives; Ingraham and Caldwell 1999). Two important frontiers can therefore be identified: (1) improve our mechanistic understanding and models of plant stable isotope ratios, including leaf water and plant organic components, and (2) develop and improve distributed data collection networks. It will be important to make progress on both fronts to enhance our understanding of these “recorders” of the biochemical and biophysical processes with which plants interact.

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