Database of published leaf wax $n$-alkane $\delta D$ values (section 4.2)

We compiled published data on hydrogen isotope values for leaf wax $n$-alkanes (C$_{27}$, C$_{29}$, C$_{31}$) for 355 plants from 59 separate localities around the world to examine variability in hydrogen isotope fractionation among plant groups and across climate gradients (Bi et al 2005, Chikaraishi & Naraoka 2003, Feakins & Sessions 2010, Hou et al 2007, Krull et al 2006, Liu et al 2006, Liu & Yang 2008, Pedentchouk et al 2008, Sachse et al 2009, Sachse et al 2006, Sessions et al 1999, Smith & Freeman 2006, Yang & Huang 2003). The samples are derived from sites on 4 continents that span estimated mean annual precipitation $\delta D$ ($\delta D_{MAP}$) values that range from -110 to -23‰. They represent a wide range of latitudes (from 23° S to 69° N), but are dominated by sites in the northern mid-latitudes (78% were collected between 30 and 60° N). These data are available in the supplementary material (Table X.2) and the global distribution is shown in Figure X.1.
Figure X.1: Distribution of sites contributing data to the global compilation of plant leaf wax hydrogen isotopic composition shown together with interpolated $\delta_{D_{MAP}}$ (Bowen, 2009) from which apparent fractionations were calculated.

We use the mean annual precipitation isoscape (Bowen 2009, Bowen & Revenaugh 2003) to constrain likely source water composition for the disparate sites in our compilation (Figure X.1). The hydrogen isotopic composition of precipitation has large and well-known spatial variations associated with changes in latitude, elevation, and continentalism (see section 1). Numerical interpolations of observational data provide a means to assess the hydrogen isotopic composition of precipitation even where observations are sparse. For most of the sites in our compilation, $\delta_{D_{MAP}}$ estimates have 95% confidence intervals of between 4‰ and 10‰ (Bowen, 2009). $\delta_{D_{MAP}}$ is less well constrained in the northwestern USA and northwestern China, where confidence in reported values is within 13‰. Inaccuracies in the mean annual precipitation isotope estimates impart some uncertainty to the apparent fractionation factors calculated here. However, the uncertainties – approximated by the reported confidence intervals – are unlikely to impart significant or regional biases in the comparisons across climatological and ecological gradients.

Precipitation isoscapes (Bowen, 2010) generally reflect broad patterns of the isotopic composition of plant source water (Bowen 2010, Liu & Yang 2008). We use modeled precipitation isotope ratio surfaces to investigate systematic patterns in the published studies of modern plant leaf wax D/H which often lack data for the isotopic composition of soil moisture.
We caution that the source of water taken up by the plant ($\delta D_w$) is not always identical to local mean annual precipitation ($\delta D_{MAP}$), especially in mountainous, arid or monsoonal climates (Brooks et al 2010, Feakins & Sessions 2010, Hu et al 2010, Krull et al 2006). We note that *in situ* measurements of plant water are invaluable to fully understand plant isotope systematics. Where additional constraints on the isotopic composition of plant source water or the seasonality of growth are available, we include these in the supplemental data and used these for $\varepsilon_{l/w}$ estimation.

We compare the calculated apparent fractionations with climate variables (temperature, relative humidity and latent heat flux) extracted by interpolation from the NCEP re-analysis data (1948-2009, 2.5° x 2.5° grid) (Kalnay et al 1996), see table X.2 (Excel spreadsheet). The NCEP resolution is sufficient to consider continent-scale but not regional climatic variables, similar to the $\delta D_{MAP}$ values. Annual mean air temperature (MAT), precipitation amount (MAP) and latent heat flux (LHF) were calculated for each site directly from the re-analysis data while evapotranspiration ($E_t$) was calculated from the latent heat flux.
Table X.1: Summary of apparent fractionations (‰) between C\textsubscript{27}, C\textsubscript{29} and C\textsubscript{31}n-alkanes and mean annual precipitation sorted by plant group divided by major life form, phylogeny and photosynthetic categories. Averages, standard deviations (S.D.), counts (n) and 95% confidence intervals (C.I.) calculated using a compilation of published values for \( \delta^{18}D_{C29} \) and \( \delta^{18}D_{MAP} \) estimates from the Online Isotopes in Precipitation Calculator version 2.2 (OIPC, [http://waterisotopes.org](http://waterisotopes.org)) or available on-site data (see Table X.2).

### Supplemental Table X.1: Apparent fractionations between leaf wax and source water compared between major taxonomic categories.

<table>
<thead>
<tr>
<th>Plant group</th>
<th>( \epsilon^{18}C_{27/MAP} ) (‰)</th>
<th>( \epsilon^{18}C_{29/MAP} ) (‰)</th>
<th>( \epsilon^{18}C_{31/MAP} ) (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{3} gymnosperms</td>
<td>-112 -112 16 14 8</td>
<td>-110 -110 24 15 12</td>
<td>-99 -103 25 15 12</td>
</tr>
<tr>
<td>C\textsubscript{3} dicots</td>
<td>-109 -110 28 7 5</td>
<td>-118 -113 30 8 4</td>
<td>-114 -110 31 6 5</td>
</tr>
<tr>
<td>C\textsubscript{3} monocots (e.g. grasses)</td>
<td>-135 -127 54 38 17</td>
<td>-147 -146 27 49 8</td>
<td>-146 -151 30 48 8</td>
</tr>
<tr>
<td>C\textsubscript{4} monocots (e.g. grasses)</td>
<td>-129 -131 22 48 6</td>
<td>-139 -132 25 56 7</td>
<td>-140 -136 25 58 7</td>
</tr>
<tr>
<td>C\textsubscript{4} dicots</td>
<td>-77 -78 18 7 13</td>
<td>-82 -84 27 8 19</td>
<td>-82 -92 27 8 19</td>
</tr>
<tr>
<td>CAM (monocots &amp; dicots)</td>
<td>-139 -142 23 4 22</td>
<td>-147 -145 13 5 12</td>
<td>-142 -142 14 6 11</td>
</tr>
<tr>
<td>Pteridophytes (ferns)</td>
<td>-103 -103 6 6 5</td>
<td>-108 -108 7 4 7</td>
<td>-114 -114 6 2 9</td>
</tr>
<tr>
<td>Bryophytes (e.g. mosses)</td>
<td>-101 -90 42 7 31</td>
<td>-135 -135 23 2 32</td>
<td>-114 -114 12 2 16</td>
</tr>
<tr>
<td>Lichens</td>
<td>-90 -91 22 4 21</td>
<td>-105 -105 6 2 9</td>
<td>-95 -95 9 2 12</td>
</tr>
</tbody>
</table>

1 Separated into categories based on life form, phylogeny and photosynthesis pathway.
2 Calculated with published source water value for local MAP if available, otherwise OIPC MAP, see Supplemental Table 1.
A Microsoft Excel workbook (Table X.2), published with the online version of the manuscript, contains the compiled dataset of leaf wax D/H and associated information extracted from the published literature. In addition we provide paired data extracted by interpolation from the precipitation isoscape and NCEP reanalysis data (1948-2009, 2.5° x 2.5° grid). Precipitation Isoscape data are derived from the Online Isotopes in Precipitation Calculator (Bowen, 2009). Climate data are derived from the NCEP Reanalysis data (1948-2009) provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA (Kalnay et al 1996).

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