1 Correlation of Bulk Sedimentary and Compound-Specific $\delta^{13}\text{C}$ Values
2 Indicates Minimal Pre-Aging of *n*-Alkanes in a Small Tropical Watershed
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25 **Abstract**

26 Inherent to sedimentary compound-specific isotopic proxies of paleoecological
27 and paleoclimate change is the assumption that biomarkers are coeval with
28 the surrounding sedimentary matrix. Compound-specific radiocarbon
29 analyses of lake and nearshore marine sediments have indicated a potential
30 offset between the ages of terrestrial biomarkers and theirsurrounding
31 sediments that could confound efforts to establish strong chronological control
32 for compound-specific isotopic data. We conducted high-resolution compound-
33 specific $\delta^{13}\text{C}$ analyses of *n*-alkanes ($\delta^{13}\text{C}_{\text{alkane}}$) in a well-studied sediment core
34 from Laguna Castilla, Dominican Republic, and compared the results to bulk
35 sedimentary $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{bulk}}$), fossil pollen, and sediment geochemistry to assess
36 potential ‘pre-aging’ of alkanes in the terrestrial environment prior to
37 deposition. We found significant positive correlations between $\delta^{13}\text{C}_{\text{bulk}}$ values
38 and $\delta^{13}\text{C}_{\text{alkane}}$ values, indicating little or no temporal lag in the response of
39 $\delta^{13}\text{C}_{\text{alkane}}$ values to vegetation change and thus little or no offset in the age of
40 terrestrially-derived compounds and the organic fraction of the sedimentary
41 matrix. While this study highlights the need for further research into the
42 variables affecting age offsets between proxy data, we propose the comparison
43 of $\delta^{13}\text{C}_{\text{bulk}}$ and $\delta^{13}\text{C}_{\text{alkane}}$ values as a method to assess potential age offsets
44 between compound-specific and other proxy datasets, particularly in small
45 watersheds with sediment recordscontaining a high proportion of
46 allochthonous organic matter. This method is more available to researchers
47 than obtaining numerous compound-specific radiocarbon analyses, which are
48 costly and not a routine service offered by radiocarbon facilities.

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50 *Key Words:* isotope; biomarker; radiocarbon; Dominican Republic; maize

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52 **1. Introduction**

53 Compound-specific carbon and hydrogen isotope analyses of sediment
54 records provide sensitive proxies of vegetation and hydrological change in
55 which sources (terrestrial vs. aquatic) of compounds such as *n*-alkanes or
56 alkanolic acids can often be determined by chain length (Brincat et al., 2000;
57 Huang et al., 2001; 2006; Tierny et al., 2008; Sachse et al., 2012; Douglas et al.,
58 2015; Schemmel et al., 2015). However, compound-specific radiocarbon
59 analyses of marine (Smittenberg et al., 2004; 2006; Drenzek et al., 2007; 2009;
60 Kusch et al., 2010) and lacustrine (Douglas et al., 2014) sediments have
61 indicated significant age offsets, sometimes millennia, between terrestrially-
62 derived organic compounds and the surrounding sedimentary matrix. This
63 ‘pre-aging’ of organic compounds is thought to result from a combination of
64 factors including long transport times, enhanced residence times in soil
65 organic carbon pools, and the slow breakdown of organic material (Douglas et
66 al., 2014). The observation of pre-aging of organic compounds in some records
67 raises questions about the chronological control for compound-specific
68 proxies and their comparability to other commonly studied proxies such as
69 fossil pollen, foraminifera, and bulk sedimentary isotopic ratios.

70 The most direct approach for assessing pre-aging of organic compounds
71 is comparison of matrix and compound-specific radiocarbon (^{14}C) content, but
72 compound-specific radiocarbon analyses are not a standard service

73 of radiocarbon laboratories and require specialized equipment (fraction
74 collectors and vacuum extraction lines) not commonly available to Quaternary
75 scientists. Another difficulty with compound-specific radiocarbon analyses is
76 that large sample sizes (several dry grams of organic material) are required to
77 obtain adequate compound mass to measure ^{14}C content, which can be
78 prohibitive when working with 5-cm diameter lake-sediment cores, especially
79 in depositional settings with low sedimentation rates. The large sample sizes
80 required can lead researchers to combine multiple compounds or organic
81 fractions to obtain adequate mass for compound- or fraction-specific ^{14}C
82 measurement, but this approach can be problematic, as each compound or
83 fraction potentially originates from different sources with different ^{14}C
84 reservoirs, residence times, or transport mechanisms (e.g. terrestrial vs.
85 aquatic). Here we take an alternate approach of assessing the temporal
86 response of a high-resolution *n*-alkane $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{alkane}}$) record to rapid
87 vegetation change through comparison with more commonly-employed proxies
88 in the field of paleolimnology, including fossil pollen, bulk stable carbon
89 isotopes, and bulk sediment geochemistry. We apply this approach to an
90 established multi-proxy sedimentary record from Laguna Castilla, Dominican
91 Republic (henceforth Castilla).

92 The bulk sedimentary stable carbon isotope value ($\delta^{13}\text{C}_{\text{bulk}}$) of lacustrine
93 sediments composed largely of allochthonous organic matter is an established
94 proxy of anthropogenic forest clearance and agriculture (Lane et al. 2004).
95 $\delta^{13}\text{C}_{\text{bulk}}$ values in lake sediments increase when native forest vegetation
96 composed of species that use the C_3 photosynthetic pathway is removed

97 and replaced by C₄ cultigens and agricultural weeds. At Castilla, rapid
98 fluctuations in $\delta^{13}\text{C}_{\text{bulk}}$ values closely match fluctuations in maize (*Zea mays*
99 subsp. *mays*) pollen concentrations and mineral influx values, indicating a
100 rapid response of the $\delta^{13}\text{C}_{\text{bulk}}$ record to short-term land use changes between
101 ~890 and 700 calyr B.P. Periods of crop cultivation near the lake are indicated
102 by increased maize pollen concentrations and mineral (allochthonous)
103 sediment influx, coinciding with increased $\delta^{13}\text{C}_{\text{bulk}}$ values (Lane et al., 2008).
104 These documented periods of rapid deforestation and subsequent crop
105 cultivation in the Castilla watershed are reflected in the proxy record (Lane et
106 al. 2008; 2009b) and offer the opportunity to assess the temporal sensitivity of
107 the $\delta^{13}\text{C}_{\text{alkane}}$ proxy to rapid vegetation change through direct comparison to
108 the $\delta^{13}\text{C}_{\text{bulk}}$ record.

109 **2. Study Site**

110 Laguna Castilla (18°47'51"N, 70°52'33"W, 976 m) is a small lake in the
111 Dominican Republic with a surface area of 1.2 ha and a watershed of ca. 25 ha
112 (Lane et al., 2008). The basin formed on a massive slump rotation block in the
113 unconsolidated sediments that make up the walls of the Río Cuevas valley.
114 Prior pollen, charcoal, and $\delta^{13}\text{C}_{\text{bulk}}$ analyses indicate prehistoric human
115 occupation, forest clearance, and agriculture from ~890–700 calyr B.P. (Lane et
116 al., 2009a).

117 **3. Materials and Methods**

118 We recovered a 7.8 m sediment core from Castilla using a PVC tube
119 fitted with a rubber piston for the uppermost sediments and a Colinvaux-
120 Vohnout locking piston corer for deeper sediments (Colinvaux et al., 1999).

121 Methods for pollen, mineral influx, and bulk organic carbon analyses are
122 described in Lane et al. (2009a), and organic compound extraction and
123 purification methods are presented in Lane et al. (2014).

124 Quantifications of *n*-alkane abundances were performed on an Agilent
125 6890 gas chromatograph (GC) equipped with a flame ionization detector at the
126 University of North Carolina Wilmington. Compounds were separated using a
127 Restek RTX-5 silica column (60 m, 0.25 mm i.d., 0.25 μm film thickness). The
128 oven temperature program for the GC was 70 °C isothermal for 1 minute, 20
129 °C/min to 180 °C, 4 °C/min to 320 °C, 320 °C isothermal for 5 minutes, 30
130 °C/min to 350 °C, and 350 °C isothermal for 1 minute. Relative contributions
131 of terrestrial vs. aquatic organic matter were estimated using the P_{aq} ratio of
132 Ficken et al. (2000), where:

$$133 \quad P_{aq} = (C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31})$$

134 Ficken et al. (2000) proposed that P_{aq} values less than 0.1 are indicative of
135 terrestrial organic matter, P_{aq} values between 0.1 and 0.4 are indicative of
136 emergent macrophyte organic matter, and P_{aq} values between 0.4 and 1.0 are
137 indicative of submerged or floating macrophyte organic matter.

138 Compound-specific carbon isotope analyses of *n*-alkanes were performed
139 on a Thermo Delta V Plus mass spectrometer interfaced with a Thermo 1310
140 gas chromatograph via an Isolink II device at the University of North Carolina
141 Wilmington. Compounds were separated using a Thermo TG-5 SILMS silica
142 column (60 m, 0.25 mm i.d., 0.25 μm film thickness). Injection temperatures
143 were 300 °C and samples were injected by a Thermo AI 1310 autosampler in
144 pulsed splitless mode. The oven temperature program for the GC was identical

145 to that used for quantification. An alkane mixture of known isotopic
146 composition provided by Indiana University (Alkane mixture B4) was injected
147 following every fourth sample to monitor instrument precision (1 s.e. = 0.2‰)
148 and for normalization of the sample data to the V-PDB (Vienna Pee Dee
149 Belemnite) scale using the methods and correction spreadsheet provided
150 by Polissar and D'Andrea (2014). All samples were analyzed in duplicate to
151 establish measurement precision.

152 4. Results

153 The Castilla P_{aq} values (mean=0.46) indicate balanced contributions of
154 aquatic and terrestrial organic matter to the sedimentary pool, with
155 notably higher aquatic contributions (increased P_{aq}) at ~730, 260, and 0 cm
156 and increased terrestrial contributions (decreased P_{aq}) at ~660, 600, and 365
157 cm (Figure 1). The C_{29} alkane (a common biomarker for terrestrial vegetation
158 (Sachse et al., 2012)) $\delta^{13}C$ record displays rapid fluctuations of up to 5‰ during
159 the period of prehistoric forest clearance and agriculture (~530–350 cm; ~900–
160 700 calyr B.P.) that correspond to increases in Poaceae (grass)
161 pollen percentages and maize pollen concentrations, decreases in *Pinus* (pine)
162 pollen percentages, and increased mineral influx rates (Figure 1). The long-
163 chain ($>C_{25}$), odd-numbered $\delta^{13}C_{alkane}$ values, typically interpreted as
164 originating from terrestrial vascular plants (Sachse et al., 2012), show
165 significant, positive correlations with sedimentary $\delta^{13}C$ values in the Castilla
166 sedimentary record (C_{25} , $r=0.63$, $F=16.2$, $p<0.01$; C_{27} , $r=0.55$, $F=11.0$, $p<0.01$;
167 C_{29} , $r=0.72$, $F=26.9$, $p<0.01$; C_{31} , $r=0.60$, $F=14.3$, $p<0.01$; Figures 1 and 2).

168 5. Discussion

169 The significant positive correlations between long-chain, odd-numbered
 170 $\delta^{13}\text{C}_{\text{alkane}}$ values and $\delta^{13}\text{C}_{\text{bulk}}$ values in the Castilla sedimentary record indicate
 171 a rapid temporal response of the $\delta^{13}\text{C}_{\text{alkane}}$ proxy to terrestrial vegetation
 172 change in the watershed. Residuals of the linear regressions between
 173 the $\delta^{13}\text{C}_{\text{alkane}}$ and $\delta^{13}\text{C}_{\text{bulk}}$ values are most likely related to the fact that $\delta^{13}\text{C}_{\text{bulk}}$ is
 174 measured on an amalgamation of organic materials from differing sources
 175 (allochthonous and autochthonous) with wide-ranging isotopic compositions
 176 (Meyers and Ishiwatari, 1993) while the long-chain alkane $\delta^{13}\text{C}$ signature is
 177 dominated by terrestrial plants (Sachse et al., 2012). Intermediate P_{aq} values
 178 for the record indicate a relatively even contribution of aquatic and terrestrial
 179 organic matter to the Castilla sedimentary organic carbon pool, likely
 180 influencing the $\delta^{13}\text{C}_{\text{bulk}}$ signal. Based on the radiocarbon chronology for the
 181 Castilla sediment record, the $\delta^{13}\text{C}_{\text{alkane}}$ record is responding to vegetation and
 182 land-use change on sub-decadal timescales and appears as temporally-
 183 sensitive to vegetation change as the $\delta^{13}\text{C}_{\text{bulk}}$, pollen, and mineral influx
 184 proxies (Lane et al., 2008). The magnitudes ($\Delta^{13}\text{C}$) of the $\delta^{13}\text{C}_{\text{alkane}}$ fluctuations
 185 closely match those of the $\delta^{13}\text{C}_{\text{bulk}}$ record, further indicating that the two
 186 proxies are responding to the same vegetation changes (Figure 1).

187 This rapid response of the Castilla $\delta^{13}\text{C}_{\text{alkane}}$ record to changes in land
 188 use contrasts with the findings of Douglas et al. (2014), who documented age
 189 offsets ($\Delta^{14}\text{C}$) of as much as 1200 years between leaf wax-derived organic
 190 compounds (*n*-alkanoic acids) and the sedimentary matrix in Lake
 191 Chichancanab, Mexico. Douglas et al. (2014) attributed this offset to long
 192 residence times of leaf waxes in the soil organic matter pool. The

193 researchers also noted a relationship between watershed area and $\Delta^{14}\text{C}$, with
194 larger watersheds showing greater pre-aging than smaller watersheds. The
195 small size of the Castilla watershed (ca. 25 ha) relative to the sites analyzed
196 by Douglas et al. (watersheds of 92 to 137 ha) may explain the rapid temporal
197 response of the Castilla $\delta^{13}\text{C}_{\text{alkane}}$ record to vegetation change and highlights the
198 need for further research on the influence of watershed size on proxy age
199 offsets. Another factor to consider is the influence of basin geology. The karst
200 geology of the Douglas et al. (2014) study sites could facilitate sub-surface
201 transport of lipids adsorbed to clays or organic matter originating from deep
202 soil horizons, a process less likely to occur in the unconsolidated marine
203 sediments of the Castilla watershed (Lane et al., 2009a).

204 The possibility does exist that all terrestrial proxies measured in the
205 Castilla record are pre-aged and correspond only because they are being
206 sourced from the same eroded sediments, particularly during the prehistoric
207 occupation phase when, based on rapid increases in mineral influx, erosion
208 rates appear to have been high. However, in this scenario, bulk and
209 compound-specific radiocarbon data would also co-vary and assessment of pre-
210 aging by direct comparison of the ^{14}C content of the two fractions would be
211 similarly deceptive. Furthermore, the P_{aq} values of the Castilla sediments
212 indicate roughly equal contributions of aquatic and terrestrial organic matter
213 to the sedimentary organic matter pool, and it is difficult to envision the
214 development of a ^{14}C reservoir effect in such a shallow basin (<5 m).

215 The notable offset in Castilla $\delta^{13}\text{C}_{\text{alkane}}$ and $\delta^{13}\text{C}_{\text{bulk}}$ values after
216 prehistoric human abandonment at Castilla (~350–150 cm; ~700–80 cal yr B.P.)

may be related to an increase in pinedominance on the landscape as indicated by peak *Pinus* pollen percentages during this period. Diefendorf et al. (2015) documented extremely low alkane abundances in the needles of pines and other conifers, and the Castilla $\delta^{13}\text{C}_{\text{bulk}}$ values may be responding to pine abundance in the watershed while the $\delta^{13}\text{C}_{\text{alkane}}$ record primarily reflects other vascular plants in the Castilla watershed and autochthonous organic matter, decreasing the match between the two records. This hypothesis is supported by the observation that the relationship between the two carbon isotope proxies is strongest when *Pinus* pollen percentages are lowest and by an increase in autochthonous inputs (as indicated by the P_{aq} values) during this interval (Figure 1).

Correlations between $\delta^{13}\text{C}_{\text{alkane}}$ and $\delta^{13}\text{C}_{\text{bulk}}$ values seem unaffected by changing sedimentation rates in the Castilla record. The strong correspondence between the two proxies that exists during periods of low (~750–550 cm; ~3500–1000 calyr B.P.; ~0.1 cm/yr) as well as high (~550–350 cm; ~1000–750 calyr B.P.; ~0.9 cm/yr) sedimentation rates indicates minimal impacts of sedimentation rates on age offsets between $\delta^{13}\text{C}_{\text{alkane}}$ and $\delta^{13}\text{C}_{\text{bulk}}$ data. Further studies assessing the potential age offsets between organic compounds and the remaining sedimentary matrix at single sites with varying sedimentation rates through time or at multiple sites with contrasting sedimentation rates will be necessary to fully assess the impacts of sedimentation rates on proxy age offsets and correspondence.

6. Conclusion

240 Compound-specific radiocarbon analyses are not offered as a standard
241 service by radiocarbon laboratories, are costly, and require very large sample
242 sizes, leading to their rare application in paleolimnological studies of
243 freshwater lakes. The one lake study that has employed this technique
244 (Douglas et al., 2014) documented pre-aging of organic compounds due to long
245 transport and residence times prior to deposition in sedimentary basins. At
246 Castilla, rapid changes in $\delta^{13}\text{C}_{\text{alkane}}$ values that correlate strongly with
247 $\delta^{13}\text{C}_{\text{bulk}}$ values indicate a rapid response of the proxy to vegetation change and
248 no apparent pre-aging of organic compounds.

249 Further research is needed to fully understand variables that can lead
250 to age offsets between organic fractions in lacustrine systems, particularly
251 watershed size, geology, and sedimentation rate. However, the Castilla record
252 indicates that age offsets between individual compounds and the sedimentary
253 matrix may be minimal in small watersheds with relatively high contributions
254 of allochthonous organic matter, regardless of sedimentation rate. We propose
255 comparison of high-resolution $\delta^{13}\text{C}_{\text{alkane}}$ and bulk sedimentary proxies as a
256 means for initial assessment of age offsets in such locations. This approach is
257 feasible as watershed size and sedimentation rates are relatively easy to
258 determine, and proxy evidence of organic matter source is commonly collected
259 in conjunction with compound-specific and bulk stable isotopic analyses of
260 sedimentary records in the form of biomarker quantification and bulk
261 geochemical ratios (e.g. the P_{aq} index or C:N ratios, respectively). At present,
262 this approach is likely to be more accessible to, and affordable for, researchers
263 than compound-specific radiocarbon analyses of multiple organic

fractions. Given the numerous variables that control $\delta^{13}\text{C}_{\text{bulk}}$ values, records that lack a significant correlation between $\delta^{13}\text{C}_{\text{bulk}}$ and $\delta^{13}\text{C}_{\text{alkane}}$ values do not conclusively demonstrate the existence of an age offset between organic fractions; however, we argue that records with a significant positive correlation between $\delta^{13}\text{C}_{\text{bulk}}$ and $\delta^{13}\text{C}_{\text{alkane}}$ values, particularly in small watersheds, are unlikely to have any such offset.

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360 **Figure Captions**

362

363 **Figure 1.** Comparison of Laguna Castilla fossil pollen, mineral influx, P_{aq} , and
 364 stable isotope data. Error bars represent 1 standard error of the mean. Pollen,
 365 mineral influx, and bulk $\delta^{13}C$ data are replotted from Lane et al. (2009a).
 366 Vertical lines on the P_{aq} graph represent likely sources of organic material
 367 based on Ficken et al. (2000).

368

369 **Figure 2.** Linear regression analyses of stratigraphically coeval bulk
 370 sedimentary $\delta^{13}C$ and n -alkane $\delta^{13}C$ values for the C_{25} , C_{27} , C_{29} , and C_{31}
 371 homologues. Error bars represent 1 standard error of the mean.

Figure 1

Figure 2