Corrigendum to: Anomalously low radiocarbon content of modern *n*-alkanes

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In our recent paper (Lane et al., 2021), we documented an anomalously low ^{14}C content of mixed *n*-alkanes isolated from modern leaves of terrestrial trees and grasses relative to bulk leaf tissue and suggested that these results indicate a potentially strong fractionation against ^{14}C during lipid biosynthesis in plants, as documented for ^{13}C and ^{2}H. In this corrigendum, we present new evidence of possible contamination of our samples as determined by ^{14}C analysis of the process (hexane) blank sample and correct our omission of the relevant work of Cisneros-Dozal et al. (2016). The hexane blank yielded insufficient CO_2 for ^{14}C measurement, but did yield a small quantity of CO_2 of unknown origin. Regardless, while this contamination may have inflated the age offsets between isolated *n*-alkane mixtures and bulk leaf tissue, it does not fully explain the apparent age offsets between isolated *n*-alkane mixtures and bulk leaf tissue.

Cisneros Dozal et al. (2016) analyzed the compound-specific ^{14}C content of individual and combined *n*-alkane homologues isolated from a modern plant specimen. They used preparative capillary gas chromatography (PCGC) to isolate individual *n*-alkane homologues and homologue mixtures prior to ^{14}C analysis, in contrast to our approach of using urea adduction to purify *n*-alkane homologue mixtures for ^{14}C analysis. Cisneros-Dozal et al. (2016) reported consistently lower ^{14}C content in their *n*-alkane homologues compared to bulk tissue (mean bulk tissue $F^{14}C = 1.224 \pm 0.006$), but with fraction modern ($F^{14}C$) values within 1–2σ of the $F^{14}C$ value of the

bulk tissue for some of their isolated C_{29} and C_{31} homologues. However, their mixed homologue samples had $F^{14}C$ values that consistently fell outside of the 2σ range of the bulk tissues ($F^{14}C$ values from 1.131 to 1.221).

Our mixed *n*-alkane homologue samples yielded $F^{14}C$ offsets relative to bulk tissue (Lane et al., 2021) that were greater on average than those reported by Cisneros-Dozal et al. (2016) (Table 1). One possible explanation for this difference is contamination of our *n*-alkane mixtures with fossil-fuel derived urea during *n*-alkane purification. We noted this possibility in our original paper, but found it unlikely that urea or other contaminants could be present in quantities sufficient to account for the full ^{14}C offsets and yet not be detectable during sample purity checks via gas chromatograph flame ionization detector (GC-FID) analyses.

In light of the contamination assessment approaches of Cisneros-Dozal et al. (2016), we obtained and present here the gas yields for our samples and the process (hexane) blank also subjected to urea adduction as measured by the NOSAMS facility during graphite conversion. The hexane blank did not yield adequate CO_2 for radiocarbon measurement, but did yield 1.287 μmol of CO_2 as reported by NOSAMS (Table 1). Conservatively assuming this CO_2 is derived purely from urea contamination containing no ^{14}C, and that contamination of all sample-derived CO_2 was equivalent to that of the hexane blank, we back calculated corrected ages of our *n*-alkane samples using the mass balance equation:

$$F^{14}C_{theoretical} = f_{alkane\_CO2} \times F^{14}C_{alkane} + f_{urea\_CO2} \times F^{14}C_{urea} \qquad \text{(Eqn 1)}$$

where $F^{14}C_{theoretical}$ represents the modern fraction ^{14}C in the analyzed sample containing lipids and presumed urea contamination, f_{alkane_CO2} represents the molar fraction of CO_2 derived from the *n*-alkanes assuming urea contamination is equivalent to that of the hexane blank, $F^{14}C_{alkane}$ represents the assumed modern fraction ^{14}C of the lipids is equivalent to the bulk tissues, f_{urea_CO2}

represents the molar fraction of CO_2 derived from the urea contamination assumed to be equivalent to that of the hexane blank, and $F^{14}C_{urea}$ is assumed to be zero representing the fossil-fuel origin of the urea.

The process (hexane) blank approach, also known as the direct method, is common practice in radiocarbon analyses to quantify potential contamination of sample batches processed in parallel (Santos et al., 2010; Zolikowski and Druffel, 2009). The results of our calculations (Table 1) show that urea contamination quantities equivalent to that of the blank does lead to corrected values but cannot explain the full magnitude of all of the ^{14}C offsets between the *n*-alkane mixtures and bulk leaf tissue. The theoretical $F^{14}C_{sample}$ values that account for urea contamination are still consistently lower than that of the measured $F^{14}C$ values for all but the *Digitaria sanguinalis* (L.) Scop. sample. This result indicates potentially large differences in biosynthetic ^{14}C fractionation between species or that urea contamination may not be consistent among samples. However, the process blank approach is the most common approach used by researchers and radiocarbon facilities to assess potential radiocarbon contamination and hence we have applied it here. This evidence of potential contamination means the quantitative magnitude of our $F^{14}C$ offsets between *n*-alkane mixtures and bulk leaf tissues may not be accurate, but our data still indicate considerable offsets between bulk tissues and *n*-alkane homologue ^{14}C content in multiple cases even after conservatively accounting for potential contamination using the process blank approach.

Some of the $F^{14}C$ offsets between *n*-alkane mixtures reported by Cisneros-Dozal et al. (2016) that are free from possible urea contamination are still quite large when converted to radiocarbon age offsets and are of similar magnitude to the age offsets we reported for our modern plant samples. For example, Cisneros-Dozal (2016) reported a corrected $F^{14}C$ value for

71 their mixed C_{23}–C_{27}, C_{33} sample of 1.131 ± 0.052. Using the radiocarbon age conversion
72 equations of Stuiver and Polach (1977), this represents a ~635 year radiocarbon age offset from
73 their bulk leaf tissue ($F^{14}C$ = 1.224 ± 0.006). Similarly, the $F^{14}C$ value reported for their total *n*-
74 alkane sample ($F^{14}C$ = 1.154 ± 0.017) equates to a ~470 year radiocarbon year offset from the
75 bulk leaf tissue ($F^{14}C$ = 1.224 ± 0.006). These centennial-scale offsets are of similar magnitude
76 to those we report for our modern plant samples and represent potentially large sources of error
77 in compound-specific radiocarbon chronologies or carbon residence time estimates. We also note
78 that Cisneros-Dozal et al. (2016) document significant column contamination in their samples,
79 indicating that the PCGC approach they used is also prone to radiocarbon contamination that
80 must be corrected for, preferably using standards of known ^{14}C content processed in an identical
81 manner to samples.
82 Our overarching conclusion remains unchanged: minor contamination of our samples is
83 possible (Lane et al., 2021), but this contamination seems unlikely to explain the full magnitude
84 of the age offsets between *n*-alkanes and bulk leaf tissue or the variation in offsets between
85 species. The data presented by Cisnero-Dozal et al. (2016) also point to potential homologue-
86 specific variations in ^{14}C incorporation during biosynthesis and evidence of significant column
87 bleed contamination of *n*-alkanes using the PCGC approach. Our results, and those of Cisneros-
88 Dozal et al. (2016), demonstrate that potential fractionations of radiocarbon during biosynthesis
89 of lipids and other biomarkers deserve further attention. Such fractionation could result in
90 misinterpretations of compound-specific radiocarbon ages and their environmental contexts.
91 Additional methodological assessments are also needed of potential contamination introduced
92 during sample purification and analysis of compound-specific radiocarbon samples.
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References

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Table 1. Calculation of theoretical $F^{14}C$ values for *n*-alkane samples assuming consistent urea contamination among *n*-alkane ^{14}C samples.

Sample	Plant Type	$F^{14}C_{Bulk\_Tissue}$	$F^{14}C_{Alkane}$	CO_2 (µmol)	f_{alkane_CO2}	f_{urea_CO2}	$F^{14}C_{theoretical}$	$F^{14}C_{Alkane} - F^{14}C_{theoretical}$
Liquidambar styraciflua L.	Angiosperm Tree (C_3)	Not Measured	0.8681	43.29	0.97	0.03	–	–
Magnolia virginiana L.	Angiosperm Tree (C_3)	1.0131	0.8156	20.67	0.94	0.06	0.9537	-0.1381
Quercus nigra L.	Angiosperm Tree (C_3)	Not Measured	0.8105	5.46	0.81	0.19	–	–
Quercus virginiana Mill.	Angiosperm Tree (C_3)	1.0138	0.9235	43.75	0.97	0.03	0.9848	-0.0613
Aristida stricta Michx	Graminoid (C_4)	1.0121	0.8658	48.79	0.97	0.03	0.9948	-0.1290
Digitaria sanguinalis (L.) Scop.	Graminoid (C_3)	1.0080	0.9373	12.28	0.91	0.09	0.9124	0.0249
Hexane blank[1]	N/A	0.0000	0.0000	1.287	–	–	–	–

[1]Hexane sample exposed to urea purification procedure.