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RADIOCARBON VARIATION IN CHARCOAL/WOOD AND SOIL FRACTIONS FROM A LOESSIC SETTING IN CENTRAL ALASKA

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ABSTRACT. The Healy's Lucky Strike site in central Alaska has an exceptional Holocene loess-paleosol sequence that has afforded us the ability to look at variation in ^{14}C dating of soil organic matter (SOM) fractions in a high-latitude loess setting. Our work has focused on comparing the radiocarbon ages of charcoal and wood to base-soluble humic acids (HA) and base-insoluble soil residue (SR) fractions from bulk soil samples. Charcoal/wood ages were younger than HA ages reflecting the later stages of vegetation development at the surface of the soils prior to being covered by loess accumulation; the HA ages generally reflect the overall timing of soil formation and mean residence time of SOM. Soil residue ages are older than charcoal/wood and HA ages. SOM ages at this location become increasingly older than charcoal/wood ages with depth, reaching 750 to 8070 yr in difference and associated with weakly developed soils at the lowest depths. We suggest the drastic SOM age differences at this site result from the differential incorporation of small particles of coal throughout the sedimentary matrices introduced older contaminants to SR fractions.

KEYWORDS: Radiocarbon dating, soil organic matter, loess, interior Alaska.

INTRODUCTION

Radiocarbon dating organic matter from buried soils can be used to establish chronologies for geological and archaeological sequences, especially when deposits are devoid of materials (such as charcoal, wood, and bone collagen) that are generally accepted to provide more accurate results for high-resolution chronologies. ^{14}C ages on soil organic matter (SOM) have been used to construct reliable temporal frameworks for understanding landscape evolutionary histories and regional archaeological sequences in several regions with relatively arid environments where charcoal, wood, and bone may have lower rates of preservation (Holliday et al. 1996, 2006; Johnson and Willey 2000; Holliday 2001; Mandel 2008; Mayer et al. 2008). ^{14}C ages of SOM have also been used to study "mean residence times" and renovation or turnover rates of organic matter and carbon in soil reservoirs (Cherkinsky and Brovkin 1993; Matthews 1993; Cherkinsky 1996; Alexandrovskiy and Chichagova 1998; Rabbi et al. 2013).

However, ^{14}C dating of SOM has also produced mixed results and is fraught with inconsistencies among the targeted fractions [i.e. acid-soluble (or fulvic acids), base-soluble (or humic acids), and base-insoluble fractions (also referred to as humins or soil residues)] (Geyh et al. 1983; Scharpenseel and Becker-Heidmann 1992; Matthews 1993; Orlova and Panychev 1993; Martin and Johnson 1995; Holliday 2001; McGeehin et al. 2001; Pessenda et al. 2001; Wang et al. 2003).

The fractions of SOM most consistently targeted for ^{14}C dating are the base-soluble acids, or *humic acids* (HA), and acid- and base-insoluble fractions, referred to here as *soil residues* (SR). It has been commonly assumed that HAs provide younger ages than soil residues, but many studies have shown an inconsistent age relationship between the two SOM fractions. Some studies show HA fractions producing younger ages or closely equivalent to those on SRs (Matthews 1980; Holliday 2004: 180; Holliday et al. 2006; Brock et al. 2010), while other studies' results exhibit the opposite relationship (Martin and Johnson 1995; McGeehin et al. 2001; Mayer et al. 2008). Decalcified bulk SOM (HA and soil residues combined) has

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also been widely dated, but with a wide variation in its reliability to chronology building due to the averaging of multiple SOM fractions whose developmental histories may not be well understood (Martin and Johnson 1995; Pessenda et al. 2001; Holliday 2004; Holliday et al. 2009; Wang et al. 2014). Acid-soluble fractions, or *fulvic acids*, of materials are infrequently ^{14}C dated, when compared to HA and SR fractions, generally due to their less resistant and more mobile character throughout the soil column that typically produce younger ages from more recent contaminants formed toward the surface soils (Campbell et al. 1967; Matthews 1980, 1993).

Recent studies have tested methods of separating volatile soil organic constituents by varying the combustion temperature between 200 and 900°C (McGeehin et al. 2001; Wang et al. 2003; Mayer et al. 2008; Brock et al. 2010; Cheng et al. 2013). Most of these studies display a progression toward older ages with higher combustion temperatures, with the volatile SOM components between 400 and 800°C potentially providing the most consistent ages when compared to paired ages on plant macrofossils from the same stratigraphic layers. Indeed, SOM has been shown to be a very complex material whose development depends on its context-specific geologic and biologic histories, which leads to difficulties in comparing the reliability of ^{14}C dating techniques targeting SOM fractions across different geological environments (Matthews 1985; Wang et al. 1996; Birkeland 1999; Holliday 2004; Brock et al. 2010).

In loess environments (wind-blown silt), eolian sediment deposition can be highly variable, shifting from slow and steady to punctuated accumulation rates (Begét 2001; Frechen et al. 2003; Muhs et al. 2003; Mason et al. 2008). If enough rapid sediment accumulation occurs, deposition may outcompete and stunt vegetation and SOM formation, creating soils that are immature in their development. But as an additional consequence, soils are buried and separated by thicker non-pedogenically altered sediments, in this case, loess or eolian sand sheet deposits (Hatté et al. 2001; Reuther 2013). A geological environment that may yield a good scenario for the use of HAs and SRs in providing reliable ages on soil development and finer chronological resolution in the stratigraphic record for paleoenvironmental and archaeological research.

There has been less work on ^{14}C dating of SOM in loess environments at higher latitudes and elevations, than other mid-latitude regions, where soil formation has a tendency to be slow on stable landscapes and may cover thousands of years, potentially compounding the discrepancies between ^{14}C dating of SOM fractions. Recent studies conducted on high-latitude loess deposits in interior Alaska and Yukon, Canada, have shown variable results with standard chemical pretreatments and varied combustion temperatures on SOM fractions to provide reliable age estimates for soil formation in these geologic environments (McGeehin et al. 2001; Brock et al. 2010). However, the number of samples and sampling locales are comparatively small when compared to studies from other regions that have more firmly established the variation within and consistent patterns among different fractions that are specific to geological environments.

Our work was designed to complement the previous studies on SOM ^{14}C dating reliability in loess environments. We focused on comparing paired ^{14}C ages of charcoal/wood macrofossils and HAs and SRs from a well-defined Holocene loess-paleosol sequence in interior Alaska. The Healy's Lucky Strike (HLS) site in Healy, Alaska (Figure 1), has an excellent record of Holocene loess deposition and soil development that has afforded us the ability to look at variation in ^{14}C dating of SOM fractions in this type of high-latitude loess setting.

STUDY SITE

Geologic and Environmental Settings

The HLS site is situated on a relatively flat toe of a southwest to northeast trending bedrock bluff that overlooks the Nenana River Gorge in the middle portion of the Nenana River Valley (Figures 1 and 2). The Nenana River heads on the southern side of the Alaska Range, bisecting the central portion of the range, and drains to the north into the Tanana River. The Nenana River and its braided secondary drainages originate in glaciated, or once glaciated, mountainous highlands. These drainages hold sands and silts from seasonal outwash that supplies sediments for subsequent wind transport. Silts in this region are primarily composed of quartz, muscovite, and chlorite, with very low calcium carbonate contents compared to the silt derived from the Tanana and Yukon River systems (Thorson and Hamilton 1977; Muhs and Budahn 2006). The dominant bedrock types in the middle Nenana Valley region consist of metamorphic (schist), volcanic (diorite, graniodiorite, rhyolite), and sedimentary (argillite, greywacke, and coarser conglomerates) substrates (Wahrhaftig 1958, 1970).

During the glacial advances of the Last Glacial Maximum (LGM) and into terminal years of the Pleistocene, intense katabatic winds funneled through the narrow pass of the Nenana River Valley and stripped much of the loess and eolian sand deposits that were deposited >15,000 yr ago (Thorson and Bender 1985; Hoffecker 1988).

The Nenana River Valley transects a vegetation transition zone between the herbaceous tundra at the higher elevations of the Alaska Range, and the mixed coniferous and deciduous forest at

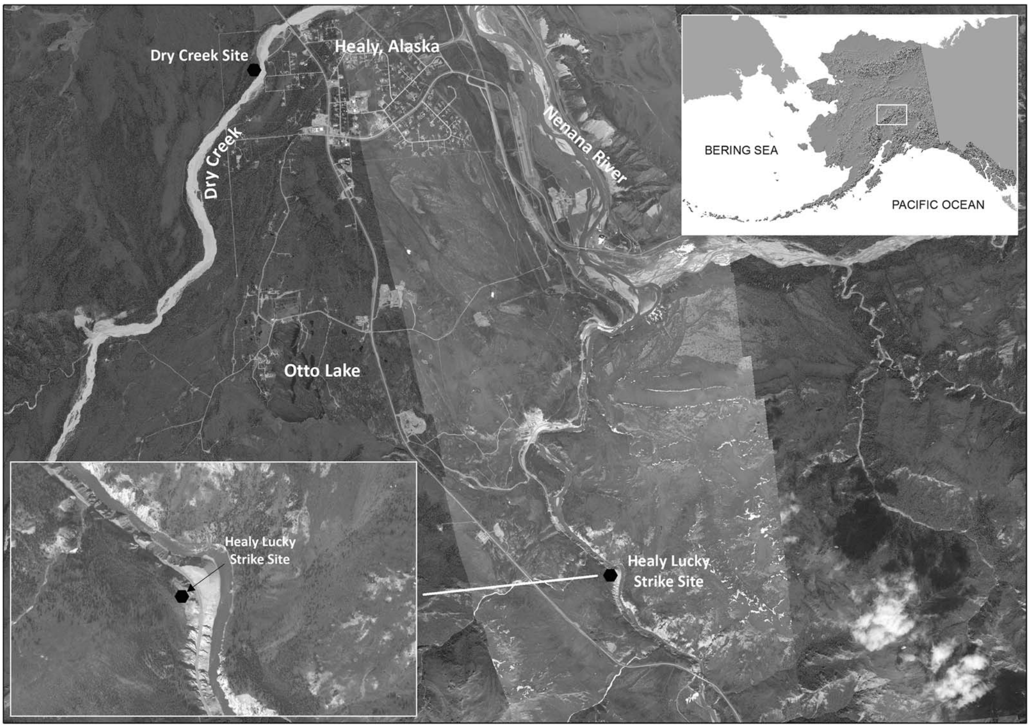

Figure 1 Google Earth image showing the location of the Healy's Lucky Strike site in the Nenana Valley, interior Alaska.

Figure 2 Terrace (lower left) on which the Healy's Lucky Strike site is situated; (upper right) the erosional surfaces at the site.

the lower elevations of the foothills down to the Tanana Lowlands. Sparse herbaceous tundra covered the landscape of the Nenana River Valley prior to 14,000 cal BP (Bigelow and Edwards 2001; Bigelow and Powers 2001). After that time, shrub tundra vegetation, dominated by birch (*Betula* sp.) shrubs, began to expand across the valley as a response to increases in effective moisture and temperature. Herbaceous tundra species (i.e., *Artemisia*, Cyperaceae, and Poaceae) expanded in the region between 12,200 and 11,700 cal BP coincident with the Younger Dryas Chronozone, likely reflecting a shift toward colder temperatures and/or increased aridity (Bigelow and Powers 2001).

Loess deposition significantly decreased, the landscape became more stable, and soil development increased throughout the region around 10,000 cal BP (Thorson and Hamilton 1977; Powers and Hoffecker 1989), coincident with increases in effective moisture, rising temperatures, and expansion of poplar (*Populus balsamifera* and *tremuloides*) and spruce (*Picea glauca* and *mariana*) trees (Bigelow and Edwards 2001; Bigelow and Powers 2001). The timing of the development of boreal forest soils in the Nenana River Valley Region is somewhat uncertain, but began appear with the expansion of spruce at least by 6000 cal BP (Thorson and Hamilton 1977; Pearson 1999).

Sampling Locale Stratigraphy

At the HLS, an erosional cut that is nearly 50 m long exposes a 3-m-thick stratigraphic record of eolian sand sheet and loess deposits that cap glaciofluvial outwash (Figure 2). We have documented nine 1- to 3-m-long stratigraphic profiles along the entire length of the erosional cut; the soil stratigraphy and depositional sequence is remarkably consistent across the cut.

A series of buried soils and five soil (pedo-) complexes are contained within the HLS site loess deposit (Figure 3; Reuther et al. 2015). Soil descriptions follow United States national conventions (USDA 1993) with modifications suggested by Holliday (2004). Pedocomplexes refer to multiple buried soils that are closely spaced together. The majority of the buried soils in the upper 205 cm of the stratigraphic column consist of immature forest soils (Cryepts and

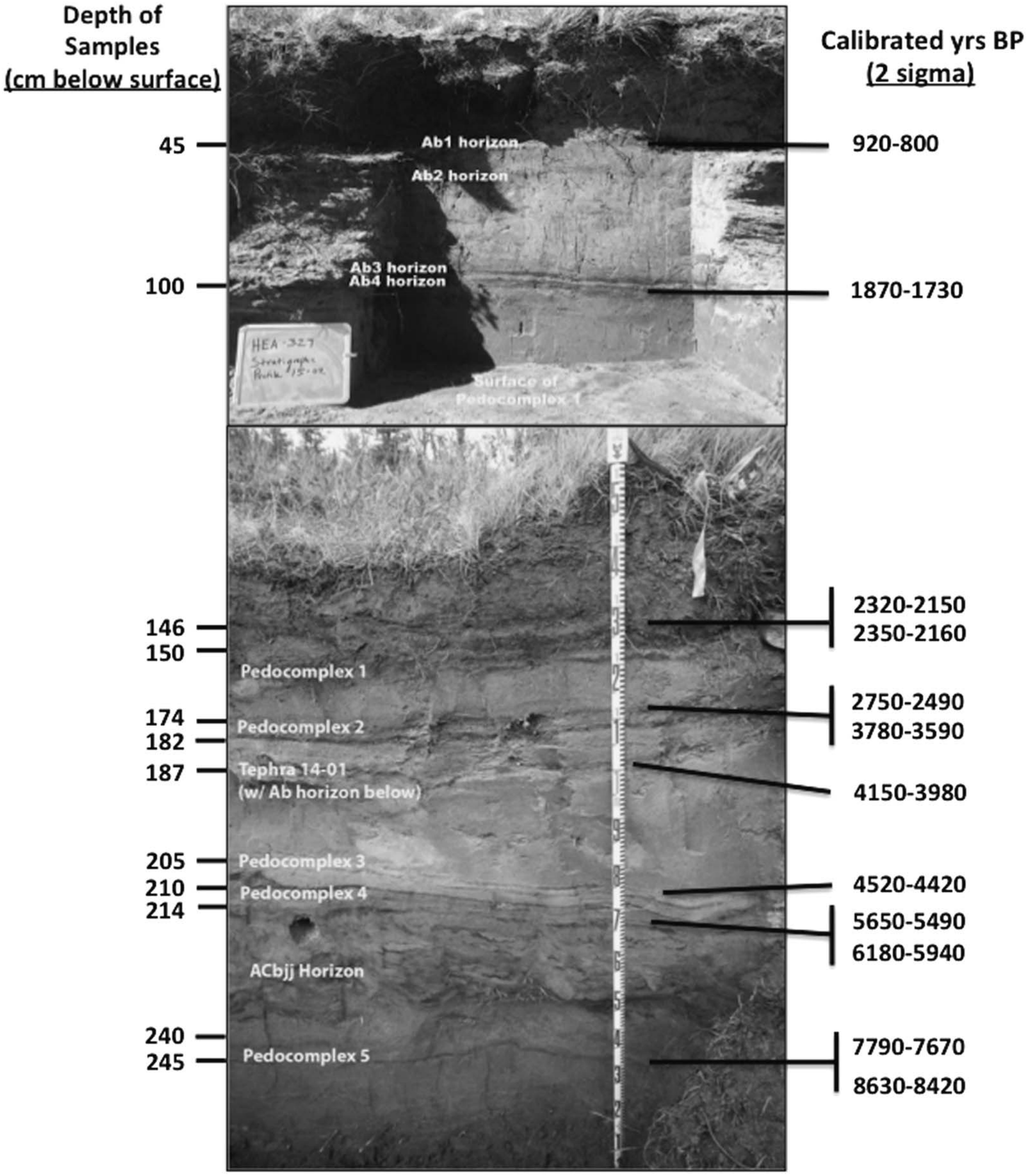

Figure 3 Stratigraphic sequence at the Healy's Lucky Strike site. Calibrated ages shown here are based on ^{14}C dates on charcoal and wood (Photograph: J Reuther).

Spodic Cryosols) with primarily humic (A) horizons and, in some cases, very incipient eluvial (E) and illuvial (B) horizons. A horizons are composed of the upper mineral and decomposed organic matter (humus); E horizons, beneath A horizons, are leached of clay, iron, and aluminum. B horizons are indicative of iron, clay, aluminum, and organic compound accumulation that are leached from overlying A and E horizons.

Very little cryoturbation was observed in these upper horizons, indicating only low-amplitude postdepositional disturbances to the HLS site sediments and soils. The upper buried soils and pedocomplexes between 205 and 145 cm below the modern surface [cm below surface (cmBS)] are high in fibrous organics, somewhat peat-like, and show only intermediate-to-high decomposition rates of plant materials before being covered with loess. Soils above 205 cmBS are likely associated with the later expansion (after 6000 yr ago) of the taiga forests into the region at these higher altitudes (Bigelow and Powers 2001). Perennially frozen sediments along this bluff appear to occur at a depth of 100 to 150 cmBS and below, and remain frozen year-round, even in the midst of the exposure to the substrata. Frozen sediments at the HLS site appear to have been kept insulated and below freezing temperatures by the development of the buried highly organic, peat-like soils.

Soils below 205 cmBS are less developed than the upper soils, consisting mostly of weakly expressed humic (A) horizons, and, in some cases, very incipient illuvial zones (B horizons). A soil (ACbjj horizon) that developed between 214 and 225 cmBS shows low-amplitude involutions and mixing of soil horizons due to cryoturbation; the largest degree of postdepositional disturbance is due to higher activity of freeze-thaw processes displayed at the HLS site. The soils at and lower than 225 cmBS show the weakest development, solely consisting of thin (1–2 cm thick) humic (A) horizons. Soils below 205 cmBS most likely relate to shrub tundra vegetative cover common in the early Holocene, although scattered trees may have presented a minor contribution also (Bigelow and Powers 2001).

METHODS

Field Sampling

In the field, we sampled five of the nine trenches, taking between 50–100 g of sediments from selected soil horizons described above. Sediment samples were extracted from horizons with a trowel that was wiped clean prior to taking each sample to reduce any residue from the previous samples taken. We made every attempt to discretely sample from each horizon despite some of them being a thin as 1–2 cm. In most cases, we sampled the upper reaches (2–3 cm) of the A horizons within the thicker buried soils (5–15 cm thick). In concept, the ^{14}C dates on these soil samples should provide a close estimation of the age of burial and on the more recent end of the mean residence time for soil development (Holliday 2004: 181).

The visible charcoal and wood samples were collected directly from the stratigraphic profile in the field. The majority of these charcoal samples was taken from the upper few cm of Ab horizons, and were our first priorities for constructing the baseline chronology described below. Otherwise, sediment samples were subsampled for charcoal and wood by sieving in nest sieves. In all cases, the charcoal and wood and sediment sample pairs were taken from the same soil horizons and depths.

Laboratory Preparations and Analyses

All samples were either directly dried at room temperature after arrival at the laboratory from the field, or they were frozen, then immediately dried at room temperature to alleviate modern bacterial or fungal contaminant growth. Our work focused on comparing ^{14}C ages of plant macrofossils to the ages of HA and SR fractions from the same stratigraphic contexts.

Charcoal and wood samples were treated with 5% HCl at 80°C for 1 hr, then washed with deionized water on fiberglass filters and rinsed with diluted NaOH to remove possible contamination by HAs. These samples were again treated with diluted HCl, washed with deionized water, and dried at 60°C.

Sediment samples were sieved through a 125-micron nylon screen, treated with 1N HCl at 80°C for 1 hr to remove any carbonates present, and then washed with deionized water using a centrifuge. Carbonate content in samples was quite low, between 0.18 and 0.34 %$CaCO_3$, as measured by gas manometer using a Chittick apparatus.

The precipitate was treated with 0.1N NaOH to extract HAs. The alkali solution was reacted with concentrated HCl to change the pH to approximately 2 to precipitate out the HAs. The precipitate was collected in centrifuge tubes and rinsed with deionized water to pH = 4–5, then the HAs were dried at 60°C.

The frequency of the NaOH washes was sample dependent and based on the amount of the base-soluble fractions (i.e. HAs) in the sample. NaOH washes were conducted until the solution became clear, and the remaining sediment residues were treated with 1N HCl at 80°C for 2 hr, washed with deionized water to a pH of ~5, and dried at 60°C.

All samples were combusted at 900°C in an evacuated sealed quartz ampoule in the presence of CuO. The resulting carbon dioxide was cryogenically purified from other reaction products and catalytically converted to graphite using the method of Vogel et al. (1984). Graphite ^{14}C/^{13}C ratios were measured at the Center for Applied Isotope Studies at the University of Georgia (NEC 0.5MV 1.5SDH-1 Pelletron AMS) and the NSF-Arizona AMS Facility at the University of Arizona (NEC 3MV Pelletron AMS). The sample ratios were compared to the ratio measured from the oxalic acid I (NBS SRM 4990). The sample ^{13}C/^{12}C ratios were measured separately using a stable isotope ratio mass spectrometer and expressed as δ^{13}C with respect to PDB, with an error of less than 0.1‰. ^{14}C ages were corrected for isotopic fractionation and calibrated using CALIB v 7.1 software (Stuiver et al. 2015) and the IntCal13 terrestrial calibration model (Reimer et al. 2013). It should be noted that we did not conduct low and high firing combustion (400°C, 600°C, 800°C) to assess the differences in volatile organics among the soil residue fractions, such as in the studies of Brock et al. (2010), McGeehin et al. (2001), Mayer et al. (2008), and Wang et al. (2003).

We have multiple ages for charcoal/wood and HAs and SR fractions from single buried soils in pedocomplexes. In these cases, we calculated pooled averages for the uncalibrated conventional ages following Ward and Wilson (1978). Median probabilities of calibrated ages were used in calculating the differences and variation among fraction ages. The ^{14}C data are detailed in Table 1.

The SR fractions from three sediment samples had repeated measurements produced at both the NSF-Arizona AMS and Center for Applied Isotope Studies facilities (Table 1) to assess if the general trends of increased older offsets were valid or consequences of laboratory error. Each repeated measurement on these SR fractions showed similar magnitudes in older age offsets for soil residues when compared to charcoal/wood and HA ages.

RESULTS

^{14}C ages for all of the materials and fractions from HLS become older with depth, with the exception of one reversal in the charcoal/wood data in Pedocomplex 1 (Figure 4) described below. This trend points to a congruency between the ^{14}C data and stratigraphy and supports the lack of extensive postdepositional disturbance to soils and sediments that would affect the "true" age values of samples.

Charcoal and Wood: The Baseline Chronology

Charcoal/wood ages (n = 15) provide the most accurate ages for the buried soil sequence at the HLS site, and indicate the soils date between 850 and 8500 cal BP. The majority of charcoal/wood ages from each separated buried soil do not overlap with one another (Figure 4). The exception being dates from Pedocomplex 1, Paleosols 1 (averaged value) and 2 that have overlapping calibrated age ranges at 2 standard deviations; however, the median probability of the two age ranges does reflect a difference of 130 yr with the deeper Paleosol 2 being the older of the values (Table 1). The overlapping ages for the Pedocomplex 1 paleosols most likely reflect the development of these soils within a relatively restricted timeframe, possibly within 330 yr given the highest and lowest values of the calibrated age ranges.

Humic Acids

At HLS, HA ages (n = 8) are generally older than their charcoal age counterparts, but show a similar older age trend with depth (Figures 4 and 5). There is a weak correlation (R^2 = 0.477) between the greater differences between paired charcoal/wood and HA ages (n = 7) and increased depth in the stratigraphic column. At and below 205 cmBS, the differences between HA and charcoal/wood ages can reach as much as 370 to 950 yr with an average difference of 694 ± 297 yr (Table 3). This results in an 8 to 11% difference between paired HA and

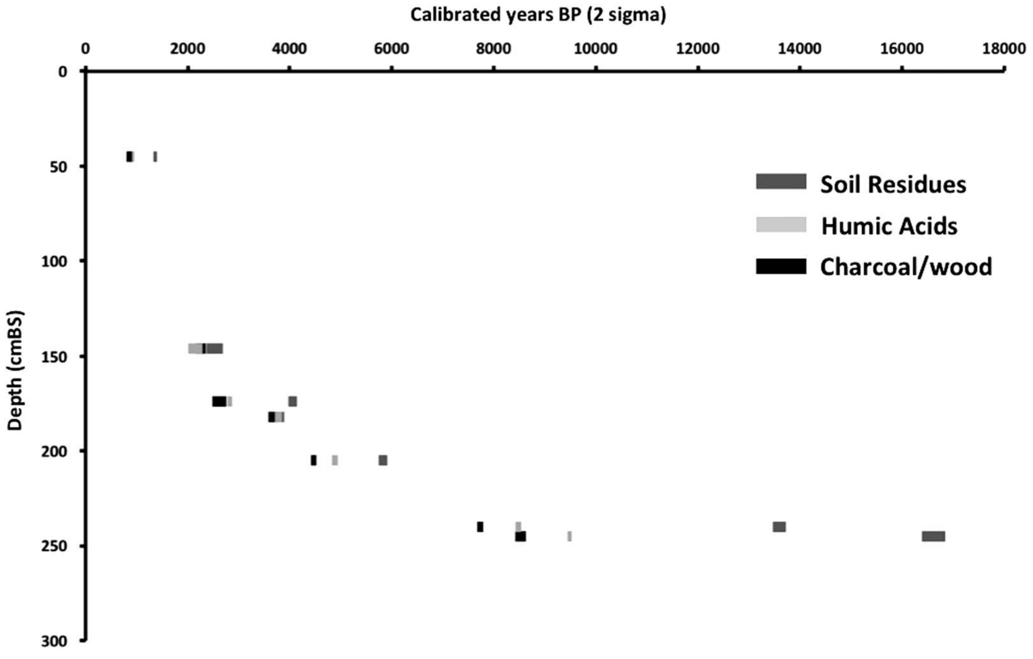

Figure 4 Plots of the calibrated ^{14}C age ranges (2σ) on charcoal/wood, humic acid, and soil residue paired ages

Table 1 Radiocarbon ages on charcoal/wood and soil organic matter fractions from the Healy's Lucky Strike site.

		Fraction								
		Charcoal/wood			Humic acids			Soil residues		
Soil horizon/ Pedocomplex	Depth, cm	δ^{13}C,% o	^{14}C age, yr BP	cal age(2σ)/ median	δ^{13}C,% o	^{14}C age, yr BP	cal age(2σ)/ median	δ^{13}C,% o	^{14}C age, yr BP	cal age(2σ)/ median
Ab1 horizon	45	−24.6	940 ± 20^{2}	920–800(850)	−25.5	1010 ± 20^{2}	960–910(930)	−25.4	1480 ± 20^{2}	1400–1320(1360)
Ab4 horizon	100	−25.6	1870 ± 20^{2}	1870–1730(1820)						
Pedocomplex 1	146	−24.6	2410 ± 40^{3}	2700–2350(2440)	−26.7	2130 ± 20^{2}	2290–2010(2120)	−27.8	2220 ± 20^{2}	2320–2150(2220)
		−30.1	2120 ± 40^{3}	2300–1990(2100)						
	150	−26.4	2210 ± 30^{3}	2320–2150(2230)						
Pedocomplex 2	174	−25.6	2530 ± 30^{3}	2750–2490(2620)	−28.1	2730 ± 20^{2}	2870–2770(2820)	−27.3	3500 ± 40^{3}	3870–3650(3770)
								−29.1	3540 ± 25^{2}	3930–3700(1850)
	182	−25.0	3460 ± 60^{3}	3780–3590(3740)	−27.1	3510 ± 25^{2}	3850–3700(3780)	−29.1	3540 ± 25^{2}	3900–3720(3830)
	187	−26.3	3720 ± 20^{2}	4150–3980(4050)						
Pedocomplex 3	205	−26.0	3980 ± 40^{3}	4530–4300(4470)	−26.3	4140 ± 40^{3}	4830–4580(4710)	−26.9	5220 ± 40^{3}	6170–5910(5970)
		−24.5	4200 ± 40^{3}	4850–4580(4730)	−26.5	4400 ± 40^{3}	5270–4860(4980)	−27.1	4950 ± 40^{3}	5750–5600(5670)
		−27.7	3920 ± 40^{3}	4500–4240(4350)						
Pedocomplex 4	210	−25.6	4860 ± 30^{2}	5650–5490(5600)						
	214	−25.6	5280 ± 40^{3}	6180–5940(6070)						
Pedocomplex 5	240	−26.1	6890 ± 30^{2}	7790–7670(7720)	−26.6	7690 ± 30^{2}	8540–8420(8470)	−27.8	12070 ± 30^{2}	14050–13780(13910)
								−25.6	10820 ± 50^{3}	12800–12670(12720)
	245	−23.3	7760 ± 50^{1}	8630–8420(8530)	−26.1	8460 ± 30^{2}	9530–9440(9490)	−24.8	13240 ± 30^{2}	16080–15750(15920)
								−24.9	16900 ± 90^{3}	20620–20110(20385)

1-this sample was analyzed at Beta Analytic; 2-the samples were analyzed at University of Georgia; 3-the samples were analyzed at University of Arizona

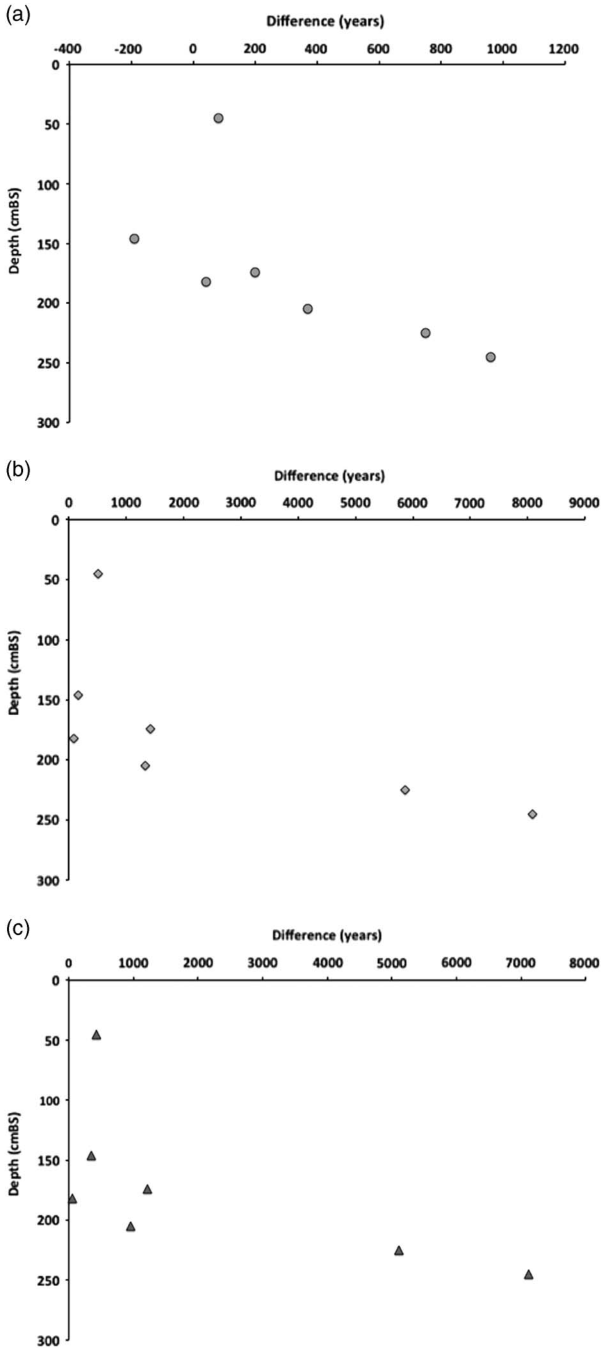

Figure 5 Plots of the differences in years between (a) humic acid and charcoal/wood ages, (b) soil residue and charcoal/wood ages, and (c) soil residue and humic acid ages by depth (cmBS).

charcoal/wood ages. While these differences are not completely surprising, the offsets within the deepest (between 225 to 245 cmBS) and less expressed soils of Pedocomplex 5 show the largest offsets at 750 to 950 yr, differences of 9 to 11% from their charcoal/wood age counterparts. Above 200 cmBS, offsets are not as pronounced ranging in difference between 18 and 203 yr with an average difference of 85 ± 82 yr. Three out of the seven calibrated age ranges for HA and charcoal/wood pairs overlap at 2 standard deviations, and are all ages on materials above 200 cmBS (Table 2).

Soil Residues

Soil residue ages ($n = 12$) are much older than charcoal/wood and HA paired ages, but show the same general age depth trends (Figures 4 and 5). Similar to paired charcoal/wood and HA age differences, there is a weak correlation ($R^2 = 0.443$) between greater differences between SR and charcoal/wood paired ages ($n = 7$) and increased depth (Tables 2 and 3). The differences between the SR and charcoal/wood ages, regardless of depth, range between 90 and 8075 yr with an average difference of 2493 ± 3166 yr and between 2 to 64% in percent difference. Between 45 and 205 cmBS, the difference between SR and charcoal/wood paired ages is between 90 and 1424 yr with an average difference of 546 ± 613 yr, resulting in percent differences between 2 to 46%. Below 205 cmBS, the ages of these materials become increasingly offset with SR ages between 1330 and 8075 yr older than their charcoal/wood counterparts, with an average difference of 5089 ± 3438 yr and 26 to 64% in percent differences. Only one of the seven calibrated age ranges for SR and charcoal/wood pairs overlaps at 2σ.

The comparison between SR and HA age differences is not as extreme as the offsets between SR and charcoal/wood ages (Tables 2 and 3). Once more, there is a weak correlation ($R^2 = 0.431$) between greater differences between SR and HA paired ages ($n = 7$) and increased depth. The differences between SR and HA ages, regardless of depth, range between 50 and 7121 yr with an average difference of 2177 ± 2788 yr and between 1 to 46% percent differences among paired ages. The differences between SR and HA ages are not as pronounced above 205 cmBS, ranging between 50 and 1221 yr with an average difference of 514 ± 499 yr and between 1 and 38% in percent difference among pairs. While at and below 205 cmBS, the differences between the ages of the two materials become more pronounced between 960 and 7121 yr, with an average

Table 2 Radiocarbon age differences between and among paired charcoal/wood and soil organic matter ages from the Healy's Lucky Strike site.

	HA-CW difference[a]		SR-CW difference[a]		SR-HA difference[a]	
Depth, cm	years[b]	%[c]	years[b]	%[c]	years[b]	%[c]
45	80	9	510	46	430	38
146	−190	−9	160	7	350	13
174	200	7	1420	43	1220	36
182	40	1	90	2	50	1
205	370	8	1330	26	960	18
240	750	9	5860	55	5100	46
245	960	11	8070	64	7120	55

[a] Fraction abbreviations: charcoal/wood = CW; humic acids = HA; soil residue = SR.

[b] The difference is the median probability of one fraction's calibrated age minus the median probability of a second fraction's calibrated age.

[c] The % is the difference between the median probabilities of two paired calibrated ages divided by their average, multiplied by 100.

Table 3 Summary of ^{14}C age differences between and among charcoal/wood and soil organic matter fractions from the Healy's Lucky Strike site.

Fraction comparisons	Mean difference (yr)[a]	Standard deviation (yrs) (1σ)[b]	Minimum difference (yr)[c]	Maximum difference (yr)[c]
HUMIC ACIDS – CHARCOAL/WOOD				
Avg. offset (all) (*n* = 7 pairs)	316	372	−190	960
Avg. offset (above 205 cmBS) (*n* = 4 pairs)	32	163	−190	200
Avg. offset (below 205 cmBS) (*n* = 3 pairs)	693	299	370	960
SOIL RESIDUES – CHARCOAL/WOOD				
Avg. offset (all) (*n* = 7 pairs)	2493	3166	90	8070
Avg. offset (above 205 cmBS) (*n* = 4 pairs)	546	613	90	1420
Avg. offset (below 205 cmBS) (*n* = 3 pairs)	5089	3438	1330	8070
SOIL RESIDUES – HUMIC ACIDS				
Avg. offset (all) (*n* = 7 pairs)	2177	2778	50	7120
Avg. offset (above 205 cmBS) (*n* = 4 pairs)	514	499	50	1220
Avg. offset (below 205 cmBS) (*n* = 3 pairs)	4395	3141	960	7120

[a] Mean difference is the average of a suite of differences between the median probabilities of paired calibrated ages.

[b] Standard deviation of the differences within a suite of differences between the median probabilities of paired calibrated ages.

[c] The minimum and maximum differences are the low and high values within the range of the difference within a suite of differences between the median probabilities of paired calibrated ages.

difference of 4395 ± 3141 yr and an 18 to 55% difference among pairs. Only one out of the seven calibrated age ranges for SR and HA pairs overlaps at 2σ.

DISCUSSION AND CONCLUSIONS

The results presented in this study illustrate the complexity of ^{14}C dating SOM fractions and, as others have suggested, the reliability of the age produced from each fraction can be regionally and environmentally dependent and context specific (Martin and Johnson 1995; Holliday 2004). A one-size-fits-all approach to pretreatment techniques in ^{14}C SOM dating may not be feasible, even in similar geological environments and closely related regions as the mixed results from interior Alaska and the Yukon, Canada, have shown (McGeehin et al. 2001; Brock et al. 2010). However, it bears pointing out that in the loessic regions of interior Alaska and the Yukon, SOM ^{14}C dating comparisons suffer from small sample sizes, both in terms of the number of comparative studies and sections, and the available paired comparisons within a section and study. Other regions such as the central Great Plains and southern High Plains have amassed much larger sample sizes across broader regions to understand sources of the variability between SOM fraction ^{14}C ages. These studies are resulting in more reliable chronologies, in the absence of charcoal, wood, and bone materials, based on the SOM fractions that provide the most consistent results for each region (Holliday et al. 1996, 2009; Johnson and Willey

2000; Holliday 2001; Mandel 2008). As stated above, our goal here was to provide additional data on ^{14}C dating of SOM in interior Alaskan loess settings to assess potential causes of variability among SOM fractions in this region; in addition, similar to those of the studies in the Great and southern High Plains, taking steps toward building broader, more reliable stratigraphic and archaeological chronologies are sections that are devoid of charcoal, wood, and bone.

At the HLS site, charcoal/wood ages were younger than HA ages reflecting the later stages of vegetation development at the surface of the soils prior to being covered by loess accumulation; the HA ages generally reflect the overall timing of soil formation and mean residency time of SOM. This trend between the HLS charcoal/wood and HA age differences is opposite that of the relationship seen in the comparative study in the middle Park region of Colorado by Mayer et al. (2008), but it is not unexpected as the charcoal/wood samples were collected within the upper few cm of the Ab horizons.

The majority of the non-overlapping charcoal/wood and HA ages between each buried soil and pedocomplex point to a relatively short duration of soil development and their rapid burial by loess, a balance of maintaining vegetative growth and soil development in the midst of loess accumulation. These results also signify that minimal exchange of illuviated younger carbon sources (e.g. HAs) has occurred between HLS pedocomplexes. However, the larger offsets between charcoal/wood and HA ages in Pedocomplex 5 may also reflect the incorporation of older carbon sources from parent material in the loess, as discussed below.

The ^{14}C age results on the SR fractions are a more complex matter. As noted above, the differences between paired charcoal/wood and SR ages become increasingly disparate with depth, as do the offsets between paired HA and SR ages (as much as 5100 to 8075 yr different). Soil residues are an amalgamation of acid- and base-resistant organic and inorganic materials that can contain many different sources of carbon depending on the geologic and pedologic history of a deposit. These fractions can include humins that are derived from pedogenesis and the parent materials, in this case the very fine fractions of silts and clays. The exact source of older carbon introduced into the soil residue fractions at HLS is still unclear. However, we can suggest two potential reasons for the drastic differences of the SR ages exhibited at HLS from dates produced on charcoal/wood and HAs: (1) clay minerals tightly bound with old carbon sources in the soil residues were combusted at temperatures >800°C creating an older date for this fraction (McGeehin et al. 2001); (2) small particles of lignite (a form of coal) were differentially incorporated throughout the sedimentary matrices, with higher percentages of lignite present in the loess deposits below 205 cmBS (Tankersley et al. 1987).

Since the samples were combusted at 900°C, the problem of incorporating older carbon from older clays into soil-derived younger carbon sources through high-temperature combustion could be an issue. However, clay content in non-reworked loess deposits in the interior Alaska is generally low (<10%; Reuther 2013), and we regard tightly bound clays as a less likely contributor to significant amounts of older ^{14}C age differences between samples that are less than 10,000 yr old. Offsets of the magnitude shown in these results would require relatively larger proportions of a clay contaminant (Mayer et al. 2008) to affect samples of this age than might be present in the HLS loess.

The presence of minute particles of lignite could also be a factor, in that seams of coal are found throughout this region (Wahrhaftig et al. 1969). Smaller clasts from these seams can be dispersed through rivers and streams, and then subsequently transported by wind and deposited on terraces and bluffs. The older ("dead") carbon from the lignite can be incorporated into younger carbon sources, including soil-derived carbon (e.g. humates and humins), creating anomalously older ages than might be expected and older ages than paired ages from charcoal and wood. Thorson and Hamilton (1977) suggested a similar process occurred at the nearby Dry Creek site, approximately 8.3 km (5.2 miles) from the HLS, where anomalously older ages occurred on charcoal from the deepest loess deposits (Figure 1). The final carbon content of these pretreated Dry Creek site charcoal samples was rather small and dead carbon contamination would have been more pronounced (Thorson and Hamilton 1977: 167). Higher amounts of lignite are likely introduced into eolian sedimentary matrices in this region during periods of higher accumulations of wind-blown particles, and may be available to be broken down and incorporated as contaminants into soil organic matrices (Tankersley et al. 1987; Tankersley and Munson 1992).

In the case of the HLS ^{14}C data, we regard lignite contamination to be more of a problem to the HA and SR fractions than older tightly bound clays, given that we see larger age offsets in both these fractions ages, when compared to paired charcoal/wood ages, in the lowest depths of the strata and associated with very weakly developed Ab horizons (1 to 2 cm thick or less). At depths below 205 cmBS, HA age differences from charcoal/wood ages are between 750 and 950 yr. These differences may indicate a mean residence age for SOM for these weak soils, and lengths of soil development in a higher altitude environment where soils may form at a slower rate. An alternative explanation is that HAs within these very immature soils incorporated carbon from lignite particulates as a soluble component causing older age differences when compared to charcoal/wood ages, and the actual mean residence time for the development of the soil is much shorter than reflected by the HA ages. Currently, we cannot pinpoint the most plausible explanation, but with studies on ^{14}C dating on SOM in coal-rich loess settings, such as the Nenana Valley, and coal-rich environments in general, lignite contamination of HAs should be taken into account.

In sum, SR ages, regardless of combustion temperature, should still be suspect given the potential problems with lignite in these regions. In spite of the equivocal HA ages in the lower soils at HLS, we feel that HA ages may be used to establish reliable mean residence time for soils in environments such as the loess settings of the Nenana Valley in interior Alaska, and still have the potential to provide consistent results in the absence of charcoal, wood, and bone. Valid HA ages may help provide broader stratigraphic chronologies, beyond those that are solely dated by the traditionally accepted organic materials mentioned above, and potentially reliable deeper time depth proxies for how carbon reservoirs in high-latitude loess settings are affected by periods of extreme environmental and climatic change. However, the HLS loess-paleosol sequence is no older than 10,000 cal BP, and given that HAs and soil residues can be generated from different biological and geological sources and affected dissimilarly by changes in climate and environment, longer sequences of SOM fraction ^{14}C dating into more climatically variable periods into the Pleistocene in higher-altitude loess settings may give us another perspective as to which SOM fraction is more reliable given a particular time period and climatic setting (Birkeland 1999; Holliday 2004).

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