Quaternary Research 72 (2009) 301–308

Contents lists available at ScienceDirect

Quaternary Research

journal homepage: www.elsevier.com/locate/yqres

The magnitude of error in conventional bulk-sediment radiocarbon dates from central North America

Eric C. Grimm [a,*], Louis J. Maher Jr. [b], David M. Nelson [c,1]

[a] Illinois State Museum, Research and Collections Center, 1011 East Ash Street, Springfield, IL 62703, USA
[b] University of Wisconsin-Madison, Department of Geology and Geophysics, Madison, WI 53706, USA
[c] University of Illinois, Institute for Genomic Biology, 1206 West Gregory Drive, Urbana, IL 61801, USA

ARTICLE INFO

Article history:
Received 28 January 2009
Available online 9 July 2009

Keywords:
Radiocarbon dating
Carbon reservoir
Hardwater effect
Rice Lake, North Dakota
Cottonwood Lake, South Dakota
Devils Lake, Wisconsin
Chatsworth Bog, Illinois
Global Pollen Database
NEOTOMA database

ABSTRACT

Although the carbon-reservoir problem with bulk-sediment radiocarbon dates from lakes has long been recognized, many synoptic studies continue to use chronologies derived from such dates. For four sites in central North America, we evaluate chronologies based on conventional radiocarbon dates from bulk sediment versus chronologies based on accelerator mass spectrometry (AMS) radiocarbon dates from terrestrial plant macrofossils. The carbon-reservoir error varies among sites and temporally at individual sites from 0 to 8000 yr. An error of 500–2000 yr is common. This error has important implications for the resolution of precise event chronologies.

Introduction

Lake-sediment records hold invaluable information for assessing past ecosystems and climates. Absolute temporal control for late-Quaternary lake-sediment records typically depends upon radiocarbon dating. High-quality chronologies are crucial for elucidating decadal to century-scale paleoenvironmental changes and for comparing event stratigraphies across sites, as is becoming increasingly common (e.g. Shuman et al., 2002; Williams et al., 2002; Wright et al., 2004; Nelson and Hu, 2008; Gonzales and Grimm, in press).

Before the advent of accelerator mass spectrometry (AMS) radiocarbon dating, investigators typically obtained conventional decay-count (radiometric) radiocarbon dates from samples of bulk sediment or occasionally from large wood fragments. The decay-count and AMS methods can provide comparable precision; however, to achieve this precision, the decay-count method requires three orders of magnitude more carbon than the AMS method, 1 g vs. 1 mg, and much more time, >24 h counting vs. <30 min for the AMS measurement (Bronk Ramsey, 2008; Hellborg and Skog, 2008). Technological advances are making it possible to obtain AMS dates from even smaller samples of a few hundred μg (Santos et al., 2007). Nevertheless, for appropriate materials, such as large wood fragments, the decay-count method can provide reliable and accurate dates. The major drawback of the decay-count method is that large masses of appropriate materials, such as wood, are not usually available from sediment cores. Consequently, investigators have typically dated samples of bulk sediment, which contains carbon from uncertain provenances. For bulk-sediment dates, the problem of the "hardwater effect," a term for the old-carbon reservoir derived from dissolved carbonate rocks, has long been known (Deevey et al., 1954; Broecker and Walton, 1959; Ogden, 1967a, 1967b; Andree et al., 1986; Saarnisto, 1988); but a more serious problem in some regions may be fine-grained clastic materials derived from lignite, coal, and carbonaceous shales (Nambudiri et al., 1980; Lowe et al., 1988; Grimm and Jacobson, 2004).

Because of these problems, AMS ^{14}C dates on terrestrial plant macrofossils have largely supplanted conventional decay-count ^{14}C dates on bulk sediment. However, a great legacy of conventional bulk-sediment ^{14}C dates exists in the literature and in paleo databases, which are widely used for synoptic paleoenvironmental studies (e.g. Shuman et al., 2002; Williams et al., 2004). For instance, in the Global Pollen Database, now a component of the NEOTOMA database (www.neotomadb.org), 90% ($n=5883$) of the ^{14}C dates are conventional, and 10% ($n=666$) are AMS. Similarly, 90% ($n=1245$) of the collection units (cores and sections) have only conventional dates, whereas 5% ($n=74$) have only AMS dates, and 5% ($n=67$) have both AMS and conventional dates. Thus, it seems critical to investigate the potential error in the conventional dates.

Here we examine four sites from central North America (Fig. 1). Carbonate rocks (limestone and dolomite) and carbonaceous rocks

---

* Corresponding author. Fax: +1 217 785 2857.
E-mail address: grimm@museum.state.il.us (E.C. Grimm).

[1] Current address: Appalachian Laboratory, University of Maryland Center for Environmental Science, 301 Braddock Rd., Frostburg, MD 21532, USA.

0033-5894/$ – see front matter © 2009 University of Washington. Published by Elsevier Inc. All rights reserved.
doi:10.1016/j.yqres.2009.05.006

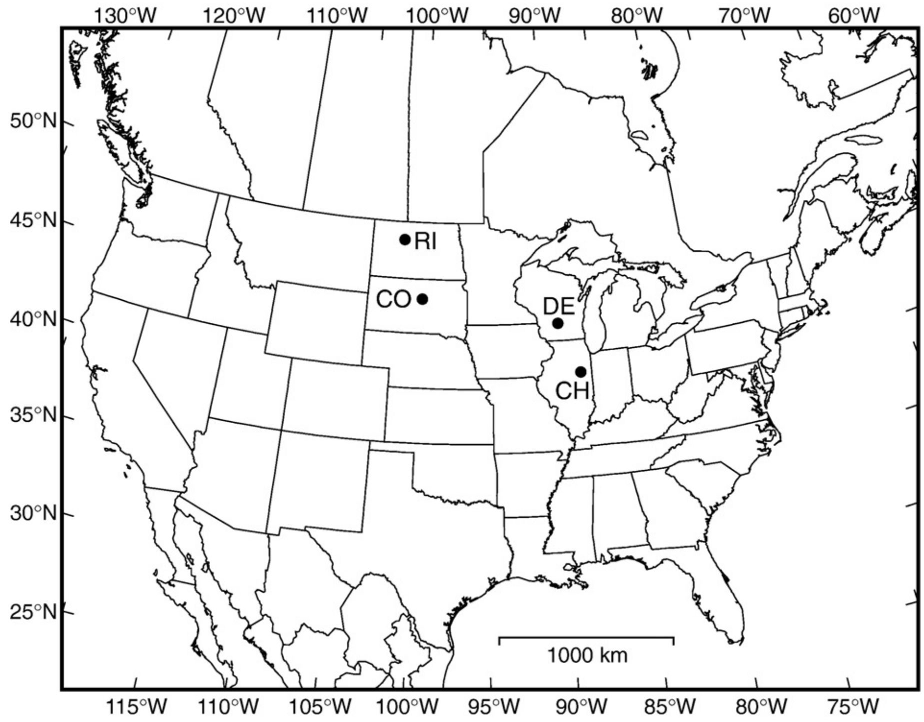

Figure 1. Site location map. RI — Rice Lake; CO — Cottonwood Lake; DE — Devils Lake; CH — Chatsworth Bog.

(lignite, coal, and shale) are widespread in this region. Much of this old carbonaceous material is ground up in glacial drift and is redeposited in lake sediment as silt-sized particles. All four of these sites were initially studied before AMS dating was widely available, and conventional dates on bulk sediment were obtained. The sites were later re-dated with AMS dates on terrestrial plant macrofossils.

Sites

Rice Lake (48°0.48′N, 101°31.82′W, 620 m a.s.l., 75 ha) lies in a kettle on glacial moraine in Ward County, North Dakota. Additional site details are in Fritz et al. (2000), Yu and Ito (1999), and Yu et al. (2002). E. Grimm initially obtained a series of conventional dates on bulk sediment and a single date on wood in the basal “trash layer.” The sediment is marly, suggesting the possibility of a significant hardwater effect. The basal wood date, presumably reliable, is ~1300 yr younger than the date on bulk lake-sediment immediately above it. Thus, a series of AMS dates on terrestrial macrofossils was obtained, on which the published age models are based (Yu and Ito, 1999; Fritz et al., 2000; Yu et al., 2002).

Cottonwood Lake (44°50.17′N, 99°54.38′W, 549 m a.s.l., 185 ha) lies on the Missouri Coteau in Sully County, South Dakota. The lake is probably a glacial kettle and lies in collapsed outwash in a buried preglacial valley (Flint, 1955; Martin et al., 2004). Barnosky et al. (1987) presented a pollen diagram with a single date near the base of the core, which they regarded as 1000–3000 yr too old based on pollen profiles from other Dakota sites. After publication of this diagram, E. Grimm obtained a series of bulk-sediment conventional dates; but the presence of lignite and carbonaceous shale in the basal sands and gravels suggested that these materials probably also occurred in the clastic component of the lake sediments, and therefore all the bulk-sediment dates were suspect. A series of AMS dates on terrestrial macrofossils was obtained later, and we report them here for the first time.

Devils Lake (43°25.08′N, 89°43.92′W, 294 m a.s.l., 153 ha) lies in a preglacial quartzite valley dammed at both ends by glacial moraines. Because the sediments have virtually no carbonate, the published age model (Baker et al., 1992), although based on bulk-sediment dates, has long been thought to be one of the more reliable age models for the Midwest. Indeed, Shuman et al. (2002) feature Devils Lake in a synoptic study arguing for warm, dry climate in Wisconsin during the Younger Dryas chronozone. However, late-glacial pollen stratigraphic events at Devils Lake appear to be ~1000 ^{14}C yr older than similar events dated with AMS at sites in northern Illinois ~200 km to the southeast. Thus, a series of AMS dates was obtained from original core to test whether the conventional ^{14}C chronology was too old or whether the pollen stratigraphic events were time transgressive.

Chatsworth Bog (40°40.55′N, 88°20.69′W, 219 m a.s.l., ~18 ha) is a marl fen, first investigated by Voss (1937) and later by King (1981), who obtained a series of ^{14}C dates on bulk sediment. Throughout most of its history, Chatsworth Bog was a lake, which gradually filled with sediment and developed into a fen ~3400 yr ago (King, 1981). The east half of the site has been quarried for marl and is now a lake again, and the rest of the fen has been tiled and drained and is planted with row crops. Chatsworth Bog is an important site in the eastern Prairie Peninsula. It anchors synoptic maps showing contrasting Holocene climate trends between the eastern and western Prairie Peninsula (Webb et al., 1983). However, because of the high marl content of the sediment, the reliability of the conventional dates from Chatsworth Bog is questionable. Nelson et al. (2006) reinvestigated Chatsworth Bog with new cores and obtained a series of AMS dates on terrestrial macrofossils. We correlated the King (1981) and Nelson et al. (2006) cores by pollen stratigraphy, which is highly similar between the two cores.

Methods

The original conventional dates were obtained from sections of core, which were cleaned of the outside smear, dried, and submitted to the radiocarbon laboratory, where they underwent acid-base treatment, which removed soluble carbonates. AMS dates were obtained from either charcoal or plant macrofossils from terrestrial or emergent aquatic plants. Some macrofossils from submerged aquatic plants were also dated for comparison. Three of the study

Table 1
Complete listing of radiocarbon dates from study sites.

Lab nr	Type	Depth (cm)	^{14}C yr BP	Material
Rice Lake, North Dakota				
Beta-37852	Conventional	1260–1270	2310 ± 70	Bulk sediment
Beta-37853	Conventional	1660–1670	5610 ± 80	Bulk sediment
Beta-37854	Conventional	2010–2020	10,510 ± 90	Bulk sediment
WIS-1873[a]	Conventional	2028–2032	9240 ± 90	*Picea* wood
CAMS-9157[b]	AMS	1046.5–1047.5	560 ± 60	Plant stem (*Schoenoplectus*?)
CAMS-9158	AMS	1250–1258	1360 ± 60	*Schoenoplectus* seeds
CAMS-9159	AMS	1430.5–1431.5	2090 ± 60	Wood
CAMS-9160	AMS	1612–1616	3730 ± 60	*Schoenoplectus* seeds
CAMS-11061	AMS	1748–1752	5260 ± 60	Charcoal
CAMS-11062	AMS	1864–1872	6350 ± 60	Charcoal
CAMS-13623[c]	AMS	1912–1920	7480 ± 60	Charcoal
CAMS-13624[c]	AMS	1912–1920	7250 ± 60	*Schoenoplectus* seeds
CAMS-9161[d]	AMS	1933.5–1934.5	9590 ± 70	Wood
CAMS-13625	AMS	1976–1980	9540 ± 60	*Schoenoplectus* seeds
Cottonwood Lake, South Dakota				
WIS-1896	Conventional	337–348	1300 ± 70	Bulk sediment
WIS-1897	Conventional	403–418	4550 ± 80	Bulk sediment
WIS-1898	Conventional	460–480	9810 ± 100	Bulk sediment
WIS-1899	Conventional	543–559	11,430 ± 110	Bulk sediment
WIS-1900	Conventional	615–626	9380 ± 100	Bulk sediment
WIS-1901	Conventional	689–700	11,060 ± 110	Bulk sediment
WIS-1902	Conventional	759–770	11,060 ± 110	Bulk sediment
WIS-1903	Conventional	835–846	11,060 ± 110	Bulk sediment
WIS-1904	Conventional	903–914	12,130 ± 110	Bulk sediment
WIS-1626	Conventional	958–968	13,410 ± 120	Bulk sediment
WIS-1905	Conventional	977–986	19,860 ± 210	Bulk sediment
CAMS-6812	AMS	385–390	240 ± 70	5 *Heliotropium curassavicum* seeds
CAMS-9859	AMS	485–488	2800 ± 140	2 *Heliotropium curassavicum* seeds, charcoal
CAMS-6818	AMS	569–573	8090 ± 70	57 *Chenopodium*, *Atriplex*, and *Amaranthus* seeds
CAMS-6817	AMS	569–573	8110 ± 90	21 *Polygonum* cf. *P. ramosissimum* seeds
CAMS-6819	AMS	606–610	8020 ± 70	36 *Polygonum* cf. *P. ramosissimum* seeds
CAMS-6813	AMS	728–730	9540 ± 90	Wood fragments
CAMS-6814	AMS	792–796	10,080 ± 80	Charcoal
CAMS-6816	AMS	868–872	9770 ± 90	Charcoal
CAMS-6815	AMS	914–921	10,300 ± 80	Charcoal
Beta-19951/ETH-2893	AMS	968–972	11,690 ± 180	*Picea* needle fragments
CAMS-6811[d]	AMS	1012–1016	> 41,400	Wood fragments
Devils Lake, Wisconsin				
WIS-993[e]	Conventional	18–25	245 ± 55	Bulk sediment
WIS-994[e]	Conventional	149–154	2055 ± 65	Bulk sediment
WIS-995[e]	Conventional	164–169	2430 ± 65	Bulk sediment
WIS-996[e]	Conventional	263–267	4105 ± 65	Bulk sediment
WIS-997[e]	Conventional	334–338	5245 ± 65	Bulk sediment
WIS-998[e]	Conventional	395–399	6920 ± 75	Bulk sediment
WIS-999	Conventional	455–459	8640 ± 85	Bulk sediment
WIS-1000	Conventional	514–518	10,080 ± 100	Bulk sediment
WIS-1001	Conventional	541–547	10,620 ± 105	Bulk sediment
WIS-1073	Conventional	599–603	12,260 ± 115	Bulk sediment
WIS-1004[f]	Conventional	599–603	12,880 ± 125	Bulk sediment
WIS-1075	Conventional	603–611	12,520 ± 160	Bulk sediment
CAMS-78446	AMS	473–475	8590 ± 50	Needles, wood, seeds, leaves
CAMS-78445	AMS	535	9740 ± 50	Needles, wood, seeds, leaves
CAMS-78444	AMS	549–551	10,110 ± 140	Needles, wood, seeds, leaves
CAMS-78443	AMS	582.5–585.0	10,730 ± 50	Needles, wood, seeds, leaves
CAMS-78442	AMS	627–639	12,580 ± 130	Needles, wood, seeds, leaves
Chatsworth Bog, Illinois[g]				
ISGS-516	Conventional	105–110	3370 ± 75	Bulk sediment
ISGS-517	Conventional	203–210	4155 ± 90	Bulk sediment
ISGS-416	Conventional	425–430	5330 ± 100	Bulk sediment
ISGS-417	Conventional	725–730	7680 ± 100	Bulk sediment
ISGS-519	Conventional	962–968	8300 ± 100	Bulk sediment
ISGS-526	Conventional	1111–1119	10,855 ± 75	Bulk sediment
ISGS-528	Conventional	1151–1159	11,280 ± 110	Bulk sediment
ISGS-527	Conventional	1250–1260	14,380 ± 150	Bulk sediment
CAMS-105965	AMS	115–118	2440 ± 40	Charcoal
CAMS-104927	AMS	269–271	4220 ± 45	Charcoal
CAMS-103618	AMS	433–437	5340 ± 50	Charcoal
CAMS-103619	AMS	704–706	5700 ± 50	Charcoal
CAMS-104928	AMS	882–886	6710 ± 60	Charcoal
CAMS-103620	AMS	1054–1056	7900 ± 60	Charcoal

(continued on next page)

Table 1 (*continued*)

Lab nr	Type	Depth (cm)	^{14}C yr BP	Material
CAMS-104929	AMS	1145–1150	9390 ± 170	2 bud scales, charcoal
UCIAMS-30983	AMS	1198–1200	9900 ± 35	*Picea* needle, 2 *Betula* seeds, *Larix* needle, *Picea* seed wing
UCIAMS-30984	AMS	1245–1252	10,315 ± 35	2 *Sagittaria* seeds, 1 *Picea* seed, charcoal
UCIAMS-30985	AMS	1334–1336	12,335 ± 30	Charcoal and 1 *Larix* needle
CAMS-103621	AMS	1389–1393	13,180 ± 140	*Picea* seed, 2 needle fragments, 2 charcoal particles, 2 seed wings
UCIAMS-30986[h]	AMS	1466–1470	14,110 ± 60	*Larix* needles, *Picea* seed wing

[a] Conventional date on wood in basal “trash layer,” not shown in Figure 2.
[b] AMS date stratigraphically above comparative conventional dates, not shown in Figure 2.
[c] AMS dates from same level averaged in Figure 2.
[d] AMS date on redeposited wood, not shown in Figure 2.
[e] Conventional date stratigraphically above comparative AMS dates, not shown in Figure 2.
[f] Date rejected as too old for conventional age model in Figure 2.
[g] Chatsworth conventional and AMS dates are from different cores, and depths are not directly comparable.
[h] AMS date stratigraphically below comparative conventional dates, not shown in Figure 2.

sites are in prairie. Plant macrofossils are relatively scarce in the sediments from these sites, but fine charcoal fragments, typically 1 mm or smaller, are frequent (Umbanhowar, 2004; Nelson et al., 2006). Charcoal, of course, is of terrestrial origin; and the fragile fragments in the Holocene sections of these lake sediments, derived primarily from herbaceous prairie vegetation, are unlikely to have resided long in the soils before being transported to the lake. We avoided dating wood and wood charcoal when possible, because they are frequently too old (Barnekow et al., 1998; Oswald et al., 2005), probably because of long residence times and inbuilt age effects (Gavin, 2001). For sites in the Great Plains, it is important to distinguish charcoal from lignite. Both appear black to the naked eye, but under the stereomicroscope, charcoal appears pure black and cellular structure is visible; whereas lignite appears very dark brown and cellular structure is not evident. If any doubt existed, the specimen was discarded. Typically, 10 to >100 charcoal fragments were combined for dates. Fires in the North American grasslands were very frequent, and charcoal is abundant in lake sediments from this region. Individual fires are not generally recognizable as distinct peaks, although decadal- to century-scale variations in fire frequency are evident in charcoal concentrations and accumulation rates (Clark et al., 2002; Nelson et al., 2004; Brown et al., 2005; Nelson et al., 2006). Charcoal dates from North American grasslands have proven to be highly reliable (e.g. Laird et al., 1996; Brown et al., 2005; Nelson et al., 2006).

Loss-on-ignition methodology follows Dean (1974). Samples were dried and weighed, ignited at 500°C (Rice Lake, Cottonwood Lake) or 550°C (Devils Lake, Chatsworth Bog) to determine organic content, and then at 900°C (Rice Lake, Cottonwood Lake) or 1000°C (Devils Lake, Chatsworth Bog) to determine carbonate content. Carbonate content was estimated by assuming that the loss of mass at 900°C or 1000°C was from decomposition of $CaCO_3$ to CaO and CO_2. The mass lost (CO_2) was multiplied by 2.27, the ratio of the molecular weights of $CaCO_3$ and CO_2. The balance of the sediment after subtracting the organic and estimated carbonate components is composed primarily of non-carbonate clastics and biogenic silica.

Results and discussion

All sites show significant deviations between the AMS and conventional chronologies (Table 1, Fig. 2). All dates obtained are listed in Table 1, whereas only those from the overlapping sections having both conventional and AMS dates are shown in Figure 2. An AMS date of >41,400 ^{14}C yr BP (CAMS-6811) on wood from the basal gravels at Cottonwood Lake indicates redeposition. Another wood date, CAMS-9161 (9590 ± 70 ^{14}C yr BP), from Rice Lake is inverted relative to the bracketing dates on *Schoenoplectus* seeds. Rice Lake has a basal trash layer with abundant wood and *Picea* needles, apparently derived from a local population of spruce trees that were growing in a swale that collapsed to form the lake, well after the regional decline of *Picea*. Thus, the dated wood fragment higher in the lake sediment is probably redeposited from elsewhere in the basin, and this date is not shown in Figure 2.

Two dates from Rice Lake, one on charcoal (CAMS-13623, 7480 ± 60 ^{14}C yr BP) and the other on *Schoenoplectus* seeds (CAMS-13624, 7250 ± 60 ^{14}C yr BP), are from the same 8-cm section of core, but the precise provenances of the charcoal and seeds within this section are unknown. The dates are significantly different at the 95% level as determined with Calib 5.0.2 (Stuiver and Reimer, 1993). However, the average deposition time for the core section is 29 ^{14}C yr/cm, so the 8-cm section represents ~230 ^{14}C yr, the same as the absolute difference between the two dates. It is possible that the younger date is on seeds from slightly higher in the section, and the two dates were averaged with Calib 5.0.2 in Figure 2.

At Cottonwood Lake the conventional and AMS chronologies differ by as much as 8000 ^{14}C yr and disagree by 1500–2000 ^{14}C yr for much of the sequence. The 8000-yr discrepancy occurs in highly inorganic sediments. These sediments also contain relatively little carbonate (Fig. 2), and the carbonate that exists may be detrital limestone or dolomite rather than authigenic calcite or aragonite. Thus, the large error in the conventional dates is probably owing to fine particles of carbonaceous shale and lignite. The organic matter in these materials is not removed by normal acid-base pretreatment. Such a large error is not unique to Cottonwood Lake. At Lost Lake, Montana, a conventional bulk-sediment date of 17,040 ± 210 ^{14}C yr BP (WIS-1791) is bracketed by AMS dates of 8965 ± 130 ^{14}C yr BP (AA-1824) and 9235 ± 150 ^{14}C yr BP (Beta-21578/ETH-3108) on *Potamogeton* and *Ruppia* seeds (Barnosky, 1989). The discrepancy between the conventional and AMS dates is ~8000 yr, similar to Cottonwood Lake, but because the AMS dates are on the seeds of submerged aquatics, which potentially have a hardwater error, the error in the conventional date may be even greater than 8000 yr. Barnosky (1989) attributes the AMS-conventional date discrepancy at Lost Lake to lignite and shale. High values of pre-Quaternary spores and pollen support this contention. Similar to Cottonwood Lake, the Lost Lake sediments are highly minerogenic. Below 6 m, the Cottonwood Lake sediments contain more organic matter and more carbonate, which probably is authigenic, and the differential between the AMS and conventional dates is less, although still 1500–2000 yr.

At Rice Lake the two chronologies disagree by 1500–2000 yr for most of the sequence. The Rice Lake sediments are marly, averaging ~40% carbonate, primarily authigenic (Yu et al., 2002). Organic matter averages 10–20%.

At Devils Lake the AMS and conventional chronologies differ by 500–1000 yr, gradually becoming greater with depth. The Devils Lake sediments have very little carbonate; and, in fact, many of the loss-on-ignition values at 1000°C were slightly negative (indicating a slight mass gain, rather than loss). Thus, consistent with its location in a quartzite basin, Devils Lake probably does not have a significant hardwater error. The carbonate in the basal sediments is probably

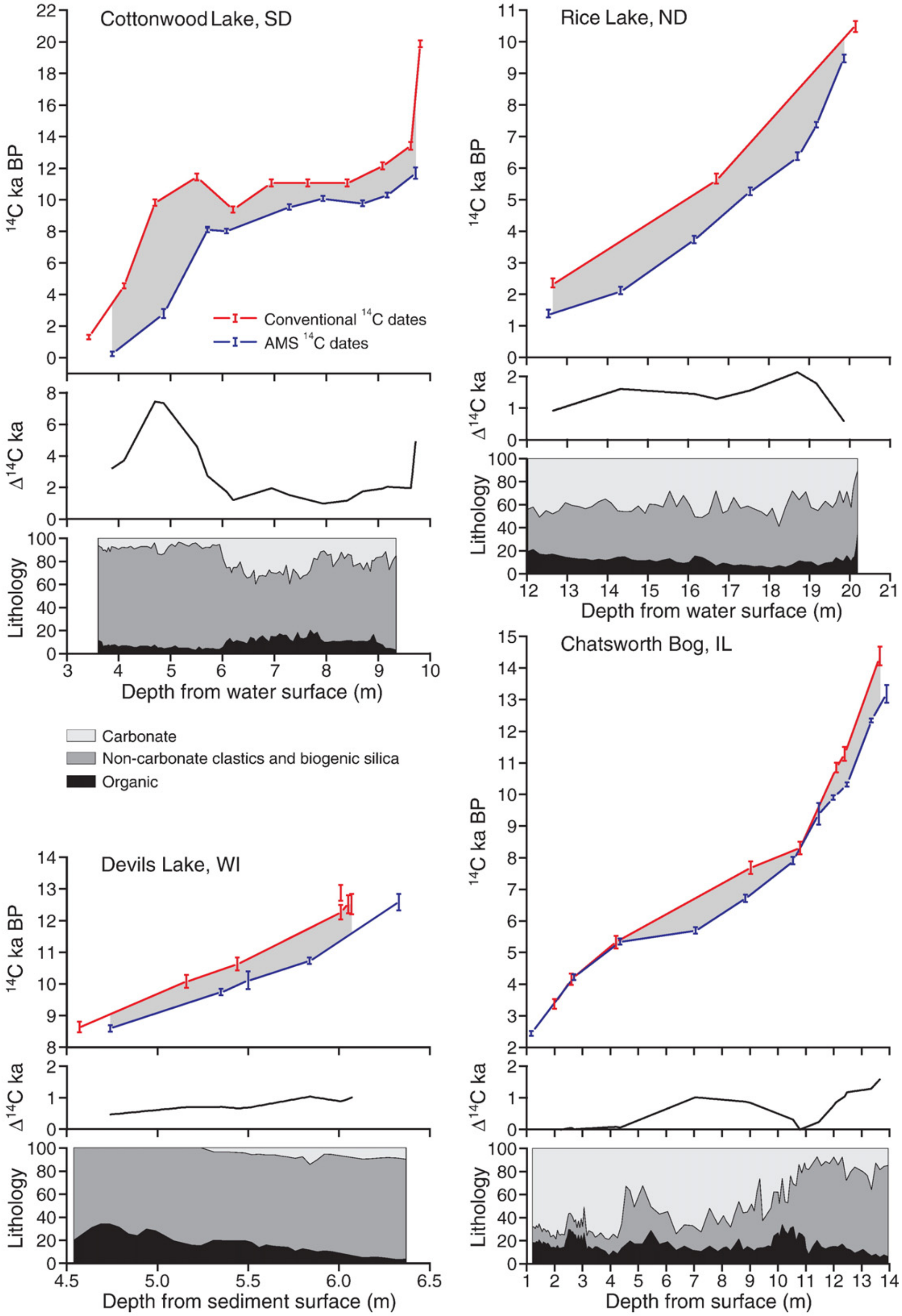

Figure 2. Age-depth graphs (^{14}C yr BP) based on conventional (red) and AMS (blue) ^{14}C dates for the four study sites. The dates are shown with 2σ error bars. Depths on the horizontal axes are shown as originally published. The vertical scales are the same for all graphs except for Cottonwood Lake, which is half the scale of the others. The vertical distance between the AMS and conventional chronologies, represented by the gray area, is the difference (Δ) or estimated reservoir, which is shown on the graph below each age-depth graph. The sediment composition based on loss-on-ignition is shown below each difference graph. The sediment key is shown below the graph for Cottonwood Lake.

detrital, originating from eolian sources or from limestone debris in the moraine dams; and we propose that the old-carbon reservoir in the highly minerogenic basal sediments is derived from eolian sources, including silt-sized carboniferous rock particles. The offset between the age models based on AMS and conventional dates leads to strikingly different interpretations of the pollen data from this site (Fig. 3). An age model based on calibrated conventional dates suggests that a marked decline in *Picea* and rise in *Pinus* occurred at the

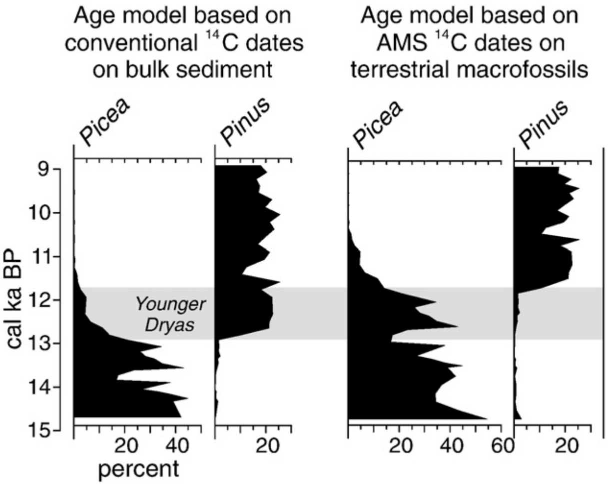

Figure 3. Alternative age models in cal yr for Devils Lake based on conventional ^{14}C dates from bulk sediment with no assumed reservoir versus AMS ^{14}C dates on terrestrial plant macrofossils. The radiocarbon dates were calibrated with Calib 5.0.2 using the INTCAL04 calibration curve (Stuiver and Reimer, 1993), and the age models are linear interpolations.

beginning of the Younger Dryas chronozone; whereas an age model based on the calibrated AMS dates shows that this transition occurred at the end of the Younger Dryas. Thus, the suggestion by Shuman et al. (2002), based on the calibrated conventional dates, that the Younger Dryas chronozone at Devils Lake was warm and dry is probably incorrect.

At Chatsworth Bog the two chronologies differ by 0–1600 yr. The divergence is essentially zero from 2000 to 5300 ^{14}C yr BP, then rises to ~1000 yr at 5700 ^{14}C yr BP, according to the AMS chronology, and then falls to zero at 8300 ^{14}C yr BP. The error increases with depth to ~1600 yr in the relatively low carbonate, minerogenic sediments at the base of the core.

Because of the high marl content in the upper sediments (40–80%), a significant hardwater error might be expected. However, little error is apparent until below 4 m depth. A transition from lake sediment to peat occurs at ~1 m depth, which dates to ~3400 ^{14}C yr BP (King, 1981). Exchange of CO_2 can maintain equilibrium in dissolved inorganic carbon between lake water and the atmosphere (Miller et al., 1999; Oswald et al., 2005), potentially mitigating the hardwater effect. This exchange is probably greater in shallower lakes, as wind and wave-action cause more mixing. This explanation may account for the diminished hardwater error in the late Holocene sediments at Chatsworth Bog, despite the high marl content. The reservoir is minimal in the low carbonate sediments of the early Holocene, but is greater in the late-Pleistocene minerogenic sediments, probably owing to carbonaceous rock particles.

The absence of an old-carbon reservoir in the upper sediments of Chatsworth Bog cannot be a function of only its shallow depth, as Cottonwood Lake is also quite shallow, and given its size and exposure to wind, certainly well mixed. However, the Cottonwood Lake sediments are much more minerogenic, more similar to the late-glacial sediments of Chatsworth Bog, which do show a reservoir effect, and the old-carbon reservoir is probably in the clastic sediments. The upper lake sediments of Chatsworth Bog—a shallow-water organic marl—are unique in our study. However, we would hesitate to generalize the Chatsworth results to other similar sediments in the absence of data from other sites.

In our study, deeper lakes with carbonate-rich sediments show a significant discrepancy between bulk-sediment conventional-date and macrofossil AMS-date chronologies, typically running 500–2000 yr. These results are consistent with results from other similar studies, for example an 800-yr offset between conventional bulk-sediment and AMS plant-macrofossil chronologies for the late-glacial interval at Lobsigensee, Switzerland (Andree et al., 1986), and a 550–2700 yr discrepancy at Lake Tibetanus, Sweden (Barnekow et al., 1998).

However, marl content is not always a good proxy for the old-carbon reservoir, as the Chatsworth data show. In fact, the greatest errors generally occur not in sediments with high contents of authigenic marl, but rather in highly minerogenic sediments with little carbonate. At Cottonwood Lake and Lost Lake (Barnosky, 1989), the error appears to be owing to clastic materials derived from lignite and carbonaceous shales, which are widespread in the northern Great Plains. At Devils Lake, a site with no authigenic carbonate and little carbonate or carbonaceous rock material in the catchment apart from the blocking moraines, the error still approaches 1000 yr towards the bottom of the core, as organic matter falls to <5%, and the potential therefore rises for small quantities of ancient carbon from eolian sources to bias the bulk-sediment dates. Both Devils Lake and Chatsworth Bog show an increase in the old-carbon error in late-glacial sediments with low organic matter.

A common practice to correct for the ancient carbon reservoir is to date the European settlement horizon and to apply the difference

Table 2
Amended age-depth controls for developing age models for Devils Lake and Chatsworth Bog.

Depth (cm)	Reported age (^{14}C yr BP)	Estimated reservoir (yr)	cal yr BP[a]	
			2σ range	Median probability
Devils Lake, Baker et al. (1992)[b]				
0	0			0
18–25	120 ± 10		130–110	120
149–154	2055 ± 65	197	1945–1618	1792
164–169	2430 ± 65	209	2349–2060	2226
263–267	4105 ± 65	282	4417–3999	4229
334–338	5245 ± 65	336	5883–5479	5649
395–399	6920 ± 75	381	7573–7312	7452
455–459	8640 ± 85	426	9423–9007	9190
473–475	8590 ± 50	0	9671–9489	9550
535	9740 ± 50	0	11,247–10,883	11,182
549–551	10,110 ± 140	0	12,340–11,237	11,717
582.5–585.0	10,730 ± 50	0	12,848–12,690	12,792
627–639	12,580 ± 130	0	15,158–14,190	14,725
Chatsworth Bog, King (1981)[c]				
20	800 ± 100	0	900–700	800
105–110	3370 ± 75	0	3828–3448	3613
203–210	4155 ± 90	0	4858–4438	4679
425–430	5330 ± 100	0	6294–5912	6103
725–730	7680 ± 100	838	7927–7512	7691
962–968	8300 ± 100	0	9480–9031	9290
1111–1119	10,855 ± 75	863	11,801–11,239	11,486
1151–1159	11,280 ± 110	1036	12,564–11,405	11,984
1250–1260	14,380 ± 150	1577	15,633–14,479	15,105

[a] Dates calibrated with the online version of Calib 5.0.2 using the INTCAL04 calibration curve (Stuiver and Reimer, 1993). The reservoir was subtracted before calibrating. Calib provides the median probability in the spreadsheet export file.

[b] The reported ages are the estimated age of the top of the core (0), the age of the *Ambrosia*-rise (120 ± 10), the conventional bulk-sediment ages from Baker et al. (1992) shown with reservoir corrections >0, and the new AMS dates reported in this paper shown with reservoir corrections of zero. Based on our age models (Fig. 2), the offset between the AMS and conventional chronologies is 464 yr at the upper AMS date at 473–475 cm. The *Ambrosia*-rise at 18–25 cm, which marks European settlement, is dated to 245 ± 55 ^{14}C yr BP. The historical date of the *Ambrosia*-rise is estimated to be ~AD 1830, or 120 BP. Thus, the implied reservoir is 125 yr. The bulk-sediment and AMS chronologies for the older section of the core show a gradually decreasing reservoir effect, and the bulk-sediment date on the *Ambrosia*-rise indicates that the reservoir continues to decrease toward the present. Thus, the reservoir for the bulk-sediment dates from the younger section of the core is prorated from 464 yr at 474 cm to 125 yr at 21.5 cm. The top of the Devils Lake core is estimated to be 0 BP.

[c] The reported ages are the bulk-sediment ages reported by King (1981). The estimated reservoir is the offset between the ^{14}C yr age models for the King (1981) core and the Nelson et al. (2006) core (Fig. 2) based on the pollen stratigraphic correlation of the two cores. King (1981) estimated the age at 20 cm to be 800 yr.

between this date and the historically known date to the entire core. This correction is perhaps better than none, but it is nevertheless inadequate. Apart from the problems with dating recent sediments due to fluctuations in atmospheric ^{14}C, the results from this study show that the correction varies with depth, as sediment lithology changes, as lake depth has changed, and as environmental and limnological conditions have changed.

Chronologies based on bulk-sediment conventional ^{14}C dates from sites in the northern Great Plains and Midwest have significant carbon-reservoir problems. The reservoir is derived from dissolved carbonate rocks, the familiar “hardwater” error, and from fine-grained clastics derived from carbonaceous rocks. Thus, the presence of groundwater and eolian sources of old carbon potentially bias the bulk-sediment dates. Another potential source of old carbon not considered here, but potentially important elsewhere, such as arctic and boreal settings, is dissolved organic carbon derived from peatlands and soils (Lowe et al., 1988; Abbott and Stafford, 1996). Additional comparisons of conventional and AMS chronologies may be useful in assessing the relative influence of dissolved organic matter versus clastics on carbon-reservoir problems in other regions.

One site that does not appear to have an old-carbon reservoir is Lake Tulane in the Florida peninsula. Bulk-sediment AMS dates from this site are consistently in line with dates on terrestrial macrofossils, so no old-carbon reservoir is indicated (Grimm et al., 2006). Lake Tulane, although a sinkhole lake, lies in acid sands in the surficial aquifer. The Florida peninsula, which juts into the ocean and for which no significant eolian source for old carbon exists, is somewhat of a special case, and these conditions for reliable bulk-sediment dates may be rarely met. Moreover, an earlier chronology from Lake Tulane (Grimm et al., 1993) based on conventional bulk-sediment dates was considerably less accurate because large sections of core, up to 20 cm in length, were dated, some of these incorporating >1000 yr of sediment. So although the AMS method cannot inherently provide a more accurate age on bulk sediment than the conventional method, the ability to date much thinner sections of sediment can provide a more highly resolved age model if there is no old-carbon reservoir.

New AMS dates from existing cores or AMS dates from new cores that are stratigraphically correlated with old cores can be used to develop corrected age models for existing data. Ideally, for the purposes of databases such as the Global Pollen Database, new sets of age-depth points would be provided in radiocarbon years with estimated old-carbon-reservoir values so that they can be calibrated by future investigators using updated calibration curves with the age-model algorithms of their choice. We provide corrected age-depth control points (Table 2) for the published chronologies for Devils Lake (Baker et al., 1992) and Chatsworth Bog (King, 1981). Attempts to derive high-resolution temporal results from the existing database of legacy bulk-sediment dates are probably futile. Without companion AMS chronologies from terrestrial macrofossils, the extent of the bias is unknown. Clearly an urgent need exists to develop more AMS chronologies on a regional basis that can be applied to existing paleo datasets.

Acknowledgments

We thank Philip Higuera and one anonymous reviewer for useful comments and improvements to the manuscript. This work was supported by National Science Foundation Grants BSR-8614916 and EAR-0622289 to E. C. Grimm and EAR-9905327 to F. S. Hu.

References

Abbott, M.B., Stafford Jr, T.W., 1996. Radiocarbon geochemistry of modern and ancient Arctic lake systems, Baffin Island, Canada. Quaternary Research 45, 300–311.

Andree, M., Oeschger, H., Siegenthaler, U., Riesen, T., Moell, M., Ammann, B., Tobolski, K., 1986. ^{14}C dating of plant macrofossils in lake sediment. Radiocarbon 28, 411–416.

Baker, R.G., Maher, L.J., Chumbley, C.A., Van Zant, K.L., 1992. Patterns of Holocene environmental change in the midwestern United States. Quaternary Research 37, 379–389.

Barnekow, L., Possnert, G., Sandgren, P., 1998. AMS ^{14}C chronologies of Holocene lake sediments in the Abisko area, northern Sweden — a comparison between dated bulk sediment and macrofossil samples. GFF 120, 59–67.

Barnosky, C.W., 1989. Postglacial vegetation and climate in the northwestern Great Plains of Montana. Quaternary Research 31, 57–73.

Barnosky, C.W., Grimm, E.C., Wright Jr, H.E., 1987. Towards a post-glacial history of the Northern Great Plains: a review of the paleoecologic problems. Annals of Carnegie Museum 56, 259–273.

Broecker, W.S., Walton, A., 1959. The geochemistry of ^{14}C in the freshwater systems. Geochimica et Cosmochimica Acta 16, 15–38.

Bronk Ramsey, C., 2008. Radiocarbon dating: revolutions in understanding. Archaeometry 50, 249–275.

Brown, K.J., Clark, J.S., Grimm, E.C., Donovan, J.J., Mueller, P.G., Hansen, B.C.S., Stefanova, I., 2005. Fire cycles in North American interior grasslands and their relation to prairie drought. Proceedings of the National Academy of Sciences of the United States of America 102, 8865–8870.

Clark, J.S., Grimm, E.C., Donovan, J.J., Fritz, S.C., Engstrom, D.R., Almendinger, J.E., 2002. Drought cycles and landscape responses to past aridity on prairies of the northern Great Plains, USA. Ecology 83, 595–601.

Dean Jr, W.E., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. Journal of Sedimentary Petrology 44, 242–248.

Deevey Jr., E.S., Gross, M.S., Hutchinson, G.E., Kraybill, H.L., 1954. The natural C^{14} contents of materials from hard-water lakes. Proceedings of the National Academy of Sciences of the United States of America 40, 285–288.

Flint, R.F., 1955. Pleistocene geology of eastern South Dakota. United States Geological Survey Professional Paper 262.

Fritz, S.C., Ito, E., Yu, Z., Laird, K.R., Engstrom, D.R., 2000. Hydrologic variation in the northern Great Plains during the last two millennia. Quaternary Research 53, 175–184.

Gavin, D.G., 2001. Estimation of inbuilt age in radiocarbon ages of soil charcoal for fire history studies. Radiocarbon 43, 27–44.

Gonzales, L.M., and Grimm, E.C., (in press). Synchronization of late-glacial vegetation changes at Crystal Lake, Illinois, USA with the North Atlantic Event Stratigraphy. Quaternary Research. doi:10.1016/j.yqres.2009.05.001.

Grimm, E.C., Jacobson Jr, G.L., 2004. Late-Quaternary vegetation history of the eastern United States. In: Gillespie, A.R., Porter, S.C., Atwater, B.F. (Eds.), The Quaternary Period in the United States. In: Developments in Quaternary science. Elsevier, Amsterdam, pp. 381–402.

Grimm, E.C., Jacobson Jr, G.L., Watts, W.A., Hansen, B.C.S., Maasch, K.A., 1993. A 50,000-year record of climate oscillations from Florida and its temporal correlation with the Heinrich events. Science 261, 198–200.

Grimm, E.C., Watts, W.A., Jacobson, G.L.J., Hansen, B.C.S., Almquist, H.R., Dieffenbacher-Krall, A.C., 2006. Evidence for warm wet Heinrich events in Florida. Quaternary Science Reviews 25, 2197–2211.

Hellborg, R., Skog, G., 2008. Accelerator mass spectrometry. Mass Spectrometry Reviews 27, 398–427.

King, J.E., 1981. Late Quaternary vegetational history of Illinois. Ecological Monographs 51, 43–62.

Laird, K.R., Fritz, S.C., Grimm, E.C., Mueller, P.G., 1996. Century-scale paleoclimatic reconstruction from Moon Lake, a closed-basin lake in the northern Great Plains. Limnology and Oceanography 41, 890–902.

Lowe, J.J., Lowe, S., Fowler, A.J., Hedges, R.E.M., Austin, T.J.F., 1988. Comparison of accelerator and radiometric radiocarbon measurements obtained from Late Devensian lateglacial lake sediments from Llyn Gwernan, North Wales, UK. Boreas 17, 355–369.

Martin, J.E., Sawyer, J.F., Fahrenbach, M.D., Tomhave, D.W., Schulz, L.D., 2004. Geologic Map of South Dakota [1:500,000]. South Dakota Geological Survey, Vermillion.

Miller, G.H., Mode, W.N., Wolfe, A.P., Sauer, P.E., Bennike, O., Forman, S.L., Short, S.K., Stafford Jr, T.W., 1999. Stratified interglacial lacustrine sediments from Baffin Island, Arctic Canada: chronology and paleoenvironmental implications. Quaternary Science Reviews 18, 789–810.

Nambudiri, E.M.V., Teller, J.T., Last, W.M., 1980. Pre-Quaternary microfossils—a guide to errors in radiocarbon dating. Geology 8, 123–126.

Nelson, D.M., Hu, F.S., 2008. Patterns and drivers of Holocene vegetational change near the prairie-forest ecotone in Minnesota: revisiting McAndrews' transect. New Phytologist 179, 449–459.

Nelson, D.M., Hu, F.S., Tian, J., Stefanova, I., Brown, T.A., 2004. Response of C_3 and C_4 plants to middle-Holocene climatic variation near the prairie-forest ecotone of Minnesota. Proceedings of the National Academy of Sciences of the United States of America 101, 562–567.

Nelson, D.M., Hu, F.S., Grimm, E.C., Curry, B.B., Slate, J.E., 2006. The influence of aridity and fire on Holocene prairie communities in the eastern Prairie Peninsula. Ecology 87, 2523–2536.

Ogden III, J.G., 1967a. Radiocarbon and pollen evidence for a sudden change in climate in the Great Lakes region approximately 10,000 years ago. In: Cushing, E.J., Wright, H.E. (Eds.), Quaternary Paleoecology. Yale University Press, New Haven, Connecticut, pp. 117–127.

Ogden III, J.G., 1967b. Radiocarbon determinations of sedimentation rates from hard and soft-water lakes in northeastern North America. In: Cushing, E.J., WrightJr Jr, H.E. (Eds.), Quaternary Paleoecology. Yale University Press, New Haven, Connecticut, pp. 175–183.

Oswald, W.W., Anderson, P.M., Brown, T.A., Brubaker, L.B., Hu, F.S., Lozhkin, A.V., Tinner, W., Kaltenrieder, P., 2005. Effects of sample mass and macrofossil type on radiocarbon dating of arctic and boreal lake sediments. The Holocene 15, 758–767.

Saarnisto, M., 1988. Time-scales and dating. In: Huntley, B., WebbIII III, T. (Eds.), Vegetation History. In: Handbook of vegetation science. Kluwer Academic Publishers, Dordrecht, pp. 77–112.

Santos, G.M., Southon, J.R., Griffin, S., Beaupre, S.R., Druffel, E.R.M., 2007. Ultra small-mass AMS 14C sample preparation and analyses at KCCAMS/UCI Facility. Nuclear Instruments and Methods in Physics Research B 259, 293–302.

Shuman, B., Webb III, T., Bartlein, P., Williams, J.W., 2002. The anatomy of a climatic oscillation: vegetation change in eastern North America during the Younger Dryas chronozone. Quaternary Science Reviews 21, 1777–1791.

Stuiver, M., Reimer, P.J., 1993. Extended ^{14}C database and revised CALIB radiocarbon calibration program. Radiocarbon 35, 215–230.

Umbanhowar Jr, C.E., 2004. Interactions of climate and fire at two sites in the northern Great Plains, USA. Palaeogeography, Palaeoclimatology, Palaeoecology 208, 141–152.

Voss, J., 1937. Comparative study of bogs on Cary and Tazewell drift in Illinois. Ecology 18, 119–135.

Webb III, T., Cushing, E.J., Wright Jr, H.E., 1983. Holocene changes in the vegetation of the Midwest. In: WrightJr. Jr., H.E. (Ed.), The Holocene. In: Late-Quaternary environments of the United States. University of Minnesota Press, Minneapolis, pp. 142–165.

Williams, J.W., Post, D.M., Cwynar, L.C., Lotter, A.F., 2002. Rapid and widespread vegetation responses to past climate change in the North Atlantic region. Geology 30, 971–974.

Williams, J.W., Shuman, B.N., Webb III, T., Bartlein, P.J., Luduc, P.L., 2004. Late-Quaternary vegetation dynamics in North America: scaling from taxa to biomes. Ecological Monographs 74, 309–334.

Wright Jr., H.E., Stefanova, I., Tian, J., Brown, T.A., Hu, F.S., 2004. A chronological framework for the Holocene vegetational history of central Minnesota: the Steel Lake pollen record. Quaternary Science Reviews 23, 611–626.

Yu, Z., Ito, E., 1999. Possible solar forcing of century-scale drought frequency in the northern Great Plains. Geology 27, 263–266.

Yu, Z., Ito, E., Engstrom, D.R., Fritz, S.C., 2002. A 2100-year trace-element and stable-isotope record at decadal resolution from Rice Lake in the northern Great Plains, USA. The Holocene 12, 605–617.