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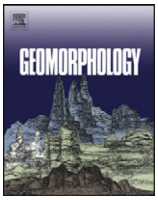

An evaluation of *Mesodon* and other larger terrestrial gastropod shells for dating late Holocene and historic alluvium in the Midwestern USA

Monica T. Rakovan [a], Jason A. Rech [a,*], Jeffrey S. Pigati [b], Jeffrey C. Nekola [c], Gregory C. Wiles [d]

[a] *Department of Geology and Environmental Earth Science, Miami University, Oxford, OH 45056, USA*
[b] *U.S. Geological Survey, Denver Federal Center, P.O. Box 25046, MS-980, Denver, CO 80225, USA*
[c] *Department of Biology, University of New Mexico, Albuquerque, NM 87131, USA*
[d] *Department of Geology, The College of Wooster, Wooster, OH 44691, USA*

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ABSTRACT

Understanding the history of stream erosion and changes in channel morphology is important for managing and restoring unstable streams. One of the significant challenges in this type of research is establishing accurate dating of late Holocene and historic alluvium. Here we evaluate the potential of using ^{14}C dating and amino acid racemization (AAR) to date large terrestrial gastropod shells that are often preserved within alluvial sediments. Many terrestrial gastropods incorporate old carbon from limestone or other carbonate rocks into their shells and therefore are unsuitable for radiocarbon dating. Recent studies, however, have shown that some taxa avoid this 'limestone problem' and can yield reliable ^{14}C ages. In this study, we measured the ^{14}C activity of specimens for the genera *Mesodon*, *Ventridens*, and *Allogona* collected live and from alluvial sequences dated independently by dendrochronology, ^{14}C dating of wood, and/or ^{137}Cs analyses. *Mesodon zaletus* contained old carbon in similar concentrations (up to ~30%) found in previous studies of other large taxa and should be avoided for ^{14}C dating when possible. In contrast, shells of *Ventridens ligera* and *Allogona profunda* showed minimal limestone effects and therefore may be suitable for dating late Holocene alluvium. These results highlight the importance of taxonomic identification of gastropod taxa prior to their use for ^{14}C dating and demonstrate that shell fragments that are not identifiable should be avoided. We also measured d/l ratios ($n = 17$) of aspartic and glutamic acid from eight different taxa of terrestrial gastropods recovered from four late Holocene and historic stratigraphic sequences. Average d/l ratios of aspartic and glutamic acid from historic sediments <300 years old are lower in shells from younger stratigraphic units, indicating that AAR can be used to differentiate between multiple historic stratigraphic units.

1. Introduction

Geomorphic studies on the impact of historic land use on streams in the central and eastern USA have documented the filling of channels with sediments eroded from upland soils and their subsequent incision as streams adjusted to modifications in sediment load (Simon, 1989; Fitzpatrick et al., 1999; Trimble, 1999; Knox, 2001; Montgomery, 2007; Walter and Merritt, 2008). Additional fluctuations in sediment load associated with changes in agricultural practices and urbanization have also modified stream channels and led to widespread stream instability (Wolman, 1967; Chin and Gregory, 2001; Rakovan and Renwick, 2011). Although the general pattern of historic (i.e., post-European settlement) changes in channel morphology in North America has been described in detail, the underlying causes are understood only at a general level. Reconstruction of changes in stream valley morphology through time is critical for determining the impact of historic land use on stream systems, identifying the relative roles of present-day land use and agricultural practices (Walter and Merritt, 2008), and predicting how streams will respond to future changes in land use and climate (Stokes and Walling, 2003).

One of the challenges in documenting the response of stream systems to land use change is the difficulty of dating late Holocene and historic alluvial deposits. Radiogenic (^{14}C, ^{210}Pb, and ^{137}Cs) and nonradiogenic (dendrochronology, luminescence, and amino acid racemization [AAR]) dating techniques have been used, but each method comes with its own set of strengths and weaknesses. In this study we evaluate the potential for using ^{14}C and AAR dating of large terrestrial gastropod shells, as well as a few other taxa, to establish the chronology of late Holocene and historic alluvial sediments in the Midwestern USA. Terrestrial gastropods are abundant in most modern floodplains, and fossil shells are common within alluvial sedimentary sequences. Gastropod shells are composed of aragonite ($CaCO_3$) and potentially can be used for ^{14}C dating. However, some gastropods incorporate old carbon from limestone or calcareous sediments into their shells and, therefore, yield radiocarbon ages that are too old (Rubin et al., 1963; Tamers, 1970; Evin et al.,

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* Corresponding author. Tel.: +1 5135291935; fax: +1 5135291542.
E-mail address: rechja@miamioh.edu (J.A. Rech).

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1980; Goodfriend and Hood, 1983; Goodfriend and Stipp, 1983; Yates, 1986; Goodfriend et al., 1999; Zhou et al., 1999; Quarta et al., 2007; Romaniello et al., 2008; Xu et al., 2011). Researchers have analyzed shells from live gastropods collected from different environments, including those with and without sources of limestone, and experimented with diets including various amounts of carbonate (Goodfriend and Stipp, 1983; Goodfriend et al., 1999; Romaniello et al., 2008; Pigati et al., 2010). The amount of carbonate incorporated into shell material is highly variable and can be as much as ~30% (Goodfriend and Stipp, 1983; Pigati et al., 2004). Thus, simple correction factors to account for this 'limestone problem' cannot be applied.

Recent studies of terrestrial gastropod taxa in North America have shown that some taxa do not ingest limestone even when living in environments in which carbonate is readily available (Brennan and Quade, 1997; Pigati et al., 2004, 2010; Rech et al., 2012). The alluvial deposits present in our study area do not contain the same taxa as those analyzed in these previous studies. Only larger (>1 cm) taxa with thick shells appear to be preserved within the alluvial sediments. Although limestone bedrock is abundant in the region, limestone outcrops and clasts are not common in modern stream floodplains where gastropods live. Thus, gastropod shells could yield reliable ^{14}C ages in this particular environmental setting.

Amino acid racemization (AAR) dating can also be applied to these gastropod shells. Dating by AAR has long been used to determine the age of shells from marine and terrestrial environments (Goodfriend, 1987; Wehmiller and Miller, 2000; Oches and McCoy, 2001; Owen et al., 2007; Yanes et al., 2007; Bateman et al., 2008; Huntley et al., 2008; Hearty and Kaufman, 2009; Penkman, 2009; Demarchi et al., 2011), and is a rapid and affordable relative dating method with resolution as low as 50–100 years for recent centuries and 200–500 years for the early Holocene (Wood et al., 2006; Kowalewski, 2009). Moreover, recent studies have shown good correlations between AAR ratios and the age of specimens in museum collections that were collected historically (Hearty and Kaufman, 2009; Huntley et al., 2012), indicating that AAR may be a robust tool for determining the age of alluvial sequences that are less than a few hundred years old.

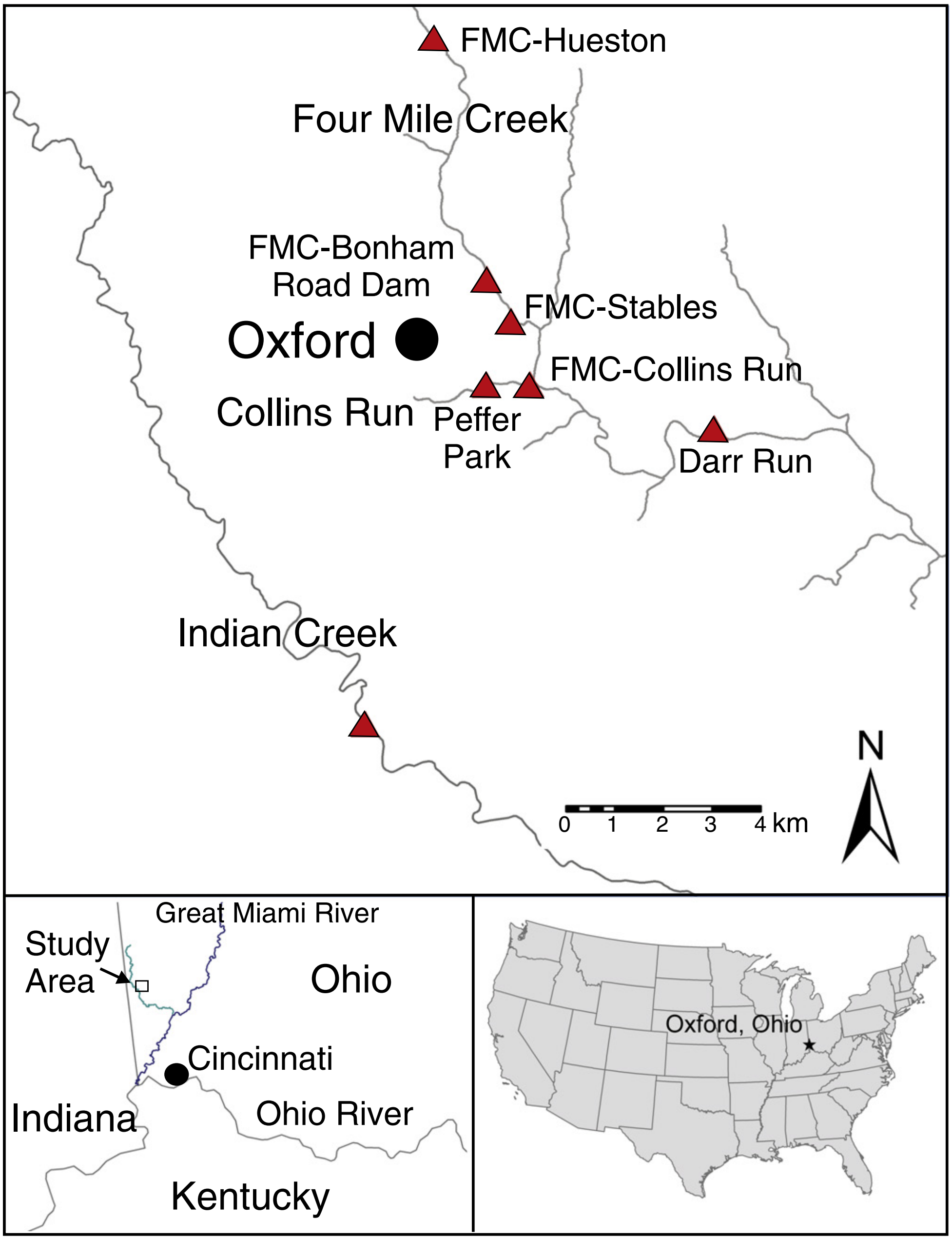

Fig. 1. Location of sampling areas along Four Mile Creek and Indian Creek in southwestern Ohio, USA.

Terrestrial gastropods are thought to be well suited for AAR dating because of their nonporous shells, which make them less vulnerable to soil contamination and hydrolysis of shell proteins that interfere with racemization and epimerization of its amino acids (Goodfriend, 1987; Yanes et al., 2007; Huntley et al., 2008). Published amino acid epimerization ratios of alloisoleucine/isoleucine of Quaternary terrestrial gastropods have shown that shell AAR ratios in alluvium and loess deposits correlate strongly with ^{14}C ages (e.g., Clark et al., 1989; Goodfriend, 1989; Oches and McCoy, 2001).

2. Study area

The study area is located in southwest Ohio, situated within the Midwestern USA (Fig. 1). The geology for this region consists of Quaternary glacial deposits that overlie a ~200-m-thick sequence of Ordovician limestone and shale. Unconsolidated glacial deposits in the area were laid down during the Last Glacial Maximum (~24 ka) (Eckberg et al., 1993).

European settlers began arriving in the area at the beginning of the nineteenth century, and by the mid-nineteenth century the landscape was largely agricultural (Knepper, 2002). By 1942, <10% of the original forest cover remained (Birch and Wharton, 1982). The mean annual temperature and precipitation in the region, based on the 30-year record from 1961 to 1990, range from 9.4 to 12.75 °C and from 91 to 107 cm, respectively (Debrewer et al., 1999).

Streams in the study area are incised within Ordovician bedrock and late Quaternary glacial deposits. The generalized alluvial stratigraphy for this region includes four sequences of alluvial fill terraces, although these terraces are not present at all locations (Fig. 2). The highest fill terrace, usually about 5 to 10 m above stream level, is capped by a well-developed soil with an argillic horizon and overlays glacial deposits that are ~24,000 years old. We designate this stratigraphic unit, thought to be latest Pleistocene in age, as unit 1. The next highest terrace, unit 2, is 4 to 6 m above stream level and capped with a soil displaying some reddening and clay accumulation. However, this soil is often highly eroded due to agricultural practices and therefore it is difficult to assess its age. The two youngest inset terraces are generally 3 to 5 m and 1 to 3 m above stream level, respectively. The higher of these terraces is thought to be historic in age and often contains a buried soil representing the pre-historic (i.e., pre-European settlement) landscape surface. We designate the stratigraphic unit below the buried soil as unit 3, whereas above the soil is unit 4. The youngest inset terrace (unit 5) has not been modified by soil development and was deposited during the latter half of the twentieth century based on analysis of aerial photography (Rakovan and Renwick, 2011).

Sites for this study are situated along Four Mile Creek (FMC), two of its tributaries (Collins Run, Darr Run), and Indian Creek (Fig. 1). Large gravel bars composed almost entirely of limestone clasts are present within stream channels. Floodplains generally do not contain limestone clasts, but floodplain sediments are calcareous with ~5 to 15% calcium carbonate.

3. Methods

Live and fossil terrestrial gastropod samples were collected from floodplains and alluvial deposits along Indian and Four Mile Creeks. Shells were cleaned and identified based on shell morphology (e.g., Nekola, 2004) and processed for radiocarbon dating and amino acid racemization. Buried trees and stumps were collected from outcrops for radiocarbon dating and dendrochronology. Samples of alluvial sediments were collected for ^{137}Cs analyses.

3.1. ^{14}C dating

Terrestrial gastropod shells and wood were processed at Miami University for accelerator mass spectrometry (AMS) ^{14}C dating using standard methods. Fossil shells were broken, and adhering detritus was physically removed; but the shells were not powdered during pretreatment to minimize the potential for adsorption of atmospheric ^{14}C. Shell samples were treated initially with 6% NaOCl for 18–24 h at room temperature to remove all organic material. Shells were then washed repeatedly in 18.2 MΩ water, sonicated for a few minutes to remove adhered solution, washed again with ultrapure water, and dried in a vacuum oven overnight at ~70 °C. Shell aragonite was converted to CO_2 using 100% H_3PO_4 under vacuum at 75 °C. Fossil wood samples were chemically pretreated with standard acid–base–acid solutions and combusted at 800 °C. For all samples, water, SO_x, NO_x, and halide species were removed using passive traps and the resulting CO_2 was split into two aliquots. One aliquot was converted to graphite by catalytic reduction of CO (modified after Slota et al., 1987) and submitted to the Arizona-NSF AMS facility for ^{14}C analysis. The second aliquot was submitted for δ^{13}C analysis to correct the measured ^{14}C activity of the shell carbonate for isotopic fractionation (Pigati, 2002). The ^{14}C ages were calibrated using CALIB v. 6.0.0 (Stuiver and Reimer, 1993) and the IntCal09 data set (Reimer et al.,

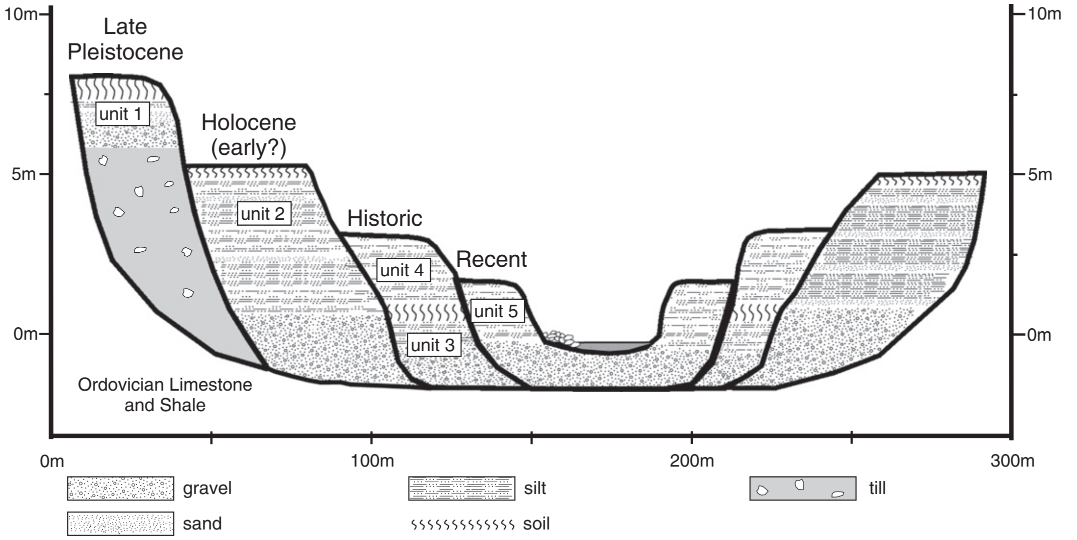

Fig. 2. Generalized alluvial stratigraphy for Four Mile and Indian Creeks in southwestern Ohio, USA.

Table 1
^{14}C results for modern gastropod shells.

Lab #	AA #	Taxon	Site	δ^{13}C (vpdb)	F^{14}C	Apparent ^{14}C age (^{14}C years)	Apparent cal age (years)[a]	P[b]	Shell Δ^{14}C	Atmos Δ^{14}C	Diet Δ^{14}C	Limestone effect[c] (^{14}C years)
MU-285	76664	*Mesodon zaletus*	Indian Creek	−9.0	0.7733 ± 0.0042	2070 ± 40	2040 ± 100	0.99	−227 ± 4	46 ± 5	77 ± 21	2900 ± 250
MU-291	76670	*M. zaletus* (aperture)	FMC Stables	−9.7	0.9066 ± 0.0028	790 ± 20	710 ± 20	1.00	−93 ± 3	46 ± 5	77 ± 21	1500 ± 200
MU-287	76666	*M. zaletus* (body)	FMC Stables	−9.1	0.8875 ± 0.0027	960 ± 20	830 ± 40 910 ± 20	0.66 0.34	−112 ± 3	46 ± 5	77 ± 21	1680 ± 210
MU-288	76667	*M. zaletus* (whorls)	FMC Stables	−9.7	0.9044 ± 0.0028	810 ± 20	710 ± 30	0.97	−96 ± 3	46 ± 5	77 ± 21	1520 ± 200
MU-283	76662	*Ventridens ligera*	FMC Stables	−13.3	1.0271 ± 0.0025	Post-bomb	–		27 ± 3	46 ± 5	77 ± 21	410 ± 180
MU-284	76663	*V. ligera*	FMC Stables	−13.9	1.0045 ± 0.0027	Post-bomb	–		5 ± 3	46 ± 5	77 ± 21	600 ± 180
MU-286	76665	*V. ligera*	Indian Creek	−11.9	1.0344 ± 0.0034	Post-bomb	–		34 ± 3	46 ± 5	77 ± 21	350 ± 180
MU-290	76669	Immature Polygyridae	FMC Stables	−8.8	0.7298 ± 0.0023	2530 ± 30	2550 ± 50 2620 ± 20 2710 ± 30	0.48 0.19 0.34	−270 ± 2	46 ± 5	77 ± 21	3420 ± 260
MU-289	76668	Immature Polygyridae	Indian Creek	−14.6	1.0040 ± 0.0031	Post-bomb	–		4 ± 3	46 ± 5	77 ± 21	600 ± 180

[a] Calibrated ages were calculated using CALIB v. 6.0.0, IntCal09.^{14}C data set; limit 50.0 calendar ka BP. Calibrated ages are reported as the midpoint of the calibrated range. Uncertainties are reported as the difference between the midpoint and either the upper or lower limit of the calibrated age range, whichever is greater. Multiple ages are reported when the probability of a calibrated age range exceeds 0.05.

[b] P = probability of the calibrated age falling within the reported range as calculated by CALIB, v.6.0.0.

[c] Defined as the theoretical difference between the measured and true ^{14}C ages for gastropods that incorporate the same amount of dead carbon in their shells as the aliquots measured here. These values are based on the difference between the modeled diet and shell carbonate Δ^{14}C values and converted into C years.

2009). Uncertainties in calibrated ages are reported at the 95% (2σ) confidence level.

The magnitude of the limestone effect on gastropod shells was calculated in two ways. For live gastropods, we compared the measured Δ^{14}C values of the shells and modeled values for the Δ^{14}C of the atmosphere and diet of the gastropod (Pigati et al., 2010). If gastropods ate only live plants, the Δ^{14}C of the gastropod diet could be determined using the atmospheric Δ^{14}C value for the year that the gastropod was collected alive and correcting for isotopic fractionation. However, gastropods consume both live and decaying organic matter, which complicates efforts to quantify their dietary isotopic value. The Δ^{14}C values of decaying organic matter could be higher than modern values because of the ^{14}C bomb spike (e.g., Manning et al., 1990; Meijer et al., 1995) or lower than modern because of isotopic decay. The impacts of these sources on the overall gastropod diet were determined using Monte Carlo simulation to encompass a reasonable range in carbon turnover rates in A-horizons of forest soils (0.16 to 0.78% y^{-1}; Brovkin et al., 2008) and the age of the organic matter consumed (modern to 200 years). Uncertainties associated with the modeled dietary values are relatively large, on the order of ~25%, because of the large range of detritus Δ^{14}C values that could be present at a given site. Thus, we are unable to quantify limestone effects that are $\lesssim$300 ^{14}C years.

For fossil gastropods, we used the difference in the apparent ^{14}C ages of the shells and wood contained in the deposit to determine the limestone effect. For wood dated independently by tree ring analysis, we determined the Δ^{14}C of the atmosphere for the last year the tree was alive using the IntCal09 calibration data set (Reimer et al., 2009). We then took the difference between the measured Δ^{14}C values of the shells and wood from the same stratigraphic unit and converted it to ^{14}C years to determine the limestone effect.

3.2. Amino acid racemization

Seventeen fossil shells and two samples of shell fragments from four sites (FMC-Stables, Darr Run, Collins Run and FMC-Hueston) were analyzed for AAR at the Amino Acid Geochronology Laboratory at Northern Arizona University following standard procedures (Kaufman and Manley, 1998). Shells were cleaned by acid leaching, demineralized, and then analyzed using reverse phase liquid chromatography. To maintain consistency, shell material closest to the aperture was analyzed in all samples. For this study, only aspartic and glutamic acid data were used because they span the range of racemization rates, are the most abundant in shell protein, and are most precisely resolved by reverse phase liquid chromatography (Kaufman and Manley, 1998; Kosnik et al., 2008).

3.3. Dendrochronology

Tree-ring dating provided calendar dates for a log buried in alluvium from Darr Run. Analyses were done at The College of Wooster Tree Ring Laboratory where logs were prepared using standard dendrochronological techniques (Stokes and Smiley, 1996). Tree ring-widths were measured to the nearest micron, and cross dating of three ring-width series was done to assemble a floating chronology. Cross-dates were initially developed using the COFECHA program (Holmes, 1983; Grissino-Meyer, 2001) and then verified graphically. The resulting floating chronology was then compared with the regional master series (http://www.ncdc.noaa.gov/paleo/treering.html, Wiles, unpublished data) to assign calendar dates to each ring.

3.4. ^{137}Cs analysis

Sediment samples from four exposures were collected to determine if samples pre- or post-dated above-ground nuclear bomb testing. The maximum ^{137}Cs concentration within a sediment profile is interpreted as the 1963 peak of ^{137}Cs emission (Walling and He, 1997). Sediment samples were collected from the FMC-Stables, Collins Run, CR-Peffer Park and FMC-Bonham Road Dam sites. Samples were collected from freshly exposed banks, dried, and passed through a 2-mm sieve. Approximately 100 g of processed sediment was sent to Missouri State University Ozarks Environmental and Water Resources Institute (OEWRI) for ^{137}Cs analysis. Sediments were analyzed using a GC4020 GE Co-Axial Detector and DSA 1000 Digital Spectrum Analyzer with 747 Series Lead Shield[1] for identifying and quantifying gamma-ray emitting radionuclides. The analyses followed the laboratory procedures outlined in the OEWRI Standard Operating Procedures (http://oewri.missouristate.edu/assets/OEWRI/Gamma_Spec_R01.pdf). Samples were run for 20-h counts and analyzed from each profile from the top down. Some samples were analyzed again for 48-h counts to verify nondetection of ^{137}Cs in samples.

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[1] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

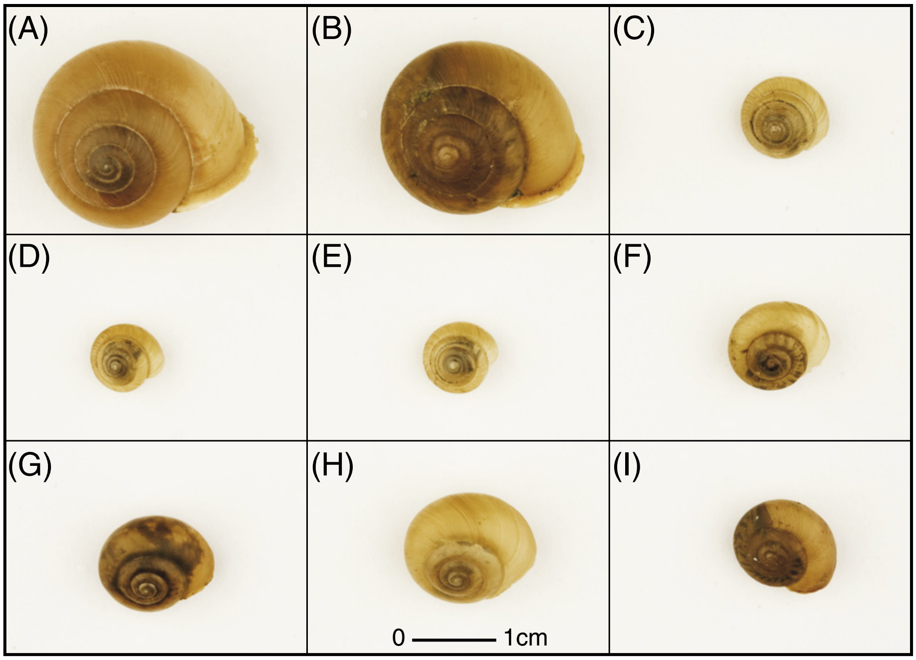

Fig. 3. Examples of terrestrial gastropods collected live from study area: (A) and (B) *Mesodon zaletus*, (C)–(F), (I) *Ventridens ligera*, and (G) and (H) immature Polygyridae.

4. Results

Three sections of results are presented. First, we compare the ^{14}C activities of terrestrial gastropod shells collected live to modeled dietary values to assess whether the shells contain old carbon. Next, we present evidence on the age of the historic and recent terraces (units 4 and 5) to constrain the age of fossil gastropods collected. Finally, we present the ^{14}C ages and amino acid racemization ratios for fossil gastropod shells.

4.1. ^{14}C activity of live shells

Live terrestrial gastropods were collected from the floodplains of Four Mile and Indian Creeks in the fall of 2009 to identify if shell aragonite was in equilibrium with atmospheric Δ^{14}C concentrations at the time of collection (45 ± 6‰; Table 1). The ^{14}C activities were determined for seven shells of species representing two different taxonomic families based on Bouchet and Rocroi (2005): Polygyridae — *Mesodon zaletus* ($n = 2$) and immature Polygyridae ($n = 2$); Gastrodontidae — *Ventridens ligera* ($n = 3$) (Fig. 3). One of the *M. zaletus* shells was analyzed in three different aliquots to determine if ^{14}C activities were similar across the shell and therefore over the growth life of the organism. The measured Δ^{14}C values in *M. zaletus* are −227 ± 4‰ for the sample from Indian Creek and −93 ± 3‰, −112 ± 3‰, and −96 ± 3‰ for the aperture, body, and inner whorls of the *M. zaletus* from FMC-Stables (Table 1). The Δ^{14}C values of the two immature Polygyridae were 4 ± 3‰ for the sample from Indian Creek and −270 ± 2‰ for the sample from FMC-Stables. The measured Δ^{14}C values for the three specimens of *V. ligera* were 27 ± 3‰, 5 ± 3‰, and 34 ± 3‰ (Table 1). These Δ^{14}C values represent apparent ^{14}C ages that range from 2530 ± 30 ^{14}C years to post-bomb (Table 1).

4.2. Age of historic deposits (units 4 and 5)

We used tree-ring and radiocarbon dating of buried logs and stumps as well as ^{137}Cs concentrations in sediment to constrain the age of units 4 and 5 and therefore assess the accuracy of ^{14}C and AAR dating of historic-age fossil gastropod shells (Tables 2, 3, and 4). Three buried logs and an in situ stump rooted in unit 3 were found at the contact between unit 3 and unit 4. The stump and one of the logs (*Carya*), found at FMC-Stables, were too decomposed for dendrochronological analysis. A second log at the FMC-Stables site was identified as *Juglans* and has 290 rings (Table 2). However, a dendrochronologic age for the *Juglans* could not be determined because there is not a regional record for this species. Conventional radiocarbon ages on the bark from the two logs at FMC-Stables are 250 ± 50 ^{14}C y BP (*Carya*) and 230 ± 50 ^{14}C y BP (*Juglans*) (Table 3; Fig. 4). The AMS ^{14}C dating of the outer ring of the *Juglans* yielded an age of 300 ± 20 ^{14}C y BP and the inner ring had a ^{14}C age of 380 ± 30 ^{14}C y BP (Table 2). The outer ring of the White Oak (*Quercus alba*) from Darr Run was dated dendrochronologically to A.D. 1799 and the inner ring to A.D. 1704 (Table 2). Based on these data, the maximum age of unit 4 at FMC-Stables is ~350 years and at Darr Run is ~210 years.

Alluvial sediments from units 4 and 5 were collected for ^{137}Cs analysis at the FMC-Stables, FMC-Bonham Road Dam, Collins Run, and CR-Peffer Park sites (Fig. 1). At the FMC-Stables site, samples

Table 2
Dendrochronology results.

Sample ID	Location	Unit	Taxa	Inner ring age (A.D.)	Outer ring age (A.D.)	Years
DTown1	Darr Run	Base of unit 4	*Quercus alba*	1704	1798	95
DTown2	Darr Run	Base of unit 4	*Q. alba*	1704	1799	96
DTown3	Darr Run	Base of unit 4	*Q. alba*	1704	1792	89
FMC Walnut	FMC-Stables	Base of unit 4	*Juglans*	Unknown	Unknown	290

Table 3
^{14}C results for wood.

Lab #[a]	Sample ID	Location	Unit	Taxa	Part of log sampled	δ^{13}C (vpdb)	^{14}C age (^{14}C years)	Cal age (years)[a]	P[b]
Beta 247943b	FMC Walnut	FMC-Stables	Base of unit 4	*Juglans*	Bark	−26.7	230 ± 50	20 ± 10	0.12
								180 ± 50	0.37
								290 ± 40	0.34
								390 ± 50	0.14
Beta 247944b	FMR Unknown	FMC-Stables	Base of unit 4	Unknown	Bark	−26.8	250 ± 50	10 ± 10	0.07
								180 ± 40	0.25
								360 ± 100	0.68
AA76671	MU#292	FMC-Stables	Base of unit 4	*Juglans*	Inner ring	−27.1	380 ± 30	360 ± 30	0.35
								470 ± 40	0.65
AA76672	MU#293	FMC-Stables	Base of unit 4	*Juglans*	Outer ring	−25.3	300 ± 20	320 ± 10	0.28
								390 ± 50	0.72

[a] Beta samples were measured by conventional ^{14}C techniques; AA samples were measured by AMS. Calibration method defined in Table 1.
[b] Defined in Table 1.

from unit 4 at depths of 0.25 to 0.50 m below the surface do not contain detectable concentrations of ^{137}Cs (Table 4). At Collins Run, 16.26 ± 0.98 Bq/kg of ^{137}Cs was detected in unit 5 at a depth of 0.25 m, but samples from 0.5 m and 0.75 m were below detection levels. At CR-Peffer Park, 6.81 ± 0.67 Bq/kg of ^{137}Cs was detected at 0.4 m, 4.11 ± 0.64 Bq/kg at 0.55 m, and levels were below detection at 0.25 m and 0.75 m. At FMC-Bonham Road Dam, 1.11 ± 0.48 Bq/kg of ^{137}Cs was detected at a depth of 0.1 m and 0.56 ± 0.39 Bq/kg at a depth of 0.2 m (Table 4). These results suggest that the age of unit 4 deposits at both localities are >50 y BP as the lack of ^{137}Cs indicates that sediment has not accumulated within these deposits since nuclear bomb testing.

In summary, we constrain the age of unit 4 to be 50–350 years old at FMC-Stables and 50–210 years at Darr Run. We estimate the age of unit 5 to be ~20–50 years based on the presence of ^{137}Cs.

4.3. ^{14}C of fossil shells

Fossil gastropod samples were collected from three locations (FMC-Stables, Darr Run, and Collins Run; Fig. 5). Six fossil shells and shell fragments from units 4 and 5, all representing members of the family Polygyridae, were radiocarbon dated. These samples included two *Mesodon thyroideus*, one *Mesodon elevatus*, one *Allogona profunda*, and two unidentifiable shell fragments (Table 5). Radiocarbon ages for gastropod shells from unit 4 at the FMC-Stables site were 690 ±20 ^{14}C y BP (*M. elevatus*) from the top of unit 4, and 340 ± 20 ^{14}C y BP (*A. profunda*) and 1050 ± 20 ^{14}C y BP (shell fragment) from the bottom of unit 4. Shell fragments from the buried soil at the top of unit 3 yielded a ^{14}C age of 1810 ± 20 ^{14}C y BP. A *M. thyroideus* shell from unit 4 at Darr Run yielded a ^{14}C age of 720 ± 20 ^{14}C y BP, and another shell fragment from unit 5 at Collins Run had an age of 1180 ± 40 ^{14}C y BP.

Radiocarbon ages of fossil *Mesodon* sp. are ~500 to ~1200 years older than the age of the sediments from which they were collected. The one fossil shell of *A. profunda* yielded a radiocarbon age that was equivalent to the independently estimated age of the strata. Radiocarbon ages on the two unidentifiable shell fragments were ~600 and ~1400 years older than the known age of the strata.

Table 4
^{137}Cs results.

Sample #	Location	Unit	Depth (m)	^{137}Cs (Bq/kg)[a]
CR 0.25	FMC-Collins Run	5	0.25	16.26 ± 0.98
CR 0.50	FMC-Collins Run	5	0.50	ND
CR 0.75	FMC-Collins Run	5	0.75	ND
CR 1.00	FMC-Collins Run	5	1.00	NA
CR 1.25	FMC-Collins Run	5	1.25	NA
CR 1.50	FMC-Collins Run	5	1.50	NA
S 0.25	FMC-Stables	4	0.25	ND
S 0.50	FMC-Stables	4	0.50	ND
S 0.75	FMC-Stables	4	0.75	NA
S 1.00	FMC-Stables	4	1.00	NA
PP 0.10	Collins Run-Peffer Park	5	0.10	1.64 ± 0.80
PP 0.25	Collins Run-Peffer Park	5	0.25	ND
PP 0.40	Collins Run-Peffer Park	5	0.40	6.81 ± 0.67
PP 0.55	Collins Run-Peffer Park	5	0.55	4.11 ± 0.64
PP 0.75	Collins Run-Peffer Park	5	0.75	ND
D 0.10	FMC-Bonham Rd Dam	5	0.10	1.11 ± 0.48
D 0.20	FMC-Bonham Rd Dam	5	0.20	0.56 ± 0.39

[a] ND = not detected; NA = not analyzed.

4.4. AAR of fossil shells

Seventeen fossil gastropod shells and two samples of shell fragments were analyzed for aspartic (Asp) and glutamic (Glu) acid d/l ratios (Table 6). The shells were collected from units 3, 4 and 5 and the buried soil between units 3 and 4. The analyses included the Polygyridae taxa *M. zaletus*, *M. clausus*, *M. thyroideus*, *M. elevatus*, *Stenotrema stenotrema*, *A. profunda*, the Discidae taxon *Anguispira kochi*, and the Gastrodontidae taxon *Ventridens intertextus*, as well as two shell fragments that were not identifiable to species. The Asp d/l values ranged from 0.061 to 0.224, and the Glu d/l values ranged from 0.018 to 0.05. The two samples of unidentifiable shell fragments yielded anomalous AAR values relative to other samples from the same stratigraphic unit and were therefore not included in the interpretation of the data. Average Asp and Glu d/l values are higher in samples from older stratigraphic units (Table 6; Fig. 6). Average Asp and Glu d/l values for gastropod shells are 0.071 ± 0.007 and 0.021 ± 0.002 for unit 5; 0.084 ± 0.019 and 0.029 ± 0.009 for unit 4; 0.165 ± 0.039 and 0.041 ± 0.008 for the soil capping unit 3; and 0.207 ± 0.015 and 0.047 ± 0.003 for unit 3, respectively (Table 6; Fig. 6).

5. Discussion

Our research objective was to determine if *Mesodon* and other large-shelled terrestrial gastropods, which are common in Holocene sediments in the midwestern USA, can be used to constrain the age of young alluvial sediments. Here we assess the potential of using these shells for ^{14}C dating and AAR geochronology of late Holocene and historic stream sediments.

5.1. Limestone effect and ^{14}C dating

The limestone effect for the combined samples of live (7 shells; 9 aliquots) and fossil (6 shells) gastropod shells ranged from 3420 ± 260 to 190 ± 210 ^{14}C years and averaged 1185 ± 190 ^{14}C y (Fig. 7; Tables 1 and 2). These values for the limestone effect are much higher than those found by Pigati et al. (2010) for smaller-shelled North American gastropods from other taxonomic families, but are similar to many previous studies that were mainly limited to large taxa

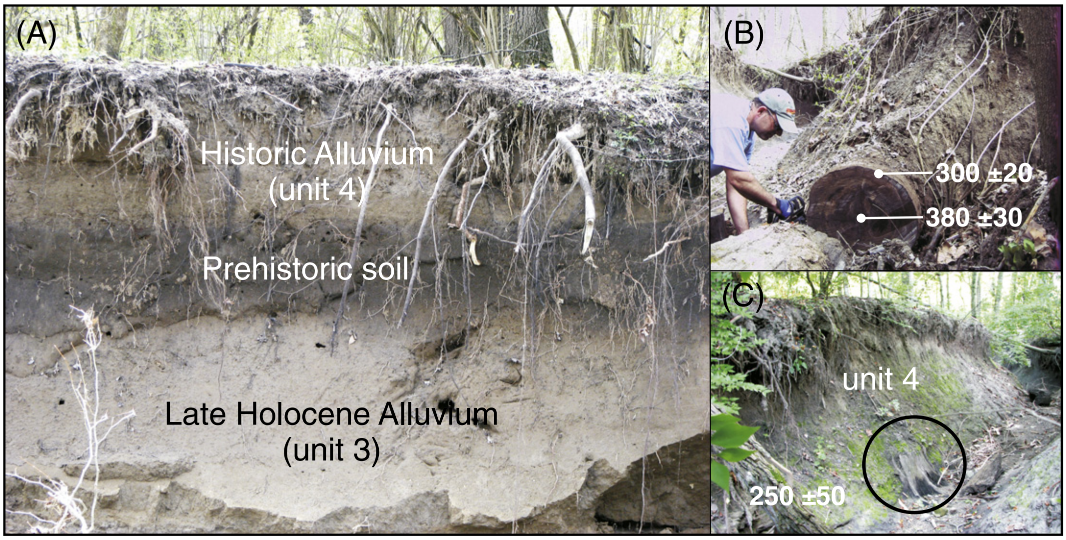

Fig. 4. Alluvium exposed at Four Mile Creek-Stables section. (A) Cut bank displaying unit 3 at base, an organic-rich prehistoric soil ~70-cm thick and ~1 m of historic alluvium (unit 4). (B) Buried walnut log, with radiocarbon ages (Table 3), lying directly on top of the prehistoric soil and buried by ~1.5 m of alluvium. (C) Hickory stump, with radiocarbon age, rooted within pre-historic soil and buried by ~2 m of historic alluvium.

within the Polygyridae (e.g., Goodfriend and Stipp, 1983). However, there are large differences in the limestone effect identified between the different taxa analyzed. Relatively low limestone effects were identified in the polygyrid *A. profunda* (190 ± 180 ^{14}C years) and gastrodontid *V. ligera* (410 ± 180, 600 ± 180, and 350 ± 180 ^{14}C y), whereas much larger limestone effects were found in *Mesodon* sp. (up to 2900 ± 250 ^{14}C y). Moreover, two immature gastropods from the Polygyridae had limestone effects of 3420 ± 260 and 600 ± 180 ^{14}C y.

In general, these results indicate that there are significant limestone effects for the *Mesodon* analyzed in this study and that these taxa will have larger ^{14}C offsets than the taxa analyzed by Pigati et al. (2010). *A. profunda* and *V. ligera* appear to ingest only small amounts of limestone and may be suitable for ^{14}C dating, but more work is needed to determine whether this is consistent at multiple locations. This variable limestone effect for individual taxa highlights the importance of taxonomic identification of gastropod shells prior to ^{14}C dating and indicates that there could be large limestone effects when dating shell fragments and immature shells that are not identifiable to taxonomic species (Fig. 7).

Pigati et al. (2010) suggested that large terrestrial land snails are more likely to ingest limestone to acquire Ca and accommodate faster rates of shell growth. These results caution that more data are needed to validate this hypothesis. Currently, only a limited number of large terrestrial gastropod taxa have been analyzed for their ^{14}C content, with most of these representing members of the Polygyridae. However, shell size alone does not predict shell ^{14}C content. The magnitude of this effect is also likely related to phylogeny, with at least some gastrodontids (e.g., *Ventridens*), polygyrids (e.g., *Allogona*) as well as all succineids (Pigati et al., 2010) demonstrating little limestone effect in spite of their relatively large shell sizes. It is thus not

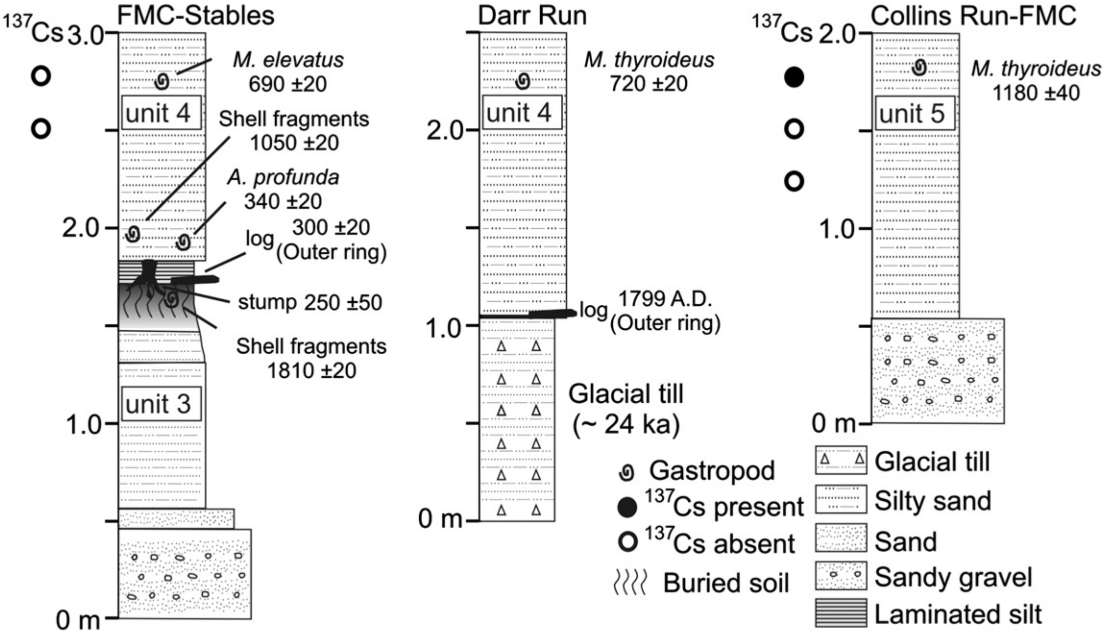

Fig. 5. Stratigraphic sections of outcrops from where fossil terrestrial gastropods were collected. Ages shown in ^{14}C years, except for log from Darr Run outcrop which is a calendar age derived from dendrochronology.

Table 5
^{14}C results for fossil gastropod shells.

Sample ID	Lab #	Location	Unit	Taxa	$\delta^{13}C$ (vpdb)	^{14}C age (^{14}C years)	Cal age (years)[a]	P[a]	Limestone effect[a] (^{14}C years)
MU-277	AA76656	Collins Run	5	*Mesodon thyroideus*	−11.4	1180 ± 40	1010 ± 30 1110 ± 70	0.16 0.81	1180 ± 40
MU-276	AA76655	Darr Run	4	*M. thyroideus*	−9.8	720 ± 20	670 ± 15	1.00	630 ± 130
MU-280	AA76659	FMC Stables	4	*Mesodon elevatus*	−8.9	690 ± 20	580 ± 10 660 ± 15	0.17 0.84	530 ± 230
MU-278	AA76657	FMC Stables	4	*Allogona profunda*	−11.6	340 ± 20	360 ± 50 450 ± 30	0.65 0.35	190 ± 210
MU-282	AA76661	FMC Stables	4	Shell fragment/no ID	−8.0	1050 ± 20	950 ± 30	0.96	880 ± 240
MU-281	AA76660	FMC Stables	3	Shell fragment/no ID	−9.0	1810 ± 20	1760 ± 60	1.00	1380 ± 100

[a] Defined in Table 1.

possible to make broad generalizations about the limestone effect for gastropod shells based upon shell mass alone. Moreover, several shells of smaller gastropod taxa are often amalgamated to obtain enough carbon for an individual radiocarbon analysis, which homogenizes the carbon from the shells and makes it less likely that high limestone effects will be identified. For example, if we had amalgamated our five *Mesodon* sp. for ^{14}C analysis, the limestone effect would have been close to ~10%. As larger and thicker gastropod shells are better preserved in the geologic record, these shells may be important for dating older strata as well as deposits from more humid environments. More work is needed to determine which of these taxa are most suitable for radiocarbon dating.

It is also interesting to note the difference in the limestone effect calculated for gastropod taxa collected live versus those for fossil shells collected from outcrops. The limestone effect was calculated for five *Mesodon* shells, including three fossil shells and two samples collected live. The three fossil shells had limestone effects of 530 ± 230, 630 ± 130, and 1180 ± 40, whereas the shells collected live had limestone effects of 1565 ± 200 and 2900 ± 250 (Tables 1 and 5). The larger limestone effects of gastropods collected live may be an artifact of the small number of samples analyzed, or may be indicative of anthropogenic effects on the habitat of these gastropods. Anthropogenic effects could include changes in the size and nature of the organic detrital reservoir used by these gastropods because of land use and land management changes. Acid rain and its impacts on the Ca reservoir in soils may also be an important factor influencing the availability of nutrients. It is uncertain what effect these and other environmental impacts may have had on the uptake of limestone and calcareous sediments by gastropods, but it is possible that anthropogenic activities have caused some gastropods to alter their dietary behavior.

5.2. Amino acid racemization (AAR)

The AAR results of large gastropod shells appear to be more promising for dating young alluvial sediments than ^{14}C dating. The aspartic (Asp) and glutamic (Glu) acid d/l ratios of older gastropod shells yielded higher average ratios than younger gastropod shells (Fig. 6). Although there is considerable spread to the data, these results suggest that AAR of fossil gastropods can be used to differentiate units of late Holocene and historic alluvium. Amino acid geochronology studies of fossils in museum collections (stored within controlled environmental conditions) have identified that AAR values correlate with the time of collection for the fossils (Hearty and Kaufman, 2009; Huntley et al., 2012). Our results show that AAR can also be used for fossils in the recent (historic) geologic record, where specimens are subjected to different diagenetic histories with variable microclimatic conditions. As long as there are some well-dated control sections that can be used to calibrate racemization rates, then this

Table 6
Amino acid racemization results.

Sample ID	Location	Unit	Taxa	Asp d/l	Glu d/l
7105C	FMC Collins Run	5	*Mesodon zaletus*	0.061	0.018
7105A	FMC Collins Run	5	*Mesodon thyroideus*	0.065	0.021
7105D	FMC Collins Run	5	*M. zaletus*	0.072	0.022
7105B	FMC Collins Run	5	*Mesodon clausus*	0.073	0.021
7106	FMC-Hueston	5	*Ventrideus intertextus*	0.080	0.023
7823	Darr Run	5	Shell fragment/no ID*	0.075	0.029
			Average[a]	*0.070 ± 0.007*	*0.021 ± 0.002*
7104C	FMC Stables	4	*M. zaletus*	0.065	0.025
7104A	FMC Stables	4	*Mesodon elevatus*	0.073	0.029
7110	FMC Stables	4	*Stenotrema stenotrema*	0.078	0.021
7104B	FMC Stables	4	*M. clausus*	0.079	0.035
7102B	FMC Stables	4	*Allogona profunda*	0.093	0.021
7102A	FMC Stables	4	*A. profunda*	0.117	0.043
			Average[a]	*0.084 ± 0.019*	*0.029 ± 0.009*
7824	FMC Stables	3 (soil)	Shell fragment/no ID*	0.077	0.025
7103C	FMC Stables	3 (soil)	*Anguispira kochi*	0.120	0.031
7103B	FMC Stables	3 (soil)	*A. kochi*	0.187	0.045
7103A	FMC Stables	3 (soil)	*A. kochi*	0.188	0.046
			Average[a]	*0.165 ± 0.039*	*0.041 ± 0.008*
7108A	FMC Stables	3	*Mesodon* sp.	0.194	0.047
7101	FMC Stables	3	*M. elevatus*	0.203	0.050
7108B	FMC Stables	3	*Mesodon* sp.	0.224	0.045
			Average[a]	*0.207 ± 0.015*	*0.047 ± 0.003*

[a] Standard deviations are reported at the 1σ confidence level.
* Excluded from average.

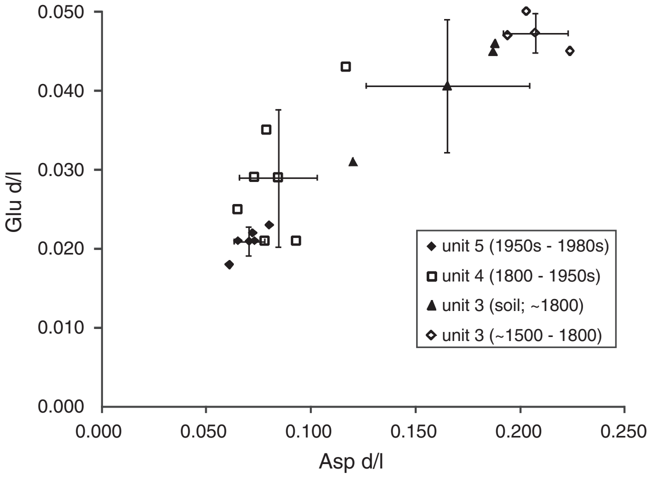

Fig. 6. Aspartic (Asp) and glutamic (Glu) acid d/l ratios of terrestrial gastropod shells from late Holocene (unit 3) and historic (Units 4 and 5) stratigraphic units. Average d/l ratios with standard deviation are shown for gastropod shells from each stratigraphic unit.

technique has potential to help resolve the age of young alluvial deposits.

The high variability of the AAR ratios could be the result of several factors, including different racemization rates among the various species analyzed, reworking of shells from older deposits, different thermal histories related to depth of burial, proximity to cut banks, the influences of microclimates, burrowing of gastropods into older stratigraphic units, and/or various residence times of shells on the landscape prior to burial. Major changes in land use (including deforestation, agriculture, changes in agricultural practices, and urbanization) have all influenced runoff rates and sediment loads to streams. Historic alluvial fill sequences are often thick (several meters), and therefore gastropod shells were likely buried rapidly and beyond the depth of large seasonal temperature fluctuations, making them well suited for AAR dating.

5.3. Late Holocene and historic geochronology

Mapping and dating late Holocene and historic stream deposits in North America is important for stream restoration, assessing the impact of land use changes on streams, and predicting the impact of future changes in climate and land use on streams. This study on the potential use of *Mesodon* and other large terrestrial gastropods for dating late Holocene and historic stream deposits in southwest Ohio was initiated out of a need to constrain the age of young alluvial deposits. In the field, thick packages of young alluvium that lacked pedogenic modification were observed in many locations; but it was unclear if these units were associated with deforestation and land use changes at the beginning of the nineteenth century or more recent (twentieth century) practices that reduced soil erosion rates, or if they predated these major changes in land use. Buried logs and stumps allowed for dendrochronological age determinations in a few locations. However, most logs were too degraded to determine growth histories or could not be tied to regional master chronologies (the only master chronology available for this area is for white oak). The ^{137}Cs concentrations can be used in alluvial deposits to identify sediment accumulated during and since aboveground nuclear testing, which was halted in 1963, and is useful for identifying very young (<50 years) fluvial deposits. However, as streams in our study area are deeply incised and a large amount of stream sediment is derived from the erosion of cut banks and mass wasting along the steep banks of the channel, ^{137}Cs concentrations were exceptionally low. For example, at FMC-Bonham Road Dam, a low-head dam constructed in the 1950s, only low concentrations of ^{137}Cs were detected even though the deposits were laid down within the last 60 years, which indicates that most of the stream sediments were derived from cut banks or deeply eroded soils.

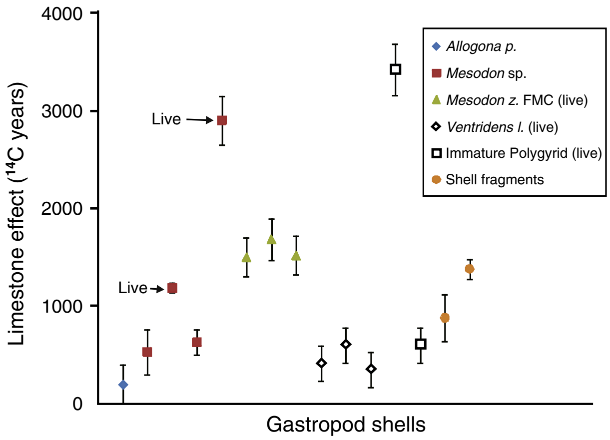

Fig. 7. Limestone effect of modern and fossil terrestrial gastropods.

6. Conclusions

This study investigated the potential use of *Mesodon* and other large terrestrial gastropods for dating late Holocene and historic stream deposits in southwest Ohio. Our study was initiated because of the minimal limestone effects found in many small-shelled North American terrestrial gastropod families (Pigati et al., 2010) and the abundance of large-shelled fossils in late Holocene and historic alluvium. Our results show that *Mesodon* in our study area are subject to significant limestone effects, obtaining up to 30% of the carbon in their shell from limestone. In contrast, other large-shelled taxa, including *V. ligera* and *A. profunda*, contained minimal dead carbon from limestone. The high variability of limestone effects in gastropod shells highlights the importance of taxonomic classification of terrestrial gastropod shells and avoiding unidentifiable shell fragments for radiocarbon dating.

Amino acid racemization (AAR) ratios were determined for 17 fossil terrestrial gastropod shells from strata of known age to determine the utility of using AAR for age control on historic sediments. Average d/l values of aspartic (Asp) and glutamic (Glu) acid for shells from four separate late Holocene and historic stratigraphic units were higher in shells recovered from older sediments. This suggests that the AAR is capable of differentiating historic alluvial sequences and may be a useful tool when mapping young alluvial fill deposits as long as suitable control sections are available.

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