Supplemental Material for: Pre-Columbian Lead Pollution from Native American Galena Processing and Land Use in the Midcontinental United States

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Sample collection

Four continuous, 10-meter-long sediment cores were collected from two locations at Avery in June 2014 using a modified Livingstone piston corer driven by an electric winch coring tower system mounted on a floating raft (Wright et al., 1984). One-meter-long overlapping Livingstone cores were offset by 50 cm at each location to ensure complete recovery. One-meter-long surface cores capturing the sediment-water interface were additionally collected at each of the Livingstone core locations using a modified piston corer. Cores were stored at 4˚C at the Indiana University-Purdue University, Indianapolis (IUPUI) Paleoclimatology and Sedimentology Laboratory prior to analysis. A composite sediment core measuring 995 cm was constructed by matching distinct stratigraphic units and sedimentological measurements (magnetic susceptibility, total organic matter, and geochemistry from X-ray fluorescence) from the A-14 coring location. The composite core penetrated to 10.0 m depth, but the lowest 5 cm were lost during the coring process because they were composed of coarse sand and gravel, which is difficult to retain with a modified Livingstone corer. Similarities in the physical and visual properties of cores from the two locations (magnetic susceptibility, stratigraphy) indicate consistent depositional patterns at both sites. Therefore, the A-14 composite core was chosen for detailed analysis since it was closest to the Kincaid Archaeological site.

Avery Lake core stratigraphy

The 995 cm composite Avery core was visually divided into a basal section between 995 and 972 and an upper section above 972 cm. The basal section from 995 to 988 cm was composed of medium to coarse sand and gravel, which is consistent with the composition of modern and paleo Ohio River channel deposits (Alexander and Prior, 1971). From 988 to 972 cm, there were alternating layers of sandy silts and sand with abundant charcoal and macro organics. At 972 cm, there was an abrupt transition to massive, tan-to-buff colored, fine-grained sediments that persisted to the top of the core (weak banding occurs above 400 cm), consistent with lacustrine swale deposits on the Black Bottom (Alexander and Prior, 1971).

Age control

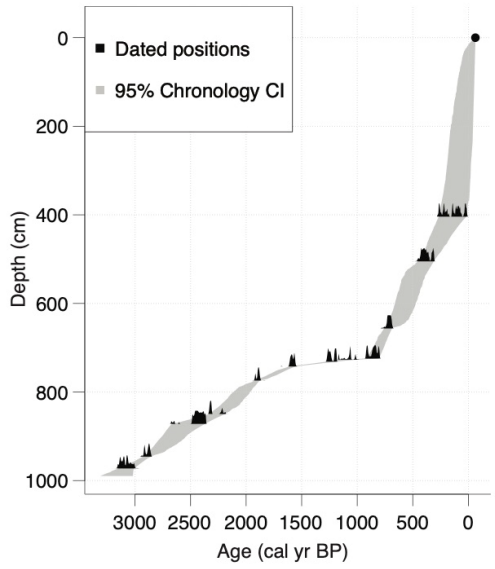
Age control for the Avery record was established by accelerator mass spectrometry (AMS) radiocarbon (^{14}C) analysis of 12 samples at the University of California, Irvine (UCI), Keck AMS Laboratory (Table 1). Charcoal and macroscopic terrestrial organic material > 63 μm was picked from a wet sieve after a brief disaggregation in a 7 % hydrogen peroxide solution.

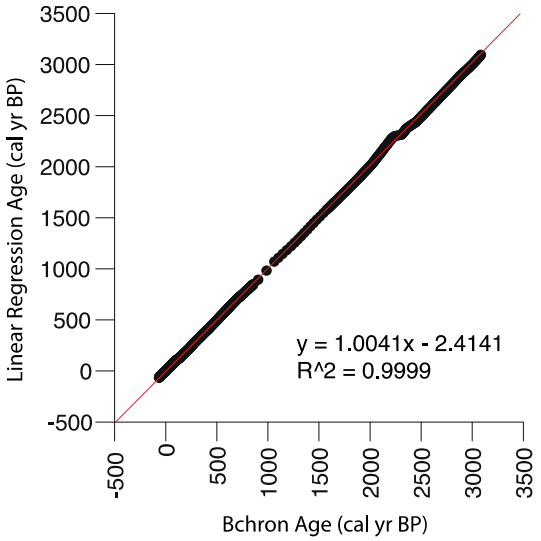
Samples were physically cleaned and chemically pretreated following acid-base-acid protocols (Abbott and Stafford, 1996; Santos, 2011). Radiocarbon ages were calibrated to calendar years before present (cal yr B.P.; present = 1950 of the Common Era) using the intcal 13 calibration curve (Reimer et al., 2013). Unless otherwise noted, dates in the text are referred to as being in the Common Era (CE) or before (BCE) with 1950 cal yr BP equal to 0 CE.

All 12 AMS ^{14}C ages were in stratigraphic order, indicating continuous, undisturbed sediment accumulation. An age model for the Avery core was developed using linear interpolation between AMS ^{14}C ages and the Bayesian age modeling software packages Bchron (Fig. S1a; Parnell et al., 2008). The two age models are virtually identical ($r^2 = 0.999$, $p < 0.001$, $m = 1.0041$), with the exception that Bchron introduced a subtle variation in the age model between 2300 and 2050 cal yr BP (Fig. S1b). Therefore, while we use the linear age model to plot all data, age model error estimates are provided based on the Bchron age model. The validity of the Avery age models for the upper ~4 meters, which represents the last ~200 years, despite few chronological constrains is supported by the agreement between Pb concentrations in the Avery sediment archive as determined by XRF and historical records of atmospheric lead pollution (Fig. S1c; Graney et al., 1995). Specifically, peak atmospheric Pb pollution and peak Avery Pb concentrations both occurred between 1968 and 1970 CE.

Table 1 Avery Lake radiocarbon age data.

UCI #	Material	Composite Depth (cm)	^{14}C Age	Error +/-	Median Probability cal yr BP	1 σ Upper Age	1 σ Lower Age	Maximum Probability
145745	Charcoal	404	135	20	130	72	116	0.365
145746	Charcoal	505	315	20	390	375	429	0.782
145747	Charcoal	656.5	805	25	720	693	730	1
145748	Charcoal	724.5	950	20	850	827	864	0.564
182487	Wood	727	1160	15	1070	1054	1085	0.534
180591	Charcoal	731.5	1285	15	1240	1239	1267	0.541
180592	Charcoal	742.25	1685	15	1590	1578	1604	0.633
180593	Charcoal	774	1945	15	1890	1875	1900	0.807
180589	Charcoal	849.5	2260	15	2310	2308	2335	0.746
180590	Charcoal	872	2425	15	2430	2376	2465	0.953
180594	Charcoal	946	2790	15	2890	2859	2890	0.654
145749	Charcoal	972.5	2930	20	3080	3091	3144	0.581





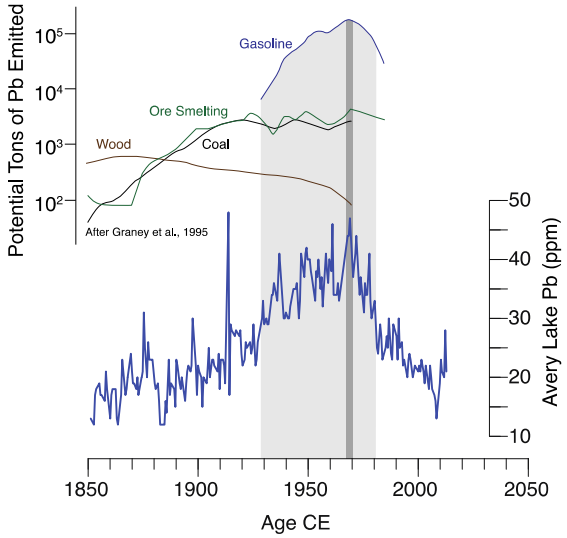


Figure S1 A) Avery Lake age model as derived using Bchron with the 90 to 10 % confidence intervals shown in gray. B) Linear regression of the Bchron and linear regression age models for Avery Lake. C) Comparison of the Avery Lake Pb record with historical atmospheric lead pollution trends after Graney et al. (1995). The light gray shading indicates the broad peak in Pb emissions. The drak gray shading indicates maximum historical Pb emissions between 1968 and 1970, which exactly match peak Pb in the Avery Lake record.

Organic carbon and total nitrogen elemental abundances and isotopic composition

The elemental abundances and isotopic composition of organic carbon (C_{org} & $\delta^{13}C_{org}$) and total nitrogen (N & $\delta^{15}N$) were determined for 150 samples (~6 cm resolution) at IUPUI (combustion with a Costech Analytical elemental analyzer coupled by continuous flow to a Thermo Delta V Plus isotope ratio mass spectrometer; IRMS) and Idaho State University (combustion with a Costech ECS 4010 elemental analyzer interfaced to a Thermo Delta V Advantage continuous flow IRMS). Approximately 10 mg of unacidified freeze-dried sample was weighed into tin capsules for isotopic analysis. The sample data are expressed in delta notation in units of per mil (‰) normalized to reference materials (USGS 40, RM 8704, RM 1577c). Analytical precision was better than ±0.2‰ for both $\delta^{13}C$ and $\delta^{15}N$ and < ± 0.5% of the sample value for %N and %C. The elemental standard acetanilide (C = 71.09%, and N =

10.36%) was used to correct elemental abundances based on the peak area response of the TCD detector.

Pollen

Pollen abundances were analyzed for 28 samples (1-cm^3 of sediment each) collected at variable depth intervals ranging between 2 and 30 cm in order to focus on temporal areas of interest. Pollen was isolated from the sediment using standard techniques (Faegri & Iverson, 1989) and mounted in silicon oil. Each sample was examined under a light microscope at 400X and a minimum of 300 terrestrial pollen grains (including Cyperaceae) were identified and counted in each sample, to the finest taxonomic resolution possible (family-level or genus-level). Raw pollen counts were then converted to percentages based on the total terrestrial pollen sum.

X-ray fluorescence geochemistry

Geochemical analyses of lacustrine sediments are routinely made using X-ray fluorescence techniques (XRF; Boyle, 2000; Mejía-Piña et al., 2016). XRF measurements were made on the Avery sediments using a handheld Olympus Innov-X Delta Pro (DPO-6000-C) X-ray fluorescence analyzer. Titanium (Ti), zirconium (Zr), and lead (Pb) measured using two energy beams, each with a measurement time of 30 seconds. Beam one had an energy of 40 Kv and beam two had an energy of 10 Kv. Results were converted from counts per second to percent (%) abundance using the system's proprietary software and an Olympus calibration standard.

Pb pollution endmembers used in the two end-member mixing model

Table 1 Endmember values

	$^{206}Pb/^{204}Pb$	Pb ppm
Endmember A *Avery Lake Sediments*	19.250	11.8
Endmember B *Galena*	21.1996	866000

Pb pollution calculations using XRF Data

Anthropogenic Pb pollution was independently determined using the XRF Pb concentration data in order to 1) assess the Pb isotope-based Mississippian period pollution estimate and 2) provide estimates of Pb pollution during the Baumer phase, which had no Pb isotopic excursion. An average background Pb concentration of 10 ppm was first subtracted from the raw Pb values during the Baumer (300 to 15 BCE) and Mississippian (1150 to 1400 CE) periods. The flux of excess Pb (Pb* $\mu g/cm^2/yr$) was then calculated by multiplying Pb* (μg /g) concentrations by the dry sediment bulk density (g/cm^3) and the sedimentation rate (cm/yr). This flux was then multiplied by the area of Avery Lake (cm^2) and the number of years between each measurement to determine the amount of Pb* (μg) deposited over the Avery Lake basin. This value was then summed for the time period of interest and converted to metric tons of Pb* to determine the total Pb* deposited in Avery Lake during the Baumer and Mississippian periods.

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