Title: Estimating anthropogenic-Pb flux using alluvial soil mass-balance geochemistry, geochronology and archaeology in eastern USA

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7 **Acknowledgments:** The research documented in this paper received support from the U.S.
8
9 National Park Service, Temple University, Baylor University Geology Department, GSA Student
10 Grants-in-Aid-of-Research, and National Science Foundation grant EAR-0823131 awarded to
11 Driese. We would like to thank Gert Verstraeten, Thomas Hoffmann, Hans Middlekoop, Andreas
12 Lang and all other organizers of the PAGES 2014 Focus-4 workshop in Leuven, Belgium, for
13 providing inspiration for writing this manuscript. Jon Harbor, Don Thieme, L.O.C. and an
14 anonymous reviewer provided helpful comments that improved an earlier version of the
15 manuscript.
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Abstract:

Predicting human impact on Earth's surface requires a quantitative understanding of past human-environmental interactions. This study uses mass-balance geochemistry of buried alluvial soils, geochronology and archaeology to constrain soil age and quantify the anthropogenic addition of lead (Pb) to alluvial soils from the Delaware River valley in northeastern USA. Mass addition of Pb was calculated for two alluvial terrace landforms. The results show that for buried soils that formed during the middle and late Holocene, the addition of Pb was estimated at $1.71 \pm 0.02 \mu\text{g cm}^{-2}$ and $-39 \pm 0.43 \mu\text{g cm}^{-2}$, respectively. The corresponding Pb addition rates were estimated at $0.04 \mu\text{g cm}^{-2} \text{ y}^{-1}$ and $-0.28 \mu\text{g cm}^{-2} \text{ y}^{-1}$, where the negative rate documents Pb loss from the soil. Conversely, the Pb addition to buried alluvial soils that formed <100 years ago were estimated at $486 \mu\text{g cm}^{-2}$ and $526 \mu\text{g cm}^{-2}$. The corresponding mean Pb addition rates were estimated to be $10.06 \pm 2.13 \mu\text{g cm}^{-2} \text{ y}^{-1}$ and $8.91 \pm 4.66 \mu\text{g cm}^{-2} \text{ y}^{-1}$. The recent Pb addition rates documented in this study are over 2 orders of magnitude higher than their middle and late Holocene counterparts. The >200 times increase in Pb and rapid deposition rates in the 19th-20th century alluvial soils coincide with the presence of historic Euro-American artifacts, providing support for human-induced Pb addition. Furthermore, the soil stratigraphic context of a tooth-crown bottle cap (maximum age = 58 y BP) and other archaeological age-based estimates allowed us to constrain the residence time of a historic alluvial soil to 58-39 y. The mass-balance results show that 19th-20th century Pb additions to these two alluvial profiles are unlike anything documented in the buried alluvial soils prior to the Industrial Era. Although human-induced mass influx of Pb had been previously documented in nearby lake cores and upland soils, quantification of Pb flux in buried alluvial soils, especially those with archaeological deposits, will further constrain the magnitude, extent and timing of anthropogenic Pb impact on Earth's surface.

1. Introduction

Quantifying human impact on Earth's surface materials is important because the mobilization of surface material may cause system-state changes on Earth that are unsustainable. One proxy for human impact is anthropogenic lead (Pb) enrichment, which could serve as both a prominent chemostratigraphic marker and a quantitative metric of human-impact on soils and sediments. For at least 2,500 years human activities, e.g., ancient silver mining, wet/dry deposition of coal fly ash, leaded gasoline combustion and metal smelting plants have mobilized Pb, often resulting in elevated concentrations in soil and sediment (Lantzy and Mackenzie, 1979; Nriagu, 1983; Weiss et al., 2007 and references therein). Pb data from a Greenland ice core show increasing Pb concentrations beginning late 19th century and up to 1970 (McConnell et al, 2002). Unlike short-lived radioactive isotopes (e.g., Cs-137), increased Pb concentrations in soil and sediment will likely stay in the Anthropocene record for millennia, making it an ideal boundary marker. Thus, understanding the timing, rate and processes of anthropogenic Pb are essential to understanding the utility of this anthropogenic marker.

Intuition holds that the modification of the Pb cycle on Earth's surface could be quantified by mapping and measuring the Pb in soil. However, anthropogenic-Pb enrichment in soils can be confounded by biological and geomorphological setting and process(es). Soils profiles are time-averaged weathering features where Pb addition (e.g., parent material, dust, anthropogenic), loss, transformation, and translocations, can affect the same profile at different intervals of time or simultaneously. The time-averaging processes of over-printing or welding can effectively mask anthropogenic-Pb enrichment. Certain types of vegetation can also concentrate Pb in high quantities in the soil. For example, roughly 0.2% of all angiosperms are heavy metal (As, Cd, Co, Cu, Mn, Ni, Pb, Sb, Se, Tl, Zn,) hyperaccumulators and metal concentrations can be 100-

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4 1000 times higher in their leaves compared to surrounding levels (Rascio and Navarri-Izzo,
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7 2011). The organic litter from hyperaccumulators is then incorporated into the soil organic
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9 matter yielding higher Pb concentrations in the soil, which could be misidentified as
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11 anthropogenic-Pb enrichment. Conversely, experimental studies show that Pb solubility can
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13 increase with decreasing pH (Reddy et al., 1995). Solubility and leaching would deplete
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15 anthropogenic-Pb in highly acidic soils.
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19 One way to overcome these issues is to quantify anthropogenic Pb impact on soils in
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21 depositional settings. Quantifying anthropogenic-Pb enrichment in buried and surface alluvial
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23 soils could yield more discrete episodes of pedogenesis (Holliday, 2004), whereas upland soils
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25 are time-averaged (Saint-Laurent et al., 2010). The study of depositional sequences in alluvial
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27 settings in conjunction with the chronological resolution and behavioral context provided by
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29 archaeology is a potential solution to some of these problems, providing a clearer view of human
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31 impact on the environment. The study documented herein attempts to quantify the
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33 anthropogenic Pb flux in an alluvial environment in northeastern USA using a combined mass-
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35 balance geochemistry, geochronology and archaeology approach. The results are compared with
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37 previous research and include a discussion of regional Pb variations.
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45 2. Materials and Methods

46 2.1 *Study area*

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48 Research along the Delaware River Valley, northeastern USA has shown that the floodplains
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50 and alluvial terraces consist of multistory buried soils that span the Holocene (Ritter et al., 1973;
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52 Stewart 1990, 1991; Stewart et al., 1991; Stinchcomb et al., 2012). Because these soils have
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4 been age-constrained in past work (Stinchcomb et al., 2011, 2012, 2013), they make a good case
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6 study for comparing background Pb with anthropogenic Pb.
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9 The study area is located within the Delaware River basin, eastern United States (Fig. 1).
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11 The middle Delaware River valley is a partly-confined river valley containing relict glacial and
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13 periglacial landforms and alluvial landforms that include alluvial fill terraces, floodplains,
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15 islands, and gravel bars (Stewart et al., 1991; Witte, 2001; Schuldenrein 2003; Witte and Epstein,
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17 2005; Stinchcomb et al., 2012; Witte, 2012). Along this portion of the river valley, glacial
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19 recession occurred ~16 ka, which led to periglacial deposition, followed by late Pleistocene
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21 incision and then alluvial deposition around 12.8 ka (Stewart et al., 1991; Witte, 2001). A 6-5
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23 ka incision event, followed by floodplain and terrace reworking for the past 6,000 years, resulted
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25 in discontinuous alluvial terrace development throughout the reach (Stinchcomb et al., 2012;
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27 Witte, 2012). The T2 alluvial terrace comprises much of the valley bottom along the middle
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29 Delaware River valley. The surface elevation above river baseflow can vary along the T2 (11-5
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31 m) and can be divided into two sub-terraces, T2a (11-7 m) and a lower T2b (7-5 m) (Stinchcomb
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33 et al., 2012). Many of the terrace profiles have evidence of >10 buried soils that span the
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35 Holocene, making this an ideal locality to constrain the timing and quantify potential human-
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37 induced Pb flux through time.
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48 *2.2 Profile description, chronology and sample collection*

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50 The T2a (high terrace) and T2b (low terrace) terraces are ideal for this research because the
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52 underlying landforms primarily consist of weathered vertical accretion deposits marked by
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54 buried soils. Two alluvial terrace profiles occurring along the Delaware River valley bottom
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56 form the basis in this study for constraining the timing and quantifying human-induced Pb flux
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4 along the reach. The two profiles were described and sampled along high and low alluvial fill
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6 terrace landforms (Fig. 1), and were the subject of previous research (Stinchcomb et al., 2011,
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8 2012, 2013). Herein, these two alluvial profiles are referred to as occurring on the high-terrace
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10 and low-terrace landforms. Surface and buried soils occurring with the high- and low-terrace
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12 landforms were described using U.S. Department of Agriculture (USDA) soil nomenclature
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14 (Schoeneberger et al., 2002) with modifications for describing lamellae horizons (see Holliday,
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16 2004). Bulk samples were collected from each terrace landform by soil horizon and at arbitrary
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18 5 or 10 cm intervals within each soil horizon for bulk geochemistry and particle-size analysis.
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20 The sample interval was selected based on overall profile thickness and not all samples were
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22 analyzed due to budget and time constraints. Oriented thin-section samples were collected by
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24 soil horizon.
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31 The age of buried soils and Pb concentrations were constrained in previous work
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33 (Stinchcomb et al., 2011, 2012; Stewart et al., 2014) using ^{14}C dating and archaeology (Table 1;
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35 See section 2.3 below). Radiocarbon ages were calibrated using CALIB 7.0 (Reimer et al., 2013)
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37 and are reported as median ages $\pm 2\sigma$ before present (BP = 1950 AD). Soils that formed before
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39 1680 AD (270 y BP) are designated as prehistoric soils. Soils that formed after 270 y BP are
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41 designated as historic soils.
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48 *2.3 Archaeology*

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51 The low-terrace landform location for this study corresponded with the Manna
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53 archaeological site (36Pi4), a contributing property to the Minisink National Historic District.
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55 Previous work at 36Pi4 provided evidence of sporadic occupations by Native Americans that
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57 began during the Middle Archaic period of regional prehistory (ca 8000-5000 BP) and persisted
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4 into the 17th century and the colonial era (Kinsey 1972: Figure 1B; Wall and Botwick 1993;
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6 Perazio et al. 2003; Stewart et al 2014). Euro-American exploration and settlement in the vicinity
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8 of the site heightened during the 18th century. The Hotel Schanno, situated adjacent to the site,
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10 opened in the mid- 19th century and continued in operation into the 20th century. Portions of the
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12 site were farmed during the 19th century and continued into the 20th century. Aerial photographs
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14 indicated that by 1956 the portion of the Manna site investigated in this study was overgrown
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16 and wooded, confirming that farming operations had ceased by this time. The federal
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18 government took over the property in the 1960s in preparation for the proposed construction of
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20 the Tocks Island Dam. The dam was never built and the lands acquired by the government
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22 became the basis for the Delaware Water Gap National Recreation Area (Fig. 1).
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28 In 2004 and 2005, seven large excavation blocks, numerous small test units, and
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30 subsurface probes were opened and completed across the terrace positions flanking the
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32 Raymondskill Creek and its junction with the Delaware River (Fig. 1). Because of the sensitive
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34 nature of archaeological site locations, 36Pi4 is not shown here. The low-terrace landform does
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36 lie within 36Pi4 boundaries (Fig. 1C). Laterally and vertically extensive bank exposures were cut
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38 and profiled along the Raymondskill Creek. Sediments and soils were described following Foss
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40 et al. (1985) and Schoeneberger et al. (2002). Excavations followed standard archaeological
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42 procedures (e.g., Stewart 2002) removing the Ap horizon (plowzone) as a single excavation level
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44 and employing 10 centimeter thick arbitrary excavation levels within deeper strata distinguished
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46 on the basis of changes in color, texture, or soil structure. The spatial context of artifacts and
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48 cultural features was controlled with reference to excavation unit, stratum, level, and three-
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50 dimensional coordinates when appropriate. Excavated matrix was dry screened through quarter
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52 inch hardware mesh. Matrix samples from all excavation levels, and all feature fill, were
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4 processed through flotation allowing for the recovery of small and highly fragmented artifacts,
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6 floral and faunal remains. Wood charcoal and other organic remains recovered from flotation and
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8 during general excavations were used for radiocarbon dating (See section 2.2).
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11 A block of excavations (Block 6) completed along the low-terrace landform (proximal to
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13 MAN-1 profile from Stinchcomb et al., 2011) documented artifacts and features in a series of 10
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15 distinctive strata to a depth of 280cm below the existing surface (Stewart et al., 2014). Block 6
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17 included 6 units measuring 1 m on a side, and two partial units $< 1 \text{ m}^2$ and is approximately 2-3
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19 meters adjacent to the low-terrace landform profile in this study. During Block 6 excavations,
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21 strata were numbered from the top to bottom and then correlated with a master stratigraphy. For
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23 the purposes of facilitating discussion, artifacts are herein designated as either being prehistoric
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25 ($>1680 \text{ AD}$ or $>270 \text{ y BP}$) or historic ($<1680 \text{ AD}$ or $<270 \text{ y BP}$). Pertinent archaeological strata
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27 were correlated with the low-terrace landform profile.
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36 *2.4 Soil and sediment characterization*

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38 Soil and sediment bulk density (ρ_{est}) was estimated using a pedotransfer function developed
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40 by Rawls (1983). The model uses particle size and % organic matter to estimate bulk density.
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42 The values were compared with modern Delaware Series measured bulk density values in a
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44 previous study (Stinchcomb et al., 2014) to help determine the validity of the approach (National
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46 Cooperative Soil Survey, 2013). The estimated bulk density values have a mean of $1.35 \pm 0.13 \text{ g}$
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48 cm^{-3} and are slightly less dense than those reported for similar USDA mapped soils in the
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50 immediate area ($1.50 \pm 0.09 \text{ g cm}^{-3}$) (NCSS, 2015). Using the USDA bulk density as actual
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52 values, the bulk density estimates reported here have an error of 10%.
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Bulk soil and sediment samples were analyzed for particle size using a Malvern 2000E laser granulometer with the HydroMU dispersion unit (Arriaga et al., 2006). Malvern quality audit standards (QAS3002, 15 – 150 µm glass spheres) were run and the results show a standard error less than 1%. Results are shown in cumulative weight percent of sand, silt, and clay, using the Udden-Wentworth (geological) grain-size scale (Wentworth, 1922). The Wentworth scale precludes genetic interpretations of soil development and is primarily used for sedimentological interpretations.

The soil pH in H₂O (1:1) was measured in the lab (NRCS, 2004). The total organic carbon % (TOC) was measured using a Costech elemental analyzer. The major and trace element whole-soil geochemistry were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) at ALS using the ME-MS61 method. Major elements are reported in wt. %. Trace elements are reported in ppm (Appendices 1 and 2).

We examined the alluvial soil bulk geochemistry using a mass-balance approach (Anderson et al., 2002; Brimhall & Dietrich, 1987). The mobile element additions and losses of Pb were calculated using the mass-transfer coefficient, τ (Anderson et al., 2002; Brimhall and Dietrich, 1987):

$$\tau_{\text{Pb,Zr}} = \frac{C_{\text{Pb},w} C_{\text{Zr},p}}{C_{\text{Pb},p} C_{\text{Zr},w}} - 1 \text{ (Eq. 1).}$$

In this equation, C equals the element concentration of the mobile element, Pb, and the immobile element, Zr, in the weathered, w , or parent, p , material. Zirconium, which is assumed to reside in zircon and is resistant to chemical weathering, was used as the immobile element for this study.

For both high- and low-terrace landforms, the lowest sample in a buried alluvial soil was designated as the parent. When $\tau_{\text{Pb,Zr}} = 0$, Pb has not been added or removed from the profile with respect to Zr. When $\tau_{\text{Pb,Zr}} = -1$, 100% of the Pb has been removed compared to Zr. When $\tau_{\text{Pb,Zr}} = 1$, 100% of the Pb has been added compared to Zr.

3. Results

3.1 Archaeology and Chronology

Archaeological data directly from or proximal to the high-terrace and low-terrace landforms provide some constraints on the timing of weathering and deposition (Fig. 2, Table 2). Although extensive archaeological excavations were not conducted along the high-terrace landform, artifacts were noted at specified depth intervals and soil horizons during trench excavation. In particular, a clay pipe and Late Woodland (950 to 350 y BP) pottery fragments were recovered between 20 and 50 cm depth below the surface (Table 2). Above this interval, a chipped-stone layer was documented at 8 cm below the surface, likely related to the private homes that were present at this locale during the mid-20th century (Table 2). The stream bank and homes were destroyed during a bank erosion event sometime after 1973 AD (-23 y BP) (Stinchcomb et al., 2012), where 1973 AD is -23 y BP because 1950 AD equals 0 BP, and therefore: 1950AD - 1973AD = -23 y. No artifacts were found in the middle and early Holocene deposits at this locality.

Excavation Block 6 is situated at the base of a low slope (3-5%) adjacent to a higher Delaware River terrace to the east. Three strata were defined in the upper 80 cm of the deposits here (Fig. 3):

Stratum 1 - Ap horizon (surface to 26-31 cm below surface), 10YR 3/4 dark yellowish brown loamy sand; crumb structure

Stratum 2 - A/C horizon (26-31cm to 43.5-49 cm below surface), 10YR 4/4 dark yellowish brown loamy sand, crumb structure; and

Stratum 3 - B/C horizon (43.5-49cm to 74-78cm below surface), 10YR 3/6 dark yellowish brown loamy sand, crumb structure.

These strata are interpreted as sheetwash deposits sourced from a higher alluvial terrace landform to the east, as these deposits are laterally traceable along extensive exposed banks in this position (see Fig. 1 in Stinchcomb et al., 2011; Stewart et al. 2014). No deposits below the Ap horizon have the mottled color or variable texture typically associated with placed fill. Land clearance and continual plowing associated with 19th and 20th century agriculture on this landscape likely facilitated conditions under which episodes of erosion and downslope movement and reworking of artifacts and sediments could have taken place (Stewart et al., 2014). The sheetwash interpretation is supported by the presence of late prehistoric artifacts mixed with those of the colonial and later periods in all three strata. A tooth-crown bottle cap and fragments of aluminum recovered from Stratum 3 (see below) indicate that the sheetwash events do not pre-date the 1890s, and most likely date to the early to mid- 20th century (Fig. 2 and 3). Although alluvial events could have contributed some sediment to these strata, the size, shape, condition and quantity of historic/modern and Native American artifacts make it highly unlikely that alluvial processes are responsible for their reworking and transport from an upstream location.

Strata 1 through 3 contain a mixture of Native American and Euro-American artifacts (Table 2). The historic artifacts range in age from 350 to -6 y BP, where this latter age is an estimate based on the observation that farming had ceased and the area was wooded by 1956. It could have ceased prior to this time, but no later than 1956 AD (roughly 0 y BP). The mean and

standard deviation of historic age estimates by stratum show no significant difference at the 95% confidence interval (Table 3) and provides further support for the sheetwash interpretation (Stewart et al., 2014). Although the maximum estimated age range extends back several centuries, the tooth-crown bottle cap recovered from stratum 3 has a maximum estimated age of 58 y BP (Table 2) and suggests that the stratum 3 sheetwash event occurred no earlier.

3.2 Geochemistry

The Delaware River alluvial soil Pb concentrations, when examined by landform and soil horizon, show a number of similarities (Table 4). The buried prehistoric A, B and C horizons in both the high- and low-terrace landforms show similar mean Pb values within error (Table 4, Fig. 3). In terms of depth trends for both landforms, the mean Pb concentration in prehistoric buried soils increases 8-16% from the A to B horizon.

Historic mean Pb concentrations in A horizons are higher than C horizons, however there is a great deal of variability in the A horizons (Table 4). Taking into account this historic A horizon Pb variability, the historic mean Pb concentrations of A and C horizons are within error. There is only one Pb value for historic B horizons, therefore no comparison was made. The lack of historic B horizons may be due to the fact that the soils were too young or sedimentation rate too high for subsoil development. When comparing historic to prehistoric horizons, historic A horizons show a >200% increase in mean Pb concentration compared to Pb in prehistoric A horizons for both high- and low-terrace soils. In the high-terrace soils, historic C horizons increase 40% in Pb concentration compared to prehistoric C horizon Pb concentrations, whereas

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4 in low-terrace soils, historic C horizons increase 83% in Pb concentration compared to
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6 prehistoric C horizon Pb concentrations.
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9 The $\tau_{\text{Pb,Zr}}$ data, which track additions and losses with respect to the parent material, show
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11 mean % addition of Pb ranging from 1 to 9 % in both the high- and low-terrace prehistoric soils.
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14 The variance in the mean $\tau_{\text{Pb,Zr}}$ for prehistoric soils shows that some soils also experienced Pb
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16 loss, <15 %. Conversely, the $\tau_{\text{Pb,Zr}}$ data from historic soils show mean addition ranging from 234
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18 to 335 % in both the high- and low-terrace landforms. The mean historic Pb additions
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20 documented here exhibit equally high standard deviations ranging from 334 to 336 %.
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25 The mean soil pH for the high- and low-terrace profiles is 5.2 ± 0.5 and 5.4 ± 0.7 ,
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27 respectively, and are classified as strongly acidic (Soil Survey Staff, 1993). Pb speciation
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29 models show that at strongly acidic pH levels, Pb^{2+} is the dominant species in soil solution with
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31 PbSO_4 and Pb-fulvate as minor components (Essington, 2004). Experimental studies show that
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33 when soil pH values are $<5.2 \pm 0.2$ Pb mobility is enhanced (Martinez and Motto, 2000).
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41 4. Discussion

42 4.1 Evidence of anthropogenic-Pb enrichment in the Delaware River Valley

43 The historic alluvial soils along both the high- and low-terrace landforms show evidence
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45 of Pb enrichment >2 orders of magnitude compared to the underlying prehistoric alluvial soils.
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48 The historic Pb enrichment is either the result of parent material variability, biological uplift
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50 (Reimann et al., 2009; Kraepiel et al., 2015), atmospheric deposition or a combination of factors.
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52 Because the Zr values for both profiles show overall minimal variation, a major change in
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54 alluvial parent material seems unlikely (Appendices 1 and 2). In a soil-Pb study from portions of
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4 the Midwest and southeastern USA, Smith et al. (2011) showed that Pb concentrations were
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6 found to be higher in regions where the parent material was mixed, as opposed to quartz-rich
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8 regions (e.g., Sand Hills, NE), suggesting that Pb concentrations more or less vary inversely with
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10 quartz concentration. Because the Delaware River valley sediments are largely quartz-rich
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12 (Stinchcomb et al., 2013, 2014), it would therefore be unlikely that the alluvial soil parent
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14 material would have a high Pb content.
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19 The argument for anthropogenic enrichment of Pb in the Delaware River Valley alluvial
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21 soils is further examined using geochemical cross plots. The cross plots show that (1) as the Pb
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23 concentrations increase, Al, Zr, P and TOC concentrations also increase, and (2) ~7 Pb values
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25 plot away from the average distribution (Fig. 4). Assuming that Al % directly reflects clay %,
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27 the positive correlation in the Pb-Al plot occurs because Pb commonly adsorbs onto clay
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29 minerals (Singh et al., 2001; Brady and Weil, 2010). The increase in Al % coincides with
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31 increasing clay % (Fig. 3, Appendices 1&2). The high Pb values that plot away from the trend
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33 coincide with samples that have high soil Pb concentrations and anomalously high $\tau_{\text{Pb,Zr}}$ values
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35 (Fig. 3). The geochemical cross plots suggest the high Pb may be sourced from a Pb-pool other
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37 than Delaware alluvial soil clay. We suggest here that anthropogenic addition of this Pb is a
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39 likely source.
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46 Pb enrichment from a source other than Delaware alluvial parent material is further
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48 confirmed by examining Pb with respect to the immobile element, Zr (Fig. 4B). In this example,
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50 Zr variations reflect the range of parent material values for the two alluvial landforms because Zr
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52 commonly resides in chemically inert minerals (e.g., zircon). The plot shows that the high soil
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54 Pb, which corresponds with anomalously positive $\tau_{\text{Pb,Zr}}$, have Zr distributions similar with
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56 respect to most Delaware alluvial parent material. The Pb-Zr plot suggests that either (1)
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4 biological uplift is concentrating Pb without affecting the Zr, or (2) the high soil Pb
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6 concentrations are sourced from a parent material foreign to that of the Delaware River alluvial
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8 soil parent material (i.e., where most Pb-Zr data are clustering).
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11 The affinity for Pb to sorb to PO_4 and organic matter makes a positive correlation
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13 between Pb, P and %TOC unavoidable (Fig. 4C). The correlation between Pb and P is likely
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15 related to Pb adsorption to phosphatic clays (Singh et al., 2001). However, the low- and high-
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17 terrace Pb peaks have P values that fall within the normal distribution of P for the two sites,
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19 suggesting no anomalous increase in phosphatic clays in these samples. The correlation between
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21 Pb and organic matter is the basis for the Pb pedotransfer function for forested Vertisols used to
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23 reconstruct ancient organic matter in a lithified paleosol (Nordt et al., 2012). Much like the Pb-P
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25 plot, the low- and high-terrace Pb peak samples have TOC values that fall within the normal
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27 range of TOC for the two sites (Fig. 4D). As with the Pb-Al and Pb-Zr plots, some Pb values
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29 deviate from the normal trend with respect to %TOC, plotting away from the trend that one
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31 might expect in pre-Anthropogenic soils (e.g., Nordt et al., 2012).
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41 *4.2 Estimating the addition of anthropogenic-Pb*

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43 The archaeology and radiocarbon data show that the maximum Pb values in Fig. 3 and
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45 Fig. 4 occur in buried historic soils that weathered during the 20th century. The timing of these
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47 maximum Pb intervals coincides with Industrial-era activities and are likely due to anthropogenic
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49 Pb addition. Because the Pb from both the high- and low-terrace landforms show anthropogenic
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51 enrichment of Pb in the historic portion of the profiles, $\tau_{\text{Pb,Zr}}$ can be used to calculate Pb mass
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53 flux at individual depths and over the entire profile for each alluvial soil. The net mass flux of Pb
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for each alluvial profile, $m_{\text{Pb, flux}}$, is calculated using the following equation (Brimhall and Dietrich; Brimhall et al., 1991; Anderson et al., 2002):

$$m_{\text{Pb, flux}} = \rho_p \int_0^{D_w} \frac{C_{\text{Pb},p} \tau_{\text{Pb,Zr}}(x)}{\varepsilon_{\text{Zr}}(x)+1} dx \approx \rho_p \int_0^{D_w} C_{\text{Pb},p} \tau_{\text{Pb,Zr}}(x) dx \text{ (Eq. 2).}$$

Here x is depth (cm), and ρ_p (g cm^{-3}) is density of parent material and $C_{\text{Pb},p}$ is the concentration of Pb in the parent material (mg kg^{-1}). The product of the numerator in Eq. 2 is divided by the strain, ε_{Zr} , for that profile, where:

$$\varepsilon_{\text{Zr}} = \frac{V_w - V_p}{V_p} = \frac{\rho_p}{\rho_w} * \frac{C_{\text{Zr},p}}{C_{\text{Zr},w}} \text{ (Eq. 3).}$$

Here ε_{Zr} is the relative change in volume, V , between the parent and weathered portion of the buried alluvial profile at the same depths used in Eq. 2. The ε_{Zr} was estimated using ρ_p and the bulk density from weathered samples, ρ_p and immobile element concentrations from the parent and weathered portion of the profile, $C_{\text{Zr},p}$ and $C_{\text{Zr},w}$, respectively (right-hand side of Eq. 3). The ε_{Zr} incorporated into Eq. 2 normalizes the volumetric changes that can occur during weathering, e.g., dilation and collapse (Brimhall et al., 1992). The product of dividing the numerator in Eq. 2 by ε_{Zr} yields the strain-corrected Pb flux for each individual x , $m_{\text{Pb, flux}}(x)$. The $m_{\text{Pb, flux}}(x)$ for each depth is integrated from the surface of the buried soil to the base of the buried soil profile, D_w , and multiplied by ρ_p . The $m_{\text{Pb, flux}}$ values are expressed in $\mu\text{g cm}^{-2}$. A negative $m_{\text{Pb, flux}}$ reflects a loss of Pb and a positive $m_{\text{Pb, flux}}$ yields an addition of Pb with respect to the parent material.

The $m_{\text{Pb, flux}}$ for two buried historic soils from the high- and low-terrace landforms are 486 ug cm^{-2} and 526 ug cm^{-2} , respectively (Fig. 3, Table 5). The $m_{\text{Pb, flux}}$ for prehistoric soils having a thickness comparable with the historic soils from the high and low terraces are -39 ug cm^{-2} and 1.71 ug cm^{-2} , respectively. The $m_{\text{Pb, flux}}$ from prehistoric to historic soils for the two profiles shows increase greater than two orders of magnitude that roughly coincides with late-19th and 20th century human activities.

The -39 ug cm^{-2} mass loss from the middle Holocene buried soil in the high terrace suggests that the historic Pb soils may have originally had more Pb that was subsequently removed through hydrolysis or translocation and illuviation of clay down profile (Fig. 3, Table 5). In fact, the underlying early Holocene buried soil in the high terrace shows Pb enrichment in the subsoil compared to the upper portion of the buried soil where there is an increase in TOC (Fig. 3). Soil pH values for the high-terrace landform are acidic and support the notion that Pb mobility may have occurred in the past (Appendix 1). An examination of soil thin sections from both the high- and low-terrace landforms show an open-pore framework in the late prehistoric and historic buried soils with no clay illuviation (Fig. 5 A&B), whereas the lower early Holocene buried soil shows illuviated clay coating channel pores (Fig. 5C). The photomicrographs support the notion that clay illuviation can move Pb lower in the profile for soils that formed for extended periods of time. Because the historic soils are incipient and have short soil residence times, illuviation and movement of Pb in the profile is unlikely.

4.3 Estimating the rate of addition of anthropogenic-Pb

We now attempt to provide some estimates on the addition rate of Pb in the high- and low-terrace buried alluvial soils (Table 5). Historic artifacts provide important constraints on the

age model input for the alluvial profiles from the two terrace landforms. Using artifacts and historic knowledge of the region, we calculate Pb addition rates for the historic buried soils.

One approach for estimating the duration of soil formation, defined herein as the soil residence time (SRT), or the amount of time the alluvial soil formed at the surface before burial, is to use diagnostic historic artifacts and their mean, maximum and minimum ages. The tooth-crown bottle cap found in the stratum 3 sheet wash deposit at Manna yields a maximum age of 58 y BP, making the Pb addition observed at ~50 cm below surface no older than 58 y BP and possibly younger. A plowed surface (stratum 1) at the low-terrace landform overlies and buries the high soil Pb concentration soil at 50 cm. Because plowing ceased ~1950 AD (0 y BP) with the formation of the Delaware Water Gap National Recreation Area, the high soil Pb would have been buried prior to plow cessation, i.e., before 0 y BP. Thus, we can approximate a residence time of 58 y BP for the high soil Pb. The 58 y BP maximum residence time is an estimate because it assumes that the soil containing high Pb concentrations began forming immediately after the sheetwash event and ceased formation around 0 y BP, when all plowing activity ceased.

It is more probable that the residence time of the soil is <58 y BP. Because the historic artifacts are a mixed assemblage due to sheetwash from a higher alluvial terrace, we thus relied upon the mean minimum age estimates for the individual archaeological strata to assign a SRT (Table 3). This approach assumes that the mean minimum artifact age is an accurate reflection of the time the sheetwash event occurred and buried the high soil Pb interval. Specifically, we subtracted the mean minimum age of stratum 2 from the corresponding mean minimum age in stratum 3. Using the archaeological data in this manner yielded a mean minimum SRT equal to 39 years (36 y BP - -3 y BP = 39 y BP). Additionally, we included the SRT estimates for both high- and low-terrace historic soils that were based on the radiocarbon age model output (see

Stinchcomb et al., 2012, 2013 for age-model output). Given the uncertainty, we calculated Pb addition rates for all three residence time scenarios (Table 5).

Along the high-terrace landform, a chip-stone layer coinciding with the high soil Pb concentration was associated with houses now since removed. The chip stone layer likely dates to the early 20th century given the age of houses that were present at the time before bank erosion. Although there is some uncertainty in our historic SRT estimates, without historical archaeology on the high- and low-terrace alluvial profiles, the radiocarbon age model output for the low-terrace landform would have produced a large, unreasonable age range for the high soil Pb interval in the alluvial soils.

The mean Pb addition rate for the high- and low-terrace historic soils along the Delaware River valley is $9.49 \pm 3.30 \text{ ug cm}^{-2} \text{ y}^{-1}$, which is based on the eight residence time scenarios discussed above (Table 5). The mean Pb addition rate is over a six-fold increase in Pb deposition compared to modern trace metal dry deposition rates in the NJ region ($1.83 \text{ ug cm}^{-2} \text{ y}^{-1}$) (Yi et al., 2006). Similar soil-Pb addition rates were calculated for an upland soil 322 km to the west-southwest (Pb addition rate of $6 - 10 \text{ ug cm}^{-2} \text{ y}^{-1}$) (Ma et al., 2014). A much slower bulk atmospheric Pb deposition rate ($0.261 \pm 0.77 \text{ ug cm}^{-2} \text{ y}^{-1}$) was documented 560 km north, in Lac Hertel, southern Quebec (Gélinas et al., 2000) (Fig. 6). The 20th century high alluvial soil Pb concentrations also coincide with the 1900AD -1970AD interval of elevated Pb flux documented in a Greenland ice core that has been attributed to leaded-gasoline emissions, non-ferrous metal processing and coal combustion (McConnell et al., 2002). The robust Greenland ice core chronology of elevated Pb flux during the 20th century does not invalidate the interpretation of a late 19th to early 20th century age designation for the high alluvial soil Pb interval in the Delaware River study area.

Pb addition since the Delaware alluvial historic soils were buried was not accounted for in our rate calculations (Fig. 3, 0.1 to 0.3 m below the surface in the low terrace landform). Also, the higher Pb concentrations in historic C horizons, compared to prehistoric C horizons, suggests that anthropogenic Pb may have been reworked and included in the primary alluvial material. Thus, Delaware alluvial Pb additions reported here are a minimum estimate of total anthropogenic Pb additions. Although there is uncertainty in the soil residence time estimates, the error is confined to $<10^2$ years. Better age control on the individual alluvial soils will refine the Pb addition rates for this region.

4.4 Potential Pb addition elsewhere in USA

Pb-enrichment has been documented elsewhere in eastern North America. Chemostratigraphic research of mill-dam sediment in south-central Pennsylvania shows a distinct geochemical signature of trace metal enrichment, including Pb, in the cores presumably sourced from metal amendments in agricultural runoff and leaded gasoline (Niemitz et al., 2013). A study of tree ring and alluvial deposit geochemistry in the Saint Francois river catchment near Montreal shows multiple Pb enrichment events suggesting several pollution events occurred during the 20th century (Saint-Laurent et al., 2010).

A $\tau_{\text{Pb,Ti}}$ map for the conterminous United States (raw data from Smith et al., 2014) shows that the quantification of Pb fluxes in the high- and low-terrace alluvial soils occur in a region where Pb is enriched in the surface with $\tau_{\text{Pb,Ti}} > 10$ in several soils (Fig. 6). The $\tau_{\text{Pb,Ti}}$ was calculated using Eq. 1 and only sites with $\tau_{\text{Pb,Ti}} > 1$ are shown. The Pb (ppm) and Ti (%) data are from A and C horizons and were collected as part of the North American Soil Geochemical Landscapes Project (NASGLP) (Smith et al., 2013) Holmgren (1993) also noted elevated Pb

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4 concentrations in northeastern USA soils and suggested industrial activities as a likely cause.
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6 Thus, the Delaware anthropogenic-Pb input represents a more widespread environmental signal.
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9 In addition to the northeastern region where these Delaware River sites are found,
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11 elevated A horizon Pb in Illinois-Missouri is centered on the long-standing mining areas for
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13 Mississippi-Valley type Pb-Zn deposits. The elevated A horizon Pb around central Colorado
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15 could be mining plus entrapment of Pb from emissions in the Denver area. Of the 4,871 sites
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17 sampled in the NASGLP project (1 site per 1,600 km²) 598 have $\tau_{\text{Pb,Ti}} > 1$, or >100% addition of
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19 Pb to the A horizon. Intriguingly, the distribution of these sites in Fig. 6 suggest that $\tau_{\text{Pb,Ti}} > 1$
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21 sites may be largely confined to woodland settings. Thus, biogenic uplifting of Pb in woodland
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23 regions (where many of the $\tau_{\text{Pb,Ti}} > 1$ in Fig. 6 occur) may be partly responsible for the high Pb
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25 concentrations in surface soils throughout much of the eastern, western and northwestern USA
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27 (Jobbagy and Jackson, 2004; Reimann et al., 2009; Kraepiel et al., 2015). A systematic
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29 evaluation of valley bottom alluvial profiles similar to those of the Delaware may help constrain
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31 the extent and timing of the Pb event in the eastern United States and throughout North America.
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41 5. Conclusions

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43 Quantifying human impact on Earth's surface requires past estimates of human impact.
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45 The results from our work show that quantifying human impact on alluvial soils using mass-
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47 balance geochemistry, geochronology and archaeology can aid in constraining the timing and
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49 magnitude of anthropogenic addition of Pb, using examples from alluvial landforms along the
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51 Delaware River valley in northeastern USA. Based on two alluvial profiles examined here,
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53 middle and late Holocene Pb additions to alluvial soils are conservative ($-39 \mu\text{g cm}^{-2}$ and $1.71 \mu\text{g}$
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55 cm^{-2}) compared to Industrial Era additions ($486 \mu\text{g cm}^{-2}$ and $526 \mu\text{g cm}^{-2}$). The corresponding
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4 middle and late Holocene Pb addition rates (-0.28 and $0.04 \mu\text{g cm}^{-2} \text{y}^{-1}$) are also conservative
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6 compared to Pb addition rates from the Industrial Era ($8.38 \mu\text{g cm}^{-2} \text{y}^{-1}$ and $9.07 \mu\text{g cm}^{-2} \text{y}^{-1}$).
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8 The >200 times increase in Pb addition in the 19th-20th century alluvial soils is the result of
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10 anthropogenic Pb addition. The mass-balance results show that 19th-20th century Pb additions to
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12 these two alluvial profiles, which span much of the Holocene, are unlike anything documented
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14 prior to the Industrial Era. Additional quantification Pb flux in alluvial profiles will constrain the
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16 extent and timing of anthropogenic Pb impact.
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Tables and Figures.

Table 1. Radiocarbon ages used in this study.

Table 2. Non-native historic and modern artifacts from the Manna archaeological site (adapted from Stewart et al., 2014). The artifacts were collected from an excavation unit ~2 m from the low-terrace profile in this study.

Table 3. Descriptive statistics of historic artifact age estimates by horizon at the Manna archaeological site (See Fig.3 for strata correlation with low-terrace landform).

Table 4. Pb concentrations and $\tau_{\text{Pb,Zr}}$ by terrace and soil horizon. See Appendices 1 and 2 for raw geochemical data.

Table 5. Pb flux and addition rates for historic and prehistoric buried alluvial soils from the high- and low-terrace landforms. See Appendices 1 and 2 for raw geochemical data and Fig. 3 for which soils were used in the flux calculations.

Figure 1. Northeastern USA study area. (A) Map of northeastern USA showing Delaware River Basin. (B) Delaware Water Gap National Recreation Area (DEWA) located along the Middle Delaware River Valley. The locations of the two alluvial profiles are shown along with their corresponding alluvial terrace designations, referred to herein as high- and low-terrace

landforms. The distribution of Quaternary alluvium (Qal) is also shown (Witte, 2001, 2012; Witte and Epstein, 2005). (C) and (D) show the exact locations of the high- and low-terrace landforms on bare-Earth LiDAR hillshades (1 m resolution). The Manna archaeological site mentioned in text corresponds with the low-terrace landform study area.

Figure 2. Delaware River alluvial profiles. (A) Upper 1.2 m of high-terrace landform. Trowel for scale. The 2006 flood deposit is the uppermost light-gray layer underlying the O horizon. (B) Upper ~1.5 m of low-terrace landform showing Block 6 archaeological excavation unit (Stewart et al., 2014). Block 6 is proximal to the low-terrace alluvial profile, the source of the particle-size, bulk density and geochemical data. The tooth-crown bottle cap has a maximum age of 58 y BP and Woodland pottery dates from 1000 to 500 y BP. Both images show approximate depth of highest Pb concentration (Pb max). Variations in grayscale denote buried alluvial soils shown in Figure 3.

Figure 3. High- and low-terrace alluvial soil profile data. Archaeological stratigraphy designations (i.e., arch' strata) are based on correlation between archaeological and geomorphological studies (Stinchcomb et al., 2011; Stewart et al., 2014). The 1000 y BP ages in both profiles coincide with observations of Late Woodland pottery and diagnostic projectile points (black triangles). Calibrated radiocarbon ages are also shown (white circles) (Table 1). See Table 2 for list of prehistoric and historic artifacts recovered from the Manna archaeological site, strata 1-3. The historic and prehistoric soil horizons mentioned throughout the text are delineated using the black horizontal dashed line and labeled on the right hand side of the figure. The historic soils used in the Pb flux calculations are denoted with a dark gray horizontal bar.

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4 The late and middle Holocene buried soils used in Pb flux calculations are denoted with light
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6 gray bars and labeled, respectively (See Table 5 for the corresponding Pb flux calculations). The
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8 early Holocene soil mentioned in Fig. 5 is also denoted using a light gray bar in the high-terrace
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10 landform.
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16 Figure 4. Geochemical cross plots for both high-terrace and low-terrace landforms showing (A)
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18 Pb-Al, (B) Pb-Zr, (C) Pb-P, and (D) Pb-organic carbon (OC). The “high-terrace Pb peak” and
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20 “low-terrace Pb peak” correspond with the maximum Pb values in both alluvial profiles and were
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22 used in the anthropogenic Pb flux calculations (Table 5). Note that the anthropogenic Pb (Pb
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24 peak) values plot away from the main Pb distribution with respect to the other elements. Thus,
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26 the Pb peak samples are not likely sourced from the same Pb pool as the majority of alluvial
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28 terrace Pb.
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36 Figure 5. Thin-section photomicrographs showing absence and evidence of illuviation. (A)
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38 Cross-polarized image from a high-terrace buried soil ~100 cm below the surface showing open-
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40 pore framework with no evidence of illuviation. (B) Cross-polarized image from a plow zone
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42 near the Manna archaeological site (low-terrace landform) that has an open and connected pore
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44 network with no illuviated clay present. (C) Cross-polarized image from an early Holocene
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46 buried soil in the high-terrace landform showing Fe-rich illuviated clay coating a tubular pore.
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50 The clay illuviation coincides with a $\tau_{\text{Pb,Zr}}$ enrichment and decline in %TOC and suggests the
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52 early Holocene pedogenesis and clay translocation enriched Pb in subsoil (see Fig. 3, high-
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54 terrace landform, 3.5 m below the surface).
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Figure 6. $\tau_{\text{Pb,Ti}}$ map for the conterminous United States (raw data from Smith et al., 2014). The $\tau_{\text{Pb,Ti}}$ was calculated using Eq. 1 and only sites with $\tau_{\text{Pb,Ti}} > 1$ are shown. The Pb (ppm) and Ti (%) data are from A and C horizons and were collected as part of the North American Soil Geochemical Landscapes Project (NASGLP) (Smith et al., 2013). Of the 4,871 sites sampled in the NASGLP project (1 site per 1,600 km²) 598 have $\tau_{\text{Pb,Ti}} > 1$, or >100% addition of Pb to the A horizon. The location of Pb addition rates calculated in (a) this study, (b) Ma et al., (2015), and (c) Gélinas et al., 2000 are also shown.

Appendix 1. High-terrace geochemical data

Appendix 2. Low-terrace geochemical data

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1

Radiocarbon lab code	landform	Depth below terrace surface (cm)	Stratigraphic context	¹⁴ C age [#] (yr BP)			Calibrated median age and $\pm 2\sigma$ range ^{**} (yr B.P.)			Source
Beta-280269	high-terrace	105	soil	1620	±	40	1507	±	98	Stinchcomb et al., 2012
Beta-289229	high-terrace	182	soil	4930	±	40	5653	±	69	Stinchcomb et al., 2012
Beta-296271	high-terrace	257	soil	5980	±	40	6819	±	108	Stinchcomb et al., 2012
Beta-282837	high-terrace	323	soil	8280	±	40	9287	±	142	Stinchcomb et al., 2012
Uga-5488	high-terrace	450	soil	9330	±	545	10629	±	140	Stewart et al., 1991
Beta-227480	low-terrace	70	soil/sediment	390	±	40	448	±	99	Stinchcomb et al., 2011
Beta-227477	low-terrace	100	soil	270	±	40	338	±	157	Stinchcomb et al., 2011
Beta-227479	low-terrace	126	soil	550	±	40	562	±	67	Stinchcomb et al., 2011
Beta-227482	low-terrace	180	soil	840	±	70	767	±	119	Stinchcomb et al., 2011
Beta-258885	low-terrace	270	soil	1900	±	40	1845	±	99	Stinchcomb et al., 2011
Beta-257433	low-terrace	342	soil	2070	±	40	2040	±	105	Stinchcomb et al., 2011

†See Stinchcomb et al., 2012 for landform details

#Conventional radiocarbon age with standard error

**Median probability age calculated in CALIB 7.0, using IntCal13 calibration curve (Reimer et al., 2013). Age error is half the maximum calibrated probability age range

Table 2

Landform	Stratum	Depth range (cm)	Historic artifact	Maximum estimated age (y BP)	Minimum estimated age (y BP)
high-terrace	-	19-39	clay pipe fragment	500	250
high-terrace	-	19-39	grit-tempered pottery	1000	500
low-terrace	1	0 - 31	Coal/clinker	~130	-6
low-terrace	1	0 - 31	Clay pigeon fragments	70	-6
low-terrace	1	0 - 31	Whiteware/ironstone ceramic fragments	130	-6
low-terrace	1	0 - 31	Clear and brown glass fragments	150	-6
low-terrace	1	0 - 31	Metal fragments	150	-6
low-terrace	1	0 - 31	22 caliber shell casing	97	-6
low-terrace	2	31-49	Coal/clinker	~130	-6
low-terrace	2	31-49	Clay pigeon fragments	70	-6
low-terrace	2	31-49	Terra cotta ceramic fragment	150	-6
low-terrace	2	31-49	Clear glass fragment	150	-6
low-terrace	2	31-49	Metal fragments	150	-6
low-terrace	2	31-49	Furniture nail	150	-6
low-terrace	2	31-49	Cut nail	150	50
low-terrace	2	31-49	Wire nail	~90	-6
low-terrace	2	31-49	22 caliber shell casing	97	-6
low-terrace	3	49-78	Coal/clinker	~130	-6
low-terrace	3	49-78	Clay pigeon fragments	70	-6
low-terrace	3	49-78	Pearlware ceramic fragments	170	130
low-terrace	3	49-78	Green bottle glass	150	-6
low-terrace	3	49-78	Clear window glass	150	-6
low-terrace	3	49-78	Tooth crown bottle cap	58	-6
low-terrace	3	49-78	Cut nails	130	50
low-terrace	3	49-78	Wire furniture nail	~90	-6
low-terrace	3	49-78	Metal tack	150	-6
low-terrace	3	49-78	Metal fragments	150	-6
low-terrace	3	49-78	Aluminum fragments	60	-6

low- terrace	3	49-78	Iron triangular arrowhead with twisted wire foreshaft	350	340
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*Archaeological strata thicknesses vary (see text).

Table 3

Stratum	Depth range (cm)	mean maximum age (y BP)	mean minimum age (y BP)
1		119±35	-6±0
2		131±33	0±19
3		144±84	39±75
Overall	0-90	134±61	16±71

Table 4

Landform	Soil	Soil horizon	Pb (ppm)		$\tau_{\text{Pb,Zr}}$		n
high-terrace	prehistoric	A	9.5	± 2.6	0.01	± 0.15	9
high-terrace	prehistoric	B	11.0	± 3.2	0.04	± 0.08	28
high-terrace	prehistoric	C	8.4	± 1.8			14
high-terrace	historic	A	32.2	± 21.7	3.55	± 3.06	3
high-terrace	historic	C	11.8				1
low-terrace	prehistoric	A	9.5	± 1.5	-0.02	± 0.13	11
low-terrace	prehistoric	B	10.3	± 1.5	-0.09	± 0.10	3
low-terrace	prehistoric	C	8.9	± 1.7			8
low-terrace	historic	A	37.0	± 21.8	2.34	± 3.34	4
low-terrace	historic	B	8.6		0.08		1
low-terrace	historic	C	16.3	± 8.7			3

Table 5

Alluvial landform	Soil	Depth of buried soil below surface (cm)	Soil thickness (cm)	$m_{\text{Pb, flux}}$ ($\mu\text{g cm}^{-2}$)	estimated age range (y BP) ¹	SRT (y) ²	Pb addition rate ($\mu\text{g cm}^{-2}$ y^{-1})
high- terrace	historic	8	31	486	34 to -18	52	9.35
						58	8.38
						39	12.46
high- terrace	prehistoric	207	45	-39		1618	-0.024
						1000	-0.039
						50	-0.78
low-terrace	historic	45	50	526	102 to - 24	126	4.17
						58	9.07
						39	13.49
low-terrace	prehistoric	228	32	1.71		800	0.002
						400	0.004
						50	0.034

¹Age ranges based on radiocarbon age model output from previous work (Stinchcomb et al., 2012, 2013)

²The 52 y and 126 y historic SRTs were calculated using the maximum absolute "estimated age range (y BP)" derived from the radiocarbon age model output. See text for additional information on SRT calculations.

Landform	Soil horizon	Historic/prehistoric	Sample depth (cm)	Estimated bulk density (g cm ⁻³)	Clay (wt. %)	Silt (wt. %)	Sand (wt. %)	Soil pH (1:1 H2O)	Pb (ppm)	Ti (wt. %)	Zr (ppm)	Al (wt. %)	TOC (%)
high-terrace	O	historic	1	1.22	2.6	38.4	59.0		9.2	0.302	137.5	2.63	2.76
high-terrace	C	historic	5	1.42	2.7	29.2	68.0	5.1	11.8	0.323	140	2.98	0.38
high-terrace	AC	historic	12	1.20	2.9	45.6	51.4	4.6	40.7	0.34	117	4.88	1.77
high-terrace	Ab	historic	17	1.42	2.5	25.4	72.1	4.7	47.2	0.224	94.7	2.14	0.38
high-terrace	ACb	historic	24	1.48	2.6	20.8	76.5	4.5	8.6	0.235	100	2.22	0.24
high-terrace	ACb	historic	34	1.48	2.8	21.9	75.3	5.2	7.1	0.239	104	2.29	0.21
high-terrace	Ab2	prehistoric	44	1.43	2.4	26.5	71.1	4.4	6.7	0.251	108	2.45	0.26
high-terrace	BCb2	prehistoric	55	1.48	2.0	22.5	75.5	5.4	6.2	0.246	98.3	2.45	0.13
high-terrace	Bwb3	prehistoric	64	1.45	2.5	25.9	71.6	5.3	6.2	0.244	96.5	2.49	0.12
high-terrace	BCb3	prehistoric	70	1.46	2.4	25.7	70.9	4.7	6.6	0.251	107	2.52	0.11
high-terrace	Ab4	prehistoric	77	1.37	3.5	36.4	60.2	5.2	7.2	0.248	110.5	2.68	0.25
high-terrace	BCb4	prehistoric	84	1.44	2.6	26.6	70.7	5.7	6.4	0.249	99.3	2.45	0.10
high-terrace	C	prehistoric	94	1.48	2.0	21.9	76.1	5.1	5.8	0.241	88.6	2.29	0.06
high-terrace	Bw1b5	prehistoric	105	1.24	6.4	61.8	31.7	4.6	10	0.34	127	3.78	0.26
high-terrace	Bw2b5	prehistoric	116	1.24	5.5	59.4	35.0	5.2	10.1	0.339	132	3.57	0.16
high-terrace	BCb5	prehistoric	130	1.35	3.6	41.5	54.9	4.8	8	0.303	121.5	3.01	0.12
high-terrace	Bwb6	prehistoric	144	1.24	5.3	61.9	32.8	5	10.6	0.357	143.5	3.56	0.16
high-terrace	Bwb6	prehistoric	161	1.30	5.9	54.2	39.8	5.3	9.8	0.329	134.5	3.55	0.13
high-terrace	A/Bb7	prehistoric	171	1.33	4.4	44.1	51.6	5	7.9	0.288	117	3.08	0.11
high-terrace	A/Bb7	prehistoric	181	1.29	5.1	47.1	47.7	5.7	8.7	0.286	112.5	3.28	0.14
high-terrace	A/Bb7	prehistoric	191	1.37	4.1	38.5	57.2	5.2	8.3	0.293	110.5	3.17	0.17
high-terrace	BCb7	prehistoric	203	1.44	2.7	29.7	67.6	5.8	6.7	0.256	107.5	2.66	0.09
high-terrace	Ab8	prehistoric	214	1.33	4.3	44.5	51.2	5.3	8.1	0.268	116	3.13	0.18
high-terrace	BwCb8	prehistoric	226	1.23	6.7	61.6	31.7	5.7	10.7	0.336	128	3.82	0.17
high-terrace	BwCb8	prehistoric	236	1.24	6.5	56.7	36.7	5.7	11	0.337	131	3.99	0.14
high-terrace	BwC2b8	prehistoric	247	1.26	5.6	59.9	34.5	5.5	11	0.326	126.5	3.67	0.14
high-terrace	Bwb9	prehistoric	257	1.26	5.9	58.4	33.9	5.5	11.6	0.358	142	4.12	0.13
high-terrace	Bwb9	prehistoric	270	1.22	6.7	64.6	28.7	5.5	11.7	0.349	136.5	4.21	0.12
high-terrace	BCb9	prehistoric	285	1.29	4.5	49.0	46.4		10.1	0.333	120.5	3.48	0.11
high-terrace	BCb9	prehistoric	295	1.34	3.6	43.5	53.1	5.1	9	0.325	124	3.25	0.07
high-terrace	Btb9	prehistoric	305	1.23	6.3	60.2	33.6	5.7	11.6	0.324	124	3.9	0.12
high-terrace	2ABtb10	prehistoric	313	1.18	5.3	69.8	24.9	5.7	11.4	0.334	129	4.04	0.24
high-terrace	2ABtb10	prehistoric	323	1.23	6.4	63.6	24.2	5	13.1	0.341	131	4.53	0.26
high-terrace	2ABtb10	prehistoric	333	1.15	5.7	72.0	22.3	5.7	13.9	0.342	136	4.23	0.23
high-terrace	2Btx1b10	prehistoric	344	1.14	6.9	72.8	20.3	4.8	13.7	0.359	136	4.64	0.21
high-terrace	2Btx1b10	prehistoric	356	1.13	7.3	75.4	17.3	5.6	15.1	0.342	130.5	4.82	0.16
high-terrace	2Btx1b10	prehistoric	368	1.13	7.3	76.9	15.9	4.7	16.5	0.367	141.5	4.84	0.13

high-terrace	2Btx2b10	prehistoric	375	1.09	5.2	79.8	15.0	5.4	18	0.382	145	5.05	0.12
high-terrace	2Btx2b10	prehistoric	384	1.15	7.6	78.3	14.2	4.8	15.7	0.386	148.5	5.07	0.12
high-terrace	2BtCb10	prehistoric	394	1.15	6.2	72.5	21.3	5.4	15	0.343	143	4.47	0.09
high-terrace	3C/Btb10	prehistoric	400	1.21	5.6	67.9	26.5	5.2	13.3	0.352	140.5	4.47	0.08
high-terrace	3C/Btb10	prehistoric	414	1.29	4.5	56.6	38.7	5.3	10.6	0.331	141.5	3.81	0.06
high-terrace	3E&Btb11	prehistoric	426	1.49	5.4	59.8	34.7	4.9	7.9	0.263	131.5	2.82	0.05
high-terrace	3Bt&Eb11	prehistoric	436	1.24	2.1	23.2	72.6	4.8	12.9	0.328	137	4.37	0.09
high-terrace	3E&Btb11	prehistoric	443	1.46	4.1	49.3	46.3	4.6	8.4	0.279	125.5	3.05	0.06
high-terrace	3Bt&Eb11	prehistoric	458	1.30	2.3	27.0	70.7	5.7	11.6	0.32	133	3.89	0.04
high-terrace	3E&Btb11	prehistoric	460	1.50	2.1	22.0	75.9	5.8	9.9	0.257	112	3.05	0.04
high-terrace	3Bt&Eb11	prehistoric	468	1.30	4.1	47.7	48.2	5.3	11.6	0.292	123	3.88	0.07
high-terrace	3E&Btb11	prehistoric	474	1.46	2.2	26.1	71.6	5.6	8.2	0.253	98.9	2.93	0.05
high-terrace	3E&Btb11	prehistoric	493	1.37	3.4	38.8	57.8	4.8	9.9	0.289	120	3.33	0.05
high-terrace	3E&Btb11	prehistoric	510	1.49	1.9	23.4	74.7	4.6	8.3	0.248	91	2.85	0.04
high-terrace	4C	prehistoric	521	1.52	1.1	13.2	85.7	4.4	7.4	0.244	99.8	2.53	0.03
high-terrace	4C	prehistoric	530	1.49	1.8	23.3	74.7	5.6	8.3	0.266	106.5	2.72	0.05
high-terrace	4C	prehistoric	540	1.51	1.5	18.4	80.2	6	7.6	0.246	91.6	2.65	0.04
high-terrace	5C	prehistoric	556	1.51	1.4	17.6	80.9	6.3	8.2	0.231	84.6	2.6	0.04
high-terrace	6C	prehistoric	566	1.52	1.0	12.5	86.5	6.3	6.8	0.213	75.7	2.6	0.04
high-terrace	6C	prehistoric	576	1.52	1.0	12.5	86.5	5.1	7.2	0.237	89.7	2.63	0.03

Appendix 2

Landform	Soil horizon	Prehistoric/historic	Sample depth (cm)	Estimated bulk density (g cm ⁻³)	Clay (wt. %)	Silt (wt. %)	Sand (wt. %)	Soil pH (1:1 H ₂ O)	Pb (ppm)	Ti (wt. %)	Zr (ppm)	Al (wt. %)	TOC (%)
low-terrace	A	historic	3	1.13	6.8	37.3	55.9	6.6	30.7	0.376	148.5	4.54	2.49
low-terrace	C	historic	9	1.30	6.4	60.6	33.0	4.8	24.9	0.317	114.5	3.54	2.16
low-terrace	Oeb1	historic	13	1.13	4.1	55.6	40.3	4.5	43.1	0.313	117.5	3.27	4.21
low-terrace	Ab1	historic	23	1.22	11.3	39.8	49.0	4.1	38.4	0.312	113.5	4.09	1.23
low-terrace	C	historic	34	1.42	4.6	68.7	26.7	4.2	16.4	0.2928	113	2.91	0.4
low-terrace	Ab2	historic	48	1.48	5.9	66.5	27.6	4.1	65.6	0.275	105	3.15	0.29
low-terrace	Ab2 Bw&Cb	historic	53	1.47	5.6	67.3	27.1	4.2	13.1	0.286	95	3.05	0.27
low-terrace	2 Bw&Cb	historic	73	1.44	3.1	70.5	26.4	4.7	8.6	0.287	105	2.84	0.17
low-terrace	2	historic	93	1.48	2.2	74.9	22.8	5.1	7.6	0.284	100.5	2.85	0.18
low-terrace	Ab3	prehistoric	103	1.49	2.3	76.1	21.5	4.6	8.1	0.287	101.5	2.82	0.15
low-terrace	C	prehistoric	113	1.53	3.4	79.7	16.9	5.1	7.8	0.282	102	3.07	0.19
low-terrace	Ab/Cb4	prehistoric	118	1.48	5.0	69.2	25.8	5.1	8.2	0.255	101	2.51	0.22
low-terrace	Ab/Cb4	prehistoric	133	1.53	2.5	82.6	15.0	5.3	6.7	0.255	98.4	2.59	0.19
low-terrace	C	prehistoric	153	1.54	1.9	83.5	14.6	5.6	6.7	0.2430	81.9	2.66	0.13
low-terrace	ABb5	prehistoric	168	1.44	3.5	67.6	28.9	5.4	9.4	0.274	114.5	2.56	0.19
low-terrace	C	prehistoric	183	1.49	2.2	79.1	18.7	5.4	8.2	0.315	103	3.12	0.17
low-terrace	Ab6	prehistoric	198	1.34	4.8	57.0	38.3	5.4	9.1	0.291	129	3.17	0.18
low-terrace	BCb6	prehistoric	213	1.44	3.6	66.9	29.5	5.5	8.6	0.308	115	3.11	0.12
low-terrace	C	prehistoric	223	1.54	8.4	65.3	26.2	5.9	9.2	0.297	107.5	4.03	0.16
low-terrace	A1b7	prehistoric	233	1.38	6.2	54.8	39.0	5.8	11.4	0.349	118	4.06	0.3
low-terrace	A2b7	prehistoric	238	1.24	4.9	47.4	47.7	5.8	11.7	0.357	135.5	3.99	0.24
low-terrace	CBb7	prehistoric	243	1.24	3.8	49.5	46.7	5.6	11.2	0.306	143	3.25	0.15
low-terrace	CBb7	prehistoric	253	1.34	3.7	60.7	35.6	6	9.3	0.307	113.5	3.26	0.11
low-terrace	A1b8	prehistoric	263	1.39	6.1	55.0	38.9	6	11	0.3130	116	3.26	0.2
low-terrace	A2b8	prehistoric	273	1.28	1.2	58.0	40.8	5.9	9.4	0.265	118.5	2.67	0.25
low-terrace	C/Bb8	prehistoric	283	1.44	0.0	74.2	25.8	6	7.4	0.296	92.2	3.14	0.12
low-terrace	ABb9	prehistoric	293	1.39	4.9	59.9	35.2	5.9	9.2	0.321	109.5	3.65	0.2
low-terrace	ABb9 Bw&Cb	prehistoric	303	1.34	3.7	58.2	38.1	5.7	10.2	0.332	116.5	3.76	0.2
low-terrace	9	prehistoric	323	1.29	2.7	57.3	40.0	5.8	11.1	0.299	130.5	3.73	0.13
low-terrace	Bwgb9	prehistoric	338	1.34	4.8	57.2	38.0	5.9	11.2	0.318	106.5	4.14	0.15
low-terrace	C	prehistoric	343	1.24	3.2	48.0	48.7	5.9	11.1	0.316	109	4.19	0.2