



Correlating floodplain geochemical profiles with archival historical mining records to establish depositional chronologies of river sediment

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ARTICLE INFO

Keywords:

Sediment budget
Heavy metals
Chronology
Historic mining statistics
Channel metamorphosis

ABSTRACT

Chronological markers in fluvial sediments can provide useful information on geomorphic response to historic catchment disturbance, and help explain historic channel morphodynamics. We concentrate on the River Nent catchment in Northern England, which was heavily impacted by lead and zinc mining in the 18th and 19th centuries. We date a 2 m deep profile of fine (<2mm) floodplain sediments using ore extraction records, covering the period 1845 to 1913, based on a significant correlation between zinc concentrations and zinc-ore extraction ($r = 0.78$, $n = 27$; $p < 0.01$). These dates were constrained with a basal OSL date of 2.7 ± 0.3 ka (Age_{min} to Age_{mean} 1.4–3.0 ka) and existing lichenometric dates for surface gravels. Earliest lead contaminated sediments at the base of the profile most likely resulted from Roman mining operations within the catchment. Local mine-worker population statistics were used to simulate pre-1845 lead ore extraction; where above-average peaks in lead concentration, recorded at the 125–130 cm, 105–110 cm and 95–100 cm horizons, were linked to respective peaks in lead ore extraction in 1825, 1850 and 1866. Estimates of historic sediment delivery volumes at a 0.062 km² sink site at Blagill, approximately 6.5 km downstream of the headwaters to the Nent, were estimated through coupling the chronological markers with accumulated sediment thickness and reach area. Sediment delivery was seen to be strongly enhanced by phases of metal mining, with peaks between 1800 and 1825 reflecting the final stages of lead mining, and later between 1892 and 1895, reflecting the peak extraction of zinc. Although lag times between ore extraction peaks and sediment delivery to the Blagill site introduce uncertainty to the proposed chronology, we conclude that where good local mining statistics are available, our approach provides a useful alternative or may be used in conjunction with other commonly used methodologies.

1. Introduction

Increased sediment supply due to historic mining activities is thought to have triggered channel metamorphosis in many rivers around the world during the Anthropocene (e.g. Lewin et al., 1977; Macklin, 1986; Miller, 1997; Wohl, 2019; Gregory, 2019). Elevated concentrations of metal contaminated sediments are often preserved in depositional sinks such as floodplains (Lewin and Macklin, 1986; Macklin 1996; Dennis et al., 2009; Ciszewski and Grygar 2016; Pavlowsky et al., 2017; Clement et al., 2017). Floodplain sediments have been widely used for reconstructing long-term historical pollution of rivers (Hudson-Edwards et al., 1999; Swennen and Van der Sluys, 2002; Bábek et al., 2011), and in the evaluation of pollution changes over the 20th century (Meybeck et al., 2007; Nguyen et al., 2009; Grosbois et al., 2012; Matys

Grygar et al., 2012; Zachmann et al., 2013; Majerová et al., 2013). Furthermore, there has been recent interest as to the possible impacts of climate-change driven increases in flood magnitude and frequency (e.g. Milan and Schwendel, 2021) upon remobilization of these contaminated stores dispersing heavy metal pollution further downstream (Pease et al., 2007; Foulds et al., 2014).

Analysis of these sedimentary records can be used to reconstruct past sedimentation rates and yields (e.g. Owens et al., 1999; Swanson et al., 2008). Establishing the depositional chronology of catchments impacted by mining activities can also be important for understanding the links between historic sediment budgets and channel response. Marron (1992), for example, established a sediment budget of floodplain material contaminated with arsenic resulting from the hydraulic extraction of gold deposits, along the Whitewood Creek and the Belle Fourche

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<https://doi.org/10.1016/j.catena.2022.106532>

Received 14 September 2021; Received in revised form 4 July 2022; Accepted 14 July 2022

Available online 29 July 2022

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River, South Dakota, USA. Similarly, [Lecce and Pavlowsky \(2001\)](#) used lead and zinc contaminated floodplain sediments to calculate sedimentation rates for the pre-mining (1830–1900), mining (1900–1920) and post-mining periods (1920–1997) within the Blue River Watershed, Wisconsin, USA. A variety of techniques have been used to constrain the age of alluvial deposits such as ^{14}C dating ([Foulds et al., 2013](#)) and environmental radionuclides ([Walling et al., 1999; 2000; Walling and He, 1997, 1999; Owens et al., 1999; Clark et al., 2014; Schillereff et al., 2016](#)). In the absence of ^{14}C or other radionuclide dating, chronostratigraphic age estimates can also be determined when good mining records are available for the study catchment (e.g. [Macklin, 1985; Lecce and Pavlowsky, 2001; Price et al., 2005; Swanson et al., 2008; Bábek et al., 2011; Ferrand et al., 2012; Foulds et al., 2013](#)). The chronology of depositional events can be determined by using variation in metal concentrations in vertical floodplain profiles as a stratigraphic tool. Indirect dating of mining-derived sediments has been achieved for rivers in the Netherlands ([Stam, 1999](#)), and Poland ([Ciszewski and Malik, 2004; Łokas et al., 2010](#)), where relative dates were ascribed to sedimentary horizons allowing pre-, during, or post-mining eras to be defined. Combined with historical records, absolute time constraints can also be determined, enabling more accurate transport and sediment storage rates to be calculated ([Lewin & Macklin, 1986](#)). In the UK, this has proven useful for dating sediment profiles in catchments influenced by metalliferous mining activities since the onset of the industrial revolution. Many authors have correlated peaks in metal concentration to periods of significant metal input within the river systems, which in turn corresponded to periods of intense mining activity further upstream in the catchment (e.g. [Macklin 1986; Miller, 1997; Rumsby, 2000; Lecce and Pavlowsky, 2001; Schillereff et al., 2016](#)), and used to indicate the onset of pollution in fluvial systems ([Grygar et al., 2010; Notebaert et al., 2011; Matys Grygar et al., 2011](#)).

The aims of this investigation were to 1) establish key chronological markers by linking historic archival mining records with metal concentrations within a vertical sequence of floodplain sediments; 2) establish historic sedimentation rates at a sink site; and 3) develop a conceptual model of historic sedimentation. Inherent in the accomplishment of these objectives was the use of a novel approach that linked mine statistics to geochemical data to constrain the age of the floodplain deposits. This paper adds to the existing body of literature by demonstrating how mine extraction and population records can be used for relative and absolute dating purposes.

2. Study location

The study area focused upon the River Nent, a principal east-bank tributary of the South Tyne, in Northern England, UK ([Fig. 1A](#)). The catchment covers an area of 29.4 km² and is underlain predominantly by Carboniferous limestone within which numerous economic mineral deposits have been identified and actively mined ([Fig. 1B, C](#)). The River Nent at Blagill is fed by a total of thirty-one tributaries, draining a mixture of agricultural (grazing) land and mine waste, including extensive areas of spoil. The headwater region southeast of Nenthead was the most heavily mined area of the catchment and exposed spoil heaps, containing an abundance of lead and zinc ores and their associated (gangue) minerals, are coupled directly with the headwater channels. Steep slopes, which lack vegetation, result in a continuous supply of lead and zinc-rich sediment into the channel ([Fig. 2A](#)).

2.1. Mining legacy

Mining within the Northern Pennines has a long history which can be traced back to at least medieval and Roman times ([Smith, 1923; Raistrick & Jennings, 1965](#)). In particular, the abundance of lead, silver and zinc reserves in the Tyne catchment indicates that mining has been very intense in this area of the UK. During the 18th and 19th centuries, the Alston Moor orefields witnessed the greatest development of mining and

smelting in the Northern Pennine region and detailed records can be traced back to 1845 ([Burt et al., 1982](#)). At least 24 mines and mine networks were established over the 18th and 19th centuries within the Nent Valley, with principal extraction sites at Long Cleugh, Nenthead and Carrs and Hanging Shaw. All these sites are situated in the headwater region of the River Nent ([Fig. 1C](#)).

A 1 km reach at Blagill on the Nent ([Fig. 3](#)) had previously been shown to have undergone channel metamorphosis in the late 1700s changing from single to wandering pattern. Channel changes have been linked to a series of large floods and enhanced sediment delivery driven by increased sediment availability from mining activities upstream ([Macklin, 1986](#)). The reach situated between Foreshield and Blagill bridge has an average slope of 0.035 compared with 0.023 in the upstream 1.5 km reach between Lovelady Shield and Foreshield bridge. This reduction in slope coupled with valley floor widening between Foreshield and Blagill bridges renders this zone a natural sediment sink. The channel morphology upstream of Foreshield bridge is single-thread sinuous with point bars, that changes to wandering in between Foreshield and Blagill bridges, before switching to single-thread, straight/sinuous with lateral bars downstream of Blagill bridge. There is a waterfall (Nentforce) situated approximately 600 m downstream of Blagill bridge, before the River Nent meets the South Tyne at Alston. Further details including the locations of paleo-bars and cross-section morphology are presented in ([Macklin, 1986](#)), and more recent Digital elevation models are given in [Chappell et al. \(2003\)](#) and [Milan et al. \(2011\)](#).

Owing to the nature of the underlying geology and the numerous natural watercourses, the mining processes often took advantage of the local river network to hydraulically remove, sort and transport the metal ore. A common technique included ‘hushing’, which involved diverting, damming and releasing headwater tributaries ([Fig. 2B](#)) to sluice the hillsides and remove any overburden (e.g. [Smith, 1923; Raistrick & Jennings, 1965; Hunt, 1970](#)). This process is believed to have originated in the Roman times and was commonly employed well into the early 19th century ([Raistrick & Jennings, 1965](#)). The washing of spoil by hushing continued until mechanised techniques became more profitable around 1842 ([Hunt, 1970](#)). Consequently, large quantities of sediment entered river channels and flooding was commonplace kilometres downstream of the hush ([Hunt, 1970; Dunham, 1990](#)). Within the Nent Valley, primary faults, known locally as ‘Lead Veins’ ([Bulman, 2004](#)), trend in a north-east/south-west direction across the valley ([Fig. 1B](#)). These faults made the hushing technique a popular method of mineral extraction. However, little documentary evidence exists for hushing along the Nent, with only passing references to the Green Hush and Dowgang Hush by [Dunham \(1990\)](#).

The mining legacy of Cumberland, including that of the Nent Valley, can be traced using the Cumberland Mineral Statistics ([Burt et al., 1982](#)), which are available for lead and zinc-ore extraction from 1845 to 1913. From these, the rapid rise in the production of zinc within the Nent Valley is clearly evident during the latter half of the 19th century ([Fig. 4A](#)), it peaked around 1898. The success of the zinc industry no doubt ensured the continued survival of the Nent Valley mines, which suffered from the decline of the lead industry during this same period ([Fig. 4A](#)). As noted by [Burt et al. \(1982\)](#), lead-ore extraction probably reached its peak before records began in 1845. The highest recorded extraction data ca. 1848 ([Fig. 4A](#)) reflect the final period of intense mining. However, an indirect indication of the changing fortunes of the lead mining industry prior to 1845 can be obtained from local population statistics ([Raistrick & Jennings, 1965](#)) and employment records of mine-workers (e.g. [Hunt, 1970](#)). Census data for Alston can be traced back to 1801 and indicates a peak between 1820 and 1850. This combined with the number of workers employed by the Alston Moor lead mines ([Hunt, 1970](#)) suggest the mid-1820s exhibited the most intense lead and silver ore extraction in this region ([Fig. 4B](#)).

Even after the peak in lead production, [Burt et al. \(1982\)](#) states that mines within the Long Cleugh and Carrs and Hanging Shaw mines,

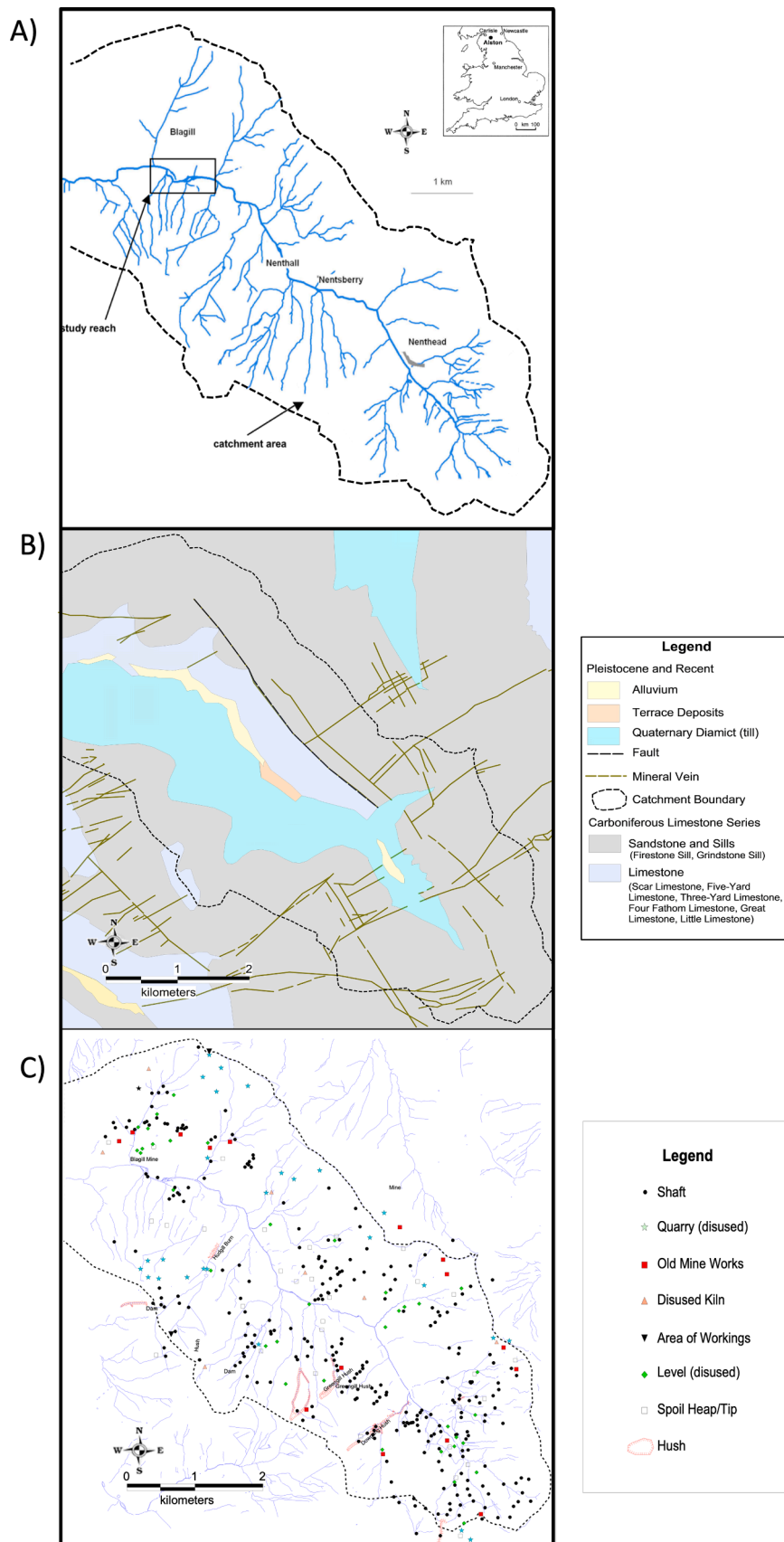


Fig. 1. River Nent study catchment, A) Drainage network with study reach highlighted, B) Geological map of the catchment, C) Spatial distribution of mining legacy.

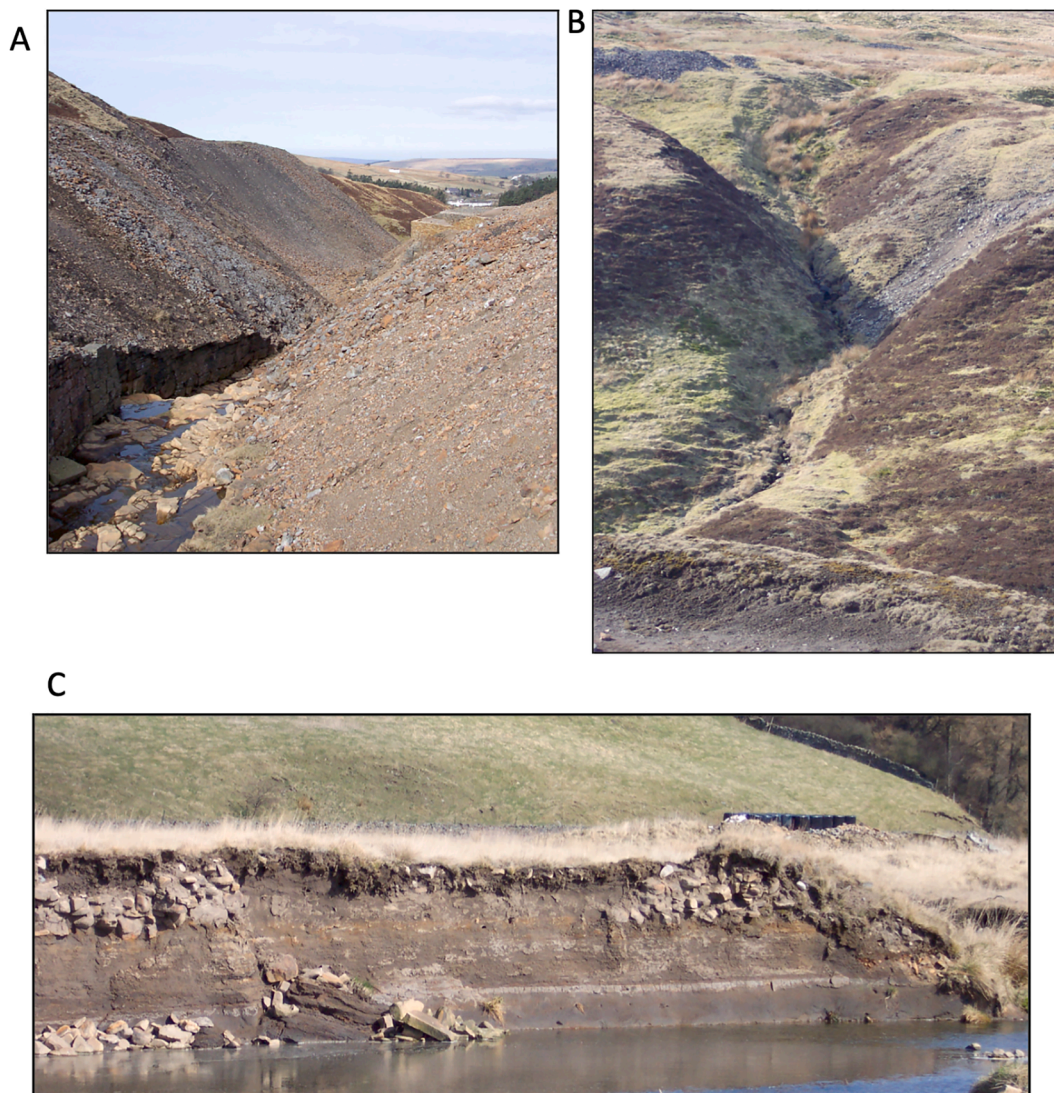


Fig. 2. Photographs of study area, a) headwaters of Nent catchment showing slope-channel coupling that supplies mine spoil directly into channel, b) relict hush, c) location of P2 profile.

within the Nent Valley, were still producing almost two thirds of Cumberland's total output in 1866. This was probably the final major output in lead ore during the mid to late 19th century, after which lead mining declined sharply, leading to the closure of many mines. From 1780 to 1820, at least 24 mines were active within the Nent Valley, but by 1848 this had fallen to 14 and as few as only two by 1886 (Smith, 1923; Burt et al., 1982; Macklin, 1986). The decline in the lead price and subsequent lead ore extraction is further reflected by a decline evident in the local population (Raistrick & Jennings, 1965). As mines closed, the associated companies were sold to those concerned with zinc extraction. During the early 1880s, zinc-ore extraction dominated, which continued well into the early 20th century, with over a quarter of a million tons of rough ore being removed between 1923 and 1938. After peaking in 1898, the mines at Nenthead were producing 39 % of the national output (Burt et al., 1982).

Oxidised zinc and lead concentrates, along with associated gangue minerals, such as barytes and fluorspar, were collected until the early-1940s, and some spoil material was reclaimed until 1963 (Dunham, 1990). However, deposits within the region are currently not regarded as sufficiently profitable to warrant further extraction. The mining legacy is still evident today, with numerous historic shafts, mine workings and spoil heaps visible within the catchment, particularly around the village of Nenthead (Fig. 1C; 2A and B).

3. Methods

3.1. Sediment sampling from cut terrace at Blagill

To establish relative and absolute depositional chronologies, a detailed profile of lead and zinc concentrations were compared against mining extraction records. The chosen sediment profile P2 was located upstream of Blagill Bridge (Fig. 3), from a low terrace unit within a present-day upstream instability zone ($54^{\circ}48'52.93''N$, $2^{\circ}23'57.54''W$). The terrace is characterised by a 2 m section of fine sediment (<2 mm) overlying gravel (Fig. 2C, 5). Although substantial channel metamorphosis appears to have taken place since 1820, the terrace in the vicinity of the sampling location appears to have remained relatively stable, and there is no evidence of substantial floodplain reworking in this area (Fig. 3). The sequence was sampled at 5 cm increments from the surface down to the baseline as determined by the contemporary gravel channel. Although this broadly represented the resolution of the natural stratigraphic divisions, sampling did cross these boundaries. Samples were collected during June 2003 using a stainless steel trowel, from the centre of each 5 cm increment. The trowel was cleaned thoroughly between sampling to avoid cross-contamination, and the samples were stored in air-tight plastic bags.

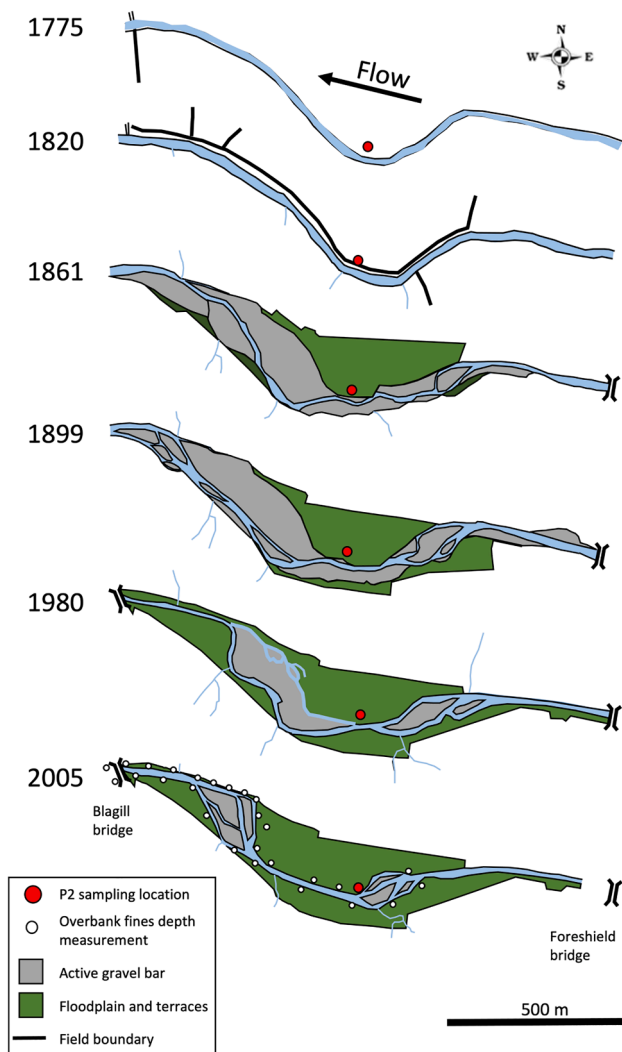


Fig. 3. Historical changes in river channel pattern. The 1775 map was drawn up during the construction of the Nentforce level, and the 1820 map was sourced from Macklin (1986). The later maps are based on Ordnance survey editions.

3.2. Laboratory analysis

The removal of metals from the sediments was conducted through a standard acid digestion technique (e.g. Cook et al., 1997). Sample were dried in an oven for 48 h at 100 °C, and passed through a 63 µm sieve. This fraction was chosen owing to the ability of metal elements to become preferentially adsorbed to the finer sediment fraction (Horowitz, 1991). One gram of the < 63 µm fraction was added to 50 ml Aqua Regia (10 % HNO₃; 30 % HCl; 60 % distilled water) and left in a fume cupboard for 24 h. The samples were then boiled on a hotplate for two hours, with the solutions checked regularly and topped up with distilled water to maintain 50 ml of liquid during the boiling process. Once cooled, the samples were passed through Glass Microfiber filter paper (MF100) into a 100 ml volumetric flask. The beakers and filter papers were washed thoroughly with distilled water to ensure the entire sample was filtered and the volumetric flask was topped up to 100 ml using distilled water. The filtrate from each sample was then analysed using a Perkin Elmer ICP-OES to determine chemical content and concentration. Although this paper just considers lead and zinc data, each sample was tested for an additional 19 elements for sediment provenancing work to be presented elsewhere. Certified Reference Material 2710a (NIST Montana highly contaminated soil standard) was used to

monitor data quality and calibration standards used dilutions of the Merck 1000 ppm multi-element solution. The final concentrations (C_{adj}) were adjusted for the original quantity of sediment used in the acid digest process and were determined using.

$$C_{adj} = C \frac{V}{m} \quad (1)$$

where C (mg kg⁻¹) is the concentration recorded by the ICP-OES in the final extract, V is the volume of final filtrate and m is the mass of the original sample (mg).

3.3. Establishing a chronology using correlations

Based upon the assumption that peaks in ore extraction would result in elevated levels of lead or zinc within the Blagill sedimentation zone, a visual and statistical correlation was made between the temporal variations in the quantity of ore extracted and the vertical pattern of changing metal concentration within P2. Positive correlation between the two datasets allow key chronological markers to be dated absolutely, and an overall relative chronology of deposition to be established. Data on ore extraction were obtained from the Cumberland Mineral Statistics covering the period 1845 to 1913 (Burt et al., 1982). For an indication of pre-1845 ore extraction, population records were used as a proxy, which suggest the peak in lead-ore extraction occurred ca. 1825. The reliability of using population as a surrogate for lead-ore extraction can be demonstrated by analysis of the post-1845 population records against the published extraction data (Fig. 6). The regression analysis shows the two parameters follow an exponential distribution which can be used to estimate the amount of lead-ore extracted prior to 1845. For 1825, Raistrick & Jennings (1965) reported a population of 7500 for Alston, which provides an estimated lead-ore yield of 4300 tons per year.

3.4. Independent dates

The age range for the full 2 m sediment sequence was constrained using an Optically Stimulated Luminescence (OSL) date for the base of the P2 sequence, and lichenometric dates of bar surfaces obtained by Macklin (1986), who reported an average date of 1905 for surface gravels within the vicinity of the P2 section. OSL takes advantage of electrical charge that builds up within quartz and feldspar grains after burial as a consequence of low-level ionising radiation from radionuclides and cosmic radiation. Trapped in the crystal lattice of the minerals, charge increases with burial time but is released when the mineral is exposed to light or heat (Wallinga, 2002). In the laboratory, thermal or optical stimulation of samples releases trapped charge which creates a small discharge of light (luminescence). The brightness of the luminescence signal reflects the amount of charge trapped and, hence, the irradiation dose the sample has received since burial (equivalent dose; D_e). From this, the age of the sample can be determined (Wallinga, 2002) through calibration against known amounts of laboratory radiation and luminescence response to these doses coupled with an assessment of dose rate (D_r).

A core sample was collected close to the base of the P2 sequence at a depth of 1.75 m. To minimise potential contamination through exposure to light, each sample was collected after dark by hammering an opaque, black PVC tube into the bank section. Once extracted, care was taken to ensure the ends of the tube were sealed immediately using black insulation tape and they were stored in photo-protective bags in preparation for OSL analysis at the Geochronology Laboratories, University of Gloucestershire, UK.

Within laboratory safelight conditions, the sample was removed from the tubing and a sub-sample was obtained from the middle of the core. Sand-sized grains (125–180 µm) of quartz were obtained through sieving and etched using 40 % hydrofluoric acid for 60 min to remove any feldspars and the outer, alpha-irradiated rind of the quartz grains. D_e

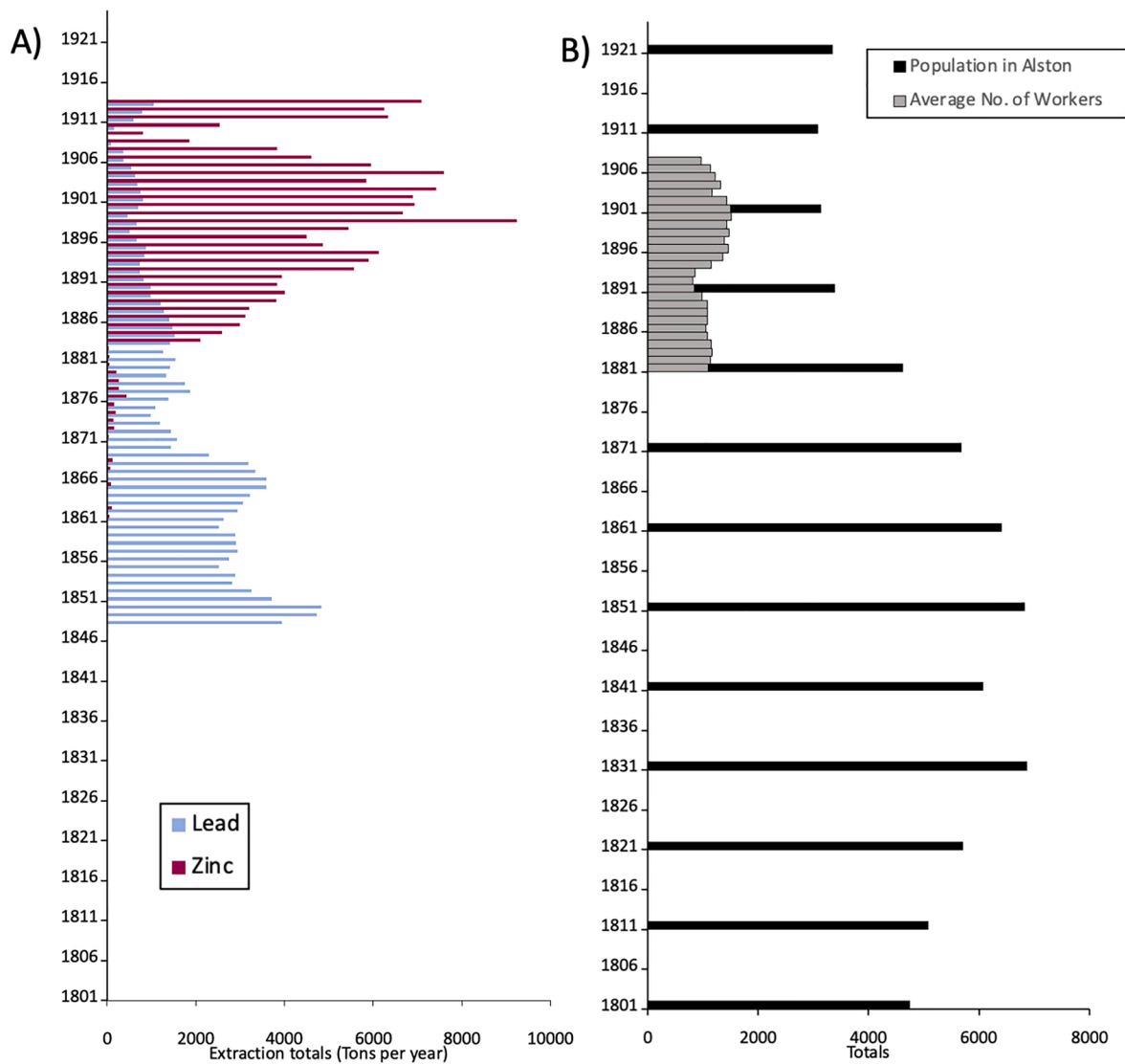


Fig. 4. A) Lead and Zinc ore extraction statistics within the Nent between 1845 and 1913 (Burt et al., 1982), B) The population of Alston from 1801 to 1921 (Raistrick & Jennings, 1965) and the number of workers employed by the Alston Moor lead mines between 1818 and 1844 (Hunt, 1970).

values for each sample were obtained from 12 multi-grained single-aliquots of quartz using a Risø TL-DA-15 irradiation and optical stimulation-detection system. D_r values were quantified through Neutron Activation Analysis of radionuclide concentrations and calculation of cosmic contributions based on geographical position and overburden thickness.

3.5. Assessing historic sedimentation

To obtain information on historic fine sediment delivery to the Blagill sedimentation zone on the Nent (Fig. 3), the parameters in Table 1 were required either through direct data collection, GIS analysis or mathematical calculation. Accurate measurements of the sedimentation zone were obtained using digitised maps obtained from Edina Digimap layers, which were uploaded and utilised in MapInfo. Measurements of length and width were determined using GIS and found to be 0.603 km and 0.102 km, respectively. These valley dimensions result in an area of 0.062 km².

To determine the average thickness of overbank fines throughout the reach, twenty-six field measurements were obtained throughout the zone, using a metre rule (Fig. 3). The vertical distance was recorded between the overbank surface and the contemporary baseline, as

determined by the current gravel bed. Where gravels were preserved within the overbank sequence, above the contemporary channel bed, the baseline was taken as the boundary between fine sediment and gravel material. Where this boundary was diffuse, resulting in an indistinct transition, the baseline was estimated. From these locations, a mean value of 0.74 m ($\sigma = 0.37$ m) was calculated. Using the depositional chronology obtained through metal stratigraphy, volumetric estimates were established between key chronological markers (dated through metal stratigraphy). Sediment volumes (V_s) were determined using the following equation, where T_s refers to sediment thickness (m) and A refers to area (61,506 m²).

$$V_s = T_s A \quad (2)$$

The results were extrapolated proportionally across the sedimentation zone, using the average thickness of overbank fines. Sedimentation rates (S) could then be established using.

$$S = \frac{V_s}{t} \quad (3)$$

where t refers to time (years).

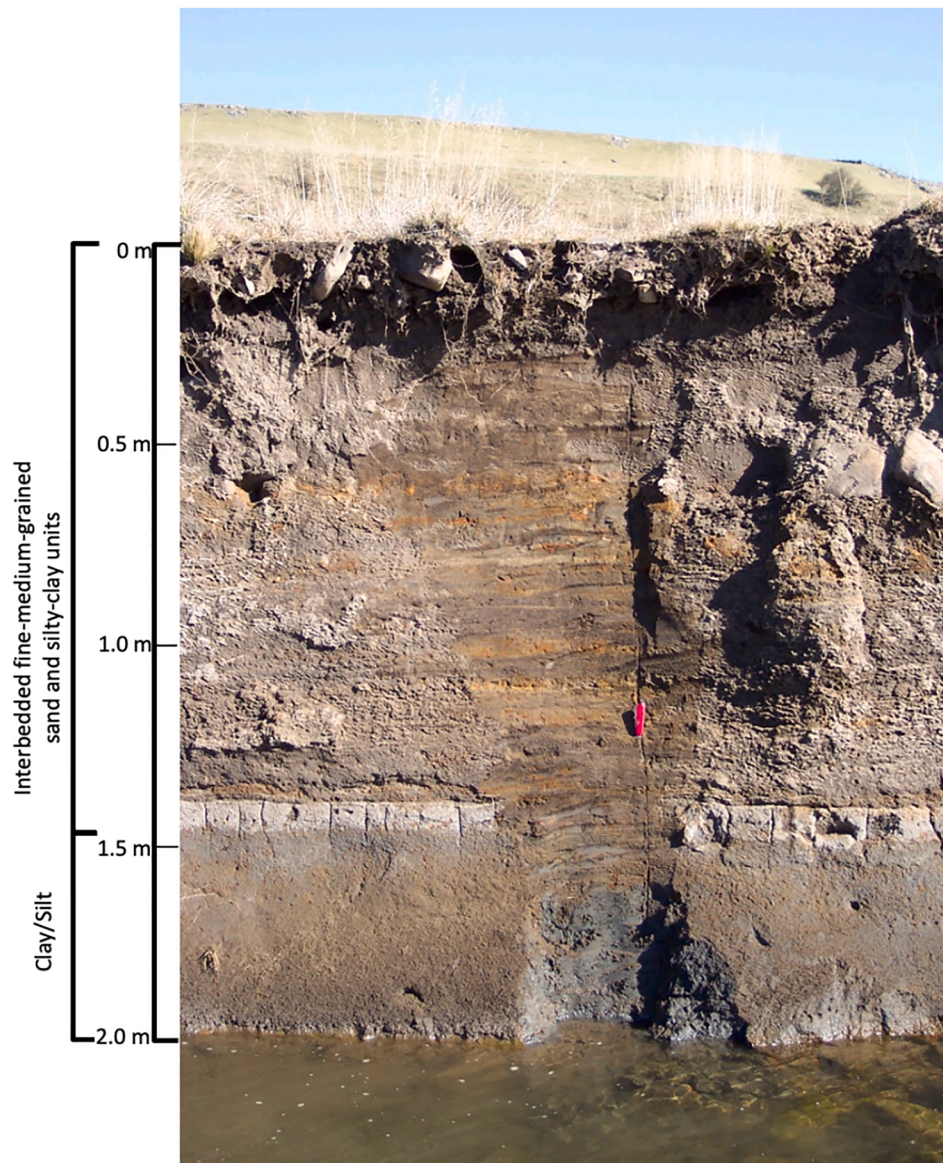


Fig. 5. The P2 profile showing 2 m of fine sediment overlying a gravel base just beneath the water surface.

4. Results

4.1. Vertical patterns

Figs. 7 and 8 demonstrate vertical variations in lead and zinc concentration at P2. Zinc demonstrates a particularly marked trend, substantially increasing in concentration above 95–100 cm. The highest concentrations occur in the top 5–10 cm of the profile with values in excess of $33,500 \text{ mg kg}^{-1}$. The lowest concentrations are found towards the base of the sequence; with 808 mg kg^{-1} being recorded at a depth of 195–200 cm. The vertical pattern of lead shows a binary profile (Fig. 8) with a main peak occurring at a depth of 125–130 cm ($17,572 \text{ mg kg}^{-1}$), and a secondary peak occurring close to the surface at a depth of 5–10 cm ($14,117 \text{ mg kg}^{-1}$).

4.2. Establishment of key chronological markers

The results from the OSL analysis for sample GL04026 taken from the base of the profile at 1.75 m just above the gravel/fine sediment transition (Fig. 5) indicated a geometric mean age estimate of $2.7 \pm 0.3 \text{ ka}$ (Age_{\min} to Age_{mean} 1.4–3.0 ka). This would indicate that sediments were

deposited in this part of the profile at the time of Roman occupation, and it is possible that the lead contamination found here, although at much lower concentrations compared with further up the profile resulted from early mining operations during this period. Sedimentary horizons above this were dated through matching zinc and lead concentration profiles with ore extraction records (Figs. 7 and 8). The reliability of using the zinc profile as a chronological tool was also supported by a Spearman's rank-order correlation (r_s 0.78 = 27; $p < 0.01$). The near-surface date of 1912, obtained through this investigation, corresponded well with lichenometric dates of bar surfaces obtained by Macklin (1986), who reports an average date of 1905 for surface gravels within the vicinity of the P2 section.

In contrast to the zinc profile, the lead concentration profile did not statistically correlate with ore extraction records. Dating of the sedimentary profile prior to 1881 therefore relied upon the lead profile, determined from ore extraction records until 1845 and then simulated from population data back to 1801 (Fig. 6). As a consequence, the lead concentration profile, above the 1881 baseline set by the zinc profile, does not reliably reflect lead production and raises doubt regarding the reliability of this sequence for obtaining an accurate chronology. Therefore the sub-90 cm profile was adopted in establishing pre-1881

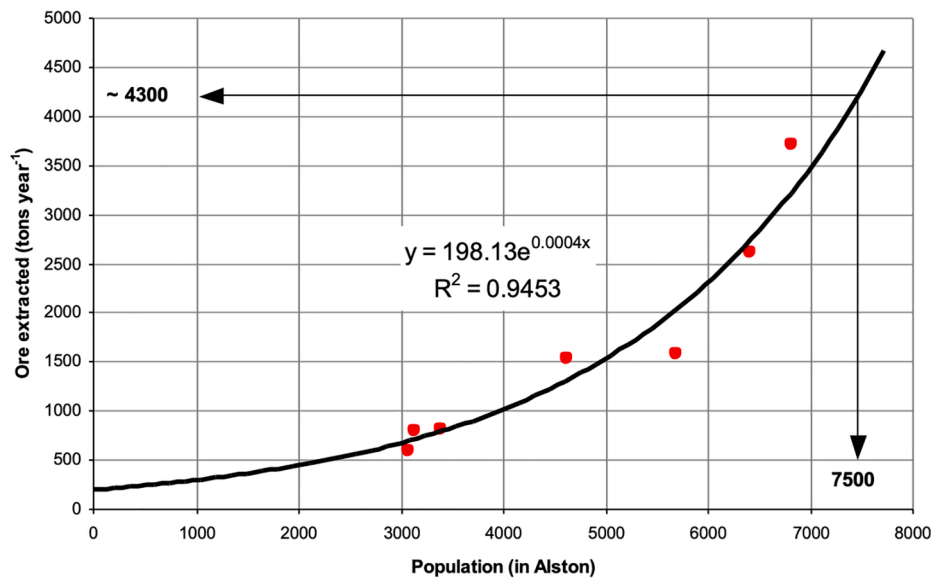


Fig. 6. Relationship between population and lead ore extraction (1801–1901). The interpolated values provide an estimation of ore extraction in 1825 as based upon the population records for that year.

Table 1

Parameters required to obtain estimates of sediment storage and sedimentation rates.

Parameter	Method of Acquisition
Length, L (m)	Field measurements, GID (Edina Digimap, MapInfo)
Width, W (m)	Field measurements, GID (Edina Digimap, MapInfo)
Area, A (m ²)	GIS (Edina Digimap; MapInfo); Mathematical calculation (LW)
Average Sediment Thickness, T_s (m)	Field measurements
Sediment Volume, v_s (m ³)	Mathematical calculation ($T_s A$)

chronologies, from which above-average peaks in lead concentration, recorded at the 125–130 cm, 105–110 cm and 95–100 cm horizons, have been attributed to respective peaks in lead-ore extraction in 1825, 1850 and 1866 (Fig. 8).

4.3. Historic sediment delivery to Blagill post 1800

The early peak in sedimentation rate ca. 1825 (Fig. 9A) can be linked to the lead mining peak, although compared the sedimentation linked with later zinc mining, the influence appears to have been minimal. A substantial increase in sedimentation rates between 1892 and 1895 corresponds with the rise and subsequent success of the zinc industry. The rapid slow-down in sedimentation rate between 1898 and 1908 further coincides with the decline in zinc ore extraction during this period, which is reversed temporarily around 1912.

5. Discussion

5.1. Interpretation of zinc stratigraphy

The onset of intense zinc mining ca. 1881 coincides with the initial transfer of mining leases from the ‘London Lead Company’ to the ‘Nenthead and Tynedale Lead and Zinc Company’ in 1883. The increase in zinc concentrations in the profiles is seen at a depth of 90–95 cm, which continues up the profile to a depth of around 60–65 cm (Fig. 7). A period of poor productivity led to the subsequent hand over to the ‘Vielle Montague Zinc Company’ in 1896 (Burt et al., 1982) which is further

reflected by the decrease in zinc concentrations between 65 and 40 cm. A renewed rise in concentrations is seen between 45 and 25 cm, with a substantial peak in zinc extraction at 25–30 cm, reflecting the peak in ore production seen in 1898. Ore production was sustained at high levels until 1904, after which, there was a rapid decline of zinc production in the early 20th century which produced lower zinc concentrations at around 15–20 cm. Production increased once again in 1912, prior to the First World War (Burt et al., 1982). The swift and dramatic nature of this event is clearly defined by excessive concentrations within the top 5–10 cm of the P2 sequence, which produces the overall peak for the profile, and allows the near-surface horizon to be dated accurately to ca. 1912.

5.2. Interpretation of lead stratigraphy

Historic records and sedimentological evidence support the dates assigned to these horizons. The initial peak in lead-ore extraction of 1825, based upon population data from Alston, is in agreement with historic records and which cites the onset of extensive lead mining as occurring in the early to mid-1820’s (e.g. Burt et al., 1982; and Raistrick & Jennings, 1965), and corresponds to the major expansion of Nenthead village specifically for the mining community (Smith, 1923). Although this does not represent the largest peak in ore extraction within the Nent valley, the rapid and sudden input of lead contaminated sediments, possibly as a consequence of prospective hushing and exacerbated by the spate of minor storms at this time (e.g. Rumsby & Macklin, 1994) would no doubt have resulted in the sudden rise in lead concentrations within the system. This evidence is preserved within the 125–130 cm horizon. The major peak in lead production for the Nent Valley in 1850 and is represented by a prominent, above average, peak in lead concentration at a depth of 105–110 cm (Fig. 8). It also corresponds with the peak in output from the Long Cleugh mine. The final peak in lead production occurred ca. 1866 (Burt et al., 1982), prior to the initiation of intensive zinc production in 1881 and, as such, is attributed to the sedimentary horizon at 90–95 cm.

5.3. Unknown sediment conveyance rates (lag effects)

When interpreting the sedimentary record held in a floodplain, possible lags or other anomalies in the primary pollution signal are of crucial importance (Matys Grygar et al., 2013). In order to establish absolute dates using metal stratigraphy, peaks in ore extraction are

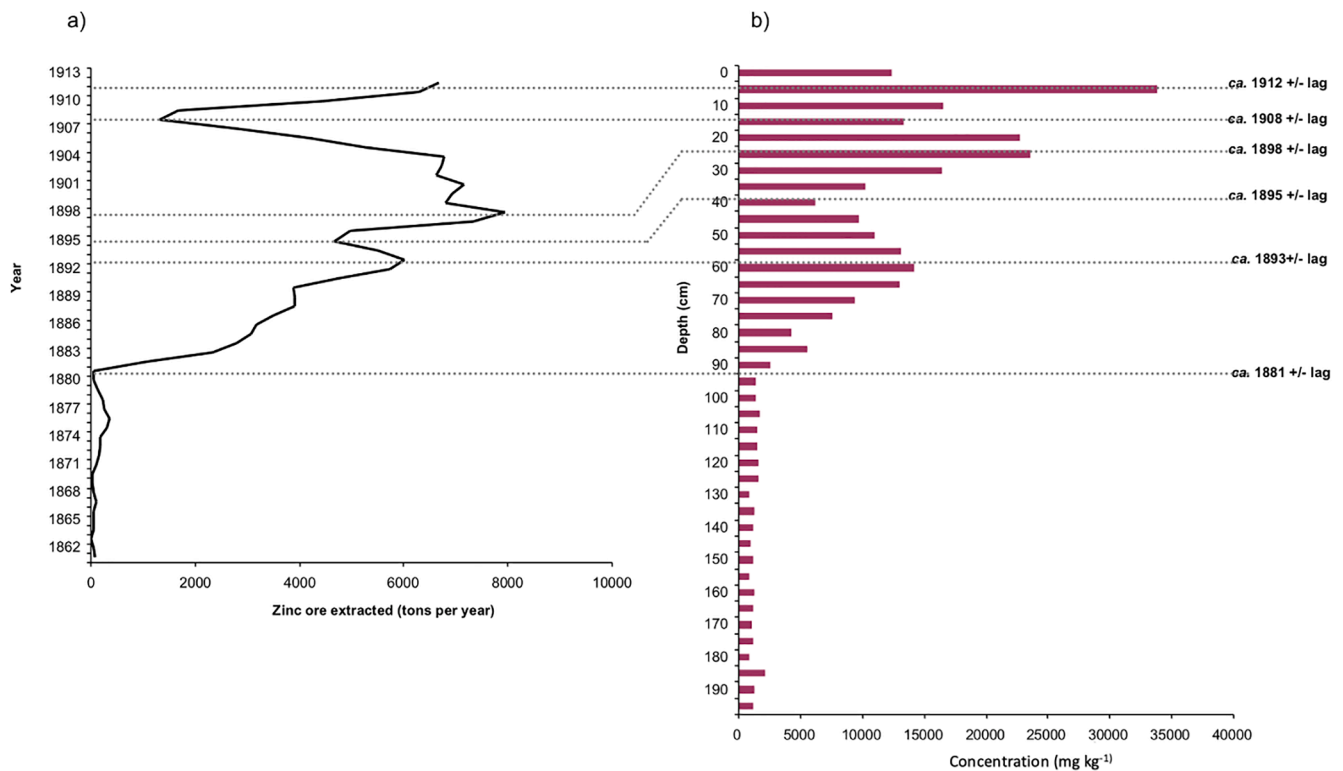


Fig. 7. Chronology of deposition at P2 (above 90 cm), using a) zinc-ore extraction records (Burt et al., 1982) and b) the zinc concentration profile.

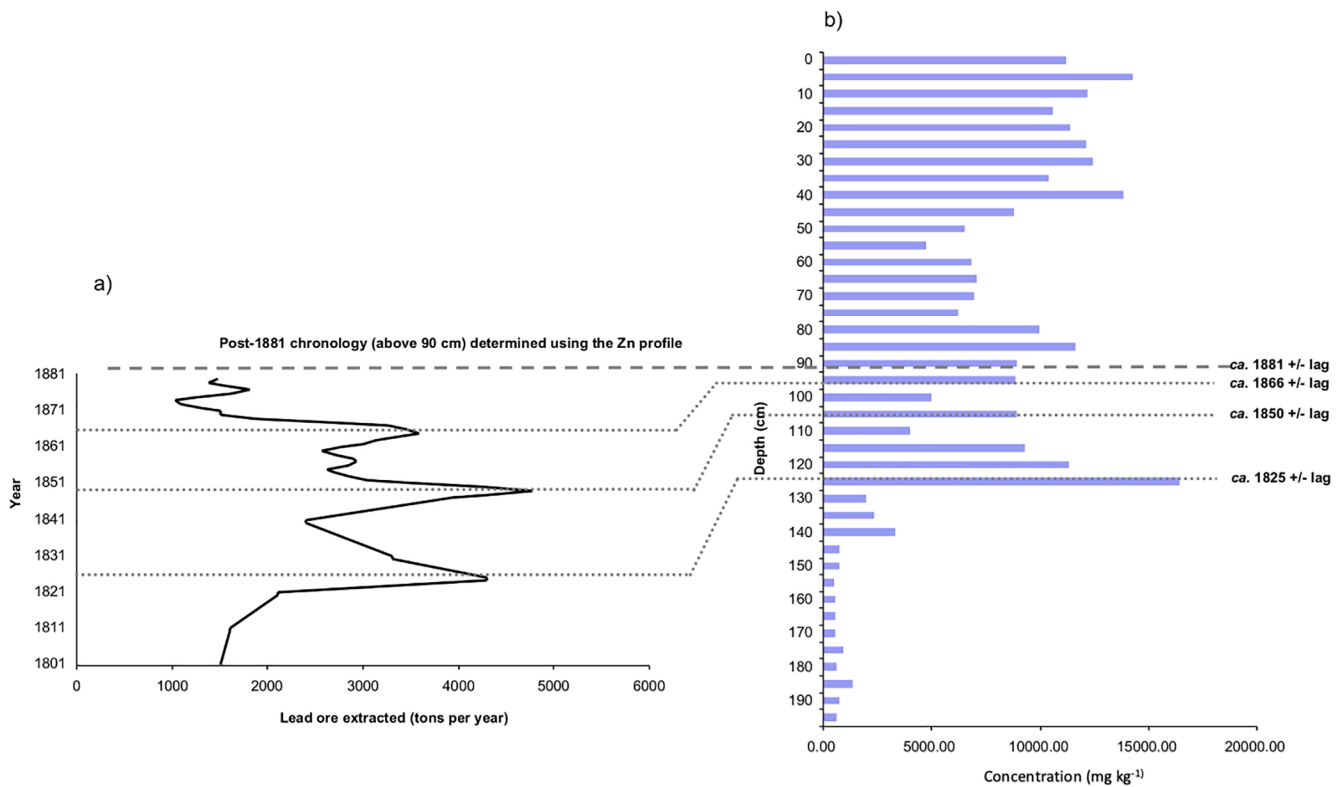


Fig. 8. Chronology of deposition at P2 (below 90 cm) using a) lead-ore extraction records (Burt et al., 1982) and b) the lead concentration profile.

assumed to relate to peaks in metal concentration. However, this assumption is only valid when the conveyance rates of metal-bearing sediments throughout the catchment can be established and lag effects between initial sediment mobility and deposition can be accounted for.

The approach used herein, when comparing individual datasets, additionally introduces a degree of subjectivity in accounting for the effects of lag and therefore only a relative chronology can be determined with confidence.

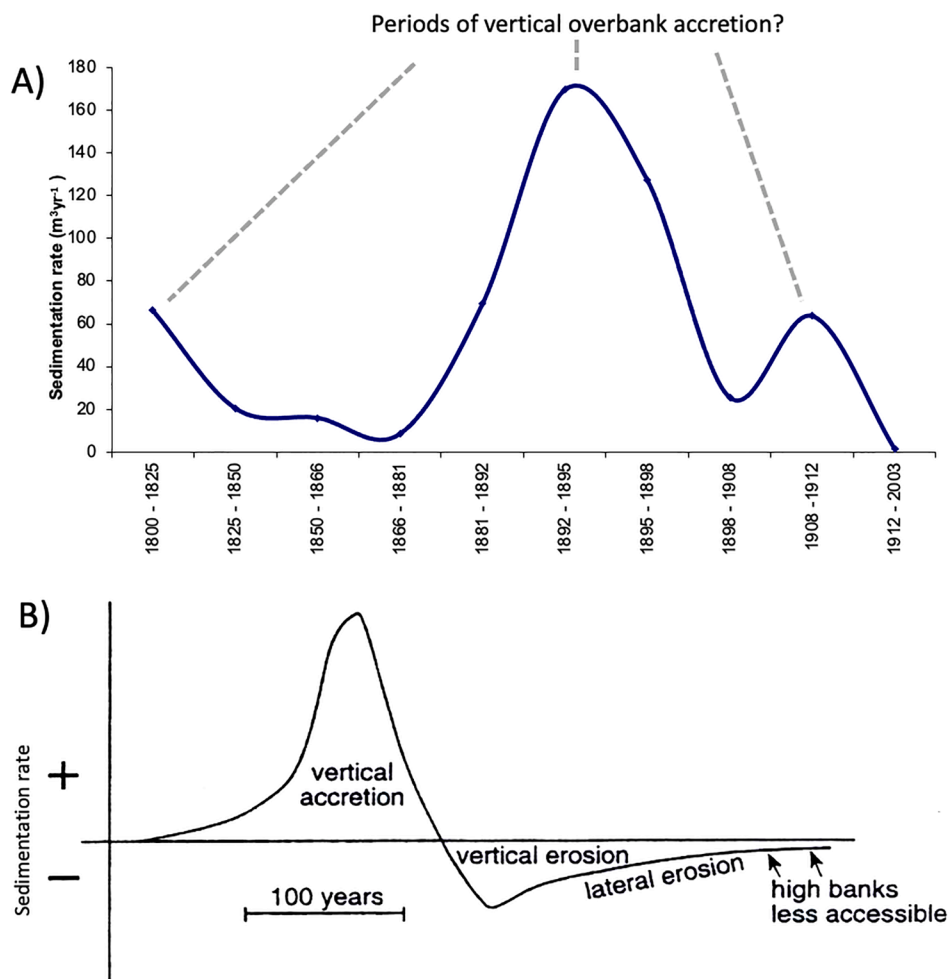


Fig. 9. Comparison of A) Historic changing sedimentation rates in the Nent catchment with, B) Trimble's (1995) Model 2, which describes channel recovery following disturbance, show effects of changes in volumetric sediment supply.

5.4. Validity of chronology

Correlations between mine-derived sediment inputs and floodplain concentrations also assume that the concentrations of metals in the floodplain are representative of the concentrations that are transported through the river. There are a number of factors that could introduce uncertainty into the validity of the proposed chronology including spatio-temporal variations in deposition, hydroclimatic factors, and post-depositional remobilisation.

5.4.1. Spatio-temporal variability of sediment deposition

The spatio-temporal variability of sediment deposition and reworking of the floodplain is an important factor (Sadler, 1981; Lewin and Macklin, 2003; Matys Grygar et al., 2013). Sediments from point bars and channel banks in direct contact with channel water can be more heavily polluted than overbank fines settling onto the floodplain surface (Matys Grygar et al., 2013). Sediment sorting also considerably affects the spatial distribution of pollutants in floodplains (Macklin et al., 1994; Wyżga and Ciszewski, 2010). For example, work on the Jizera River, Czech Republic has demonstrated spatial variations in contamination of Copper, Nickel and lead on floodplains, where sediment sorting appears to result in higher concentrations in laterally deposited sediments than in distal floodplain sediments (Matys Grygar et al. 2013). Sediments in direct contact with the river water may also acquire secondary pollution and become enriched. The sorting and settling dynamics of fine sediments on floodplain surfaces is also a factor (e.g. Grygar et al. 2010), as a result of flow energy variation across the floodplain surface, topographic

variations and the influence of vegetation or structures.

5.4.2. Hydrological influences

The decline in lead production since 1866 contradicts with the apparent increase in lead concentration within the P2 profile above 75 cm (Fig. 8) and may reflect remobilised lead from spoil during the period of intense zinc mining. Flood magnitudes, duration, event sequencing and sediment availability are also known to influence both sediment delivery and alter the concentrations of contaminants delivered to sites downstream of their source (Magilligan et al. 1998; Benedetti 2003; Lecce et al., 2004; Pease et al., 2007). Hence the depth profiles of the contaminants should be interpreted in accord with complex depositional environments of floodplains (Lewin and Macklin 2003; Miall 2006).

Hydroclimatic conditions that result in changes to the frequency of high magnitude events are likely to alter the frequency of fine sediment delivery to the floodplain. Likewise, the predominance of in-channel flows could result in channel incision and progressive abandonment of the floodplain. Several high-flow events (exceeding 150 m³s⁻¹) occurred along the Tyne between 1868 and 1914, and intense storm activity has been identified by Rumsby & Macklin (1994) between 1875 and 1895 within the Thinhope Burn catchment, a tributary to the South Tyne 9 km north of the junction of the Nent with the South Tyne. Many of the high flow events coincide with mining activity within the Nent Valley, and it is possible that a combination of storm activity and mining is recorded within the sediment profile at Blagill. Although these storm events may have been responsible for channel metamorphosis at Blagill (Fig. 3), the channel and floodplain in the vicinity of the sampling location for P2

appears to have remained relatively laterally stable.

The initial aggradation high shown as a falling limb between 1800 and 1825 on Fig. 9A, does not appear to have initiated channel change straight away when viewing the 1820 map, where the channel remains single-thread (Fig. 3). However change does appear later on the 1866 map, during a period of reduced aggradation, and possibly indicating a lag in response. The main period of aggradation peaking between 1892 and 1895 does appear to be associated with channel response at Blagill with the 1899 map showing the greatest braiding intensity, most likely in response of increased sediment supply and large floods (Rumsby & Macklin, 1994). During periods of accretion sediment supply to the floodplain is likely to have increased, with both lower and higher magnitude floods able to deliver sediment to the floodplain surface. Increased frequency of overbank events during aggradational phases is also likely to have allowed floodplain surface sorting of fines, potentially leading to spatial variations in accumulated sediment thickness as differences in grain-size. It is likely that grain size changes in the profile also result from differences in flood magnitude as well as whether the system is in an aggradational or incisional phase. Higher energy floods may deliver coarser material for example. However, any size differences resulting from such floods are geochemically minimized by analysing the < 63 μm sediment fraction, as was done herein – hence adding confidence to the proposed chronology.

5.4.3. Post-depositional processes

Chemostratigraphy assumes that the metal concentrations reflect the primary depositional signature. However, a number of studies have provided evidence for post-depositional re-remobilisation (Bradley and Cox, 1990; Taylor, 1996; Hudson-Edwards et al., 1998; Miller and Miller, 2007; Du Laing et al., 2009), within deposited sediments. The forms of metal may be modified through changes in redox potential and pH, driven by fluctuating water tables, and acidification through pedogenesis or atmospheric deposition (Hudson-Edwards et al., 1998). In addition, biological processes such as uptake by plants and organisms are responsible for metal remobilisation. Metals can also be leached out of soils (Salomons and Forstner, 1984). Channel incision subsequent to fine sediment deposition on floodplains can lead to a drop in water table and the weathering of existing minerals (e.g. sulphides), as well as changing the frequency of overbank deposition (Miller and Miller, 2007). Some incision at Blagill is likely in between aggradational phases (Fig. 9), however the extent to which this lowered the water table in the floodplain, and the possible impact on metal remobilisation, is unclear.

Hudson-Edwards et al. (1998) have investigated secondary remobilisation of metals in the South Tyne catchment, including floodplain sediments on the river Nent at Blagill. They indicated that lead, zinc, cadmium and copper were stored in floodplain sediments as sulphides and carbonates, and iron and manganese oxyhydroxides, and suggested evidence for both primary (depositional) and secondary (remobilisation) processes. Down-profile weathering paragenesis was suggested whereby sulphides converted to carbonates and were either altered or are replaced by iron and manganese oxyhydroxides. Evidence for chemical remobilisation included mineral breakdown and pseudomorphing, high levels of exchangeable and specifically adsorbed contaminant metal in zones of relatively low pH, and the accumulation of secondary iron and manganese oxyhydroxides at levels related to a fluctuating water table or the breakdown of organic matter. Despite the possibility of remobilisation lead and zinc within profile P2, correlation of zinc concentrations with mining, does offer contrary support. Remobilisation may have been more significant for lead, which may explain the lack of a correlation between lead concentrations and mining records.

5.5. Conceptual model of historic sedimentation at Blagill

Catchment disturbance from human activities is well documented to increase sediment supply downstream (Jackson et al., 2005; Donovan et al., 2015; Miller et al., 2019), and often resulting in depositional

archives stored in lower energy zones within a catchment. Understanding the legacy effects and fate of anthropogenic sediment deposition in river systems is essential for future management of riverine ecosystems and their management (Bain et al., 2012), and may be used to help reconstruct past fluvial system-scale response to changes in flow and sediment supply (Grabowski et al., 2014).

Trimble (1995) presented a sediment budget model (Model 2 – Perturbation of Humid Area Quasi Steady State) demonstrating the temporal response of the channel and floodplain forced either by climatic factors (e.g. Knox, 1972), or from anthropogenic alterations to the catchment such as mining, and appears to show parallels to the sedimentation rates shown over time for the River Nent (Fig. 9). In response to disturbance, excessive sediment supply may induce aggradation on both the floodplain and in the channel downstream. If there is a reduction in sediment supply caused by an amelioration or reversal of the conditions causing the disturbance, then if sediment supply remains low, the river will remove the accumulated sediment. This may be manifest as incision, which at first can be rapid, but as the long profile equilibrium is reached, the vertical cutting will slow down, and lateral erosion becomes more significant. As this proceeds sediments become less accessible from the high banks and terraces, and new deposition on a new floodplain may begin to offset erosion, leading to a return to steady state conditions (Schumm and Lichty, 1965).

The pattern of changing sediment volumes varies markedly throughout the development of the sedimentation zone at Blagill, and strong links with mining activity can be made. An increase in the vertical aggradation of overbank fines is implied prior to the peak in lead mining between 1825 and 1850, and observed prior to the onset of intensive zinc mining between 1881 and 1892. This excessive sediment input and subsequent pattern of declining sedimentation broadly agrees with the Trimble's (1995) model for catchments recovering from disturbance (Fig. 9B), however deviates slightly from the model by only exhibiting incision through the mining deposits back the former gravel bed elevation, rather than substantial further incision through these gravels. This is evidenced by the comparable elevations of the contemporary gravel bed elevation and the gravel-fine sediment transition at the base of the P2 profile. Subsequent to the demise of the zinc industry, a substantial decrease in aggradation rate is recorded up to 1912, indicating reduced sediment generation and mobility. This reflects the general decline in mining throughout the catchment. Post-1912 rates and volumes should be viewed with caution as no chronological markers after 1912 can be determined from the profile at P2. However, as the 1912 marker occurs within the top 0–5 cm of P2, further aggradation is unlikely to have exceeded 1 or 2 cm, suggesting the channel has incised through the mining deposits back down to the gravel bed at this location, and that the river Nent is undergoing recovery in the manner described by Trimble (1995).

6. Conclusions

This paper demonstrates the value of combined archival and field-based analyses in reconstructing historic sediment budgets in fluvial systems. It links zinc and lead concentrations in accumulated sediment to historic mining records for the River Nent catchment in Northern England. A clear relationship exists between zinc concentrations within the P2 profile and zinc ore extraction, enabling a post 1881 chronology to be established. Lead records were used to establish the pre-1881 chronology, where lead concentrations are closely linked with 1825, 1850 and 1866 ore extraction figures. Historic sedimentation at Blagill was reconstructed through combining historic chronological markers, sedimentation depths and reach area. Changes in sediment delivery showed clear links to ore extraction records, with a response very similar to the catchment disturbance conceptual model proposed by Trimble (1995). Coupled with sediment provenancing approaches, using multi-geochemical fingerprinting, the chronology has the potential to establish historical sediment budgets, and elucidate historic catchment scale

adjustments in sediment sources and connectivity, driven by mining activities, and is the focus of ongoing work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research was funded from a University of Gloucestershire Studentship to A. Parker. We would like to thank the Graham family for access to their land during fieldwork. Thanks also to Professor Phil Toms for undertaking the OSL analysis, Professor Mike Fowler for oversight and guidance with the ICP-OES analysis, and to Dr George Heritage for help in collecting the OSL samples.

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