



# Mediaeval Lead Pollution in the River Ouse at York, England

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The City of York in northern England has a long history of being flooded by the River Ouse. Excavations of a 9 m sedimentary profile were carried out by the York Archaeological Trust on the site of a pumping station associated with a flood prevention scheme at North Street on the south-west bank of the River Ouse. This profile records evidence of human activity and episodic river sedimentation over a period from the 2nd to the 14th century AD. Anthropogenic materials in the profile include waterfront timber and wattle structures, and dumps of organic domestic debris and industrial waste. Evidence of historic floods is preserved in interleaved alluvial deposits. This study reports on the degree of lead (Pb) contamination at the site from Roman to Mediaeval times and the sources of both alluvial and manufactured lead deposited in the profile. Archaeological, sedimentological, geochemical and mineralogical evidence suggest that Yorkshire Dales mining activity during the 9th–13th centuries AD may have both directly and indirectly caused lead contamination of the alluvial deposits at North Street. © 1999 Academic Press

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## Introduction

In Britain as elsewhere in the world, rivers have long been the foci of human settlement and activity (Evans, 1991; Needham & Macklin, 1992). Human exploitation of natural resources from prehistoric times through to the present day, however, has had a very significant impact on the hydrology, sediment regime and ecology of most of Britain's rivers. This has arisen sometimes inadvertently after deforestation or land-use change but also deliberately, for example, by construction of weirs for navigation or embankments for flood protection. Increases in flooding and flood peaks, river sediment loads and rates of valley floor alluviation following human disturbance, or disturbance of vegetation, are now well documented (Robinson & Lambrick, 1984; Brown & Barber, 1985; Macklin *et al.*, 1991). Widespread river pollution

associated with the Industrial Revolution, particularly from base metal mining and manufacture, has also been the subject of considerable recent research (Lewin & Macklin, 1987; Bradley & Cox, 1990; Macklin, 1996; Taylor, 1996). What is less clear from these studies, however, is precisely when mining, manufacture and use of base metals first increased contaminant metal concentrations in British river systems above pre-industrial, "natural" levels. It has generally been believed that localized contamination of some rivers may have begun in the Roman period (e.g., Macklin, Bradley & Hunt, 1985) but evidence for this is largely circumstantial primarily because few geochemical investigations of Roman age alluvial deposits have been undertaken. Indeed, one of the very few studies that has been carried out on well-dated Roman alluvium at Doncaster, northern England, on the River Don (Macklin, 1997), shows no metal contamination and that significant river pollution, at least in this region, began much later in the 13th century AD.

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Similarly, in a post-1st millennium BC alluvial sequence at Lambley on the River South Tyne (Passmore & Macklin, 1997), significant lead contamination is not encountered in material younger than the 12th century AD.

Recent archaeological investigations at York, northern England, of a 9 m thick river bank sequence dating from the 2nd to the 15th century AD, provided a unique opportunity to study flooding and pollution during the Roman and Mediaeval periods in the Yorkshire Ouse, one of Britain's major rivers affected by historic metal mining (Macklin, Hudson-Edwards & Dawson, 1997). Excavations revealed a series of superimposed waterfront structures which interdigitated with domestic and industrial waste, and river sediments. A range of geochemical, mineralogical and sedimentological analyses were carried out on these deposits with three principal aims. The first was to establish the degree of lead contamination at the site and document how this had varied over Roman and Mediaeval times. The second was to determine whether lead in alluvium originated from metalliferous waste discharged by mines located in the headwater tributaries of the River Ouse 40–50 km upstream of York, or from local domestic and industrial sources from within the city itself. The third aim was, using lead isotopic ratios, to identify if ore from the Yorkshire Dales was the primary source of lead used in metal manufacturing, or whether material was imported from mining areas outside the region.

## Study Area

### *The City of York—history and geological setting*

The area occupying the present-day City of York has had a long history of human habitation. It has been demonstrated that prehistoric settlement was present in the Vale of York, although no evidence of structures has yet been found in the city itself (Radley, 1974). Roman occupation began with the construction of a legionary fortress on the north-east bank of the River Ouse in the last quarter of the 1st century AD. Civilian settlement soon followed until the Roman town of Eboracum covered a large area on both banks of the river Ouse. The settlement prospered, becoming a market for domestic and industrial goods from all over Europe (Salway, 1981; Ottaway, 1993). The focus of settlement appears to have moved just south of the confluence of the rivers Ouse and Foss during the Anglian period but returned to overlie the Roman town when the thriving Viking settlement of Jorvik was constructed. Excavations at Coppergate (Figure 1) have revealed evidence (antler, jet, amber, leather, metal) of extensive Viking Age commercial activity (e.g., Bayley, 1992).

The City of York lies at the confluence of the Rivers Ouse and Foss (Figure 1) where the Ouse breaks through a glacial morainic ridge. The City has had a

long history of flooding. Radley & Simms (1971) used archaeological evidence to suggest that in Roman times, sea level was lower than at present and that the Vale of York was less susceptible to flooding. This period was followed by a rise in sea level and an abandonment of settlements dated to AD 350–370. Farrant (1953) suggested that there has been a gradual increase in average flood levels at York since the 13th century AD, but Radley & Simms (1971) suggested that by AD 1150, serious flooding became less frequent and continued so for about 700 years. Records for this period, however, are poor, with large floods documented only in the years 1263 (Environment Agency, 1995), 1315 (Radley & Simms, 1971; Environment Agency, 1995), and 1316 and 1360 (Pugh, 1961).

The major tributaries of the River Ouse upstream of York are the Rivers Swale, Ure and Nidd (Figure 1). These rivers drain the southern part of the Yorkshire Dales lead–zinc fluorite–baryte Orefield (Figure 1; Dunham & Wilson, 1985). The ore deposits occur as vein and replacement bodies in carboniferous limestone, sandstone and shale. Galena [PbS] is the major lead ore mineral, but several secondary lead minerals also occur, including cerussite [PbCO<sub>3</sub>], anglesite [PbSO<sub>4</sub>] and occasionally, pyromorphite [Pb<sub>5</sub>Cl(PO<sub>4</sub>)<sub>3</sub>] (Dunham & Wilson, 1985). The largest deposits occur in upper Swaledale (c. 85 km upstream of York), and in Nidderdale (c. 45 km upstream of York) (Figure 1).

Evidence and records of lead mining in the Yorkshire Dales are sparse prior to the major phase of mining during the 17th–19th centuries. Lead smelting is first documented in the Pennines during Roman times in Nidderdale, Yorkshire, at the end of the 1st century AD (Jennings, 1967). Roman pigs of lead have been documented at Heyshaw Bank near Greenhow in Nidderdale (Emperor Domitian, AD 81; Kirkshaw, 1735; Raistrick, 1930), at Nussey Knot, Greenhow (Emperor Trajan, AD 98), and at Hurst in Swaledale (Emperor Hadrian, AD 117–138), but it is not known definitely whether these were derived from local lead. Very little is known of lead mining during the Mediaeval period, but it is recorded that the roof of York Minster was protected with leaden sheets (William of Malmesbury, 690), and 12th century AD state and abbey records show that mining was being carried out at Greenhow and in upper Swaledale (Dunham & Wilson, 1985).

### *The North Street excavation*

The North Street excavation was carried out by York Archaeological Trust from March to July 1993. The excavation was located on the south-west bank of the River Ouse (NGR SE 6009 5178; Figure 1). It consisted of a single circular trench, 5.50 m in diameter, on the site of a pumping station associated with a flood prevention scheme. The uppermost 1.80 m of sediment was removed by machine and the remainder was excavated by hand. Detailed archive report

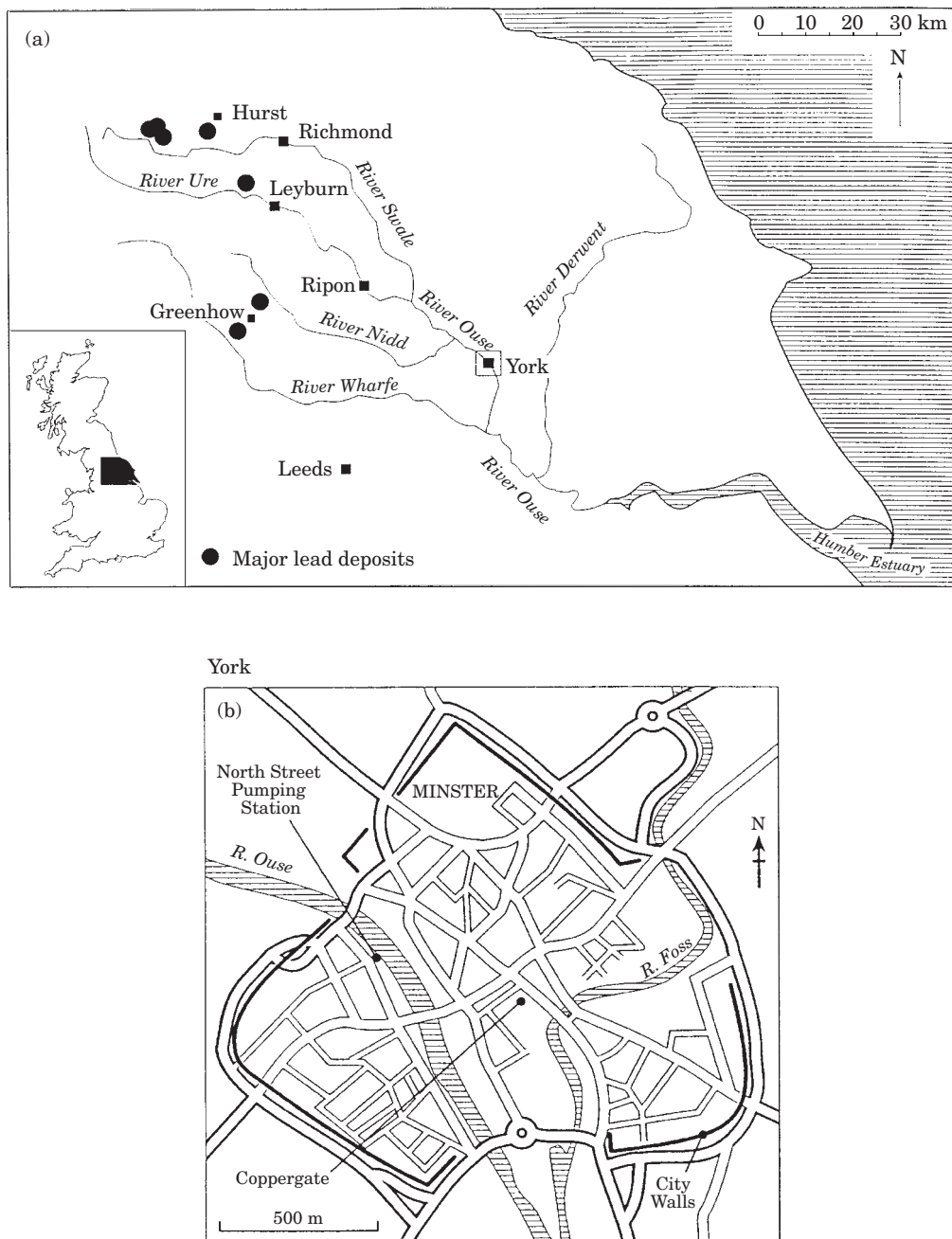


Figure 1. (a) Location map of Yorkshire Ouse River basin, showing major Yorkshire Dales lead deposits; (b) the City of York, showing the locations of North Street, Coppergate, and the Rivers Ouse and Foss.

information is summarized in [Finlayson \(1993\)](#). Excavations exposed a well-stratified, 9 m thick sequence which, on the basis of included pottery assemblages, was deposited over a period from the 2nd to the 15th century AD ([Figure 2](#)). The pottery was recovered from 161 excavated contexts, of which 25 produced characteristic Roman pottery dating from the 2nd to 4th centuries AD. There was a gap in the ceramic sequence from the end of the 4th century to the mid-9th century, followed by an unbroken sequence from the mid/late 9th century up to the 15th century.

Three types of deposit were evident. The first is a succession of timber, stone and wicker waterfront structures and revetments ([Figure 2](#)). A sequence of buildings dating from the late 13th century AD also demonstrates that the area was protected by a river wall after this time. Second, a wide range of dumped material including shells, tile, brick, mortar, pottery, burnt grain, charcoal, animal bone, glass beads, wattle, slag and lead “run-offs” (fragments of roofing material), had been tipped down the river bank and accumulated against, or within, the waterfront

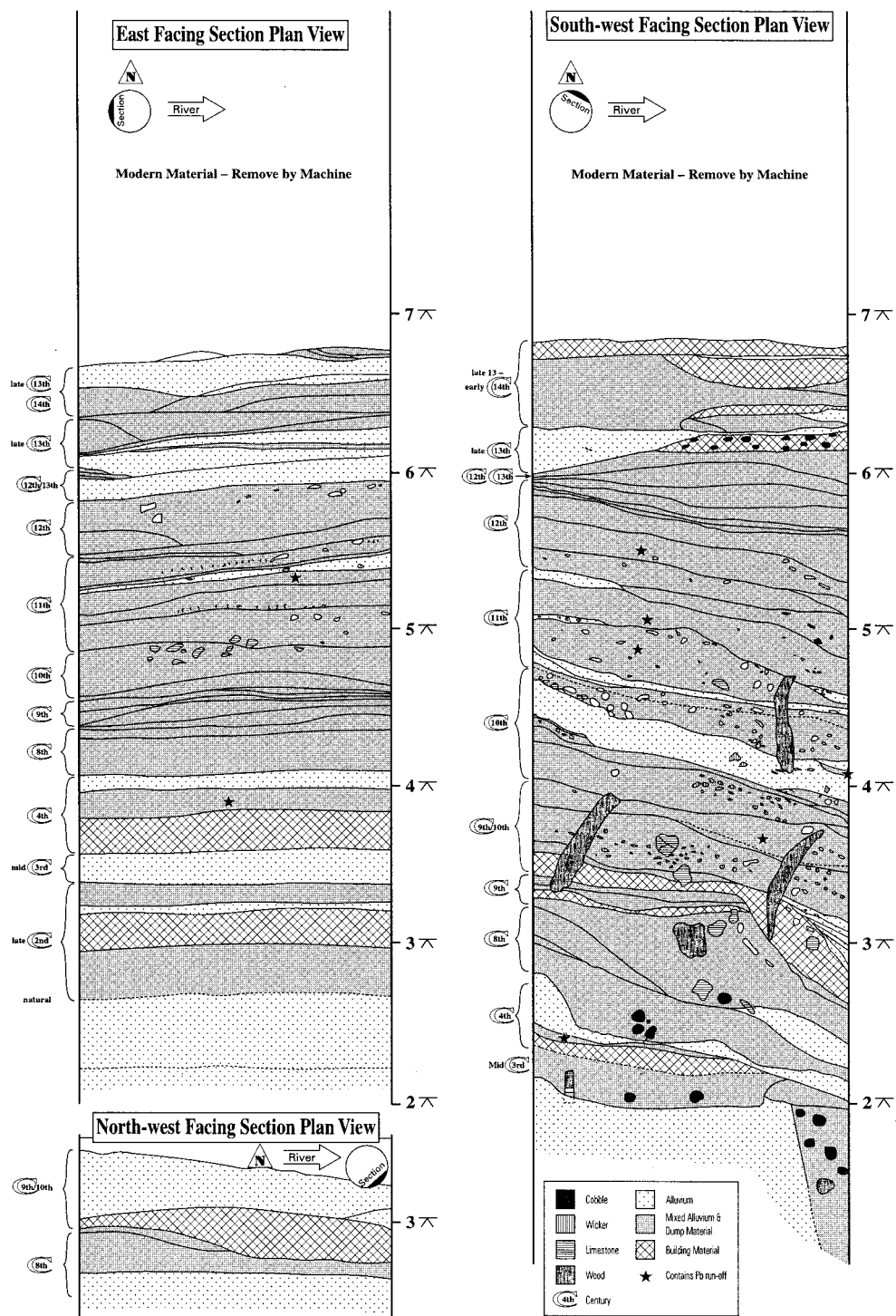


Figure 2. East, south-west and north-west facing stratigraphic sections at North Street excavation.

structures described above. Most of the dumped material had been reworked by the river and mixed with river sediment. The third group of deposits were well-sorted beds of sandy alluvium (with minor amounts of silt and clay), ranging in thickness from 3 to 30 cm, which had been sedimented on, and in some

cases, over the top of the river bank. Some alluvial units, notably those deposited between the 2nd to 4th, and 12th to 14th centuries, could be traced right across the circular trench and are likely to represent major floods that overtopped the channel. Other alluvial units, generally those dated to the 9th to 10th century



Table 1. Lead isotope ratio analyses (corrected values against SRM-981) for North Street alluvium, mixed alluvium and dump material and lead "run-offs"

Sample	Century	$^{208}/^{206}\text{Pb}$	$^{207}/^{206}\text{Pb}$	$^{206}/^{207}\text{Pb}$	$^{204}/^{206}\text{Pb}$
<i>Alluvium</i>					
1103	late 13	2.0623 ± 0.003 (0.13%)	0.84247 ± 0.0009 (0.11%)	1.1870 ± 0.0013 (0.11%)	0.05417 ± 0.00001 (0.2%)
1113 10–15	late 13	2.0704 ± 0.010 (0.47%)	0.84269 ± 0.0018 (0.21%)	1.1867 ± 0.0025 (0.21%)	0.05424 ± 0.00007 (0.13%)
1181	11	2.0631 ± 0.008 (0.38%)	0.84382 ± 0.0024 (0.29%)	1.1851 ± 0.0034 (0.29%)	0.05424 ± 0.00011 (0.20%)
1195a	11	2.0586 ± 0.011 (0.55%)	0.84282 ± 0.0028 (0.33%)	1.1865 ± 0.0039 (0.33%)	0.05377 ± 0.00011 (0.21%)
1281a	10	2.0631 ± 0.019 (0.94%)	0.84382 ± 0.0014 (0.17%)	1.1879 ± 0.0020 (0.17%)	0.05424 ± 0.00008 (0.15%)
1281b	10	2.0607 ± 0.011 (0.52%)	0.84048 ± 0.0039 (0.46%)	1.1898 ± 0.0055 (0.46%)	0.05385 ± 0.00020 (0.37%)
1287	10	2.0652 ± 0.007 (0.34%)	0.84171 ± 0.0023 (0.27%)	1.1881 ± 0.0032 (0.27%)	0.05363 ± 0.00017 (0.31%)
1390 2–9	9–10	2.0580 ± 0.005 (0.26%)	0.84440 ± 0.0011 (0.13%)	1.1843 ± 0.0015 (0.13%)	0.05429 ± 0.00006 (0.11%)
1391	9–10	2.0728 ± 0.009 (0.42%)	0.84646 ± 0.0018 (0.21%)	1.1814 ± 0.0025 (0.21%)	0.05443 ± 0.00005 (0.09%)
1438	8	2.0672 ± 0.008 (0.38%)	0.84660 ± 0.0016 (0.19%)	1.1812 ± 0.0022 (0.19%)	0.05454 ± 0.00020 (0.37%)
1440	4	2.0591 ± 0.020 (0.98%)	0.84223 ± 0.0010 (0.12%)	1.1873 ± 0.0014 (0.12%)	0.05428 ± 0.00018 (0.33%)
<i>Mixed alluvium and Dump Material</i>					
1026	late 13–14	2.0756 ± 0.014 (0.68%)	0.84363 ± 0.0015 (0.18%)	1.1854 ± 0.0021 (0.18%)	0.05397 ± 0.00010 (0.19%)
1102	late 13	2.0664 ± 0.015 (0.75%)	0.84557 ± 0.0005 (0.06%)	1.1826 ± 0.0007 (0.06%)	0.05427 ± 0.00003 (0.05%)
1188	11	2.0617 ± 0.013 (0.61%)	0.84221 ± 0.0031 (0.37%)	1.1874 ± 0.0044 (0.37%)	0.05412 ± 0.00024 (0.45%)
1195b	11	2.0576 ± 0.015 (0.73%)	0.84403 ± 0.0030 (0.35%)	1.1848 ± 0.0041 (0.35%)	0.05412 ± 0.00010 (0.18%)
1272	10	2.0570 ± 0.015 (0.75%)	0.84473 ± 0.0018 (0.21%)	1.1838 ± 0.0025 (0.21%)	0.05412 ± 0.00016 (0.29%)
1274	10	2.0748 ± 0.011 (0.53%)	0.84438 ± 0.0010 (0.12%)	1.1843 ± 0.0014 (0.12%)	0.05392 ± 0.00009 (0.17%)
1279	10	2.0583 ± 0.011 (0.52%)	0.83960 ± 0.0021 (0.25%)	1.1910 ± 0.0030 (0.25%)	0.05385 ± 0.00018 (0.34%)
1386	9–10	2.0607 ± 0.007 (0.35%)	0.84180 ± 0.0032 (0.38%)	1.1879 ± 0.0045 (0.38%)	0.05398 ± 0.00015 (0.27%)
<i>Lead "run-offs"</i>					
1174	12	2.0720 ± 0.004 (0.20%)	0.84040 ± 0.0009 (0.11%)	1.1899 ± 0.0013 (0.11%)	0.05390 ± 0.00001 (0.01%)
1289	9–10	2.0767 ± 0.006 (0.31%)	0.84224 ± 0.0015 (0.18%)	1.1864 ± 0.0021 (0.18%)	0.05409 ± 0.00001 (0.02%)
1295	9–10	2.0773 ± 0.003 (0.16%)	0.84291 ± 0.0003 (0.03%)	1.1864 ± 0.0004 (0.03%)	0.05411 ± 0.00001 (0.01%)
1441	4	2.0851 ± 0.001 (0.05%)	0.84928 ± 0.0013 (0.15%)	1.1775 ± 0.0018 (0.15%)	0.05452 ± 0.00001 (0.01%)

AD, were found only in the western-facing parts of the section, closest to the river (Figure 2). They probably relate to more moderate flood events where sedimentation was confined within the channel. Both the alluvial and dump deposits dip towards the River Ouse, although the angle of dip decreases up-section from 20° at the base to less than 3° at the top of the profile, consistent with a progressive north-easterly shift in the position of the river bank at this site. Previous excavations in the centre of York (York Archaeological Trust, 1988b) have shown a similar pattern with evidence that the banks of the River Ouse have narrowed by as much as 40 m since the 1st century AD.

## Methodology

Seventy-three samples of river sediment, mixed dump and alluvium, and building materials were collected during the excavation. Duplicate samples were collected by the York Archaeological Trust and archaeological materials extracted. Samples were air-dried and sieved to <2 mm. Sediment pH was measured in a 1:2.5 air-dried sediment: de-ionized water (DIW) slurry. The samples were placed in porcelain crucibles and ashed for 15–24 h at 450°C. The ashed material was then pulverized using a porcelain mortar and pestle. Two hundred and fifty milligrams of ashed sample was

digested in 2 ml of concentrated Aristar HNO<sub>3</sub> for 1 h at 95°C. The amount of lead in acid was <1 ppb. After cooling, 8 ml of 18 MΩ DIW from a NANOpure system was added and the samples were transferred to polypropylene vials. Analysis for lead concentration was carried out using flame atomic absorption (Pye Instrument). Standards ranging from 5 to 20 µg/g were used, and blank values were below detection limits. Lead values were approximately within 10% of the lead concentration of the reference standard GBW07311 (Office of Reference Materials, Laboratory of the Government Chemistry, U.K).

Isotope ratios of  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{204}\text{Pb}/^{206}\text{Pb}$  were determined for a representative subset of the 73 original samples, comprising 19 alluvial and mixed alluvial/dump material samples, and for four samples of lead "run-off". The lead "run-offs" were cleaned thoroughly by scraping away the weathering crust, washed with 5% HNO<sub>3</sub> and finally DIW. Approximately 100 mg of each sample was then scraped off with a stainless steel knife to form mm-sized particles. The sediment and "run-off" samples were digested in nitric acid as described above, and the lead concentration of the sample solution adjusted to approximately 50 ng/g using 100 ml volumetric flasks and 18 MΩ DIW prior to isotope analysis. The lead isotope ratio in solution was measured using inductively coupled plasma-mass spectrometry (ICP-MS,

VG Plasma Quad, Fisons Instruments). The certified common lead isotope standard SRM-981 from the National Institute of Standards and Technology (NIST) was used to calibrate the instrument. Observed mass range was 201–210. Each sample was measured six times, and the average lead isotope ratios were calculated. These were corrected for mass fractionation and were normalized against values obtained from the standard SRM-981. Accuracy was found to be  $-0.01$  to  $-0.19\%$  for  $^{208/206}\text{Pb}$ ,  $+0.05$  to  $-0.20\%$  for  $^{207/206}\text{Pb}$  and  $-0.04$  to  $-0.20\%$  for  $^{204/206}\text{Pb}$ . Values of short-term precision were calculated as percent relative standard deviation (RSD %; Table 1) for  $^{208/206}\text{Pb}$ ,  $^{207/206}\text{Pb}$  and  $^{204/206}\text{Pb}$ , and varied between 0.05 and 0.98%, 0.03 and 0.46%, and 0.01 and 0.45%, respectively.

Polished thin sections of unwashed, dried sediment samples and lead “run-off” were examined using a Jeol JSM 6400 scanning electron microscope (SEM) combined with energy dispersive X-ray spectrometry (EDX) and equipped with a Link Analytical back-scattered electron detector. Operating conditions were 15 kV accelerating voltage and 1.5 nA incident specimen current. Analytical data were obtained using a standardless Link Analytical eXL energy dispersive analysis system with a ZAF4-FLS deconvolution/recalculation package. Counting time was 45 s for each analysis.

## Results

### Lead concentrations

Four types of sedimentary units within the North Street section have been distinguished (Figure 2), and include (i) “alluvium”, composed of sand, silt and some clay; (ii) “mixed alluvium and dump material”, which contains alluvium and discarded material including shells, tile, brick, mortar, pottery, burnt grain, charcoal, animal bone, glass beads and wattle; (iii) “mixed alluvium and dump material with lead ‘run-off’”, which is comprised of the materials in unit type (ii) along with lead “run-off” (see below); and (iv) “building material”, comprising cobbles, mortar and sand. Concentrations of total lead for these four types are plotted against height and age in Figure 3, and are summarized in Table 2.

Just over 50% of the North Street samples exceed the maximum lead concentration (100 mg/kg) for pre-Roman alluvium in the Yorkshire Ouse basin (Table 2; Hudson-Edwards & Macklin, unpubl. data). Tenth and 11th century AD mixed alluvium and dump material with lead “run-off” samples exhibit the highest lead concentrations. Values for the mixed alluvium and dump material units are highest in the 9th to 12th centuries AD, and for alluvium in the 10th, 11th and 13th centuries AD. The mixed alluvium and dump material with lead “run-off” exhibit the highest mean values, followed by mixed alluvium and dump

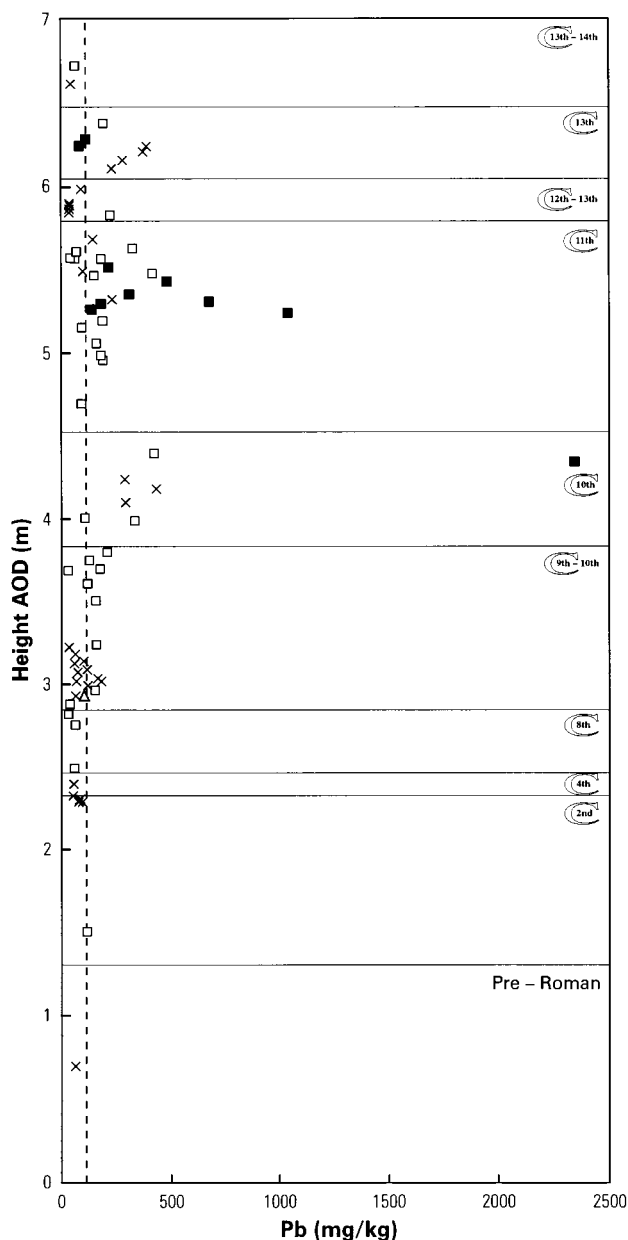


Figure 3. Lead contents in North Street alluvium, alluvium and dump material with and without lead “run-off”, and building material. Depth down-section is given in metres (m) above ordnance datum (AOD). Vertical dashed line shows the maximum pre-Roman Yorkshire Ouse basin alluvial lead concentration.

material, the building material sample, and alluvium (Table 2).

### Sediment composition and forms of lead

The alluvial sediment at York is composed of quartz [ $\text{SiO}_2$ ], shale bedrock, calcite [ $\text{CaCO}_3$ ], baryte [ $\text{BaSO}_4$ ], and zircon [ $\text{ZrSiO}_4$ ] detrital fragments, and authigenic gypsum [ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ], vivianite [ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ] and framboidal pyrite [ $\text{FeS}_2$ ]. Lead occurs in the North Street profile in two major forms. “Run-offs” and

Table 2. Lead concentrations in North Street alluvium, mixed alluvium and dump material, and building material

Unit type	N	Pb concentration (mg/kg) arithmetic mean	Range
Alluvium	30	90	21–42
Mixed alluvium and dump material	32	110	20–420
Mixed alluvium and dump material with lead “run-off”	10	310	72–2300
Building material	1	97†	—
Pre-Roman Yorkshire Ouse basin alluvium*	122	24	4–100

N, number of samples.

\*Hudson-Edwards & Macklin, unpubl. data.

†Concentration of single sample.

folded scraps of lead alloy occur in 4th, 9th–10th (Figure 4(a)), 11th, 12th and 13th century AD mixed dump and alluvial units. The “run-offs” are the waste products of the manufacture of lead sheets for use in roofing and other activities. They generally are elongate to equant, flattened fragments with rounded edges, and range in length and thickness between 0.5–7 cm and 0.5–1 cm, respectively. They exhibit fine, mm-thick, weathering rinds composed of iron–lead oxyhydroxides.

Lead is also found as 10–50 µm, rectangular and irregular, zoned minerals occurring on the edges of, and enclosed by, shale bedrock grains (Figure 4(b), (c)) in alluvial and mixed alluvial/dump units. Semi-quantitative SEM-EDX analysis reveals that these are all lead phosphates with an average composition (PbO 67.0 weight%, CaO 11.5 weight%, P<sub>2</sub>O<sub>5</sub> 15.2 weight%, FeO 1.5 weight% and Cl 1.2 weight%) near calcium-rich chloro-pyromorphite [(Pb,Ca)(PO<sub>4</sub>)<sub>3</sub>Cl].

### Lead isotopes

Measurements of lead isotope ratios using ICP-MS in environmental materials with accuracies and precisions of better than 0.5% (e.g., Russ, 1989), can be used to identify major sources of lead. The ratios of lead isotopes to each other vary with the geological ages and the geographical locations of lead ores. Lead isotopes have thus been used for provenancing lead sources in environmental (Chow & Earl, 1972; Grousset *et al.*, 1994) and archaeological materials (Brill & Wampler, 1967; Gale, 1989; Ghazi, 1994).

The <sup>208</sup>Pb/<sup>206</sup>Pb, <sup>207</sup>Pb/<sup>206</sup>Pb, <sup>206</sup>Pb/<sup>207</sup>Pb, and <sup>204</sup>Pb/<sup>206</sup>Pb North Street isotope results are summarized in Table 1. The <sup>206</sup>Pb/<sup>207</sup>Pb ratio is generally used as an environmental tracer because it can be measured most accurately (Maring *et al.*, 1987). <sup>206</sup>Pb/<sup>207</sup>Pb ratios for York alluvium, mixed alluvium and dump material and lead “run-offs” are depicted in Figure 5. These results show that the alluvium, mixed alluvium and dump material, and all lead “run-offs” except the 4th century AD sample have similar signatures. Statistical comparisons were made using mean <sup>206</sup>Pb/<sup>207</sup>Pb ratios using a Mann–Whitney *U*-test (Swan & Sandilands, 1995). Comparisons were made between mean values

for the North Street alluvium, mixed alluvium and dump material and lead “run-offs”, and galena ores from the Yorkshire Dales (Mitchell & Krouse, 1971; Rohl, 1996). Statistically significant differences were not found in all cases, suggesting that all of these North Street materials may have been derived from Yorkshire Dales sources.

Statistical comparisons were also made between mean <sup>206</sup>Pb/<sup>207</sup>Pb ratios for the North Street samples and galena ores from other U.K. deposits (Rohl, 1996) which were mined at least as far back as Roman times (Derbyshire, north-west Wales, the Mendips, west Cumbria, Leadhills; Woodward, 1876; Gough, 1930; Davies, 1935; Lewis, 1967; Buchanan & Cossans, 1969). Although these tests showed that the mean isotopic values are significantly different than mean values for the other galena ores, it is appreciated that some of the North Street alluvium and mixed alluvium and dump material values (within 1 standard deviation) correspond to some of the Derbyshire values and two of the north-west Wales orefield values (Figure 5). This is confirmed by Mann–Whitney *U*-tests. Similarly, Mann–Whitney *U*-tests for the individual North Street “run-off” samples show that only the “run-off” from the 4th century AD gives a non-statistically significant difference from isotopic values for galena are from Derbyshire, north-west Wales, the Mendips, and west Cumbria.

## Discussion

### Lead phosphate minerals

Mineralogical compositional and textural information can be used to provenance sediment sources (e.g., Hudson-Edwards, Macklin & Taylor, 1997). The lead phosphate minerals in the North Street profile are likely to originate from three possible sources: (1) secondary weathering products of the mineral veins in the Yorkshire Dales orefield (cf. Dunham & Wilson, 1985) which have been transported down-river and deposited in the North Street profile; (2) *in situ* authigenic precipitates which formed directly in the sediment pile; or (3) *in situ* weathering products of river-transported lead-bearing minerals.

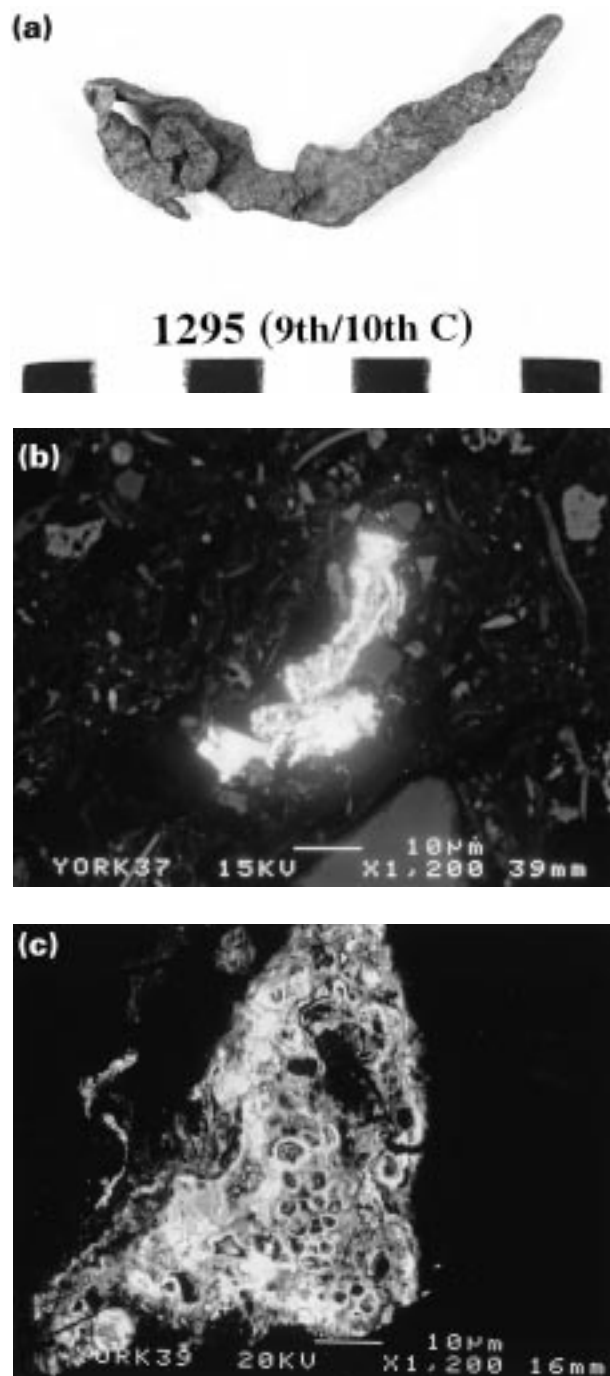


Figure 4. Photograph and photomicrographs of lead “run-off” and shale-hosted lead phosphate minerals. (a) Ninth–tenth century AD lead “run-off” (roofing material). Scale is 7 cm long. (b) Calcium-bearing lead phosphate embedded within shale bedrock grain in 10th century AD mixed alluvial/dump unit. (c) Calcium-bearing lead phosphate on edge of shale bedrock grain in 10th century AD alluvial unit, exhibiting zoned growth texture.

Secondary lead phosphate mineral vein weathering products (option 1) are extremely rare in the lead ore deposit areas (Dunham & Wilson, 1985) and would thus probably not be the major source of North Street lead phosphates.

The weathering rinds on the lead “run-offs” suggest that some movement of lead may have occurred within the North Street profile. Such redistribution of lead could have given rise to precipitation of secondary, authigenic lead minerals at North Street (option 2). If this had been the mechanism of lead phosphate formation, then these minerals would probably be found on a variety of substrates. All of the lead phosphate grains observed, however, occur on and within shale bedrock grains. In addition, the present high pHs of the North Street samples (7.3–9.3) suggest that the lead mobility may have been extremely limited (Korte *et al.*, 1976), although pH conditions may have differed in the past. Finally, the lead “run-offs” are relatively scarce in the profile and of small size (e.g., Figure 4(a)) suggesting that weathering alone may not have caused the general enrichment of lead seen in the profile.

The precursors of the “option 3” North Street lead phosphates could be lead-bearing ore minerals such as galena and cerussite, or lead-bearing ore mineral weathering products such as ferromanganese oxyhydroxides. Evidence for this comes from the Tyne and Tees Rivers north of the Yorkshire Ouse basin, which also drain Yorkshire Dales/Northern Pennine lead ore deposit areas and are contaminated with lead-bearing sediment (Macklin & Dowsett, 1989; Macklin *et al.*, 1994; Hudson-Edwards, Macklin & Taylor, 1997). Downstream of the mining areas, the sediment lead mineralogy is dominated by ferromanganese oxyhydroxides which often occur on and within shale bedrock grains (Hudson-Edwards *et al.*, 1996; Hudson-Edwards, Macklin & Taylor 1997). The association of the North Street lead phosphates with shale bedrock fragments, and relationship of York to the lead ore deposit areas of the Yorkshire Dales (Figure 1(a)) suggests that lead-bearing ferromanganese oxyhydroxides may have been the original lead-bearing minerals deposited at North Street. The North Street lead phosphates could then have formed as pseudomorphs of ferromanganese oxyhydroxides which experienced reduction and dissolution (cf. Nriagu & Dell, 1974; Nriagu, 1984). Thus, option 3 (above) is the most reasonable for the origin of the lead phosphate minerals.

Pyromorphite is only very slightly soluble ( $K_{sp} = 10^{-84.4}$ ) (Nriagu, 1974) and has a greater field of stability at earth surface conditions than other lead sulphides, oxides and carbonates (Nriagu, 1984). This suggests that once formed, the York calcium-bearing pyromorphites would have not weathered to any great extent, thus preserving the integrity of the lead concentration versus age profile (Figure 3).

#### *Sources of lead and implications of lead contamination*

Elevated lead concentrations in 9th–13th century AD alluvium and mixed alluvium and dump material with and without lead “run-off” at North Street reflect river contamination from both production- (mining,



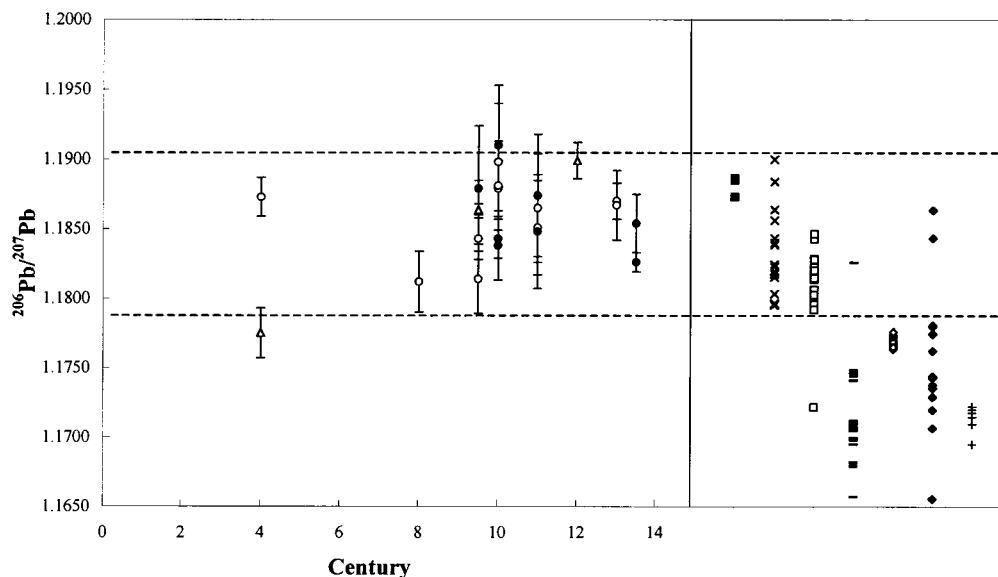


Figure 5.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in North Street alluvium, mixed alluvium and dump material, and lead “run-offs”. Ratios are also shown for Yorkshire Dales and Northern Pennines (Mitchell & Krouse, 1971; Rohl, 1996; range defined by horizontal dashed lines) and other British lead ores (Rohl, 1996), for comparison. Bars indicate 1 s.d. ●, Alluvium; ○, mixed alluvium and dump material; △, lead “Run-off”; ■, Yorkshire Dales lead ore (Rohl, 1996); ×, Yorkshire Dales lead ore (Mitchell & Krouse, 1971); □, Derbyshire lead ore (Rohl, 1996); –, NW Wales lead (Rohl 1996); ◇, Mendips lead ore (Rohl, 1996); ♦, west Cumbria lead ore (Rohl, 1996); +, Leadhill lead ore (Rohl, 1996).

smelting) and consumption- (use, wear and disposal of domestic and industrial products) related activities. Given the dynamic nature of the sedimentation at North Street, it is possible that the sediments at a particular level do not contain reworked lead from an older horizon. Several lines of evidence, however, suggest that this is probably not the case. Excavations at Coppergate (Figure 1(b)) in the City of York which have yielded extensive evidence for 9th–11th century AD metal working including cubes of galena (Bayley, 1992), and the general persistence of elevated lead concentrations at North Street during this time (Figure 3) suggest that the 9th–11th century-dated North Street sediments contain contemporaneous material. In addition, the unit type exhibiting the highest lead concentrations from the 13th century is alluvium which does not appear to contain reworked 9th–11th century lead-rich dump material.

Lead isotopic evidence suggests that the lead-bearing material in the North Street alluvial and mixed alluvial/dump material deposits could have been derived from Yorkshire Dales lead deposit areas. If true, then Mediaeval lead mining in the Yorkshire Dales, resulting in the 9th–13th century river contamination as far downstream as York, may have been more significant than previously thought. The nearest lead deposits to York are those approximately 45 km upstream at Greenhow (Figure 1(a)). Although this appears to be a large distance, similar lead concentrations have been documented in Tyne basin floodplain sediment located more than 40 km from the nearest mine (Macklin *et al.*, 1994).

Overlap of some of the North Street isotopic lead values with values from galena ores from Derbyshire and north-west Wales (Figure 5) suggests that ores from these areas may have been imported to York for metal working. This is not supported by lead isotopic data for the 9th–12th century manufactured “run-off” samples from North Street. The 4th century AD “run-off”, however, may have been produced from a combination of Yorkshire Dales lead ore and material imported from other parts of England including Derbyshire, north-west Wales, the Mendips or west Cumbria. This is supported by historical records (York Archaeological Trust, 1988a), which suggest that lead ore mined from the Mendips and from west Cumbria was imported to York in Roman times.

## Conclusions

Elevated lead concentrations occur in 9th, 10th, 11th and 13th century AD alluvium and dump material mixed with river sediment revealed in an excavation at North Street on the River Ouse, York. The lead occurs in the sediment pile mainly as phosphate minerals and as “run-off” (scraps and fragments of roofing material). Mineralogical textural evidence and lead isotope ratios suggest that most of the lead could have been derived from the carboniferous terrain drained by tributaries of the River Ouse, and more specifically, from lead deposits of the Yorkshire Dales orefield. The lead appears to have been transported from the orefield by the river, altered to lead phosphate after deposition,

and subsequently, not moved appreciably in the profile. This information, combined with elevated lead values in the North Street alluvial sequence and extensive evidence of 9th–11th century AD metal working at Coppergate in York, suggests that lead mining was taking place in the Yorkshire Dales during this period. Furthermore, this mining activity appears to have resulted in significant river contamination in the Ouse downstream at least as far as York. Information on lead levels and river pollution in the Yorkshire Ouse during the Roman period between the 2nd–4th century AD, and during the 5th–8th centuries AD is, however, more limited. At North Street, lead concentrations are at or below pre-Roman levels, suggesting that metal production- and consumption-related activities at this time had relatively little impact on the river environment at York.

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