# Regional lead isotope study of a polluted river catchment: River Wear, Northern England, UK

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## Abstract

High precision, lead isotope analyses of archived stream sediments from the River Wear catchment, northeast England (1986-88), provide evidence for three main sources of anthropogenic lead pollution; lead mining, industrial lead emissions and leaded petrol. In the upper catchment, pollution is totally controlled and dominated by large lead discharges from historic mining centres in the North Pennine Orefield ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ ratios range from 2.0744 - 2.0954 and 0.8413 - 0.8554 respectively). In the lower catchment, co-extensive with the Durham Coalfield and areas of high population density, pollution levels are lower and regionally more uniform. Isotope ratios are systematically higher than in the upper catchment ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ ratios range from 2.0856 -2.1397 and 0.8554 - 0.8896 respectively) and far exceed values determined for the geogenic regional background. Here, the pollution is characterised by the atmospheric deposition of industrial lead and petrol lead. Lead derived from the combustion of coal, although present, is masked by the other two sources. Recent sediments from the main channel of the River Wear are isotopically indistinguishable from older, low order stream sediments of the North Pennine Orefield, indicating that contamination of the river by lead mining waste (up to several 1000 mg/kg Pb at some locations) continues to pose an environmental problem; a pattern that can be traced all the way to the tidal reach. Using within-catchment isotope variation and sediment lead concentrations, estimates can be made of the discharges from discrete mines or groups of mines to the overall level of lead pollution in the River Wear. As well as providing information pertinent to source apportionment and on-going catchment remediation measures, the database is a valuable resource for epidemiologists concerned with the health risks posed by environmental lead.

*Keywords:* Lead isotopes; Stream sediments; Pollution; Mining; Industrial emissions Leaded petrol; Source apportionment; England; Laser ablation-ICP-MS

## 1. Introduction

Using the catchment of the River Wear (Fig. 1), a study was undertaken to examine regional variation in the isotopic composition of lead in stream sediments in order to establish the principal sources of lead pollution in northeast England. Northeast England, like many other industrial and highly populated regions of the UK, is synonymous with coal and has a long history of underground and opencast mining, especially during the 19th and 20th centuries. Geologically the eastern part of the region encompasses the onshore Durham Coalfield and its North Sea offshore extensions. During the same period, the western part of the region, referred to as the North Pennine Orefield, was the UK's main producer of lead and zinc (Dunham 1990). Coal and non-metalliferous mining have now effectively ceased and other industries are in sharp decline. Despite ongoing remediation measures, centuries of intense industrial activity (steel making, ship building, mining, chemical processing) have left a legacy of environmental pollution. Streams and rivers in former lead mining areas have fine-grained sediments that contain more than 600 mg/kg Pb (British Geological Survey, 1996; Macklin et al., 1997; Hudson-Edwards et al., 1997; Lord & Morgan, 2003; Robson & Neal, 1997). Extensive areas in both the orefield and coalfield have soils with 100-300 mg/kg Pb and locally > 400 mg/kg Pb (McGrath & Loveland, 1992). Geochemical data for the city/urban areas of northeast England are less comprehensive but in Newcastle upon Tyne for example (population 250,000), lead in soils frequently exceeds UK Soil Guideline Values for residential (450 mg/kg Pb) and commercial land-use (750 mg/kg Pb) (Rimmer et al., 2006; DEFRA 2005). As yet the implications for public health, especially the concerns of low level lead neurotoxicity in young children **(**Canfield et al., 2003; Lanphear et al., 2005**),** have not been fully evaluated. However, one of the fundamental problems in determining health risk is source apportionment. In the case of lead, lead isotopes have proved extremely valuable in identifying the sources and pathways by which this metal enters the environment (Farmer et al., 1999; Gulson et al., 1994; Hansmann et al., 2000; Labonne et al., 2001; Monna et al., 1997). Potential anthropogenic sources in northeast England (past and present) are numerous; the most important of which include local lead ores, leaded petrol, industrial emissions and coal combustion.

Previous lead isotope studies have focussed almost exclusively on the historically important North Pennine Orefield, either to elucidate the origin of the ores (Moorbath, 1962) or to provide information for archaeological investigations (Rohl, 1996). With the exception of two coal analyses for the Durham Coalfield (Farmer et al., 1999), there are no lead isotope data for areas of the River Wear catchment outside the confines of the North Pennine Orefield. The overall aim of this study therefore was to use high precision lead isotope analysis of stream sediments to identify the principal sources of lead pollution. In creating a lead isotope database, it was hoped the information would be a resource for future epidemiological studies where regional variation might provide a basis for assessing lead body burdens for people living in area.

## 2. Materials and Methods

### *2.1 Study area*

The River Wear has a catchment area of approximately 1300km$^2$ and is one of several major river systems in northeast England (Fig. 1**)**. It comprises (1) a western, upper catchment that includes part of the more extensive North Pennine Orefield (1600km$^2$) and is characterised by substantial pollution from historical lead mining activities, and (2) a multi-sourced, polluted lower catchment that drains the highly populated, heavily industrialised Durham Coalfield to the east.

#### *2.1.1 Upper catchment 'Orefield'*

The upper catchment is underlain by the Carboniferous Limestone Series (limestones, shales, sandstones) and overlying Millstone Grit Series (predominantly sandstones) that rest unconformably upon an older, Lower Palaeozoic granite 'Weardale Granite'. The granite is not exposed at the surface but has been proved by drilling and geophysics (Dunham et al., 1961). A distinctive feature of the orefield is the spatial zoning of ores, with an inner zone of lead, zinc and fluorspar located over the top of the granite (Fig. 1) surrounded by an outer zone of barite and lead (Dunham, 1990). Though disputed evidence exists for Roman mining, the upper Wear valley has been a centre of mining activity for the last 400 years (1665-1985) and accounts for 30% of the total recorded North Pennine Orefield production of 2.9 Mt lead. The ores were worked primarily from sub-vertical mineral veins of which several hundred are recorded. The range of fine-grained, stream sediment lead concentrations is extremely large (60 to 20,000 mg/kg Pb) with most streams having >250 mg/kg Pb which is several times greater than the expected geological background. Typical regional background concentrations for fine-grained sediment in streams draining unmineralised Carboniferous limestones are <35 mg/kg Pb and ≈100 mg/kg Pb for shales and sandstones (British Geological Survey, 1993, 1996).

*2.1.2 Lower catchment 'Coalfield'*

Downstream, the lower catchment is underlain by the Coal Measures; a thick sequence of shales, sandstones and coal seams that lie stratigraphically above the Carboniferous lithologies referred to above. This is the Durham Coalfield *sensu stricto*. As in the upper catchment, centuries of mining have left their environmental scar. Fine-grained stream sediment values range from ~60 to ~600 mg/kg Pb. However, in contrast to the highly variable lead concentrations in streams draining the orefield, there is a more even but nevertheless significantly elevated level of 100-200 mg/kg Pb in streams across most of the coalfield. Only in the relatively unworked, western fringe of the Durham Coalfield, where industrial activity has been least, is there a preponderance of streams with values <90 mg/kg Pb. In the absence of other evidence, the least contaminated streams are taken to be a good approximation of the regional lead background. The regional scale distribution of streams with fine-grained sediment containing 100-220mg/kg Pb is consistent with the concept of diffuse anthropogenic pollution (D'Arcy et al., 2000).

*2.2 Samples*

Use was made of 118 archived stream sediment samples collected from low order streams by the British Geological Survey during 1986-88 (British Geological Survey, 1996) and supplemented by 27 sediment samples (this study 1999-2001) from the main channel of the River Wear (Fig. 2; Table 1). Low order stream sediments (i.e. the fine-grained, <150 μm size clay and fine silt fractions) have the advantage over soil samples in averaging the lead over a much greater area. They comprise a well-mixed composite of eroded soil, weathered bedrock and chemical precipitates and, although the sampled area may vary from stream to stream, they tend to minimise the influence of very localised soil anomalies. The sampling methods used were those described by Plant (1971) and Plant and Moore (1979), and subsequently incorporated into the international standard for geochemical mapping (Darnley et al., 1995). Stream sediments collected using these protocols were considered satisfactory for revealing regional scale variation without recourse to a high-density soil survey involving 1000s samples. Moreover, the density of archived low order stream sediments was considered robust enough to detect important within-catchment variation. For completeness, the sampled area was extended to include adjacent parts of the Tyne and Tees river catchments. Samples from the main channel of the River Wear were taken by sediment suction pump (Lord & Morgan, 2003). This method was adopted because it facilitates the sampling of wider, more slowly flowing rivers in water depths up to 1m. It does not however take into account sediment accumulation rates, so the time span of contamination (years or decades) represented by the sample is unknown. In faster flowing, low order streams, the accumulation of fine-grained sediment is minimal and subject to shorter time scale changes. No attempt was made to take water samples or to recover suspended particulate matter for analysis.

To validate the isotopic composition of lead entering the streams from abandoned lead mines, 44 galena samples (lead ores) were collected from individual, well-documented, mineral veins in the North Pennine Orefield (Fig. 2; Table 1). Sampling was based on geological criteria relating to vein orientation and the relative age of mineral deposition (Dunham, 1990) to give a broader perspective on isotopic variation than had been possible from previous studies (Moorbath, 1962; Rohl, 1996).

To supplement the limited coal data (Farmer et al., 1999) and provide better control on the lead isotope composition of coal waste, use was made of unpublished data for coal and shale samples from the Durham Coalfield (Pearson & Worrall pers.comm.).

The study benefited greatly in having total lead concentrations for all of the archived samples prior to isotopic analysis (British Geological Survey, 1996). Chemical analysis of the additional River Wear samples was carried out at the University of Sunderland and at a commercial laboratory (ACME, Canada).

## 2.3 Analytical procedures

High precision lead isotope analysis was performed by laser ablation, multi-collector, ICP mass spectrometry (LA-MC-ICP-MS). The sediment samples were prepared as 1cm diameter pressed powder discs using a styrene-wax binder (van Zyl, 1982). This provided a flat, even surface for laser ablation with the minimum degree of spalling. Ablation was carried out using a one-pass raster pattern over an area of $25 mm^2$ and a spot size of 300µm. For the galenas, ablation was carried out on fresh, cleavage fragments using the lowest possible laser fluence and a spot size of 30µm. To reduce fluctuations in ion intensities and signal spikes caused by variable degrees of vapourisation, a particle trap was mounted between the ablation cell and ICP.

Isotope ratio analysis was carried out using either a VG Elemental Axiom or P54 multi-collector ICP MS linked to a New Wave Research Microprobe II, 266 nm Nd:YAG laser ablation system. Instrumental mass bias was determined by simultaneous aspiration of a thallium solution through the laser cell (Longerich et al., 1987; Ketterer et al., 1991). Isobaric interference of $^{204}$Hg on $^{204}$Pb was corrected by reference to $^{202}$Hg.

For each analytical session (by day), multiple analyses of the Standard Reference Material NBS981 (in solution) were used to monitor instrument performance and allow normalization to internationally accepted values (Thirwell, 2002). Repeatability and overall uncertainty were assessed by laser analysis of an in-house reference material (urban soil: 407 mg/kg Pb) before and after each analytical session. Total, combined, overall uncertainties (2σ %) for the period of analysis (2001-2005) after quadratic error propagation are as follows: $^{206}$Pb/$^{204}$Pb 0.113%; $^{207}$Pb/$^{204}$Pb 0.087%; $^{208}$Pb/$^{204}$Pb 0.095%; $^{207}$Pb/$^{206}$Pb 0.070%; $^{208}$Pb/$^{206}$Pb 0.033%.

Analyses provided by Pearson & Worrall (pers. comm.) were acquired using a Nu Plasma MC-ICP mass spectrometer in solution mode. All analyses were corrected for mass bias and Hg isobaric interference as described above, and normalized to NBS981 (Todt et al., 1996). Overall uncertainties (2σ %) for the period of analysis (May 1999-January 2000) are estimated as follows: $^{206}Pb/^{204}Pb$ 0.030%; $^{207}Pb/^{204}Pb$ 0.032%; $^{208}Pb/^{204}/Pb$ 0.032%.

## 3. Results and Discussion

Lead isotope analyses for the stream sediments and galenas are summarised in Table 1 and shown in Figs. 3 to 7. Also included in Table 1 are the unpublished data (Pearson & Worrall) for coal and shale samples from northeast England. Throughout the following discussion the terms 'upper catchment and Orefield' and 'lower catchment and Coalfield' are used synonymously. Absolute uncertainty errors (2 sigma) on the isotope ratios shown in Figures 3 to 7 are ±0.0005 for $^{207}Pb/^{206}/Pb$ and ±0.0006 for $^{208}Pb/^{206}/Pb$.

### *3.1 Spatial Variation*

The foremost feature of the stream sediment data is the strong lead isotope contrast between the Orefield and Coalfield (Fig. 3). Over the Orefield, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios range from 2.0744 to 2.0954 and 0.8413 to 0.8554 respectively, thereafter increasing to 2.1397 and 0.8896 over the Coalfield. Given the large range of lead concentrations considered, this pattern is independent of lead concentration and represents a true picture of regional variation.

A second, equally significant feature is the degree of variation seen within the upper catchment. Here, the lowest $^{208}Pb/^{206}Pb$ ratios (<2.083) are located within the inner zone of the North Pennine Orefield, directly above the top of the concealed Weardale Granite (see Fig. 1). Streams in the Rookhope and Stanhope valleys, in particular, define a cluster of noticeably low values. Outside this cluster, the stream sediments have higher $^{208}Pb/^{206}Pb$ ratios typical of the outer zones of the North Pennine Orefield. Within the outer zone, samples from the lower section of the

Bollihope valley, immediately downstream of mining activity, show a marked enrichment in $^{208}Pb$ and have unusually high $^{208}Pb/^{206}Pb$ ratios >2.091. In both cases (Rookhope and Bollihope), the anomalously low and high $^{208}Pb/^{206}Pb$ ratios are a direct measure of the locally mined lead ores. Throughout the orefield there is excellent isotopic agreement between stream sediments and lead ores and, where mines have worked several veins with different isotope compositions, the sediments provide an average value (see section 3.2 for discussion). Because the upper catchment is wholly within the North Pennine Orefield, no stream can be regarded as being outside the influence of mineralization and hence the natural ‘geogenic’ background could not be unequivocally established.

Whilst considered outside the scope of this paper, the isotope data make an important contribution to theories concerning the origin of the lead ores. The apparent zonation noted above is in accordance with current metallogenic models for the North Pennine Orefield (Cann & Banks, 2001; Bouch et al., 2006). These invoke a channelling of lead-rich fluids (originating in adjacent sedimentary basins) inwards and upwards through the Weardale Granite. The development of galenas with low $^{208}Pb/^{206}Pb$ ratios in the upper Wear valley adds support to the assertion that the mineralizing fluids responsible for the deposition of these ores have leached part of their lead from the high U-Th, radiogenic, sub-surface granite (Brown et al., 1980; Bouch et al., 2006).

For the Coalfield, within-catchment variation ($^{208}Pb/^{206}Pb$ 2.0856-2.1397, $^{207}Pb/^{206}Pb$ 0.8554-0.8896) shows no obvious spatial correlation with opencast coal sites or the extensive spoil tips from underground coal workings. Many stream sediments have extremely high $^{208}Pb/^{206}Pb$ ratios (>2.100) that fall well outside the regional background (~2.088-2.098) as estimated for samples with lead concentrations <90mg/kg Pb, for streams on the western fringes of the Coalfield where coal extraction has been least. Neither does the range of $^{208}Pb/^{206}Pb$ ratios for stream sediments overlap with the range of $^{208}Pb/^{206}Pb$ ratios (2.058-2.085; Table 1) determined for Carboniferous coals or shales from NE England (Farmer et al., 1999; Pearson & Worrall pers.comm.). Thus the elevated levels of lead are not solely a function of the fluvial dispersal of finely ground coal waste from abandoned mine sites, and implies one or more additional anthropogenic sources. Given the diffuse nature of the regional distribution of lead, the most likely source of pollution is atmospheric deposition (dry and wet aerosols) linked to industrial lead emissions and petrol lead, but also including a contribution of lead from centuries of coal combustion. A more detailed discussion of source apportionment is presented below.

*3.2 River Wear Pollution Profile*

Variation in the lead content of the River Wear sediments (Fig. 4, Table 1), from the highest sampling point on the river at Wearhead (Site 1) to the tidal reach near Sunderland (Site 27), a distance of 87km, suggests an exponential decrease in concentration due to the dilution of lead-rich mine waste by relatively uncontaminated sediment. At Wearhead (Site 1), mine waste from a large cluster of abandoned mines and associated smelt mills charges the river sediment with more than 6000 mg/kg Pb. Within 7 km downstream (Site 5), the lead concentration has fallen to less than 1000 mg/kg Pb. Such a sharp fall in concentration is attributed to a combination of dilution and the density settling of finely milled lead ore that gives exceptionally high levels of lead in the <150 μm sediment fraction at Sites 1 and 2. From Site 5 to Site 9, the Wear is joined by two major tributaries; Rookhope Burn and Stanhope Burn. Both valleys were the loci of extensive mining and smelting, and their contaminated sediment input raises the lead concentration in the main channel of the River Wear to >3500 mg/kg Pb. After an initial rapid fall in concentration downstream from Site 9, similar to that shown at Site 1, the lead concentration remains fairly constant at about 1200-1500 mg/kg Pb for a further 18km until Site 14. Thereafter there is a progressive decrease in concentration as the river flows through the Coalfield to a value of about 350 mg/kg Pb near the tidal reach (Site 27).

Combining the isotope and total lead data, important detail is revealed concerning the effect of specific tributaries on the source and level of lead pollution in the River Wear. Fig. 4 shows the co-variation in lead concentration and $^{208}Pb/^{206}Pb$ ratios for five consecutive river sections.

*Section I (Sites 1-5: 0-7km)*

Site 1, as mentioned above, reflects an intense level of pollution from a plexus of veins and mines around the old processing plant and waste dumps at Kilhope, where it is estimated that more than 60,000 tonnes of lead concentrate were treated (Dunham, 1990). The isotopic composition ($^{208}Pb/^{206}Pb$ 2.0865) is characteristic of the outer zone of the orefield in having a high $^{208}Pb/^{206}Pb$ ratio. Downstream from Site 1, the lead concentration continues to decrease as a result of sediment dilution but the isotope composition remains fairly constant. Thus Site 5 ($^{208}Pb/^{206}Pb$ 2.0834) may be regarded as the end member isotope component of lead pollution in the River Wear from mines in the western, outer zone of the orefield.

*Section II (Sites 6-9: 7-15km)*

Between Sites 6 and 9, although there is a marked rise in lead concentration due to fresh inputs of mine waste from the Rookhope and Stanhope valleys, there is a steady fall in the $^{208}Pb/^{206}Pb$ ratio. This is a result of the mixing between lead, as measured at Site 5 ($^{208}Pb/^{206}Pb$ 2.0834), with lead from mines in the inner zone of the orefield characterised by lower $^{208}Pb/^{206}Pb$ ratios. The mean ratio for mine waste released into the Rookhope and Stanhope streams is 2.0783 (Table 1, samples 323486, 323461, Rh8 and Rh9). Using these two end member components, lead in the River Wear at Site 10 (1610 mg/kg Pb) comprises about 50% lead from mines in the Rookhope and Stanhope valleys.

*Section III (Sites 10-14: 15-28km)*

Between Sites 10 and 11 the Wear is joined by Bollihope Beck; a stream that brings in additional lead from an important cluster of mines close to its confluence with the River Wear. The mean Bollihope component ($^{208}Pb/^{206}Pb$ 2.0920) as defined by samples BB2 and BB3 (Table 1) mixes with lead in the Wear to raise the $^{208}Pb/^{206}Pb$ ratio to 2.0828 (Site 11). Applying similar reasoning, the Bollihope mine waste at this point on the River Wear constitutes ~18% of the total lead (1226 mg/kg Pb). Below Site 11 there is no further input of anthropogenic lead from the North Pennine orefield and the $^{208}Pb/^{206}Pb$ ratio can be used as the isotopic end member component of mine-related pollution in the River Wear before it enters the Coalfield. Any changes further downstream are due to other anthropogenic sources. For the next 6.6km until Site 14, the $^{208}Pb/^{206}Pb$ ratio remains relatively unchanged.

*Section IV (Sites 15-23: 28-65km)*

From Site 15 to Site 22, the sediment lead concentration slowly decreases to about 700 mg/kg Pb. This is accompanied however by a steady increase in the $^{208}Pb/^{206}Pb$ ratio to approximately 2.0845. If this were due to dilution by relatively uncontaminated, local sediments (i.e. derived from the weathering of Coal Measure shales and sandstones), one would have expected the $^{208}Pb/^{206}Pb$ ratio to remain fairly constant. This is not observed and suggests an increasing contribution from another source having a higher $^{208}Pb/^{206}Pb$ ratio. Given the regional pattern of isotopic variation shown by streams in the lower catchment, it is thought the $^{208}Pb/^{206}Pb$ increase is due to a steady input of diffuse anthropogenic pollution from tributaries throughout the abandoned Coalfield.

*Section V (Sites 24-27: 65-87km)*

For the final section of the Wear, there is a very sudden rise in the $^{208}Pb/^{206}Pb$ ratio to 2.0882 (Site 24), followed by an equally sharp fall (Site 27) to a value similar to that of Site 23. The rise occurs as the River Wear enters the city of Durham. This could be due to either (1) an increased input of diffuse pollution or, (2) contamination by locally high levels of tetra-ethyl lead (TEL). TEL, the principal lead additive to UK petrol prior to it being phased out in the late 1990s, had an average $^{208}Pb/^{206}Pb$ composition of ~2.189 for the period 1989-91 (based on $^{207}Pb/^{206}Pb$ data from Sugden et al. (1993) recalculated according Haack et al. (2004) ). Only 2-3 % of this lead would be needed to raise the $^{208}Pb/^{206}Pb$ ratio to 2.088. Since the rate of river sedimentation is unknown, older inputs of TEL may also be present. However, taking an even lower $^{208}Pb/^{206}Pb$ ratio of ~2.16 for French-UK petrol for the period 1980-87 (based on $^{207}Pb/^{206}Pb$ data from Veron et al. (1999) recalculated according Haack et al. (2004)), the same shift is evident. During this earlier period, the European manufacturer of TEL (Octel Co.) supplied both the UK and French markets (Monna et al., 1997). By contrast, in all cases, at least 10-20% of anthropogenic lead with a $^{208}Pb/^{206}Pb$ range of ~2.10-2.12, typical of the Coalfield, would be required to create the same isotopic shift. Whilst it is not possible to discriminate between these two hypotheses, a higher petrol lead component seems most probable in that it does not require a major change in sediment influx.

*3.3 Source Apportionment*

The following interpretation is based on information for the Wear catchment (this study), unpublished data for coal and shale from the Durham Coalfield (pers.comm. Pearson & Worrall), data for North Pennine lead ores (Rohl, 1996), UK coals (Farmer et al., 1999), peat and freshwater sediments (Farmer et al., 1997), industrial/urban aerosols in the UK and Western Europe (Sugden et al., 1993; Monna et al., 1997; Bollhöfer et al., 1999; Veron et al., 1999; Farmer et al., 2002; Haack et al., 2003; Noble et al., 2007) and UK leaded petrol (Sugden et al., 1993; Monna et al., 1997; Veron et al., 1999).

*3.3.1 Orefield*

Fig. 5 shows the co-variation in $^{208}$Pb/$^{206}$/Pb and $^{207}$Pb/$^{206}$Pb for stream sediments and galenas (lead ores) in the upper Wear catchment 'Orefield'. It is evident that pollution of upper catchment streams is determined by the discharge of lead-rich waste from abandoned mines. The degree of correspondence in $^{208}$Pb/$^{206}$/Pb, $^{207}$Pb/$^{206}$Pb ratios between stream sediments and galenas is very high and there is no apparent indication of mixing with other sources. Theoretically one would expect to detect, albeit minor, a component of airborne pollution (petrol lead and/or coal lead) as observed by Farmer et al. (2002) for localities in Scotland or a component of global anthropogenic lead (Boutron et al., 1994). This is not observed. In the absence of such evidence we conclude that the archival stream sediments for the period 1986-88 only record the dominant North Pennine lead ore component. Weaker anthropogenic sources, if present, are masked. To detect and quantify the contribution of airborne pollution to the upper Wear catchment it will be necessary to use other media such as herbage, peat or undisturbed lake sediments. Galena samples with $^{208}$Pb/$^{206}$/Pb ratios <2.070 are from mineralised veins intersected by the Weardale borehole (Dunham et al., 1961). Although of geological interest, these veins were never economically exploited. Thus their $^{206}$Pb-enriched isotopic signature is not reflected in the mine waste-polluted stream sediments of Rookhope Beck or other streams in the upper

Weardale valley that sit topographically above the sub-surface Weardale Granite (Fig. 1). With regard to the extent and significance of mine-related pollution, comparison of Figs. 4 and 5 clearly indicates that the environmental lead loadings of present day river sediments in the lower reaches of the River Wear (main channel) are dominated by discharges from abandoned mines in the North Pennine Orefield; up to 70km upstream.

*3.3.2 Coalfield*

Fig. 6 shows the corresponding co-variation in $^{208}Pb/^{206}/Pb$ and $^{207}Pb/^{206}Pb$ for stream sediments in the lower Wear catchment 'Coalfield'. Previous work by Farmer et al. (1997, 1999, 2002) has shown that notwithstanding the withdrawal of leaded petrol and decreased coal consumption, the contribution from coal continues to affect the content and $^{207}Pb/^{206}Pb$ ratios of atmospheric lead in Scotland and, by inference, the rest of the UK. Even allowing for scatter in the coal-shale data, streams in the Coalfield are not dominated by a coal lead component. Instead, excluding those few measurements that fall within the regional background ($^{208}Pb/^{206}/Pb$ 2.088-2098), they define a linear array ($^{208}Pb/^{206}/Pb$ ~2.100-2.1398; $^{207}Pb/^{206}Pb$ ~0.8265-0.8896) that shows very little overlap with representative samples of coal and shale from the Durham Coalfield.

The Coalfield array (Fig 7) does however extend to higher $^{208}Pb/^{206}/Pb$, $^{207}Pb/^{206}Pb$ ratios indicative of UK leaded petrol and includes the field for UK airborne particulate matter (Southampton and London) reported by Monna et al. (1997) for 1994-96 ($^{208}Pb/^{206}/Pb$ 2.100-2.175, $^{207}Pb/^{206}Pb$ 0.865-0.911) and Veron et al. (1999) for 1968-96 ($^{207}Pb/^{206}Pb$ ~0.882-0.907). Similar ratios have been found for present day airborne pollution in Germany, Japan and the UK (Monna et al., 1997; Noble et al., 2007). Such pollution is interpreted as a mixture of industrial lead, petrol lead and lead from the combustion of coal. As noted by Monna et al. (1997), the trend to lower ratios in the 1994-96 data probably reflects the withdrawal of leaded petrol allowing industrial sources to become more evident.

Discriminating between these three anthropogenic sources is far from easy. The problem is especially difficult for industrial lead for which there is no unique end-member isotope composition and which varies from region to region depending upon local inputs. Data for industrial emissions, specifically for northeast England, are lacking but by comparability with airborne pollution in southern England for 1994-96 (Monna et al., 1997; Veron et al., 1999), industrial emissions in northern France for 1993-94 (Monna et al., 1997) and atmospheric deposition in Scotland for 1980-89 using an archival moss record (Farmer et al., 2002), it is reasonable to infer a similar range of values.

With regard to the petrol lead component, Fig. 7 shows the composition of UK leaded petrol for 1994-95 (Monna et al., 1997), the composition for 1989-91 (Sugden et al., 1993) and, for reference, the average of French-UK petrol for 1980-87 (Veron et al., 1999). In the case of data from Sugden et al. and Veron et al., $^{208}$Pb/$^{206}$Pb ratios were estimated from measured $^{207}$Pb/$^{206}$Pb ratios using parameters for the 'European Leaded Gasolines' regression given by Haack et al. (2004). For the period of interest therefore, UK leaded petrol lies on a linear extension of the Coalfield array at higher $^{208}$Pb/$^{206}$Pb, $^{207}$Pb/$^{206}$Pb ratios.

The coal combustion end-member component is similarly hard to define. Individual UK coalfields show significant variation in the lead isotope composition of coal (Farmer et al., 1999).  This complicates any attempt to assign a degree of certainty to the isotopic composition of resultant pollution. The data reported by Pearson and Worrall (this study) are the most comprehensive to date for the Durham Coalfield but do not account for the more radiogenic nature (i.e. higher ratios) of the stream sediment samples. We infer therefore that any contribution from coal combustion in the stream sediments is isotopically masked by contributions from industrial and petrol lead. As a consequence, the contribution of lead from the commercial and domestic burning of coal is difficult to estimate.

There remains the question of the geogenic component and its contribution to total lead isotope composition. Fine grained stream sediment is the product of soil erosion and surface weathering and will always carry a finite component of natural lead. In the case of the lower Wear catchment, the regional background provides an approximation of natural lead and, based on streams in areas with little history of coal mining, is unlikely to exceed 100mg/kg Pb and have a $^{208}$Pb/$^{206}$/Pb ratio $<2.100$ and $^{207}$Pb/$^{206}$Pb ratio $<0.865$.

The best interpretation is that the Coalfield array is a mixing array between a coal lead component, comprising coal combustion lead and regional background lead, and a petrol lead component that includes an inferred but unknown proportion of industrial lead. The exact amount of petrol lead in any one stream sediment sample will depend upon many factors, not least, the proximity of the local catchment to major roads or urban centres. Thus, elevated levels of lead in the lower Wear catchment are considered to be a mixture of geogenic lead and three principal components of anthropogenic lead (petrol lead, industrial lead, coal combustion lead).

## 4. Conclusions

The study successfully demonstrates that stream sediments are a very effective sampling medium for determining regional variation in the isotope composition of environmental lead. As a result of differences in industrial activity, the upper and lower catchments of the River Wear are isotopically distinctive, allowing different sources of anthropogenic pollution to be identified and characterised. As expected, pollution in the upper catchment is controlled and dominated by waste from abandoned mines and smelter sites in the North Pennine Orefield. Furthermore, within-catchment variation due to natural variation in the isotope composition of the lead ores, allows one to trace the fluvial dispersal of lead from specific mines or groups of mines into the River Wear. In the lower catchment, the dispersal of finely divided coal/shale waste from abandoned coal workings does not appear to be a major source of lead pollution, either in terms of total concentration or isotope composition. Lead levels across the Durham Coalfield are lower than those of the upper catchment and display a more uniform, regional distribution. However they are significantly elevated above background levels, indicating a major source of anthropogenic pollution. Isotope ratios suggest that the pollution, as represented by the archival stream sediments, is dominated by variable amounts of petrol lead and lead from diverse industrial emissions. The presence of both components is attributed to the deposition of airborne particulate matter over extended periods of time. Because of their dominance they tend to mask the contribution of other anthropogenic sources. Since the stream sediment samples (as distinct from the River Wear samples) were collected prior to the phasing out of leaded petrol, the data must be interpreted cautiously with respect to present day lead loadings. Nevertheless, the close isotopic agreement between 1999-2001 and pre-1990 sediment samples provides compelling evidence that contamination of the River Wear by lead mining waste continues to pose an environmental problem. Even at its tidal reach, the river carries an overwhelming lead isotope signature of the North Pennine Orefield. Given the similarity of northeast England to other regions of the world with long histories of coal and non-metalliferous mining, there is considerable scope for extending this type of work. The pollution of rivers by mine waste is a worldwide problem and source apportionment is an important factor in achieving effective remediation. Finally, it is hoped the data will stimulate more informed discussion by health authorities concerning lead in the environment and the use of stable lead isotopes in epidemiological studies.

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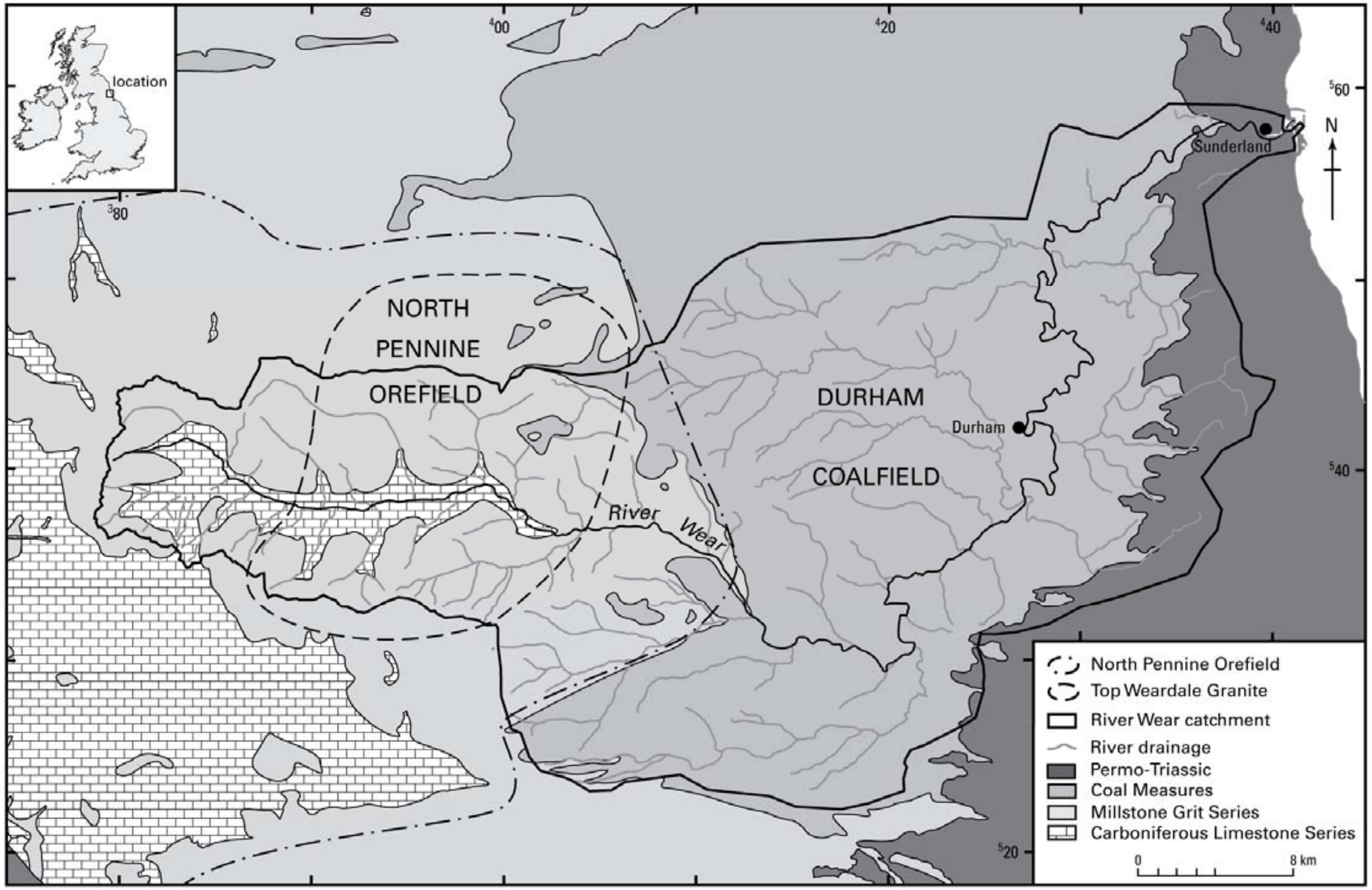



Figure 1 STOTEN-D-08-01278R1

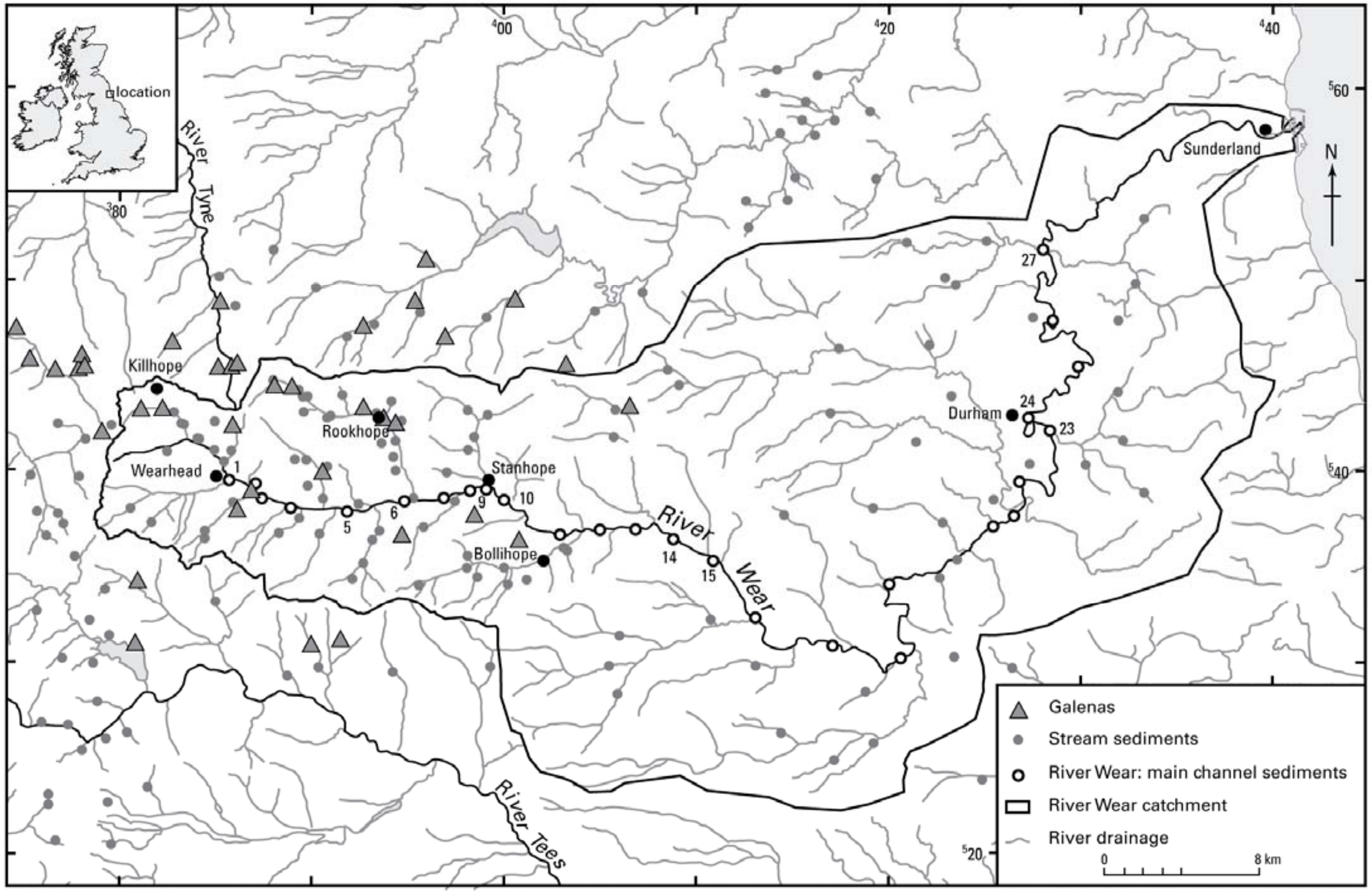



Figure 2  STOTEN-D-08-01278R1

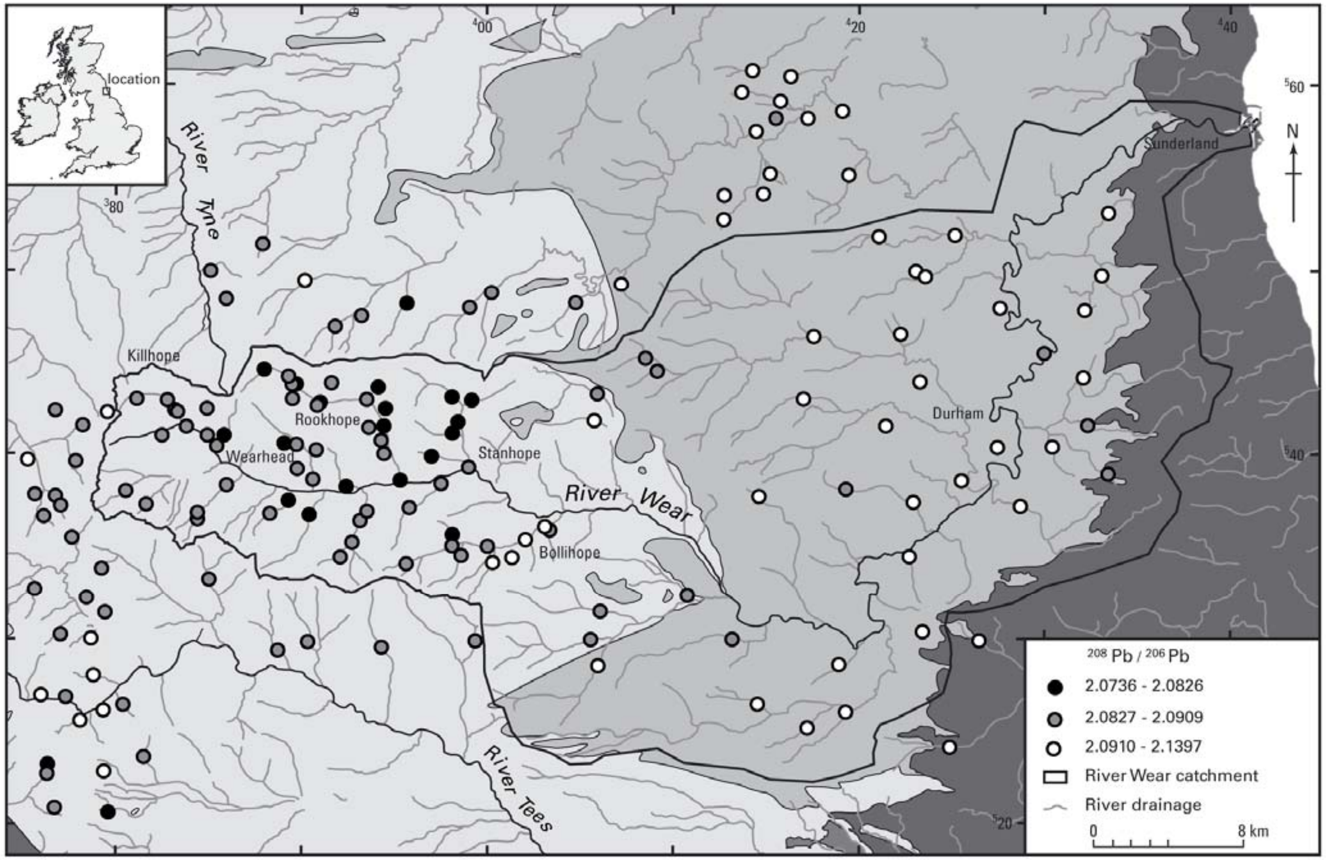
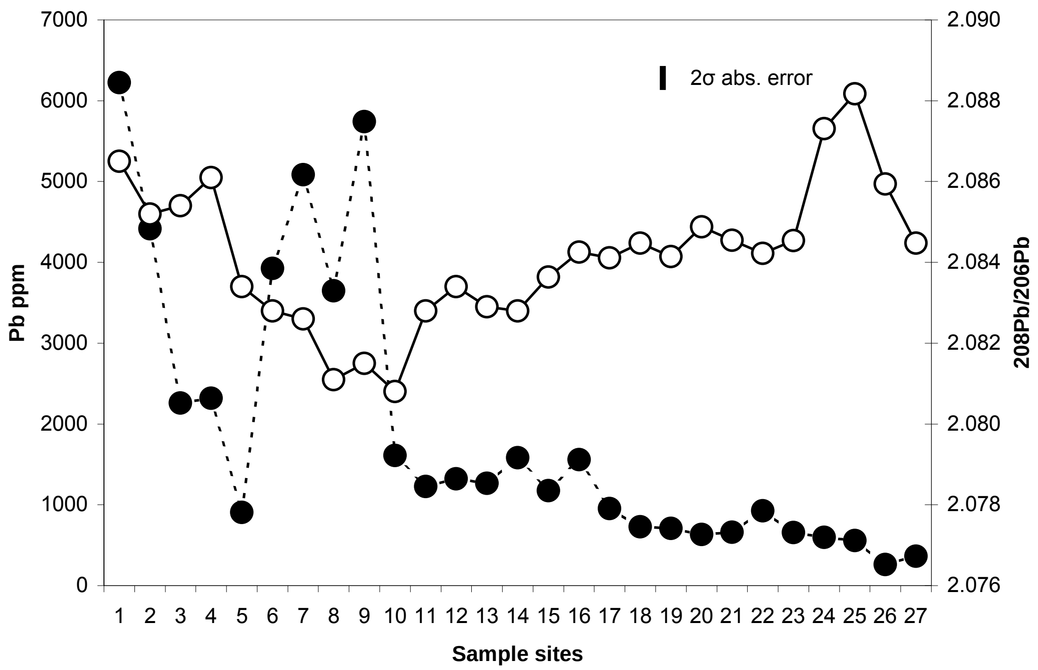



Figure 3 STOTEN-D-08-01278R1

Figure 4  STOTEN-D-08-01278R1



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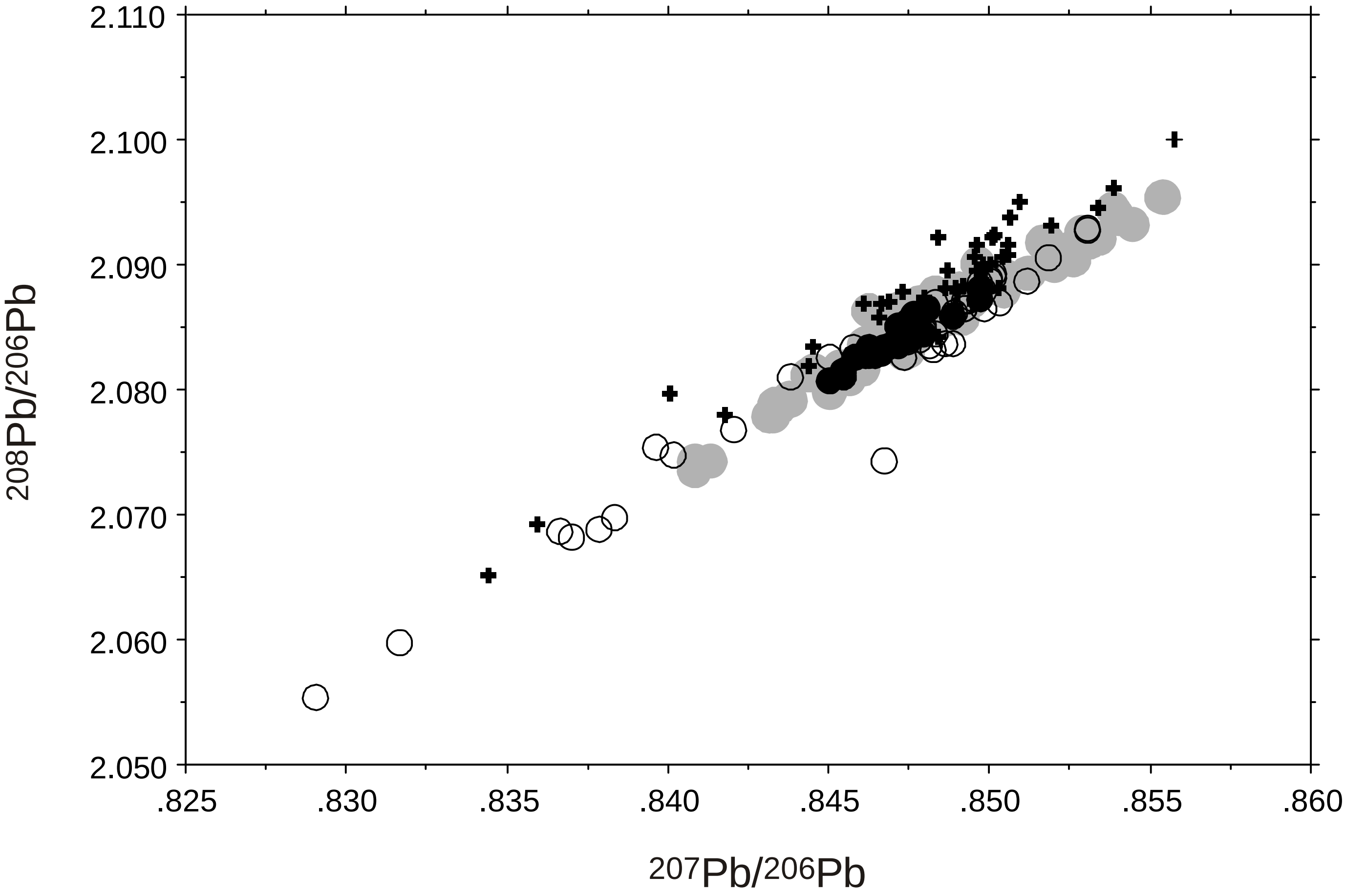

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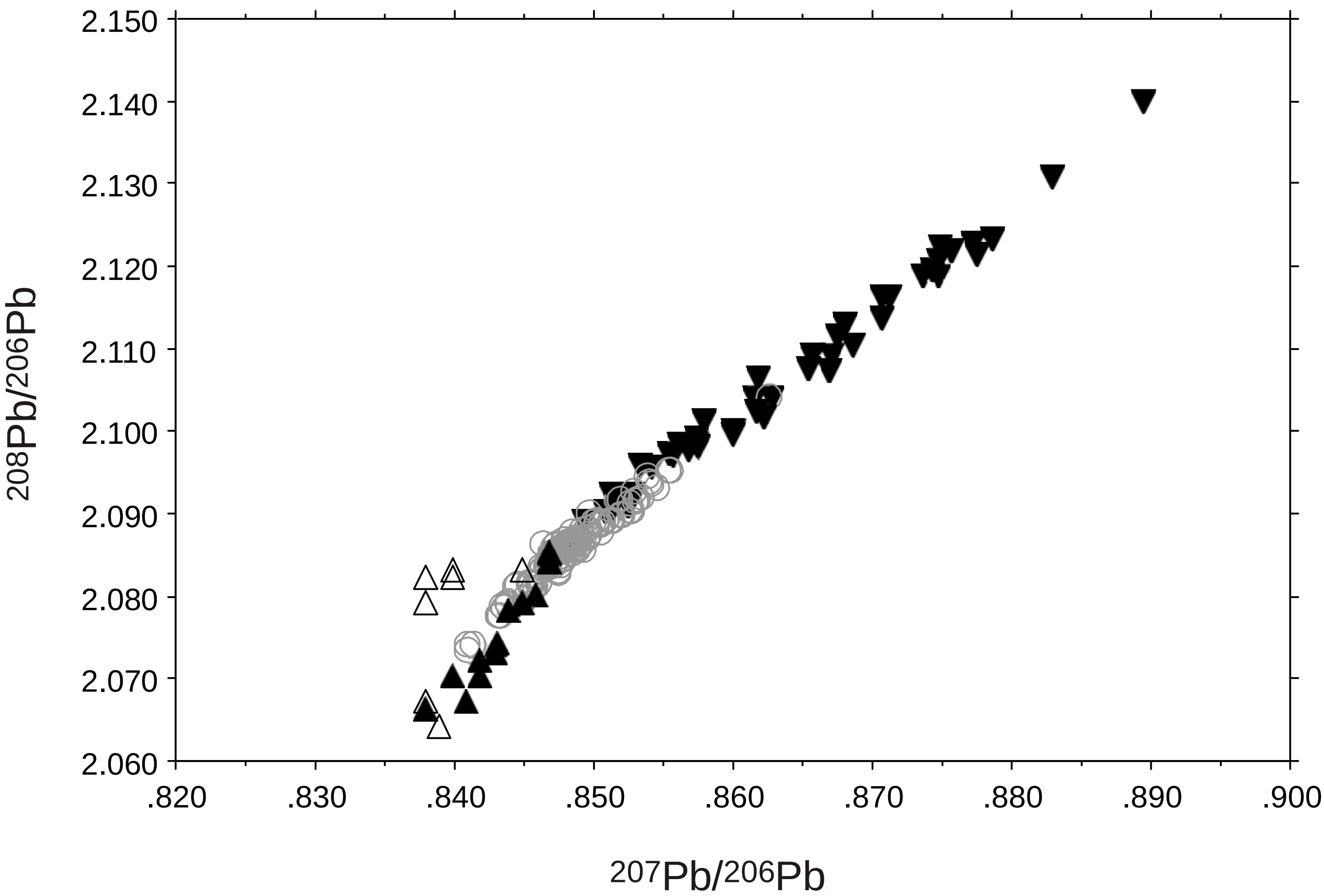

Figure 7  STOTEN-D-08-01278R1

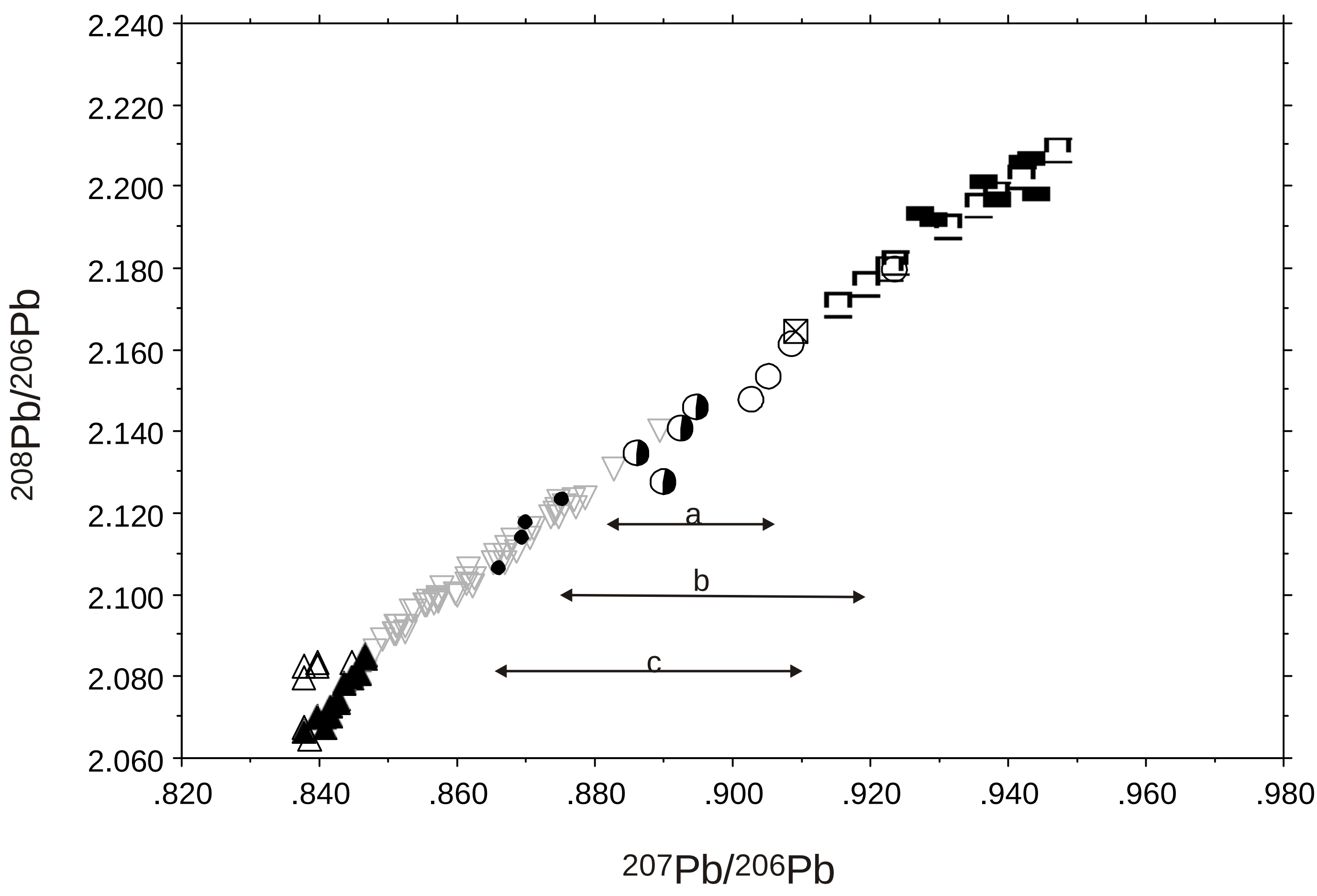

**Figure Captions and Table STOTEN-D-08-01278R1**

Fig. 1 Simplified geological map of northeast England showing the River Wear catchment. The lower catchment 'Coalfield' is defined as that area underlain by Coal Measures (Durham Coalfield). The upper catchment 'Orefield' is underlain by the Millstone Grit and Carboniferous Limestone Series and occupies part of the more extensive North Pennine Orefield. Also shown is the sub-surface top of the Weardale Granite that delimits the central 'inner' zone of the orefield (see text for details).

Fig. 2 River Wear catchment showing the location of sediment sampling points for 1st and 2nd order streams, lead ores (galenas) and sediments collected from the main channel of the River Wear (numbered 1-27). Sample points are also shown for sediments and lead ores collected in the contiguous catchments of the Rivers Tyne and Tees.

Fig. 3 Regional variation in $^{208}Pb/^{206}Pb$ for stream sediments from 1st and 2nd order streams with respect to the upper and lower catchments of the River Wear (excluding data for the River Wear main channel samples). Geological legend as for Fig. 1. Note the anomalously high ratios for the Bollihope area and clustering of very low ratios in the Stanhope and Rookhope valley areas (see text for details).

Fig. 4 Profile along the River Wear showing co-variation in lead concentration and $^{208}Pb/^{206}Pb$ ratios for sediments taken from the main river channel. Numbers 1 to 27 along the ordinal axis are the sediment sample sites shown in Fig.2 and described in Table 1. Site 1 represents the highest point on the Wear and Site 27 the lowest point on the Wear - a total distance of 86.5km. Ordinal axis is not linear. Filled circles refer to lead concentrations; open circles to $^{208}Pb/^{206}Pb$ ratios. Vertical error bar indicates the 2σ absolute uncertainty assigned to the $^{208}Pb/^{206}Pb$ measurements.

Fig. 5 $^{208}Pb/^{206}/Pb$-$^{207}Pb/^{206}Pb$ co-variation for archival stream sediments (1986-88) and lead ores from the upper catchment of the River Wear 'Orefield' indicating their close relationship to more recent sediment samples (1999-2001) taken from the main channel of the River Wear. Also shown are the data of Rohl (1996) for North Pennine galenas (lead ores). 2σ analytical uncertainties for $^{208}Pb/^{206}/Pb$ and $^{207}Pb/^{206}Pb$ are 0.033% and 0.070% respectively (grey filled circles stream sediments; black filled circles recent River Wear sediments; open circles lead ores; crosses galenas (Rohl 1996).

Fig. 6 $^{208}Pb/^{206}/Pb$-$^{207}Pb/^{206}Pb$ co-variation for archival stream sediments (1986-88) from the lower catchment of the River Wear 'Coalfield'. Also shown, for reference, are data for the upper catchment sediments and the lead isotope composition of Carboniferous coals and shales (data from Pearson & Worrall pers.comm.). See text for 2σ analytical uncertainties (inverted filled triangles lower catchment stream sediments; grey open circles upper catchment stream sediments; filled triangles coal (this study and Farmer et al., 1999); open triangles shale).

Fig. 7 $^{208}Pb/^{206}/Pb$-$^{207}Pb/^{206}Pb$ co-variation showing the relationships between stream sediments for the lower catchment of the River Wear 'Coalfield' (1986-88), coal and shale from the Durham Coalfield, UK leaded petrol and UK airborne particulates (inverted open triangles stream sediments; filled triangles coal (this study and Farmer et al., 1999); open triangles shale; solid squares petrol England 1994 (Monna et al., 1997); open squares petrol Scotland 1981-91 (Sugden et al., 1993); crossed square mean UK-French petrol 1980-87 (Veron et al., 1999); open circles airborne particulates Scotland 1994-95 (Bollhöfer et al., 1999), half filled circles airborne particulates England 1996-98 (Veron et al., 1999; Bollhöfer et al., 1999); small filled circles industrial emissions France 1993-94 (Monna et al., 1997). Bar ‘a’ is the range of UK airborne particulates 1968-96 (Veron et al., 1999). Bar ‘b’ is the range of airborne particulates for Scotland 1980-89 using archival mosses (Farmer et al., 2002). Bar ‘c’ is the range of airborne particulates for England 1994-96 (Monna et al., 1997). All ranges are with respect to $^{207}Pb/^{206}Pb$.

Table 1 Location and lead isotope composition of samples from the River Wear catchment and adjacent areas, Northern England.

**Table 1 STOTEN-D-08-01278R1**

Table 1. Location and lead isotope composition of samples from the River Wear catchment and adjacent areas, Northern England.

**Sediments: 1st and 2nd order streams**

| Sample no | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{206}Pb$ | $^{208}Pb/^{206}Pb$ | Pb ppm | Grid Ref | Eastings | Northings | Regional Location |
|---|---|---|---|---|---|---|---|---|---|---|
| 300012 | 17.9608 | 15.5501 | 37.8764 | 0.8658 | 2.1091 | 139 | NZ | 425150 | 551900 | Coalfield |
| 300033 | 17.7578 | 15.5361 | 37.6210 | 0.8749 | 2.1185 | 169 | NZ | 423230 | 543910 | Coalfield |
| 300048 | 18.1552 | 15.5699 | 38.0976 | 0.8575 | 2.0983 | 93 | NZ | 422170 | 546500 | Coalfield |
| 300073 | 18.3576 | 15.5949 | 38.3454 | 0.8495 | 2.0888 | 112 | NZ | 415500 | 558200 | Coalfield |
| 300077 | 18.0431 | 15.5193 | 37.8878 | 0.8601 | 2.0998 | 104 | NZ | 421400 | 541530 | Coalfield |
| 300087 | 17.8004 | 15.5533 | 37.7095 | 0.8738 | 2.1186 | 393 | NZ | 419400 | 555100 | Coalfield |
| 300088 | 18.0460 | 15.5497 | 37.9641 | 0.8616 | 2.1038 | 190 | NZ | 416990 | 543010 | Coalfield |
| 300092 | 17.8727 | 15.4977 | 37.6929 | 0.8672 | 2.1091 | 78 | NZ | 423520 | 549660 | Coalfield |
| 300093 | 18.2213 | 15.5123 | 38.1123 | 0.8514 | 2.0921 | 99 | NZ | 417510 | 546350 | Coalfield |
| 300101 | 17.6690 | 15.5273 | 37.5159 | 0.8788 | 2.1231 | 179 | NZ | 422990 | 549980 | Coalfield |
| 300111 | 17.9945 | 15.5299 | 37.8564 | 0.8629 | 2.1038 | 108 | NZ | 421060 | 551800 | Coalfield |
| 300112 | 18.1315 | 15.5560 | 38.0998 | 0.8580 | 2.1011 | 124 | NZ | 416300 | 560500 | Coalfield |
| 300118 | 17.7744 | 15.5488 | 37.6878 | 0.8748 | 2.1205 | 255 | NZ | 415700 | 559100 | Coalfield |
| 300136 | 17.8577 | 15.5525 | 37.7814 | 0.8709 | 2.1159 | 169 | NZ | 414200 | 560800 | Coalfield |
| 300142 | 18.0526 | 15.4818 | 37.8737 | 0.8576 | 2.0980 | 156 | NZ | 413600 | 559600 | Coalfield |
| 300146 | 18.2218 | 15.5942 | 38.2071 | 0.8558 | 2.0969 | 227 | NZ | 414800 | 554100 | Coalfield |
| 300154 | 17.7859 | 15.5537 | 37.6942 | 0.8745 | 2.1194 | 196 | NZ | 427570 | 547930 | Coalfield |
| 300185 | 17.8667 | 15.5675 | 37.8061 | 0.8714 | 2.1160 | 236 | NZ | 415200 | 555200 | Coalfield |
| 300224 | 18.2060 | 15.5764 | 38.1734 | 0.8556 | 2.0970 | 112 | NZ | 412700 | 554000 | Coalfield |
| 300226 | 17.7281 | 15.5529 | 37.6284 | 0.8773 | 2.1226 | 164 | NZ | 419100 | 558600 | Coalfield |
| 300234 | 17.4550 | 15.5254 | 37.3497 | 0.8896 | 2.1398 | 163 | NZ | 416200 | 557400 | Coalfield |
| 300255 | 18.2735 | 15.5955 | 38.2828 | 0.8535 | 2.0956 | 109 | NZ | 414400 | 557500 | Coalfield |
| 300271 | 17.6034 | 15.5461 | 37.5061 | 0.8831 | 2.1305 | 181 | NZ | 417200 | 558200 | Coalfield |
| 300281 | 18.0478 | 15.5561 | 38.0100 | 0.8619 | 2.1061 | 189 | NZ | 412700 | 552700 | Coalfield |
| 300305 | 18.3906 | 15.5992 | 38.3531 | 0.8483 | 2.0856 | 246 | NZ | 419290 | 538120 | Coalfield |
| 300312 | 18.3964 | 15.6135 | 38.3708 | 0.8487 | 2.0858 | 879 | NZ | 400200 | 548740 | Orefield |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 300316 | 17.9182 | 15.5565 | 37.8568 | 0.8682 | 2.1128 | 110 | NZ | 426460 | 529890 | Coalfield |
| 300321 | 18.1596 | 15.5476 | 38.0836 | 0.8562 | 2.0982 | 83 | NZ | 422900 | 537390 | Coalfield |
| 300341 | 17.6826 | 15.5186 | 37.5035 | 0.8776 | 2.1211 | 128 | NZ | 425480 | 538600 | Coalfield |
| 300364 | 18.2131 | 15.5636 | 38.1631 | 0.8543 | 2.0955 | 72 | NZ | 422700 | 534500 | Coalfield |
| 300374 | 18.2218 | 15.5369 | 38.0939 | 0.8527 | 2.0907 | 62 | NZ | 433400 | 538900 | Coalfield |
| 300381 | 18.1472 | 15.5617 | 38.0925 | 0.8575 | 2.0990 | 373 | NZ | 428650 | 537200 | Coalfield |
| 300533 | 18.3738 | 15.5911 | 38.3498 | 0.8486 | 2.0872 | 197 | NZ | 409100 | 544500 | Orefield |
| 300534 | 17.7733 | 15.5658 | 37.7083 | 0.8758 | 2.1216 | 805 | NZ | 423420 | 530410 | Coalfield |
| 300542 | 18.2120 | 15.5298 | 38.0717 | 0.8526 | 2.0904 | 90 | NZ | 405890 | 543250 | Orefield |
| 300548 | 18.4032 | 15.6202 | 38.3892 | 0.8488 | 2.0861 | 1771 | NZ | 404740 | 548210 | Orefield |
| 300595 | 18.0228 | 15.5444 | 37.9268 | 0.8625 | 2.1044 | 166 | NZ | 405690 | 541790 | Orefield |
| 300623 | 17.7328 | 15.5206 | 37.6392 | 0.8750 | 2.1222 | 444 | NZ | 433410 | 553100 | Coalfield |
| 300624 | 18.0365 | 15.5560 | 37.9036 | 0.8624 | 2.1016 | 147 | NZ | 432040 | 544180 | Coalfield |
| 300629 | 18.0247 | 15.5341 | 37.8978 | 0.8618 | 2.1021 | 117 | NZ | 432110 | 547830 | Coalfield |
| 300674 | 17.9087 | 15.5277 | 37.7370 | 0.8671 | 2.1072 | 76 | NZ | 430340 | 540390 | Coalfield |
| 300684 | 18.2489 | 15.5305 | 38.1402 | 0.8510 | 2.0901 | 119 | NZ | 432290 | 541600 | Coalfield |
| 300685 | 17.9671 | 15.5513 | 37.8611 | 0.8656 | 2.1074 | 127 | NZ | 427400 | 540400 | Coalfield |
| 300694 | 17.9521 | 15.5745 | 37.8911 | 0.8676 | 2.1113 | 269 | NZ | 433060 | 549730 | Coalfield |
| 300739 | 18.3161 | 15.5848 | 38.2731 | 0.8509 | 2.0896 | 204 | NZ | 408500 | 545200 | Orefield |
| 300764 | 18.1154 | 15.5812 | 38.0290 | 0.8602 | 2.0993 | 11160 | NZ | 407210 | 549200 | Coalfield |
| 301914 | 17.9728 | 15.5587 | 37.8759 | 0.8656 | 2.1073 | 146 | NZ | 418870 | 528570 | Coalfield |
| 301925 | 17.8433 | 15.5376 | 37.7163 | 0.8708 | 2.1135 | 104 | NZ | 417210 | 525150 | Coalfield |
| 301933 | 18.2086 | 15.5034 | 38.0526 | 0.8215 | 2.0899 | 91 | NZ | 413140 | 529950 | Coalfield |
| 301943 | 18.1331 | 15.5404 | 38.0380 | 0.8570 | 2.0976 | 107 | NZ | 419280 | 526000 | Coalfield |
| 301972 | 18.2155 | 15.5380 | 38.1048 | 0.8529 | 2.0921 | 127 | NZ | 414620 | 537740 | Coalfield |
| 302104 | 18.2967 | 15.5829 | 38.2821 | 0.8516 | 2.0918 | 184 | NZ | 405930 | 528500 | Orefield |
| 302132 | 18.4499 | 15.6269 | 38.4657 | 0.8470 | 2.0850 | 1097 | NZ | 406040 | 531450 | Orefield |
| 302146 | 18.4547 | 15.6305 | 38.4768 | 0.8470 | 2.0852 | 3227 | NZ | 405530 | 529950 | Orefield |
| 302155 | 18.4149 | 15.6245 | 38.4200 | 0.8486 | 2.0864 | 644 | NZ | 410750 | 532360 | Orefield |
| 302169 | 17.8733 | 15.5282 | 37.7158 | 0.8688 | 2.1101 | 156 | NZ | 424910 | 524100 | Coalfield |
| 302506 | 18.2660 | 15.5557 | 38.2104 | 0.8517 | 2.0918 | 102 | NZ | 414510 | 526480 | Coalfield |
| 302517 | 18.3011 | 15.6095 | 38.2809 | 0.8529 | 2.0917 | 11295 | NZ | 400220 | 534120 | Orefield |
| 302541 | 18.4316 | 15.6205 | 38.4473 | 0.8475 | 2.0859 | 1428 | NZ | 403360 | 535860 | Orefield |
| 302562 | 18.2837 | 15.6037 | 38.2576 | 0.8534 | 2.0922 | 1473 | NZ | 401290 | 534400 | Orefield |
| 320209 | 18.4256 | 15.6309 | 38.4684 | 0.8483 | 2.0878 | 4064 | NY | 378150 | 541550 | Orefield |
| 320222 | 18.4755 | 15.6331 | 38.5501 | 0.8462 | 2.0864 | 2725 | NY | 376700 | 537700 | Orefield |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 320270 | 18.4482 | 15.6282 | 38.4691 | 0.8471 | 2.0855 | 3220 | NY | 377000 | 537200 | Orefield |
| 320276 | 18.4076 | 15.6114 | 38.3929 | 0.8482 | 2.0857 | 140 | NY | 375600 | 537800 | Orefield |
| 320293 | 18.4252 | 15.6176 | 38.4320 | 0.8476 | 2.0856 | 413 | NY | 376100 | 536600 | Orefield |
| 320305 | 18.3084 | 15.6214 | 38.3019 | 0.8531 | 2.0918 | 1743 | NY | 379500 | 542250 | Orefield |
| 320622 | 18.4117 | 15.6259 | 38.4381 | 0.8490 | 2.0882 | 15392 | NY | 376700 | 542350 | Orefield |
| 320627 | 18.3311 | 15.5815 | 38.2904 | 0.8501 | 2.0888 | 194 | NY | 375600 | 532700 | Orefield |
| 320647 | 18.3078 | 15.5978 | 38.2666 | 0.8520 | 2.0900 | 138 | NY | 377000 | 530200 | Orefield |
| 320691 | 18.3521 | 15.6086 | 38.3367 | 0.8505 | 2.0890 | 496 | NY | 379400 | 531400 | Orefield |
| 320693 | 18.3748 | 15.6162 | 38.3866 | 0.8498 | 2.0891 | 6359 | NY | 378400 | 532200 | Orefield |
| 320806 | 18.3252 | 15.5826 | 38.2610 | 0.8504 | 2.0879 | 115 | NY | 388700 | 529350 | Orefield |
| 320824 | 18.4419 | 15.6272 | 38.4489 | 0.8474 | 2.0848 | 1372 | NY | 384990 | 533190 | Orefield |
| 321039 | 18.4037 | 15.6229 | 38.4069 | 0.8489 | 2.0870 | 469 | NY | 394290 | 529500 | Orefield |
| 321041 | 18.3822 | 15.6140 | 38.3840 | 0.8495 | 2.0884 | 391 | NY | 379200 | 533800 | Orefield |
| 321099 | 18.4175 | 15.6231 | 38.4260 | 0.8483 | 2.0864 | 3024 | NY | 390310 | 529780 | Orefield |
| 321230 | 18.4765 | 15.6251 | 38.4548 | 0.8456 | 2.0810 | 672 | NY | 376300 | 523200 | Orefield |
| 321249 | 18.6125 | 15.6479 | 38.5943 | 0.8408 | 2.0736 | nr | NY | 379600 | 520600 | Orefield |
| 321254 | 18.2305 | 15.5937 | 38.2006 | 0.8553 | 2.0954 | 200 | NY | 379400 | 522800 | Orefield |
| 321273 | 18.3208 | 15.6049 | 38.2900 | 0.8518 | 2.0901 | 166 | NY | 381500 | 523600 | Orefield |
| 321279 | 18.3075 | 15.6064 | 38.2688 | 0.8525 | 2.0905 | nr | NY | 376300 | 522700 | Orefield |
| 321281 | 18.3774 | 15.6036 | 38.3327 | 0.8491 | 2.0858 | 105 | NY | 376700 | 520800 | Orefield |
| 321454 | 18.4132 | 15.6264 | 38.4112 | 0.8487 | 2.0860 | 4096 | NY | 385080 | 549960 | Orefield |
| 321460 | 18.4117 | 15.6205 | 38.3953 | 0.8484 | 2.0854 | 1401 | NY | 385910 | 548410 | Orefield |
| 322463 | 18.2816 | 15.5910 | 38.2547 | 0.8283 | 2.0921 | 211 | NY | 390150 | 549400 | Orefield |
| 322488 | 18.3028 | 15.5610 | 38.2265 | 0.8502 | 2.0888 | 124 | NY | 387890 | 551380 | Orefield |
| 322607 | 18.3389 | 15.5605 | 38.2500 | 0.8485 | 2.0857 | 103 | NY | 393210 | 547480 | Orefield |
| 322672 | 18.5042 | 15.6362 | 38.4936 | 0.8450 | 2.0799 | 14867 | NY | 395600 | 548140 | Orefield |
| 322808 | 18.6047 | 15.6432 | 38.5798 | 0.8408 | 2.0743 | 6509 | NY | 394510 | 542450 | Orefield |
| 322812 | 18.3360 | 15.5767 | 38.2676 | 0.8494 | 2.0872 | 142 | NY | 399050 | 547910 | Orefield |
| 322820 | 18.4622 | 15.6213 | 38.4607 | 0.8461 | 2.0832 | 327 | NY | 393620 | 541400 | Orefield |
| 322840 | 18.5329 | 15.6362 | 38.5353 | 0.8437 | 2.0794 | 2647 | NY | 399150 | 542900 | Orefield |
| 322841 | 18.4139 | 15.6208 | 38.4232 | 0.8483 | 2.0866 | 716 | NY | 389490 | 542980 | Orefield |
| 322858 | 18.3490 | 15.5775 | 38.2847 | 0.8490 | 2.0866 | 131 | NY | 391790 | 546890 | Orefield |
| 322872 | 18.4318 | 15.6229 | 38.4129 | 0.8475 | 2.0840 | 2714 | NY | 394400 | 540010 | Orefield |
| 322877 | 18.4385 | 15.6223 | 38.4059 | 0.8473 | 2.0829 | 7803 | NY | 394250 | 540700 | Orefield |
| 322880 | 18.4877 | 15.6099 | 38.4702 | 0.8443 | 2.0813 | 96 | NY | 394150 | 543610 | Orefield |
| 322881 | 18.4519 | 15.6201 | 38.4463 | 0.8465 | 2.0836 | 530 | NY | 389490 | 543800 | Orefield |

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|---|---|---|---|---|---|---|---|---|---|---|
| 322886 | 18.4563 | 15.6287 | 38.4858 | 0.8468 | 2.0852 | 212 | NY | 390800 | 542660 | Orefield |
| 322887 | 18.4125 | 15.6198 | 38.4084 | 0.8483 | 2.0860 | 163 | NY | 391610 | 543870 | Orefield |
| 323026 | 18.4430 | 15.6253 | 38.4599 | 0.8472 | 2.0853 | 5694 | NY | 380490 | 538000 | Orefield |
| 323031 | 18.4799 | 15.6228 | 38.4675 | 0.8454 | 2.0816 | 2045 | NY | 398100 | 543100 | Orefield |
| 323038 | 18.4756 | 15.6331 | 38.4949 | 0.8461 | 2.0837 | 1118 | NY | 382430 | 541000 | Orefield |
| 323056 | 18.4067 | 15.6186 | 38.4045 | 0.8485 | 2.0864 | 2402 | NY | 383180 | 542380 | Orefield |
| 323080 | 18.4550 | 15.6259 | 38.4676 | 0.8467 | 2.0844 | 1364 | NY | 384890 | 542470 | Orefield |
| 323086 | 18.4264 | 15.6224 | 38.4435 | 0.8478 | 2.0863 | 6910 | NY | 381600 | 537280 | Orefield |
| 323201 | 18.4598 | 15.6286 | 38.4770 | 0.8466 | 2.0844 | 2536 | NY | 384380 | 536460 | Orefield |
| 323246 | 18.4655 | 15.6359 | 38.4977 | 0.8468 | 2.0848 | 18538 | NY | 399360 | 529850 | Orefield |
| 323257 | 18.4234 | 15.6189 | 38.4310 | 0.8478 | 2.0860 | 338 | NY | 385920 | 538310 | Orefield |
| 323264 | 18.4920 | 15.6333 | 38.4975 | 0.8454 | 2.0818 | 6029 | NY | 389070 | 540580 | Orefield |
| 323281 | 18.4057 | 15.6229 | 38.4083 | 0.8488 | 2.0868 | 4622 | NY | 384390 | 536830 | Orefield |
| 323283 | 18.4559 | 15.6276 | 38.4553 | 0.8467 | 2.0836 | 1777 | NY | 390760 | 540210 | Orefield |
| 323295 | 18.3526 | 15.6191 | 38.3449 | 0.8511 | 2.0893 | 1230 | NY | 392100 | 534420 | Orefield |
| 323419 | 18.4473 | 15.6279 | 38.4495 | 0.8471 | 2.0840 | 4656 | NY | 389780 | 539190 | Orefield |
| 323423 | 18.4249 | 15.6240 | 38.4384 | 0.8480 | 2.0862 | 280 | NY | 393140 | 536380 | Orefield |
| 323434 | 18.5874 | 15.6389 | 38.5585 | 0.8413 | 2.0744 | 1520 | NY | 392390 | 538260 | Orefield |
| 323457 | 18.4322 | 15.6259 | 38.4268 | 0.8478 | 2.0846 | 4879 | NY | 388280 | 536770 | Orefield |
| 323458 | 18.4776 | 15.6281 | 38.4583 | 0.8457 | 2.0815 | 2848 | NY | 398100 | 535610 | Orefield |
| 323461 | 18.5298 | 15.6330 | 38.5223 | 0.8435 | 2.0788 | 1353 | NY | 396980 | 539880 | Orefield |
| 323474 | 18.5237 | 15.6295 | 38.5148 | 0.8438 | 2.0792 | 1609 | NY | 398080 | 541110 | Orefield |
| 323486 | 18.5475 | 15.6370 | 38.5395 | 0.8431 | 2.0779 | 2078 | NY | 398430 | 541730 | Orefield |
| 323652 | 18.3635 | 15.6117 | 38.3682 | 0.8502 | 2.0893 | 234 | NY | 398600 | 534510 | Orefield |
| 323665 | 18.4378 | 15.6246 | 38.4095 | 0.8474 | 2.0832 | 9723 | NY | 395600 | 534030 | Orefield |
| 323808 | 18.3382 | 15.6096 | 38.3160 | 0.8512 | 2.0894 | 184 | NY | 380400 | 526400 | Orefield |
| 323814 | 18.2704 | 15.5993 | 38.2663 | 0.8538 | 2.0946 | 202 | NY | 379300 | 526100 | Orefield |
| 323849 | 18.2400 | 15.6025 | 38.2201 | 0.8554 | 2.0954 | 146 | NY | 378000 | 525500 | Orefield |
| 323870 | 18.2874 | 15.6156 | 38.2945 | 0.8539 | 2.0940 | 460 | NY | 378600 | 530000 | Orefield |
| 323871 | 18.2537 | 15.6006 | 38.2150 | 0.8544 | 2.0933 | 273 | NY | 378800 | 528000 | Orefield |
| 324038 | 18.2661 | 15.5978 | 38.2378 | 0.8540 | 2.0938 | 218 | NY | 375900 | 526900 | Orefield |
| 324093 | 18.3533 | 15.6078 | 38.3375 | 0.8504 | 2.0888 | 123 | NY | 377300 | 526800 | Orefield |
| 324408 | 18.3709 | 15.6069 | 38.3507 | 0.8496 | 2.0877 | 413 | NY | 377800 | 539600 | Orefield |
| 324425 | 18.4256 | 15.6103 | 38.4472 | 0.8472 | 2.0866 | 222 | NY | 377600 | 535500 | Orefield |
| 324441 | 18.3359 | 15.6186 | 38.3562 | 0.8518 | 2.0918 | 503 | NY | 375200 | 539700 | Orefield |
| BB2 | 18.3196 | 15.6177 | 38.3132 | 0.8525 | 2.0914 | 2131 | NZ | 403100 | 536100 | Orefield |

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|---|---|---|---|---|---|---|---|---|---|---|
| BB3 | 18.3138 | 15.6183 | 38.3258 | 0.8528 | 2.0927 | 4054 | NZ | 402000 | 535400 | Orefield |
| BB5 | 18.4265 | 15.6250 | 38.4527 | 0.8480 | 2.0868 | 3134 | NZ | 400000 | 535000 | Orefield |
| BB7 | 18.3776 | 15.6144 | 38.4131 | 0.8496 | 2.0902 | 572 | NY | 398100 | 535000 | Orefield |
| DS1 | 18.4887 | 15.6418 | 38.4877 | 0.8460 | 2.0817 | 267 | NY | 389300 | 537500 | Orefield |
| HB1 | 18.4344 | 15.6246 | 38.4297 | 0.8476 | 2.0847 | 213 | NY | 397500 | 538400 | Orefield |
| HB4 | 18.4636 | 15.6290 | 38.4741 | 0.8465 | 2.0838 | 131 | NY | 395800 | 537100 | Orefield |
| KB02 | 18.4435 | 15.6197 | 38.4510 | 0.8469 | 2.0848 | 262 | NY | 381100 | 543200 | Orefield |
| KB06 | 18.4342 | 15.6282 | 38.4716 | 0.8478 | 2.0870 | 1561 | NY | 382800 | 542900 | Orefield |
| KB09 | 18.4233 | 15.6217 | 38.4287 | 0.8479 | 2.0859 | 1834 | NY | 383300 | 542300 | Orefield |
| KB11 | 18.4093 | 15.6222 | 38.4203 | 0.8486 | 2.0870 | 7832 | NY | 383800 | 541500 | Orefield |
| KB13 | 18.4028 | 15.6251 | 38.4126 | 0.8491 | 2.0873 | 2118 | NY | 384900 | 541000 | Orefield |
| KB14 | 18.4283 | 15.6288 | 38.4533 | 0.8481 | 2.0866 | 4060 | NY | 385400 | 540400 | Orefield |
| MhB2 | 18.4639 | 15.6415 | 38.5186 | 0.8471 | 2.0862 | 1145 | NY | 390200 | 540800 | Orefield |
| MhB7 | 18.4728 | 15.6405 | 38.5079 | 0.8467 | 2.0846 | 5432 | NY | 390600 | 538600 | Orefield |
| Rh2 | 18.4473 | 15.6224 | 38.4495 | 0.8445 | 2.0815 | 183 | NY | 388000 | 544600 | Orefield |
| Rh3 | 18.4683 | 15.6300 | 38.4791 | 0.8463 | 2.0835 | 279 | NY | 389300 | 544200 | Orefield |
| Rh4 | 18.5196 | 15.6402 | 38.5484 | 0.8445 | 2.0815 | 811 | NY | 389700 | 543800 | Orefield |
| Rh5 | 18.4939 | 15.6330 | 38.5076 | 0.8453 | 2.0819 | 2030 | NY | 391000 | 542800 | Orefield |
| Rh7 | 18.4383 | 15.6237 | 38.4311 | 0.8472 | 2.0843 | 1128 | NY | 393500 | 542900 | Orefield |
| Rh8 | 18.5476 | 15.6413 | 38.5579 | 0.8433 | 2.0789 | 1811 | NY | 394400 | 541500 | Orefield |
| Rh9 | 18.5572 | 15.6478 | 38.5603 | 0.8432 | 2.0779 | 9518 | NY | 395300 | 538600 | Orefield |
| SeB2 | 18.4833 | 15.6452 | 38.5203 | 0.8465 | 2.0820 | 3806 | NY | 385800 | 541000 | Orefield |
| StB1 | 18.4592 | 15.6318 | 38.5120 | 0.8469 | 2.0864 | 105 | NY | 399000 | 539300 | Orefield |
| SwB2 | 18.5994 | 15.6342 | 38.7269 | 0.8406 | 2.0822 | 56 | NY | 390700 | 536700 | Orefield |
| WhB2 | 18.3862 | 15.6198 | 38.3737 | 0.8495 | 2.0871 | 495 | NY | 393500 | 536900 | Orefield |
| WhB4 | 18.4049 | 15.6188 | 38.3905 | 0.8486 | 2.0859 | 303 | NY | 392700 | 535200 | Orefield |

**Sediments: Main Channel River Wear**

| Sample no | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{206}Pb$ | $^{208}Pb/^{206}Pb$ | Pb ppm | Grid Ref | Eastings | Northings | Regional Location |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 18.4360 | 15.6333 | 38.4695 | 0.8480 | 2.0865 | 6225 | NY | 385600 | 539700 | River Wear |
| 2 | 18.4596 | 15.6381 | 38.4922 | 0.8471 | 2.0852 | 4417 | NY | 386800 | 538800 | River Wear |
| 3 | 18.4503 | 15.6355 | 38.4762 | 0.8474 | 2.0854 | 2259 | NY | 387500 | 538500 | River Wear |
| 4 | 18.4467 | 15.6348 | 38.4819 | 0.8476 | 2.0861 | 2319 | NY | 389000 | 538000 | River Wear |

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|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 18.4661 | 15.6351 | 38.4736 | 0.8467 | 2.0834 | 905 | NY | 392000 | 537900 | River Wear |
| 6 | 18.4664 | 15.6286 | 38.4640 | 0.8464 | 2.0828 | 3927 | NY | 395000 | 538500 | River Wear |
| 7 | 18.4869 | 15.6352 | 38.4954 | 0.8458 | 2.0826 | 5085 | NY | 397000 | 538500 | River Wear |
| 8 | 18.4891 | 15.6312 | 38.4776 | 0.8454 | 2.0811 | 3648 | NY | 399000 | 539100 | River Wear |
| 9 | 18.5014 | 15.6380 | 38.5110 | 0.8454 | 2.0815 | 5742 | NZ | 400000 | 538500 | River Wear |
| 10 | 18.5003 | 15.6332 | 38.4961 | 0.8450 | 2.0808 | 1610 | NZ | 403000 | 536800 | River Wear |
| 11 | 18.4788 | 15.6357 | 38.4882 | 0.8461 | 2.0828 | 1226 | NZ | 405000 | 537100 | River Wear |
| 12 | 18.4786 | 15.6368 | 38.4977 | 0.8462 | 2.0834 | 1320 | NZ | 407000 | 537000 | River Wear |
| 13 | 18.4693 | 15.6366 | 38.4706 | 0.8466 | 2.0829 | 1265 | NZ | 409000 | 536400 | River Wear |
| 14 | 18.4836 | 15.6404 | 38.4975 | 0.8462 | 2.0828 | 1584 | NZ | 411000 | 535400 | River Wear |
| 15 | 18.4611 | 15.6354 | 38.4698 | 0.8471 | 2.0836 | 1177 | NZ | 412872 | 532314 | River Wear |
| 16 | 18.4491 | 15.6359 | 38.4584 | 0.8474 | 2.0843 | 1559 | NZ | 417038 | 530861 | River Wear |
| 17 | 18.4561 | 15.6348 | 38.4674 | 0.8471 | 2.0841 | 955 | NZ | 420714 | 530367 | River Wear |
| 18 | 18.4469 | 15.6287 | 38.4521 | 0.8472 | 2.0845 | 727 | NZ | 420078 | 534205 | River Wear |
| 19 | 18.4454 | 15.6307 | 38.4478 | 0.8474 | 2.0841 | 710 | NZ | 423583 | 535481 | River Wear |
| 20 | 18.4339 | 15.6295 | 38.4738 | 0.8478 | 2.0849 | 632 | NZ | 425488 | 537164 | River Wear |
| 21 | 18.4480 | 15.6303 | 38.4593 | 0.8473 | 2.0845 | 662 | NZ | 426585 | 537778 | River Wear |
| 22 | 18.4506 | 15.6334 | 38.4576 | 0.8472 | 2.0842 | 927 | NZ | 426823 | 539427 | River Wear |
| 23 | 18.4376 | 15.6288 | 38.4322 | 0.8476 | 2.0845 | 658 | NZ | 428563 | 542105 | River Wear |
| 24 | 18.3907 | 15.6277 | 38.3933 | 0.8497 | 2.0873 | 596 | NZ | 427331 | 542847 | River Wear |
| 25 | 18.3885 | 15.6240 | 38.3874 | 0.8497 | 2.0882 | 557 | NZ | 429932 | 545484 | River Wear |
| 26 | 18.4068 | 15.6228 | 38.3966 | 0.8488 | 2.0859 | 262 | NZ | 428606 | 547842 | River Wear |
| 27 | 18.4283 | 15.6248 | 38.4167 | 0.8479 | 2.0845 | 365 | NZ | 428224 | 551193 | River Wear |

**Galenas: North Pennine Orefield**

| Sample no | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{206}Pb$ | $^{208}Pb/^{206}Pb$ | Grid Ref | Eastings | Northings | Location |
|---|---|---|---|---|---|---|---|---|---|
| NE-02-14 | 18.4547 | 15.6530 | 38.4460 | 0.8482 | 2.0833 | NY | 49375 | 54279 | Rookhope Borehole |
| NE-02-15 | 18.4333 | 15.6336 | 38.4076 | 0.8481 | 2.0836 | NY | 49375 | 54279 | Rookhope Borehole |
| NE-02-16 | 18.4414 | 15.6528 | 38.4279 | 0.8488 | 2.0838 | NY | 49375 | 54279 | Rookhope Borehole |
| NE-02-17 | 18.6797 | 15.6582 | 38.6639 | 0.8383 | 2.0698 | NY | 49375 | 54279 | Rookhope Borehole |
| NE-02-19 | 18.4807 | 15.6473 | 38.3370 | 0.8467 | 2.0744 | NY | 49375 | 54279 | Rookhope Borehole |
| NE-02-21 | 18.7080 | 15.6516 | 38.7023 | 0.8366 | 2.0687 | NY | 4927 | 55433 | Rookhope |
| NE-02-22 | 18.8987 | 15.6674 | 38.8456 | 0.8290 | 2.0555 | NY | 4944 | 5425 | Rookhope |

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|---|---|---|---|---|---|---|---|---|---|
| NE-02-23 | 18.6921 | 15.6458 | 38.6584 | 0.8370 | 2.0683 | NY | 3868 | 5390 | Ireshopeburn |
| NE-02-24 | 18.6292 | 15.6425 | 38.6636 | 0.8396 | 2.0755 | NY | 48896 | 54432 | Rookhope |
| NE-02-25 | 18.6292 | 15.6490 | 38.6458 | 0.8401 | 2.0748 | NY | 48896 | 54432 | Rookhope |
| NE-02-26 | 18.4813 | 15.6292 | 38.5055 | 0.8457 | 2.0835 | NY | 38100 | 5432 | Killhopehead |
| NE-02-27 | 18.8338 | 15.6614 | 38.7943 | 0.8316 | 2.0598 | NY | 39470 | 53675 | Eastgate |
| NE-02-28 | 18.5722 | 15.6359 | 38.5693 | 0.8420 | 2.0768 | NZ | 40080 | 53648 | Frosterley |
| NE-02-29 | 18.4651 | 15.6453 | 38.4358 | 0.8473 | 2.0826 | NY | 38590 | 54235 | Cowshill |
| NE-02-30 | 18.4238 | 15.6204 | 38.3950 | 0.8478 | 2.0840 | NY | 3905 | 5400 | Westgate |
| NE-02-31 | 18.6733 | 15.6444 | 38.6322 | 0.8378 | 2.0689 | NY | 3985 | 5378 | Stanhope |
| NE-02-32 | 18.4251 | 15.6221 | 38.4171 | 0.8479 | 2.0852 | NY | 3861 | 5379 | Ireshopeburn |
| NE-02-33 | 18.3672 | 15.5855 | 38.2699 | 0.8486 | 2.0838 | NZ | 40663 | 54348 | Wolsingham |
| NE-02-34 | 18.4972 | 15.6312 | 38.5234 | 0.8450 | 2.0826 | NY | 38218 | 54325 | Killhope |
| NE-02-35 | 18.5374 | 15.6421 | 38.5783 | 0.8438 | 2.0811 | NY | 38505 | 54534 | Allenheads |
| NE-02-36 | 18.3724 | 15.6181 | 38.3850 | 0.8501 | 2.0893 | NY | 37520 | 54575 | Nenthead |
| NE-02-37 | 18.4331 | 15.6295 | 38.4320 | 0.8479 | 2.0849 | NY | 38515 | 54876 | East Allendale |
| NE-02-38 | 18.3033 | 15.6130 | 38.3048 | 0.8530 | 2.0929 | NY | 40056 | 54888 | Edmundbyers |
| NE-02-39 | 18.3691 | 15.5991 | 38.3289 | 0.8492 | 2.0866 | NY | 586 | 606 | Brampton |
| NE-02-40 | 18.3155 | 15.5875 | 38.2575 | 0.8511 | 2.0888 | NY | 8260 | 6610 | Haydon Bridge |
| NE-02-41 | 18.3731 | 15.6193 | 38.3844 | 0.8501 | 2.0891 | NY | 37790 | 54797 | West Allendale |
| NE-02-43 | 18.3919 | 15.6189 | 38.3764 | 0.8492 | 2.0866 | NY | 39690 | 54703 | Edmundbyers |
| NE-02-44 | 18.3063 | 15.6155 | 38.3115 | 0.8530 | 2.0928 | NZ | 40320 | 54566 | Muggleswick |
| NE-02-45 | 18.3899 | 15.6172 | 38.3836 | 0.8492 | 2.0872 | NY | 3826 | 5466 | Allenheads |
| NE-02-46 | 18.4443 | 15.6358 | 38.4660 | 0.8477 | 2.0855 | NY | 38569 | 54532 | Allenheads |
| NE-02-47 | 18.3776 | 15.6203 | 38.3887 | 0.8500 | 2.0889 | NY | 37812 | 54534 | Nenthead |
| NE-02-48 | 18.3738 | 15.6150 | 38.3650 | 0.8498 | 2.0880 | NY | 37410 | 54730 | Nenthead |
| NE-02-49 | 18.3944 | 15.6230 | 38.3933 | 0.8493 | 2.0872 | NY | 39266 | 54750 | Hunstanworth |
| NE-02-50 | 18.4454 | 15.6312 | 38.4391 | 0.8474 | 2.0839 | NY | 39590 | 55102 | Blanchland |
| NE-02-51 | 18.3062 | 15.4938 | 38.2714 | 0.8518 | 2.0906 | NY | 37775 | 54525 | Nenthead |
| NE-04-02 | 18.3247 | 15.5807 | 38.2477 | 0.8503 | 2.0870 | NY | 3855 | 5688 | Stonecroft |
| NE-04-03 | 18.3579 | 15.5999 | 38.3031 | 0.8498 | 2.0865 | NY | 3790 | 5420 | Smallcleugh |
| NE-04-05 | 18.3858 | 15.6223 | 38.4008 | 0.8497 | 2.0886 | NY | 3954 | 5488 | East Allendale |
| NE-04-06 | 18.3700 | 15.6152 | 38.3725 | 0.8500 | 2.0888 | NY | 3765 | 5452 | Nentsbury |
| NE-04-07 | 18.4022 | 15.6225 | 38.3930 | 0.8489 | 2.0862 | NY | 3860 | 5455 | Allenheads |
| NE-04-08 | 18.3788 | 15.6115 | 38.3648 | 0.8494 | 2.0873 | NY | 3915 | 5313 | Flushiemere |
| NE-04-09 | 18.4064 | 15.6160 | 38.3791 | 0.8483 | 2.0846 | NY | 3808 | 5311 | Cow Green |
| NE-04-11 | 18.4615 | 15.6364 | 38.4662 | 0.8469 | 2.0836 | NY | 3880 | 5445 | Frazers Hush |

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|---|---|---|---|---|---|---|---|---|---|
| NE-04-12 | 18.4258 | 15.6301 | 38.4528 | 0.8483 | 2.0870 | NY | 3900 | 5310 | Pike Law |

**Carboniferous Coal and Shale: Durham-Northumberland Coalfield (Pearson & Worrall pers. comm.)**

| Sample no | $^{206}$Pb/204Pb | $^{207}$Pb/$^{204}$Pb | $^{208}$Pb/$^{204}$Pb | $^{207}$Pb/$^{206}$Pb | $^{208}$Pb/$^{206}$Pb | Pb ppm | Sample Type/Age |
|---|---|---|---|---|---|---|---|
| GP1 | 18.5773 | 15.6072 | 38.7031 | 0.8401 | 2.0834 | nr | Shale (Westphalian) |
| GP2 | 18.6317 | 15.6376 | 37.4515 | 0.8393 | 2.0638 | nr | Shale (Westphalian) |
| GP4 | 18.6511 | 15.6225 | 38.5512 | 0.8376 | 2.0670 | nr | Shale (Westphalian) |
| GP8 | 18.4722 | 15.6036 | 38.4765 | 0.8447 | 2.0829 | nr | Shale (Westphalian) |
| GP10 | 18.6379 | 15.6231 | 38.7396 | 0.8382 | 2.0785 | nr | Shale (Westphalian) |
| GP14 | 18.8721 | 15.6304 | 38.8432 | 0.8282 | 2.0582 | nr | Shale (Westphalian) |
| GP20 | 18.6116 | 15.6327 | 38.7576 | 0.8399 | 2.0824 | nr | Shale (Westphalian) |
| GP21 | 18.7124 | 15.5946 | 38.5482 | 0.8334 | 2.0600 | nr | Shale (Westphalian) |
| GP26 | 18.6489 | 15.6358 | 38.8328 | 0.8384 | 2.0823 | nr | Shale (Westphalian) |
| GP5 | 18.5461 | 15.6121 | 38.3950 | 0.8418 | 2.0702 | nr | Coal (Westphalian) |
| GP6 | 18.5787 | 15.6116 | 38.4594 | 0.8403 | 2.0701 | nr | Coal (Westphalian) |
| GP9 | 18.5924 | 15.6340 | 38.4266 | 0.8409 | 2.0668 | nr | Coal (Westphalian) |
| GP12 | 18.6467 | 15.6203 | 38.5249 | 0.8377 | 2.0660 | nr | Coal (Westphalian) |
| GP13 | 18.5564 | 15.6196 | 38.4569 | 0.8417 | 2.0724 | nr | Coal (Westphalian) |
| GP17 | 18.4302 | 15.6119 | 38.4217 | 0.8471 | 2.0847 | nr | Coal (Westphalian) |
| GP18 | 18.4063 | 15.5973 | 38.3624 | 0.8474 | 2.0842 | nr | Coal (Westphalian) |
| GP22 | 18.4323 | 15.5895 | 38.3415 | 0.8458 | 2.0801 | nr | Coal (Westphalian) |
| GP24 | 18.5130 | 15.6019 | 38.3824 | 0.8428 | 2.0733 | nr | Coal (Westphalian) |
| GP27 | 18.4495 | 15.5985 | 38.3527 | 0.8455 | 2.0788 | nr | Coal (Westphalian) |
| GP29 | 18.4682 | 15.5832 | 38.3781 | 0.8438 | 2.0781 | nr | Coal (Westphalian) |

nr not reported. Further details relating to all samples can be obtained from the Corresponding Author.