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A 500 Year Sediment Lake Record of Anthropogenic and Natural Inputs to Windermere (English Lake District) Using Double-Spike Lead Isotopes, Radiochronology, and Sediment Microanalysis

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Supporting Information

ABSTRACT: A high-resolution record of pollution is preserved in recent sediments from Windermere, the largest lake in the English Lake District. Data derived from X-ray core scanning (validated against wavelength dispersive X-ray fluorescence), radiochronological techniques (^{210}Pb and ^{137}Cs) and ultrahigh precision, double-spike mass spectrometry for lead isotopes are combined to decipher the anthropogenic inputs to the lake. The sediment record suggests that while most element concentrations have been stable, there has been a significant increase in lead, zinc, and copper concentrations since the 1930s. Lead isotope down-core variations identify three major contributory sources of anthropogenic (industrial) lead, comprising gasoline lead, coal combustion lead (most likely source is coal-fired steam ships), and lead derived from Carboniferous Pb–Zn mineralization (mining activities). Periods of metal workings do not correlate with peaks in heavy metals due to the trapping efficiency of up-system lakes in the catchment. Heavy metal increases could be due to flood-induced metal inwash after the cessation of mining and the weathering of bedrock in the catchment. The combination of sediment analysis techniques used provides new insights into the pollutant depositional history of Windermere and could be similarly applied to other lake systems to determine the timing and scale of anthropogenic inputs.

INTRODUCTION

Lake sediments provide an archive of environmental change and may be used to examine temporal changes in natural and anthropogenic element input allowing the reconstruction of heavy metal pollution history within a catchment. Within the UK and Europe, a number of studies attribute the enrichment of heavy metals in lacustrine sediments to human and industrial activity during the late 19th and early 20th centuries, and leaded gasoline usage during the 20th century.[1−3] Lead isotope ratios have been increasingly used to yield information on geochemical origin, to establish the principal sources of lead pollution, and to identify the pathways by which lead enters the environment.[4−7] Local point sources of heavy metals from mining activities have also been correlated with pollution records in lake sediments.[8,9] These studies demonstrate that point sources (such as mining activities) have a significant impact on the surrounding environment and local pollution history.[10] The development of the high precision double-spike lead isotope technique now enables significantly more sensitive environmental investigations.[11]

Within the English Lake District, significant amounts of heavy metal pollution linked to changes in mining activity have been identified within the sediments of Ullswater,[12,13] Bassenthwaite,[14,15] and Brotherswater,[16] to the north of Windermere (Figure 1). In the recreationally important Windermere, there was interest in evaluating frequency of flood events and the extent of heavy metal pollution derived historically from the catchment.[17] In the South Basin, low resolution analysis of 1 m sediment cores have previously identified enriched levels of lead, zinc, copper, and mercury which were attributed to anthropogenic inputs such as mining activities, sewage discharge, denudation of land surfaces (erosion and surface runoff of sediment containing enriched levels of heavy metals), heavy industry, and burning of fossil fuels.[18−20]

This paper investigates the pollutant deposition of Windermere and the surrounding catchment, and assesses the timing and scale of anthropogenic inputs in recent lacustrine sediments using two methods not previously applied. Non-destructive, high-resolution (200 μm scale) Itrax micro-X-ray fluorescenece and microradiographic analysis has the potential

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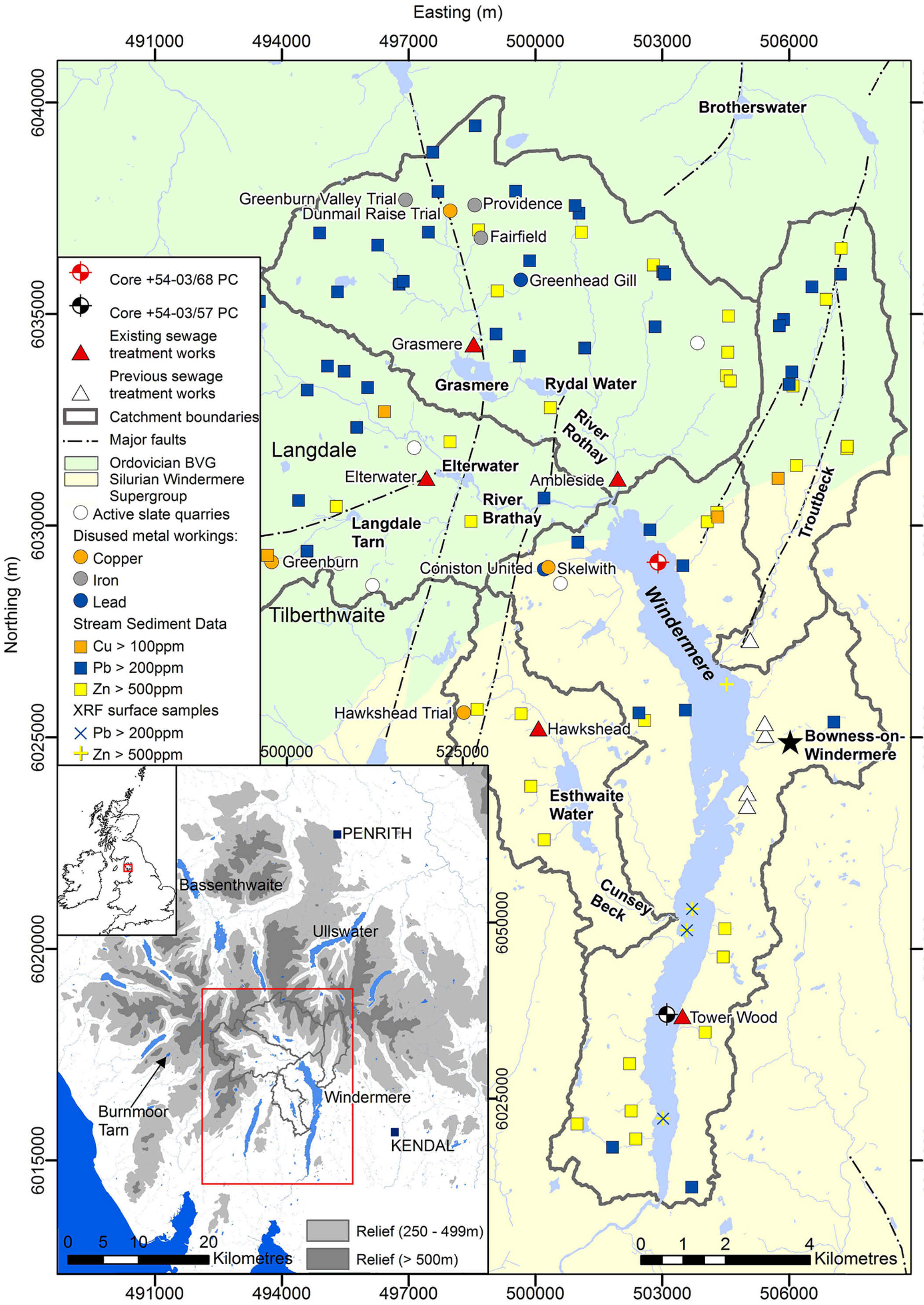

Figure 1. Location map, showing Windermere catchment, rivers, lakes, valleys, Bowness-on-Windermere (black star), sewage treatment works, and BGS sediment cores. The location of disused metal workings, currently active slate quarries, and stream sediment and WD-XRF samples with elevated concentrations of Pb, Zn, and Cu is also shown. Solid geology, stratigraphy, and faults are from British Geological Survey.[23] BVG: Borrowdale Volcanic Group; catchment areas calculated using 5 m resolution NEXTMap data. Inset shows location map of the study area in relation to the Lake District and the British Isles. Figure contains British Geological Survey materials reproduced with permission. Copyright 2013 NERC.

to identify fine scale compositional change (e.g., mining inputs and seasonal events). The data are validated against conventional wavelength dispersive X-ray fluorescence (WD-XRF) using centimeter-scale subsamples. In addition, high-precision, double-spike lead isotope measurements, offering 10 times the precision of the conventional single spike method, are used to examine multisource inputs of lead. The data interpretations are constrained by radiochronology and extensive historical research of former mining landscapes.

Study Site. Windermere is the largest freshwater lake in the English Lake District, occupying a radial preglacial river valley and as such represents a major recreational attraction in a UK

National Park. It comprises two basins (North and South) separated by an area of low islands and shallow water (Figure 1). The lake is orientated NNW to SSW, measuring ca. 17 km in length with a maximum width of ca. 1.5 km. It has a total area of ca. 14.7 km^2 and a maximum depth of 62 m. The lake bed is characterized by several sub-basins separated by steps, ridges, and isolated topographic highs, interpreted as the surface expression of recessional moraines related to retreat of the British and Irish Ice Sheet.[21,22] The sedimentology of the lake bed is dominated by gyttja (fine to very coarse organic rich silt).[21]

The bedrock of the catchment (area ca. 242 km^2) predominantly comprises the Borrowdale Volcanic Group (BVG) in the north, and the Silurian Windermere Supergroup (slates, shales, and sandstones) in the south[17] (Figure 1). There are two major fault systems in the region, orientated NNW-SSE and ENE-WSW which produce kilometre-scale map offsets (Figure 1).[23,24] The two main inlets of Windermere (River Rothay and Brathay) are located at the northern end of the lake and are sourced in the central Lake District, draining several streams and small lakes, including Elterwater, Grasmere, and Rydal Water. Troutbeck represents the main river catchment to the east of the North Basin. In the South Basin, the predominant inflow enters as flow from the North Basin and via Cunsey Beck. Except on the steeper and denuded surfaces, land cover in the north is largely grassland on poor soils and acidified podsols, with mixed woodland and improved grassland to the west.[25,26] Land use to the east is more urban, with the settlements of Ambleside and Bowness-on-Windermere.

Sewage Treatment. There are five existing sewage treatment works (STW) within the Windermere catchment: at Grasmere; Elterwater and Ambleside in the North; Hawkshead and Tower Wood in the South (Figure 1). Wastewater entering the North Basin was not treated until the opening of the STW at Ambleside in 1886, and the smaller Grasmere and Elterwater plants were later installed in the early 1970s.[27] In the South Basin, wastewater was first treated in 1888 at Beemire and subsequently diverted to Tower Wood in 1924, the largest STW in the catchment. Regular monitoring since 1945 has assessed the level of nutrient enrichment and biological production in the water column, and has revealed a progressive change toward eutrophy.[28] Large increases in nutrients from the mid-1960s are attributed to a growing human population, changes in agricultural practice, and increased sewage discharge.[29] Centralization of wastewater treatment in the 1960s led to an increase in direct discharge of treated sewage effluents, promoting algal growth, increasing phosphorus availability, and reducing oxygen concentration in deep water.[25,28] The implementation of a tertiary phosphate stripping treatment in 1992 at Tower Wood and Ambleside STW helped reduce phosphate loading.[29,30]

Mining and Quarrying in the Lake District. The Lake District has a long recorded history of metalliferous mining and quarrying that dates back to the 16th century. Skilled systematic mineral exploration steadily increased until the mid 18th century, followed by a large expansion due to the formation of private mining companies. In the Windermere catchment, mining for copper, lead, and iron was greatest in the latter half of the 19th century[25] and was followed by a rapid decline in 1870. During the 20th century there have been sporadic bursts of mining activity; however, all mining activity has now ceased.[31] Quarrying for slate, building stone, and aggregates was an important commercial industry; however, many small quarries closed during the early 20th century and only a few commercial operators are currently active.[32]

■ METHODOLOGY

Historical Research. Catchment boundaries were determined using onshore terrain data (5 m spatial resolution) from NEXTMap Britain (a national IfSAR digital elevation database)[33] and spatial analyst tools in ArcGIS. Information on metal workings was compiled from several sources, including published books, reports, and publications from local groups, such as the Cumbrian Amenity Trust Mining History Society and the Kendal and District Mine Research Society (KDMRS) (for refs, see Supporting Information). Further information was acquired though the BRITPITS Mineral Occurrence Database, the Lake District Historic Environment Record (LDHER), the English Heritage Archive (PastScape Record), and the National Trust Historic Buildings, Sites and Monuments Record. This paper represents the most extensive synthesis to date of the former mining landscapes, mining sites, and metal inputs into Windermere.

Active quarries were derived from the LDHER and refs 17 and 34. Stream sediment geochemical data (acquired in 1978−1980) were derived from BGS Geochemical Baseline Survey of the Environment (G-BASE) (analysis through direct current optical emission spectrometry).[35−37]

Sediment Analysis. Two piston cores from the North and South Basin were acquired in 2012 (core diameter 90 mm) using a piston corer designed by Uwitec.[38] The North Basin core +54-03/68 PC (53.7 m water depth; UTM coordinates, 502900, 6029136; core length, 10 m) and South Basin core +54-03/57 PC (37.3 m water depth; UTM coordinates, 503267, 6018702; core length, 6 m) (Figure 1) were analyzed using an Itrax micro-XRF core scanner (step size 200 μm, counting time 30 s, Mo anode X-ray tube, XRF conditions 30 kV, 50 mA) in accordance with the methodology detailed in ref 39.

The cores were also subsectioned at 1 cm resolution, and 35 samples from each core were analyzed by WD-XRF to quantitatively determine compositional changes. Further analysis of 16 representative lake bed sediment samples acquired by a Van Veen F42A grab (lightweight sediment sampler used to collect accurate representative samples of the top layer of sediment) in 2011 (Figure 1) was also completed via WD-XRF analysis according to the same methodology. The conventional WD-XRF data provide lower resolution compositional variations on homogenized centimeter-scale subsamples, whereas the Itrax micro-XRF core scanner provides continuous, nondestructive, high-resolution elemental profile data. The high frequency compositional changes identified by the Itrax are often missed when using lower resolution subsamples. The Itrax produces elemental data in counts but numerous studies (e.g., ref 40) have shown that these data highly correlate with quantitative analytical data (e.g., ICP-OES or WD-XRF). This aspect, along with its nondestructive analytical and radiographic capability, combine to make the Itrax a unique high-resolution core scanner.

Additional analysis included using radiochronology (^{210}Pb and ^{137}Cs) to determine accumulation rates. ^{210}Pb activity was determined through the measurement of its granddaughter ^{210}Po using alpha spectrometry. A Constant Flux−Constant Sedimentation (CF:CS) model of ^{210}Pb dating was used.[41] The CF:CS model assumes that both the flux of unsupported ^{210}Pb to the sediment and the sedimentation rate are constant. When

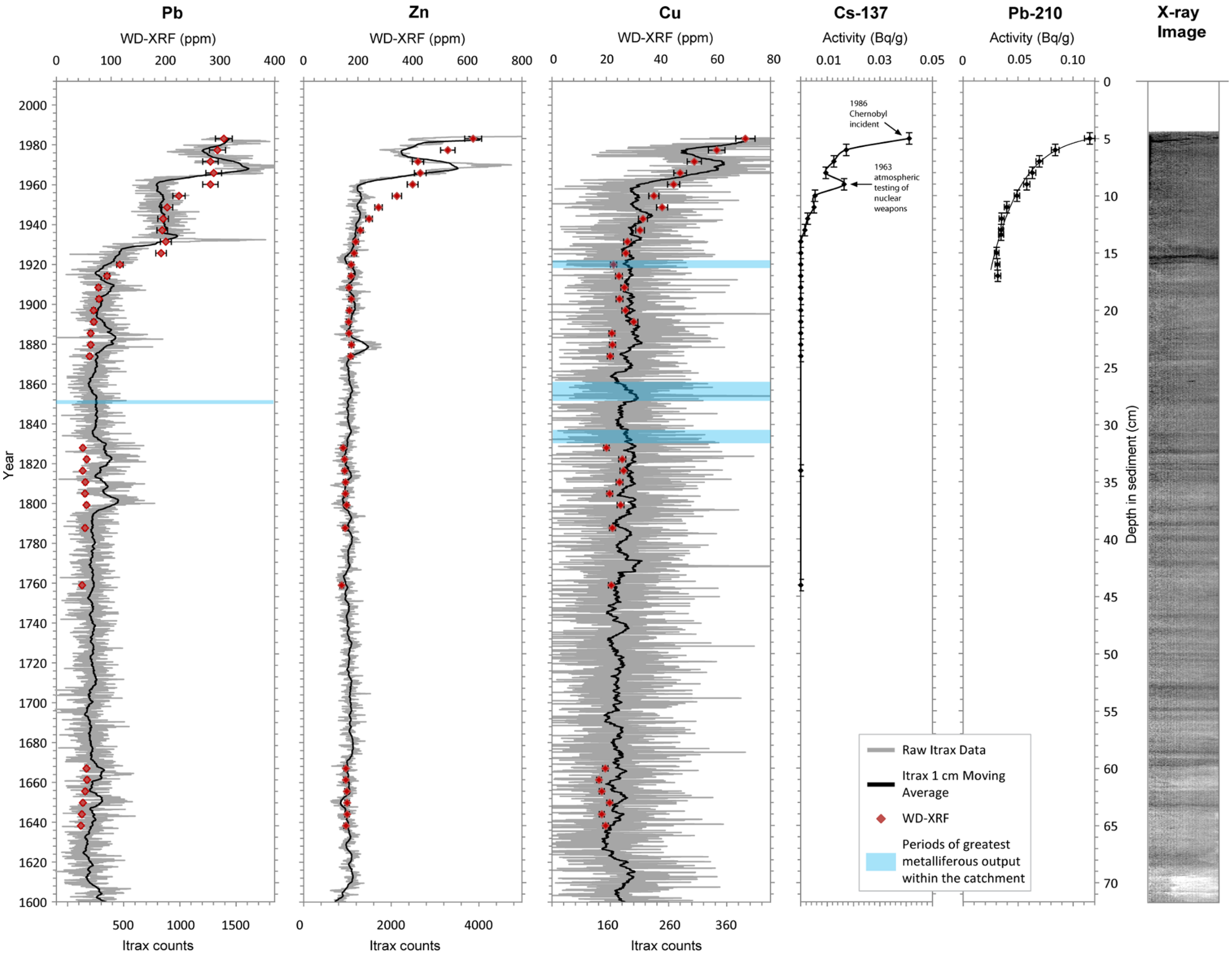

Figure 2. Pb, Zn, and Cu profiles, ^{137}Cs activity and total ^{210}Pb activity profile with exponential fit in core +54-03/68 PC (North Basin), with periods of metalliferous output labeled; 4.52 cm is added to the sample depth to compensate for loss of sediment in the top of the core (see Discussion section). Continuous lines show Itrax peak areas, points show concentrations determined from subsamples using WD-XRF, and the X- ray image is from the Itrax core scanner.

the assumptions are satisfied, the ^{210}Pb concentration will vary exponentially in accumulating sediment due to the exponential nature of radioactive decay. The sedimentation rate is calculated by plotting the natural logarithm of the unsupported lead concentration and determining the least-squares fit. The ^{137}Cs activity of samples (sampled at 1 cm resolution) was determined using a Canberra well-type HPGe gamma-ray spectrometer (counting for 100 000 s). High precision lead isotopic abundances were also determined to yield information on geochemical origin. Isotopic data were acquired using a Thermo Scientific NEPTUNE multicollector ICP-MS. Instrumental mass bias was corrected using the SBL74 ^{207}Pb–^{204}Pb double spike developed at the University of Southampton.[11] For more details of sediment analysis, see Supporting Information.

■ RESULTS

Mining and Quarrying. Within the Windermere catchment, mining exploited mineral (copper, lead–zinc, hemeatite) veins within the heavily faulted Ordovician (BVG) rocks around Grasmere and within Tilberthwaite and Langdale Valley, particularly during the latter half of the 19th century (Figure 1). Copper mining mostly took place to the west of Windermere at Greenburn, Skelwith, and Hawkshead (see Table S1, Supporting Information). The largest mine was at Greenburn where five E-W copper veins yielding copper pyrites and a large quantity of oxide of copper were worked.[42] Stream sediment geochemical data acquired in 1978–1980 identifies elevated levels of copper (above the background level of 10–25 ppm) near the mine, most likely derived from spoil heaps and workings (Figure 1).

Veins in which lead and zinc minerals form the main metallic component have been mined on a considerable scale in the Lake District.[36] In the Windermere catchment, two disused lead mines (Greenhead Gill and Coniston United Mine) worked mineral veins within the fault system (Figure 1 and Table S1, Supporting Information). Greenhead Gill mine was worked for lead and silver, and although zinc was present in higher quantities it was not mined because it had little commercial value.[43] Stream sediment geochemical data identifies elevated levels of lead (>200 ppm) in this region. Iron ore mines exploited hemeatite-bearing veins within the heavily faulted BVG rocks NE of Grasmere (Figure 1 and Table S1, Supporting Information). The mines were closed in 1877 due

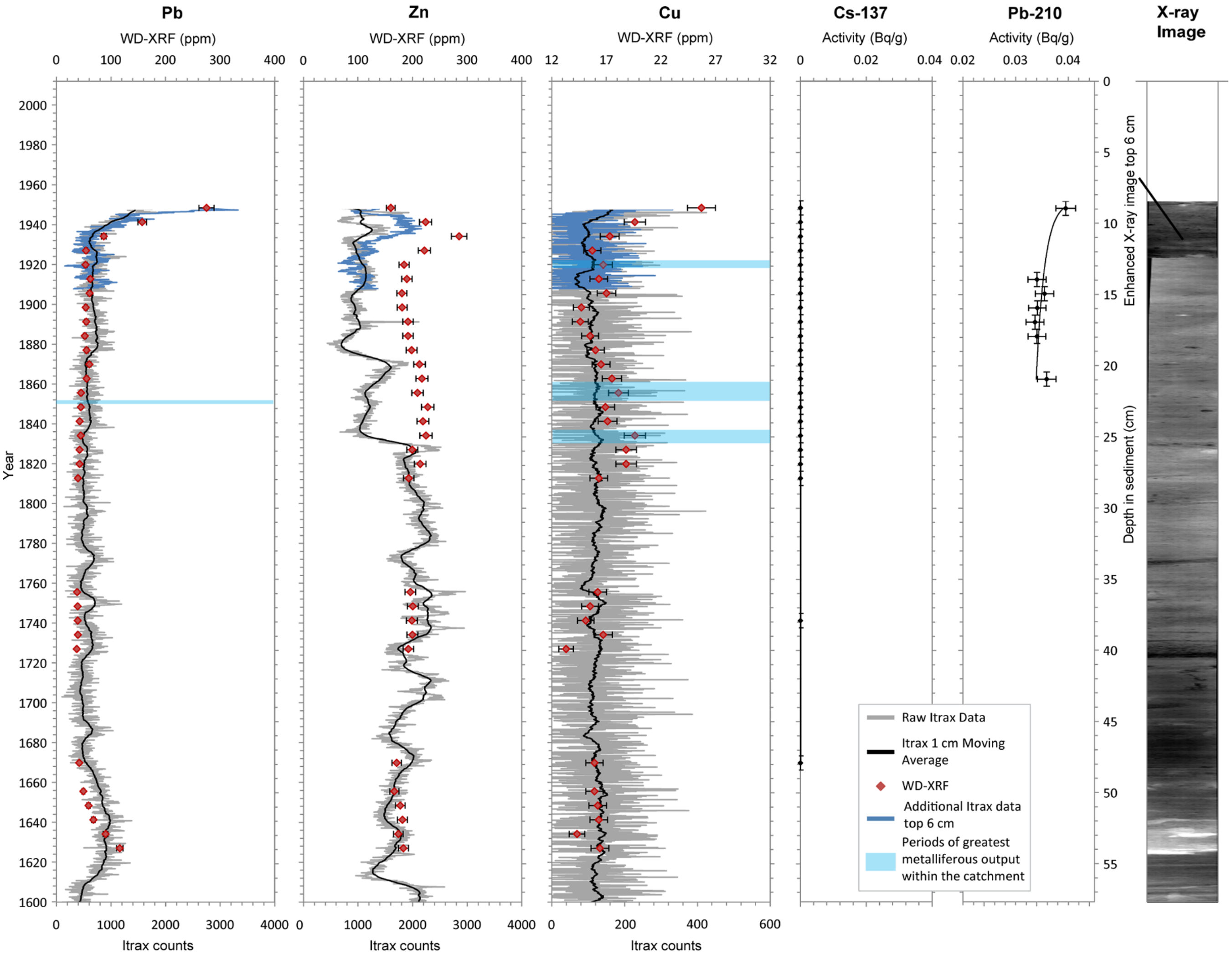

Figure 3. Pb, Zn, and Cu profiles, ^{137}Cs activity and total ^{210}Pb activity profile with exponential fit in core +54-03/57 PC (South Basin), with periods of metalliferous output labeled; 8.4 cm is added to the sample depth to compensate for loss of sediment in the top of the core (see Discussion section). Continuous lines show Itrax peak areas, points show concentrations determined from subsamples using WD-XRF and the X- ray image is from the Itrax core scanner. Additional Itrax data from the top 6 cm of the recovered core is derived from further analysis to supplement incomplete Itrax data from the top of the core.

to low production, high transport costs, and falling prices, but were later worked during the 1930s due to the high price of iron.[42] Quarrying for slate is the only active extractive industry in the catchment with five quarries (Elterwater, Peatfield, High Fell, Petts, and Brathay) currently active (Figure 1).[17,34] The past quarrying has led to increased sediment loads of fine rock-flour entering Windermere, particularly in the North Basin.[25,44]

Historical research has revealed the greatest period of metalliferous output within the Windermere catchment was in the latter half of the 19th century (see Table S1, Supporting Information). These periods of metal workings do not correspond with notable increases in heavy metals (Figures 2 and 3). In addition, elevated concentrations of lead, zinc, and copper in stream sediment geochemical data in the northern portion of the Windermere catchment are also observed in headwater regions which are not influenced by mining activities downstream (Figure 1). The high concentrations are possibly due to the weathering of bedrock, and it is likely that the presence of mineral veins acts as conduits for heavy metals.

Sediment Accumulation Rates. Sediments were dated to determine accumulation rates using the CF:CS ^{210}Pb model. In the North Basin (core +54-03/68 PC), the supported ^{210}Pb activity is estimated to be 0.019 Bq/g, based on observing the activity in the deepest samples where the excess Pb activity tends toward a baseline of zero. The average sediment accumulation rate is 0.17 cm/yr (2 SE limits 0.15−0.21 cm/yr). We were able to validate this accumulation rate over the last 49 years by measuring ^{137}Cs activity. The impact of the Chernobyl disaster (1986) is known to be significant in the Lake District, with the input of most Chernobyl-derived Cs through direct atmospheric deposition during a few hours of intense convective rainfall after the incident. A peak in ^{137}Cs activity at the top of the core is taken to correspond to the 1986 Chernobyl incident,[45] and a peak at a depth of 4.5 ± 0.5 cm is taken to correspond to the 1963 atmospheric testing of nuclear weapons (bomb maximum), suggesting an average sediment accumulation rate from 1963 to 1986 of 0.17 ± 0.02 cm/yr. This is consistent with the ^{210}Pb determined accumulation rate (Figure 2).

In the South Basin (core +54-03/57 PC), no ^{137}Cs activity was measured and results from ^{210}Pb dating were more variable with several outlier values, particularly between 1 and 5 cm

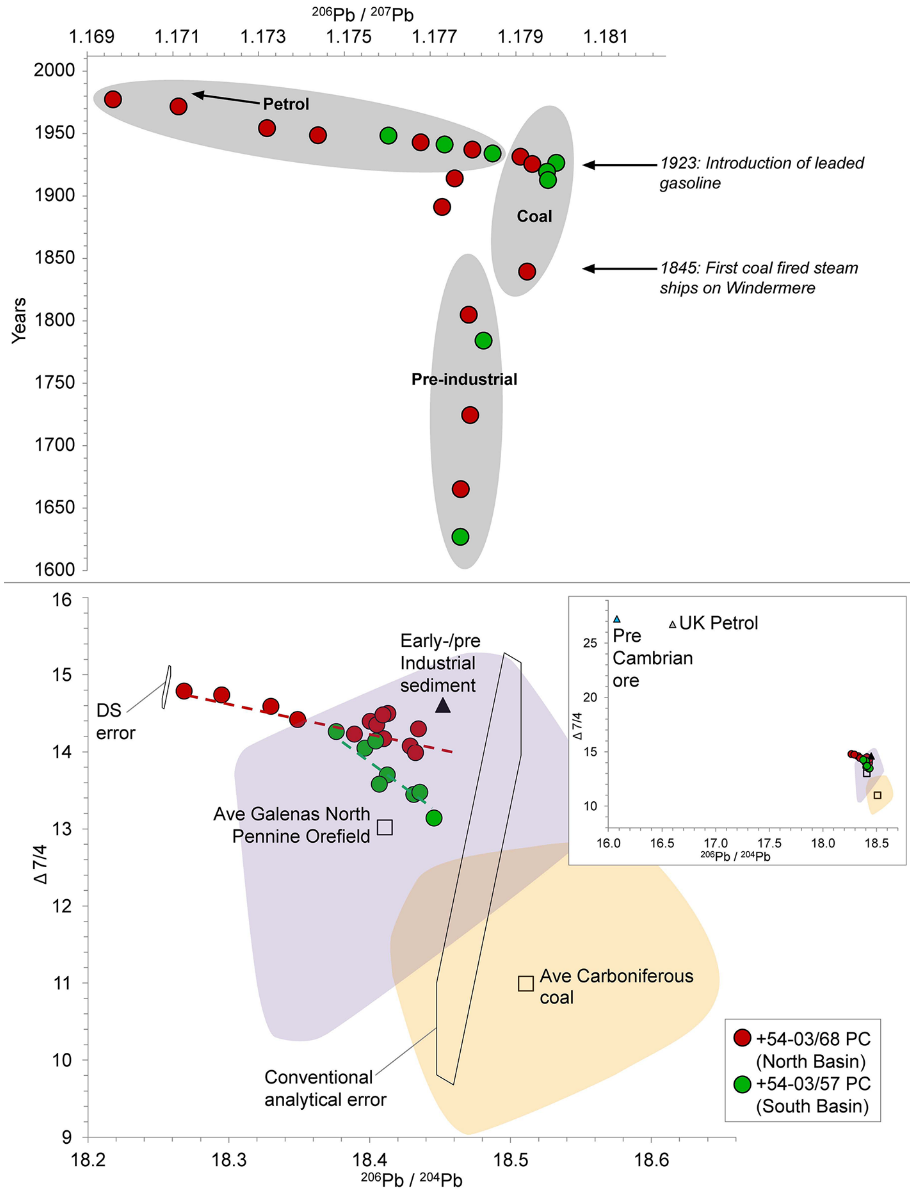

Figure 4. Upper panel: lead isotope ratios, showing change in $^{206}Pb/^{207}Pb$ over time. Lower panel: Δ7/4 versus $^{206}Pb/^{204}Pb$ showing the scale of the double-spike error (conventional analytical error for comparison). The average end-member ratio for pre/early industrial sediment[46,47] is taken as approximate to that of preindustrial deposits from Windermere. The field for Carboniferous coal and galena ratios[7] were derived by conventional lead isotope measurement techniques. Inset shows Pre-Cambrian ore ratios from Australia (likely source of gasoline antiknock agent)[48] and end-member ratio for UK gasoline[4] (see Supporting Information Tables S2 and S3 for details).

depth. Following removal of these values, supported ^{210}Pb activity was estimated to be 0.033 Bq/g, and a linear fit through a plot of the natural logarithm of the determined excess ^{210}Pb activities for each sample suggests an average accumulation rate of 0.14 cm/yr (2 SE 0.08−0.56 cm/yr) (Figure 3). In core +54-03/68 PC and +54-03/57 PC, the likely presence of erosion surfaces will be discussed further in the Discussion section.

Heavy Metal Profiles. In the North Basin (core +54-03/68 PC), Itrax elemental profiles reflect conventional WD-XRF compositional variations and show a lake catchment that has been fairly stable over the period of sediment accumulation (Figure 2). However, there are significant deviations from this stability within the top 12 cm of the recovered core (69 year period). In particular, the Itrax data (which reveal much higher resolution variations at the submillimeter level compared to the WD-XRF data) show a stepwise increase in lead from 1935 to 1960. In addition, there is a significant increase in lead, zinc, and copper from 1960 to 1968, a decline from 1968 to 1978, and a subsequent increase from 1978 to 1984 (Figure 2). This covariation of lead, zinc, and copper indicates a common source for these contaminants, and discounts the possibility that there have been separate Pb and Zn mineralization episodes.

In the South Basin, Itrax elemental profiles for lead and copper reflect conventional WD-XRF compositional variations and are relatively stable over the period of sediment accumulation; however, an increase in lead is observed within the top of the recovered core from 1935 to 1950 and a corresponding increase in copper is observed from 1940 to 1950 (Figure 3). The Itrax zinc profile shows an increase similar to lead and copper in the top of the recovered core (validated by the WD-XRF data). Deeper in the core, the Itrax zinc profile shows deviation over the period of sediment accumulation, whereas corresponding WD-XRF concentrations show a fairly stable profile with no significant deviation from the background level of ca. 180 ppm (Figure 3). The disagreement between Itrax and WD-XRF data is caused by variations in iron. A clear negative correlation exists between iron (relatively high concentration) and zinc (trace concentration) which represents an interelement effect. In WD-XRF fundamental parameter software corrects for interelement effects and provides an authentic profile which is similar to that seen for lead and copper. This capability is not provided with the Itrax.

Lead Isotope Analysis. In the North and South Basin core, ^{206}Pb/^{207}Pb of excess lead shows a similar profile over time (based on the sediment accumulation rates detailed above). In core +54-03/68 PC (North Basin), 4.52 cm is added to the sample depth and in core +54-03/57 PC (South Basin), 8.4 cm is added to the sample depth to compensate for loss of sediment in the top of the core (see Discussion section). The depth-shifted data reveals the oldest samples in both cores (ranging in age from 1810 to 1620) have a relatively constant ^{206}Pb/^{207}Pb around 1.177 and trend toward end-member ratios for early-industrial/preindustrial sediments (taken as approximate to that of preindustrial deposits from Windermere) (Figure 4). Samples with a ^{206}Pb/^{207}Pb around 1.179 (ranging in age from the 1920s to the 1840s) trend toward end-member ratios for Carboniferous coal, and samples ranging in age from 1980 to the 1920s are characterized by low ^{206}Pb/^{207}Pb and trend toward the isotopically distinguishable UK gasoline end-member ratio[4] (Figure 4).

DISCUSSION

The approach used for dating (using the CF:CS ^{210}Pb model) yielded an accumulation rate for the sediment of 0.17 cm/yr in the North Basin (core +54-03/68 PC) and 0.14 cm/yr in the South Basin (core +54-03/57 PC). In Windermere and other lakes in the catchment, a number of studies have dated recent sediments using similar methods to provide a record of environmental change.[18,49−51] In the North Basin, ^{210}Pb dates from a 1997 mini-core located ca. 600 m SW of core +54-03/68 PC suggest a mean accumulation rate of approximately 0.18 cm/yr,[52] which is in agreement (within the estimated uncertainty) with the accumulation rate determined for core +54-03/68 PC. In the ^{137}Cs record, Appleby[52] identified two distinct peaks at 4.5 and 10.5 cm, which are related to the 1986 Chernobyl incident and the 1963 atmospheric testing of nuclear weapons (bomb maximum). The ^{137}Cs record from core +54-03/68 PC also shows two peaks in activity at the top of the core and at a depth of 4.5 ± 0.5 cm. The peak at the top of the core is taken to correspond to the 1986 Chernobyl incident, suggesting a loss of at least 4.52 cm (rate of 0.17 cm/yr over 26 years) of sediment from the top of the core (Figure 2).

In the South Basin, given the lack of ^{137}Cs and outlier ^{210}Pb values, we infer disturbance and likely loss of sediment from the top of core +54-03/57 PC. The absence of ^{137}Cs suggests a loss of at least 60 years of accumulation (initial input of ^{137}Cs into the global environment estimated to be 1952, related to atmospheric nuclear weapons testing). At our estimated accumulation rate of 0.14 cm/yr (based on ^{210}Pb activity) this equates to a loss of at least 8.4 cm (Figure 3). Sediment loss is possibly the result of the coring process. It is important to note that the accumulation rate for the North and South Basin core (derived from ^{210}Pb dating and validated by reference to chronostratigraphic dates from the ^{137}Cs record), is only valid in surface sediments, and the rate for surface sediments may not be representative at depth. The extrapolated chronology to 1600 is tentative, and therefore the depth in the core is also displayed for comparison (Figures 2 and 3).

Reconstruction of the sediment record in the North Basin using high-resolution Itrax data (validated against WD-XRF data) suggests that while most element concentrations have been stable over the period of sediment accumulation, there was a stepwise increase in lead concentration from 1935 to 1960, and a significant increase from 1960 to 1968. In the South Basin, an increase in lead is similarly observed from 1935 to 1950 (Figures 2 and 3). In addition, ultrahigh precision, double-spike lead isotope measurements reveal a significant decline in ^{206}Pb/^{207}Pb from the 1920s to 1980. This is attributable to the introduction and use of (^{206}Pb-depleted) leaded gasoline post-1923, demonstrating a significant anthropogenic input of lead in recent sediments (Figure 4). Increased industrialization, urbanization, and road traffic at this time led to a dramatic increase in atmospheric lead emissions in other parts of the UK, particularly during the 1960s and 1970s.[2,7,53] The increases observed in stable lead, particularly from 1960 to 1968 is the result of increased industrialization and urbanization at this time. When using high-precision lead isotopes (measured by double spike, errors < ±0.002%), Δ7/4 (calculated relative to the Northern Hemisphere Reference Line)[54] is used to visualize the subtle differences which are difficult to observe in the traditional 64−74 plots. In Windermere, Δ7/4 further suggests leaded gasoline is a common source of lead in recent sediments, and Δ7/4 trend toward the isotopically distinguishable UK gasoline end-member ratio (Figure 4, lower panel).[4]

The double-spike lead isotope measurements further reveal samples ranging in age from the 1840s to the 1920s trend toward end-member ratios for Carboniferous coal (Figure 4). The most likely source of Carboniferous coal is coal-fired steam ships, the first of which was launched in Windermere in 1845.[25,27,55] The opening of the Kendal to Windermere railway in 1847 saw the introduction of additional steamers to the lake and led to a rapid expansion in the use of these boats. In 1869, the railway was built as far as Lakeside, and round trips on the streamers and trains were offered, further boosting tourist traffic. In 1872, the Furness Railway Company combined the new railhead with a steam cargo service, further increasing use and transporting cargo such as coal, timber, saltpeter, and sulfur.[55] By 1922, the roads had improved and motor vehicles were common, and steamers were no longer required to transport cargo. The age of steam on Windermere gradually came to a close, with most coal-fired steamers ceasing operation by 1956, after which some vessels were refitted with diesel engines. In 1899, the first motor boat was used on the lake, and motor boats and steamers operated alongside each other for several years. From the 1920s onward, a decline in ^{206}Pb/^{207}Pb is most likely due to the introduction and use of leaded gasoline, and the end of coal-fired steamer operation on the lake. Other possible sources of Carboniferous coal include coal combustion (coal ash associated with the Industrial Revolution), which entered Windermere through two major pathways, via fluvial dispersal of finely ground coal waste and through diffuse atmospheric emissions from heavy industry.

In addition to Carboniferous coal, analysis of Δ7/4 identifies a further component of lead: galena ore from mineral veins

(Figure 4). Possible sources include mining activities and the discharge of lead-rich waste from abandoned mines (lead derived from Carboniferous Pb−Zn mineralization). In addition, isotopic ratios trend toward end-member ratios for early-industrial/preindustrial sediments (Figure 4, lower panel).[46,47] We infer a finite component of natural lead, derived from surface weathering, soil erosion, and Pb−Zn mineralization, is contained within the fine grained stream sediment entering Windermere. Elevated concentrations of lead, zinc, and copper in stream sediment data from headwater regions not influenced by mining activities downstream further suggest weathering of bedrock has contributed to the stream sediment entering Windermere. Thus, the elevated levels of lead in Windermere are considered to be a mixture of natural lead, and three major components of anthropogenic (industrial) lead, comprising gasoline lead, coal combustion lead, and lead derived from Carboniferous Pb−Zn mineralization.

The sediment record also identifies an increase in the concentration of copper: in the North Basin, concentrations significantly increased from 1960 to 1968, declined from 1968 to 1978 and increased from 1978 to 1984 (Figure 4). Concentrations of lead and zinc show similar variations, suggesting a covariance of these contaminants, and a common source. In the South Basin, concentrations of copper increased from 1940 to 1950 (Figure 3). The majority of metal mining and smelting in the catchment is located to the north of Windermere (Figure 1) and given the location in relation to up-system sediment traps (e.g., Grasmere, Elterwater, Langdale Tarn, Rydal Water) it is unlikely that a significant amount of mining related heavy metals would have been transported to Windermere. For example, copper contamination is recorded in sediments downstream from the Greenburn Mine in Elterwater,[25] and stream sediment data identifies elevated levels of copper near the mine (Figure 1), most likely derived from spoil heaps and workings. This indicates Elterwater acted as an efficient sediment trap, limiting the amount of mining related heavy metals entering Windermere. As a result of the trapping efficiency of up-system lakes, periods of metal workings in the Windermere catchment do not correlate with peaks in mining related heavy metals. The more recent increases in copper (and also lead and zinc) observed in the North and South Basin (in the 1940s and 1960s) could instead be due to flood-induced metal inwash after the cessation of mining (similar to findings in other upland regions of Britain).[56] The higher concentrations could also be due to the weathering of bedrock in the catchment, which contributes to the stream sediment load entering Windermere and leads to covariation of lead, zinc, and copper. In addition, increases in zinc can also be attributed to anthropogenic activity within the catchment, in the form of processed waste and human sewage inputs. High-resolution data from the North Basin reveal a marked increase in zinc in the 1960s (Figure 2), which corresponds with an increase in direct discharge of treated sewage effluents in the catchment at this time. The decline in concentration from 1968 to 1978 (North Basin), and from 1940 onward (South Basin) does not correspond with historical records of changes in sewage treatment practices.

This study has shown that the application of a specific combination of nondestructive and high precision analytical techniques has enabled determination of the timing and scale of anthropogenic inputs to Windermere. High-resolution Itrax analysis (validated against WD-XRF), radiochronology (^{210}Pb and ^{137}Cs), and ultrahigh precision, double spike lead isotopes provide new insights into the pollutant depositional history of Windermere and demonstrate the effectiveness of an integrated approach when investigating pollution signals in lacustrine environments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables providing information on metal workings in the Windermere catchment and lead isotope ratios in Windermere core samples, major ore deposits and contemporary environmental materials. Details of sediment analysis and references are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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