

Modern pollution signals in sediments from Windermere, NW England, determined by micro-XRF and lead isotope analysis

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Abstract: High resolution geochemical (Itrax micro-XRF and wavelength dispersive XRF) data, radiochronology (²¹⁰Pb and ¹³⁷Cs analyses) and ultra-high precision double-spike lead isotope measurements from lacustrine sediment cores are used in combination with historical research of former mining landscapes to investigate modern pollution signals in sediments from Windermere, the largest lake in the English Lake District. The sediment record suggests that while most element concentrations have been stable, there has been a significant increase since the 1930s in lead, zinc and copper concentrations. Double-spike lead isotope measurements reveal a mixture of natural lead, and three major contributory sources of anthropogenic (industrial) lead, comprising gasoline lead, coal combustion lead (from coal-fired steam ships) and lead derived from Carboniferous Pb-Zn mineralisation (mining activities). A number of up-system sediment traps have limited the amount of mining related heavy metals entering Windermere, and as a result, periods of metal workings do not correlate with peaks in heavy metals. Increases could also be due to flood-induced metal inwash or weathering of bedrock in the catchment. Application of these non-destructive and high precision analytical techniques provides new insights into the pollutant depositional history of Windermere.

Introduction

Lacustrine sediments provide an archive of environmental change and a high resolution record of catchment level anthropogenic activity, and can be used to examine temporal changes in natural and anthropogenic trace element input. Several studies attribute the enrichment of heavy metals in lacustrine sediments to human and industrial activity during the late 19th and early 20th centuries, and more recent leaded gasoline usage (Williams, 1991; Farmer et al., 1996; Yang et al., 2002; Yang and Rose, 2005). In particular, lead isotope ratios have been increasingly used to establish the principal sources of lead pollution and yield information on geochemical origin (Gulson et al., 1994; Monna et al., 1997; Farmer et al., 1999; Hansmann and Köppel, 2000; Shepherd et al., 2009). Development of the high precision double-spike lead isotope technique (Ishizuka et al., 2003) has also led to more sensitive environmental investigations.

Within the English Lake District, contamination of heavy metals as a result of direct human and industrial activity has been identified in several lacustrine settings. In particular, local point sources of heavy metals from mining activities have been identified within the sediments of Ullswater (Anderton et al., 1998; Kember, 2001; Grayson and Plater, 2009), Bassenthwaite (Hatfield et al., 2008; Chiverrell et al., 2012) and Brotherswater (Schillereff et al., 2013) (Fig.1). In the Windermere catchment, the historical extent of heavy metal pollution is believed to be considerable (Millward et al., 2000). Concentrations of heavy metals in sediment cores (0.5 – 1 m long) from the South Basin have identified enriched levels of lead, zinc, copper and mercury related to anthropogenic inputs such as mining activities, denudation of land surfaces, sewage discharge, heavy industry and burning of fossil fuels (Aston et al., 1973; Hamilton-Taylor, 1979; Hamilton-Taylor, 1983).

Regional Setting

Windermere is the largest natural lake in England and is divided into a North and South Basin, separated by an area of low islands and shallow water (Fig. 1). The lake occupies a radial pre-glacial river valley and is orientated NNW to SSW, measuring c. 17 km in length with a maximum width of c. 1.5 km and depth of 62 m in the north. The sedimentology of the lake bed is dominated by gyttja (fine to very coarse organic rich silt) and the geomorphology is characterised by several steps and ridges, interpreted as the surface expression of recessional moraines formed during ice retreat (Miller et al., 2013; Pinson et al., 2013). The bedrock of the catchment is predominantly comprised of the Borrowdale Volcanic Group (BVG) in the north, and the Silurian (Windermere Supergroup) in the south (Mitchell, 1956; Millward et al., 2000) (Fig. 2). There are two major fault systems in the region (orientated NNW-SSE and ENE-WSW) (Postlethwaite, 1975; BGS, 1996). These faults produce kilometre-scale map offsets within the oldest orientated Silurian formations, however large offsets are not seen to the north of Windermere (Woodcock and Soper, 2006) (Fig. 2). The major fluvial inputs in the North Basin are the River Rothay, Brathay and Troutbeck, and in the South Basin the predominant inflow enters as flow from the North Basin and via Cunsey Beck (Fig. 1). The fluvial inputs drain several streams and small lakes, including Elterwater, Grasmere and Rydal Water in the north, and Esthwaite Water in the west. Land cover to the north is largely grassland on poor soils and acidified podzols, to the west is mixed woodland with improved grassland and to the east is more urban with the towns of Ambleside and Bowness-on-Windermere (Pickering, 2001; Barlow et al., 2009a).

Within the Windermere catchment there are five existing sewage treatment works (STW) at Ambleside, Elterwater, Grasmere, Hawkshead and Tower Wood (Fig. 1). Wastewater entering Windermere was not treated until the opening of two STW, at Ambleside in 1886 and Beemire (near Bowness-in-Windermere) in 1888 (McGowan et al., 2012). Sewage from Beemire was subsequently diverted to a new STW at Tower Wood in 1924, which is currently the largest STW in the catchment, processing waste water from the Bowness/Windermere area. The level of nutrient enrichment and biological production in the water column has been assessed through regular monitoring since 1945, revealing a progressive change towards eutrophy (Reynolds and Irish, 2000). Increases in nutrients to the lake are attributed to a growing human population in the catchment, changes in agricultural practice and increased sewage discharge (Talling, 1999). In particular, an increase in the direct discharge of treated sewage effluents in the 1960s (due to centralisation of wastewater treatment) led to an increase in algal growth and phosphorus availability and a reduction in oxygen concentration in deep water (Reynolds and Irish, 2000; Pickering, 2001). In 1992, the introduction of a “phosphate stripping” treatment at Tower Wood and Ambleside STW led to a reduction in phosphate loading, particularly in the South Basin (Talling, 1999; Parker and Maberley, 2000). Similar findings were observed further north at Grasmere, where the onset of eutrophication is dated to 1855, analogous with the expansion of human settlement (Barker et al., 2005; Sabater and Haworth, 1995).

The Lake District has a long history of metalliferous mining and quarrying dating back to the 16th century, with some evidence for earlier activity in the 13th, 14th and 15th centuries. In the Windermere catchment, the greatest period of mineral output (for lead, copper and iron) was in the latter half of the 19th century (Pickering, 2001) and was followed by a rapid decline in the industry in 1870 due to foreign competition. There have been sporadic bursts of activity in the 20th century, but all mining activity has now ceased (Adams, 1988, 1995). Quarrying for slate, building stone and aggregates increased in the 16th century and developed into an important

commercial industry, particularly during the 19th century. The industry declined during late Victorian times and many small quarries closed during the early 20th century, leaving only a few commercial operators active (BGS, 2000).

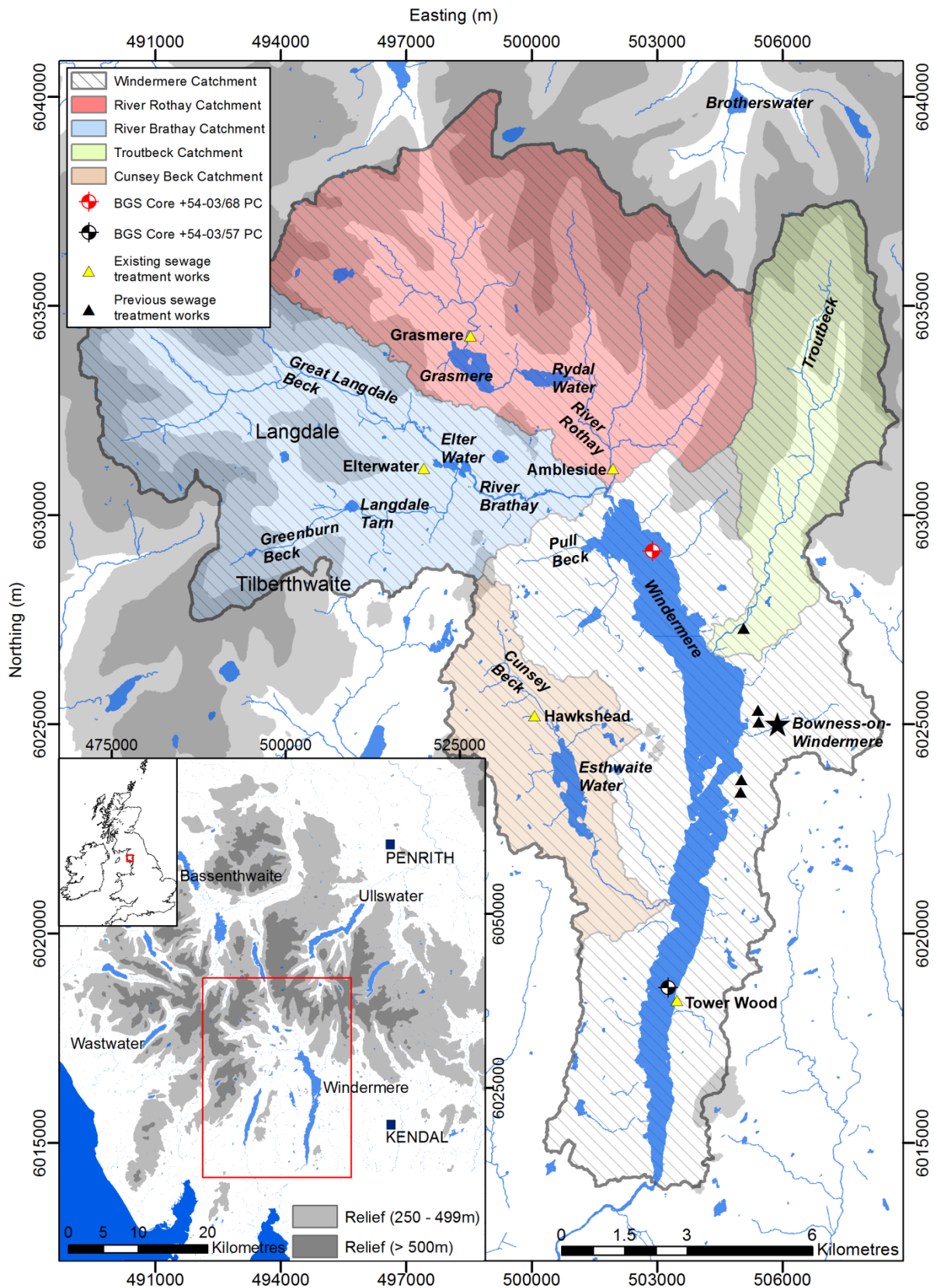


Fig. 1: Location of study area, showing the Windermere catchment, rivers, lakes, valleys, Bowness-on-Windermere (black star) and the location of existing and previous sewage treatment works and BGS sediment cores. Onshore DEM and catchment areas calculated using 5 m resolution NEXTMap data. Insert shows location map of the study area in relation to the Lake District and the British Isles.

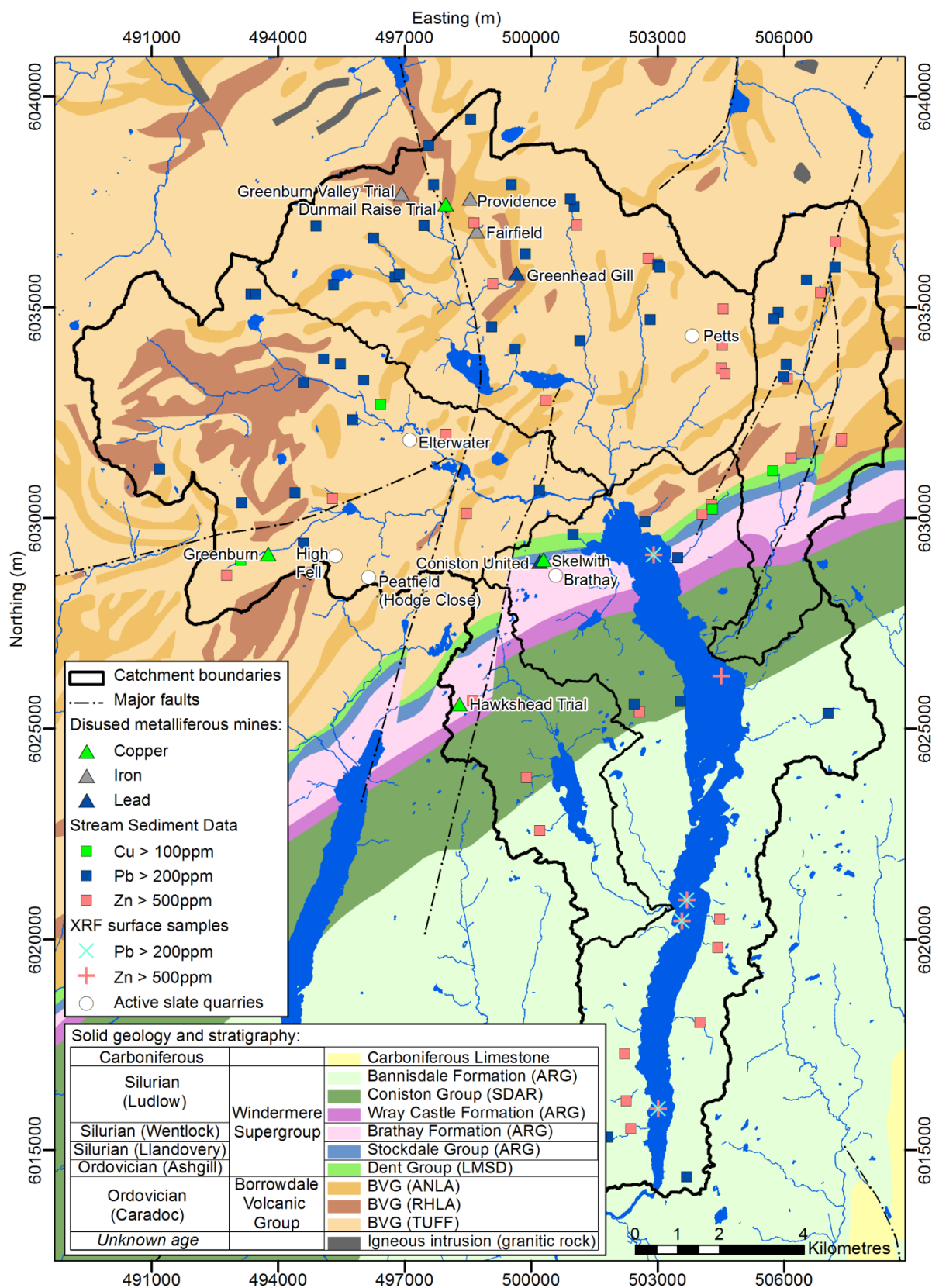


Fig. 2: Location of disused metalliferous mines and currently active slate quarries. Stream sediment and WD-XRF samples with elevated concentrations of Pb, Zn and Cu are shown. Solid geology, stratigraphy and faults (BGS, 1996). BVG: Borrowdale Volcanic Group; ARG: siliciclastic argillaceous rocks; ANLA: andesitic, lava; RHLA: rhyolitic, lava; SDAR: sandstone and (subordinate) argillaceous rocks interbedded; LMSD: limestone and (subordinate) sandstone interbedded. Figure contains British Geological Survey materials © NERC [2013].

Methodology

Historical Research

Catchment boundaries were determined using 5 m resolution onshore terrain data from NEXTMap Britain (a national IfSAR digital elevation database, Dowman et al., 2003) and spatial analyst tools in ArcGIS. Information on the former mining landscapes and metalliferous mining sites, output and locations within the Windermere catchment was then compiled from multiple sources, including published books and reports (Eastwood, 1921; Shaw, 1970; Postlethwaite, 1975; Adams, 1988, 1995; Tyler, 2005, 2006) and publications from local groups including the Cumbrian Amenity Trust Mining History Society (CATMHS) and the Kendal and District Mine Research Society (KDMRS). The BRITPITS Mineral Occurrence Database (MOD), the Lake District Historic Environment Record (LDHER)¹, the English Heritage Archive (PastScape Record)², the National Trust Historic Buildings, Sites and Monuments Record (HBSMR) and two additional websites^{3,4} were used to provide further information of mineral workings.

The BGS BRITPITS database and the LDHER were used to generate a complete list of disused quarries in the catchment. Active quarries were derived from these searches, and also the BGS BRITPITS Directory of Mines and Quarries 2010 (Cameron et al., 2010) and Millward et al., (2000). Stream sediment geochemical data were derived from BGS Geochemical Baseline Survey of the Environment (G-BASE)⁵. Small, first order streams were sampled from 1978 – 1980 and analysis was through direct current optical emission spectrometry (BGS, 1992; Johnson et al., 2005).

Sediment Analysis

Two piston cores from the North and South Basin were acquired in 2012 using a floating platform and piston corer designed by Uwitec⁶ (Fig. 1). The North Basin core +54-03/68 PC (53.7 m water depth, UTM coordinates 502900, 6029136) and South Basin core +54-03/57 PC (37.3 m water depth, 503267, 6018702) were longitudinally split (core diameter 90 mm) and photographed at high resolution, with one half archived at the British Geological Survey Core Store (Keyworth, UK). U-channels were extracted from the working halves of each core and analysed using an Itrax micro-XRF core scanner at the British Ocean Sediment Core Research Facility (BOSCORF, National Oceanography Centre, UK) in accordance with the methodology detailed in Croudace et al., (2006). **Itrax settings were as follows: step size 200 µm, counting time 30 seconds, molybdenum anode X-ray tube, XRF conditions 30 kV, 50 mA.** The Itrax micro-XRF core scanner provides continuous, non-destructive, high-resolution elemental profile data, and is capable of identifying high frequency compositional changes. In addition, a number of studies (e.g. Croudace et al., 2012) have shown that Itrax elemental data (in counts) correlates well with quantitative analytical data (e.g. ICP-OES or WD-XRF). These combine to make the Itrax a unique high-resolution core scanner.

The cores were also sub-sectioned at 1 cm resolution and samples were freeze-dried. 35 samples from each core were analysed by wavelength dispersive X-ray fluorescence (WD-XRF) using a Philips MagiX-Pro XRF spectrometer to measure concentrations of elements of atomic mass greater than or equal to sodium. Samples were homogenised by grinding and compressed into powder pellets in accordance with the standard

¹ <http://www.heritagegateway.org.uk>

² <http://www.english-heritage.org.uk/professional/archives-and-collections/nmr>

³ <http://www.cumbria-industries.org.uk>

⁴ <http://www.mine-explorer.co.uk>

⁵ <http://www.bgs.ac.uk/gbase>

⁶ <http://www.uwitec.at>

methodology (Croudace and Williams-Thorpe, 1988). A certified reference sample (BE-N, basalt, Centre de Recherches **Petrographiques et Gochimiques**, France) was used as a control and calibrations previously established by analysis of 15 International Geochemical Reference samples were used. Further analysis of 16 representative lake bed sediment samples acquired in 2011 by a lightweight sediment sampler (Van Veen F42A grab) (Fig. 2) were also completed via WD-XRF analysis according to the same methodology.

Sediment accumulation rates were determined using ^{210}Pb through the measurement of its granddaughter ^{210}Po using alpha spectrometry (Flynn, 1968). Each sample (1-3 g, 1 cm downcore) was spiked with ^{209}Po (nominally 50 mBq), digested using double acid leaching and Po separated onto silver discs by auto-deposition before counting by alpha spectrometry (100,000 seconds). A Constant Flux - Constant Sedimentation (CF:CS) model of ^{210}Pb dating (which assumes that both the flux of unsupported ^{210}Pb to the sediment and the sedimentation rate are constant) was used (Robbins, 1978). A Canberra well-type HPGe gamma-ray spectrometer (counting for 100,000 seconds) was used to determine the ^{137}Cs activity of samples from 0 - 20 cm, 29.5 cm and 39.5 cm (sampled at 1 cm resolution). The standard method of evaluating the 661 keV peaks of the spectra (Ritchie and McHenry, 1990) was used, and each activity was corrected for sample mass and volume.

High precision lead isotopic abundances were also determined using a Thermo Scientific NEPTUNE Multi Collector (MC) inductively-coupled plasma mass spectrometer (ICPMS) to yield information on geochemical origin. Samples from both cores ranging from 0.5 - 66.5 cm depth (1 cm downcore sampling resolution) were digested using double acid leaching followed by the isolation of lead from the matrix using AG1-X8 200-400 mesh anion exchange resin. All samples were measured with a ^{208}Pb ion beam intensity of $>1 \times 10^{-10}\text{A}$ as an integration of >20 measurements, each integrating 5 seconds. Instrumental mass bias was corrected using the SBL74 ^{207}Pb - ^{204}Pb double spike developed at the University of Southampton (Ishizuka et al., 2003). Pb standard NBS 981 gave results, 16.9403 ± 27 (2SD) for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.4973 ± 21 for $^{207}\text{Pb}/^{204}\text{Pb}$ and 36.7169 ± 66 for $^{208}\text{Pb}/^{204}\text{Pb}$. The lead isotopic standard NBS 981 was measured to assess accuracy, a procedural blank was treated in the same manner as the samples to determine possible contamination from reagents and general handling and clean laboratory techniques and high purity reagents were used to avoid contamination of samples with additional lead.

Results

Mining and Quarrying

Metalliferous mining exploited mineral (copper, haematite and lead-zinc) veins within Ordovician (BVG) rocks to the north of the Windermere catchment, particularly during the latter half of the 19th century (Fig. 2, Table 1). Copper mining took place at Greenburn, Skelwith and Hawkshead to the west of Windermere, and at Dunmail Raise Trial to the north. The largest mine was at Greenburn where five named E-W copper veins (through coarse ashes and breccias of the BVG) yielding copper pyrites and a large quantity of oxide of copper were worked to varying degrees (Postlethwaite, 1975). The low-grade ore was treated in lead lined stone tanks, by leaching the copper from the ore and then recovering by precipitation onto scrap iron (Blundell, 1994; Holland, 2000). Stream sediment geochemical data acquired in 1978 - 1980 (BGS G-BASE) identifies elevated levels of copper (above the background level of 10 - 25 ppm) near Greenburn Copper Mine, most likely derived from spoil heaps and workings (Fig. 2). Iron ore mines in the catchment exploited haematite-bearing veins within the heavily faulted BVG rocks NE of Grasmere within the River Rothay catchment (Shaw, 1970) (Fig. 2, Table 1). Providence and Fairfield mine were closed in 1877 due to low production, high transport costs and falling prices, but were later worked during the 1930s due to the high price of iron (Postlethwaite, 1975). Lead mines in the catchment worked mineral veins within the fault system at Greenhead Gill and Coniston United. The lead mine high up Greenhead Gill to the north of Grasmere was worked for lead and silver and tried by opencasts, deep shafts and short levels driven along the four E-W coursing veins. Although zinc was present in higher quantities it was not mined because it had no commercial value (Shaw, 1939). Stream sediment geochemical data in this region identifies elevated levels of lead (>200 ppm).

Slate quarrying in the Windermere catchment has taken place since the 17th century (Tyler, 2006) predominantly to the north of the catchment in the upper part of the volcanoclastic sedimentary rocks of the

BVG which yield sea-green slate in large quantities (Postlethwaite, 1975; Millward et al., 2000). Slate quarrying is the only active extractive industry in the catchment operating on a small scale, with five quarries at Elterwater, Peatfield, High Fell, Petts and Brathay currently active (BGS BRITPITS database; Millward et al., 2000; Cameron et al., 2010) (Fig. 2). In addition to slate quarrying, small scale open-pit or surface workings extracted igneous and metamorphic rocks (from the BVG), sandstone (from Silurian siltstones and mudstones within the Coniston Group and Bannisdale Formation) and sand and gravel. Quarrying in the catchment has led to increased fine sediment supply to Windermere, particularly evident in the North Basin (Pickering, 2001; Barlow et al., 2009b).

The greatest period of metalliferous output within the Windermere catchment was in the latter half of the 19th century (Table 1). These periods of metal workings do not correspond with notable increases in heavy metals (Figs. 3 and 4). In addition, in the northern portion of the Windermere catchment, some headwater regions (which are not influenced by mining activities) have high concentrations of lead, zinc and copper in stream sediment geochemical data. This could be 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

The CF:CS model of ^{210}Pb dating was used to determine accumulation rates. Supported ^{210}Pb activity in the North Basin (core +54-03/68 PC) was estimated to be 0.019 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 0.17 cm/yr (2 S.E. 0.15 - 0.21 cm/yr). In the Lake District, the impact of the Chernobyl disaster (1968) is significant, with the input of most Chernobyl-derived Cs through direct atmospheric deposition during a few hours of intense rainfall after the incident. ^{137}Cs activity in core +54-03/68 PC was measured in order to validate the ^{210}Pb accumulation rate over the last 49 years. At the top of the core, a peak in ^{137}Cs activity is taken to correspond to the 1986 Chernobyl incident (Ritchie and McHenry, 1990). An additional peak in ^{137}Cs activity at a depth of 4.5 ± 0.5 cm is taken to correspond to the 1963 atmospheric testing of nuclear weapons (bomb maximum) (Fig. 3). This suggests an average sediment accumulation rate of 0.17 ± 0.02 cm/yr from 1963 to 1986, which is consistent with the ^{210}Pb accumulation rate.

^{137}Cs activity was not observed in the South Basin (core +54-03/57 PC) and ^{210}Pb results were more variable, with outlier values between 1 – 5 cm depth. Following removal of outliers, ^{210}Pb activity was estimated to be 0.033 Bq/g (based on observing the activity in the deepest samples where the excess Pb activity tends towards a baseline of zero) giving an accumulation rate of 0.14 cm/yr (2 S.E. 0.08 - 0.56 cm/yr) (Fig. 3). The likely presence of erosion surfaces in core +54-03/68 PC and +54-03/57 PC will be discussed further in the discussion section.

Heavy metal profiles

Itrax elemental profiles in the North Basin (core +54-03/68 PC) reflect conventional WD-XRF compositional variations and show a lake catchment that has been fairly stable over the period of sediment accumulation (Fig. 3). Within the top 12 cm of the recovered core (69 year period) there are significant deviations from this stability. The Itrax data show a stepwise increase in lead from 1935 to 1960, and increases in lead, zinc and copper are also observed from 1960 to 1968 and 1978 to 1984 (Fig. 3). This co-variation of elemental profiles indicates a common source for these contaminants.

In the South Basin (core +54-03/57 PC), Itrax and WD-XRF concentrations of lead and copper are relatively stable over the period of sediment accumulation; however, a marked increase is observed in lead from 1935 to 1950 and in copper from 1940 to 1950 (Fig. 4). Although zinc concentrations show a similar increase, deeper in the core the Itrax zinc profile shows deviation whereas corresponding WD-XRF concentrations show a fairly stable profile (Fig. 4). This disagreement between Itrax and WD-XRF data is caused by an inter-element effect due to variations in iron (there is a negative correlation between relatively high concentrations of iron and trace concentrations of zinc). WD-XRF fundamental parameter software corrects for inter-element effects, whereas this capability is not provided in the Itrax software.

Lead isotopes

$^{206}\text{Pb}/^{207}\text{Pb}$ of excess lead in the North and South Basin core shows a similar profile over time (based on the sediment accumulation rates derived from ^{210}Pb dating). The data, which has been depth shifted to compensate for loss of sediment in the top of the cores (see discussion section), reveals the oldest samples (from 1810 to 1620) have a relatively constant $^{206}\text{Pb}/^{207}\text{Pb}$ around 1.177. These samples trend towards end-member ratios for early-/pre industrial sediments (Hamilton and Clifton, 1979; Croudace and Cundy, 1995). Samples ranging in age from the 1920s to the 1840s are characterised by a $^{206}\text{Pb}/^{207}\text{Pb}$ around 1.179 and trend towards end-member ratios for Carboniferous coal (Shepherd et al., 2009). Samples characterised by a low $^{206}\text{Pb}/^{207}\text{Pb}$ (ranging in age from 1980 to the 1920s) trend towards the isotopically distinguishable UK gasoline end-member ratio (Monna et al., 1997) (Fig. 5).

Mine	Mineral	Coordinates (UTM)	Period of Operation	Greatest period mineral output	Details
Greenburn (Great Coniston Mine/New Coniston)	Copper	493746, 6029173	1845, evidence for 1690; closed 1942 (Adams, 1988, 1995; Blundell, 1994)	1854 – 1861 (mid 19 th century) (Millward and Robinson, 1974)	Suspension in late 19 th century, re-opened in early 20 th century
Hawkshead Trial	Copper	498289, 6025614	c. 1830 (Tyler, 2006)	-	Small copper trial
Skelwith	Copper	500290, 6029024	Opened 1540 (English Heritage Archive), closed 1901	1850s	Post Medieval copper mine
Dunmail Raise Trial	Copper	499665, 6035813	c. 1920 (Adams, 1988, 1995; Tyler, 2005, 2006).	-	Good quality copper ore, not in commercial quantities
Providence (Tongue Gill Iron Mines)	Iron	4986619, 6037515	Providence and Fairfield: start unknown, although mine supplied ore to the smelter in Langdale around 1700; re-opened in 1873, closed in 1877 (Tyler, 2005). Re-opened in 1930s (Postlethwaite, 1975).	Providence and Fairfield: early 17 th century, revival 1874 - 1876 (Shaw, 1970)	Providence and Fairfield: ancient iron ore mines
Fairfield	Iron	498659, 6036880			
Greenburn Valley Trial	Iron	496900, 6037679	1880s	-	Small trial (Tyler, 2006)
Greenhead Gill (Grasmere Lead Mine)	Lead	499665, 6035813	Opened 1564, closed 1573 (Shaw, 1970; Tyler, 2005). Re-worked in 1870s but soon abandoned (KDMRS newsletter, 1983, Tyler 2005, 2006)	-	Extensive account, including production data (Tyler, 2005)
Coniston United	Lead	500196, 6028966	c. 1853 (Adams, 1988, 1995)	-	Group of trials, two levels, little mineralisation

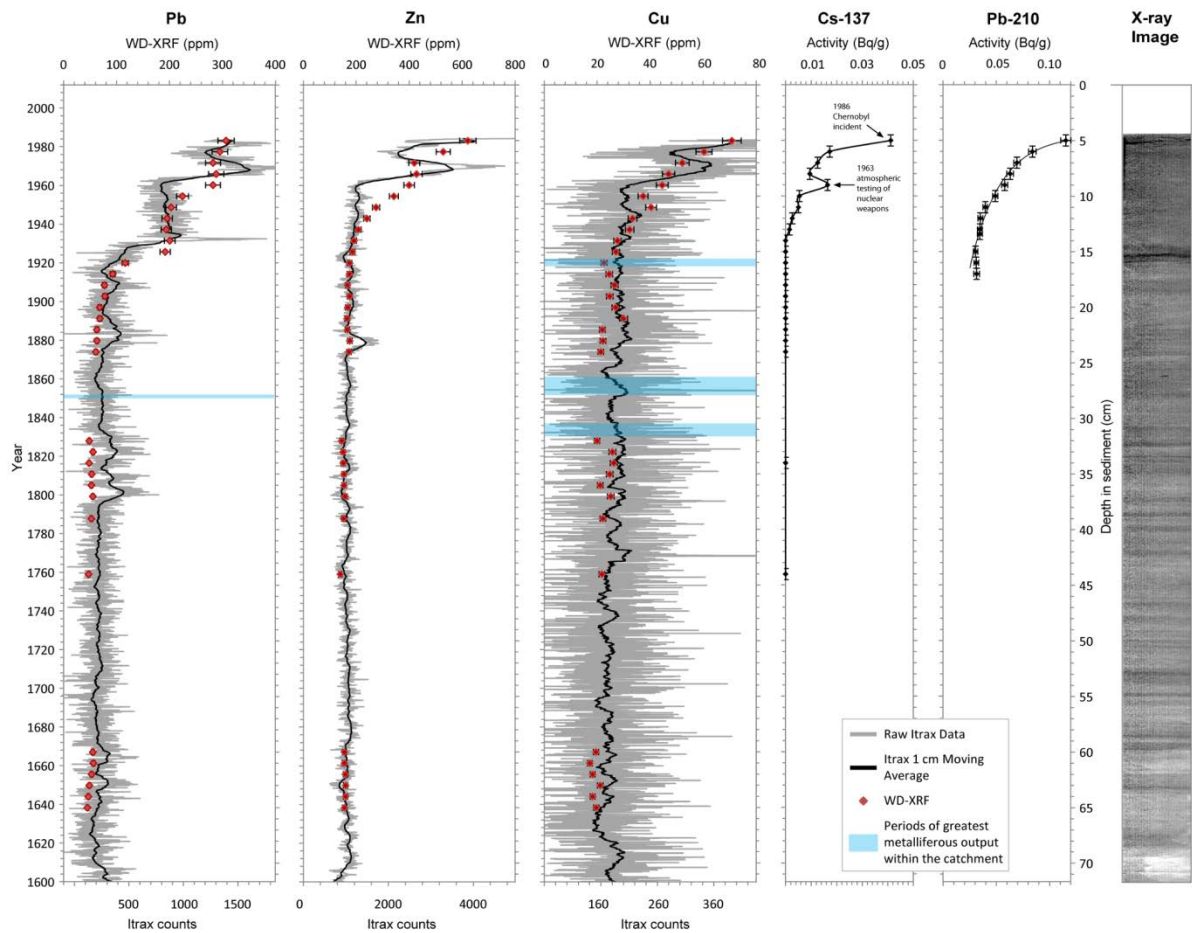
Table 1: Disused copper, lead and iron mines in the Windermere catchment.

Fig 3: Elemental profiles, ^{137}Cs activity and total ^{210}Pb activity in core +54-03/68 PC (North Basin). Periods of metalliferous output are highlighted, continuous lines show Itrax peak areas, points show concentrations determined from sub-samples using WD-XRF and the X-ray image is from the Itrax core scanner. 4.52 cm is added to the sample depth to compensate for loss of sediment in the top of the core.

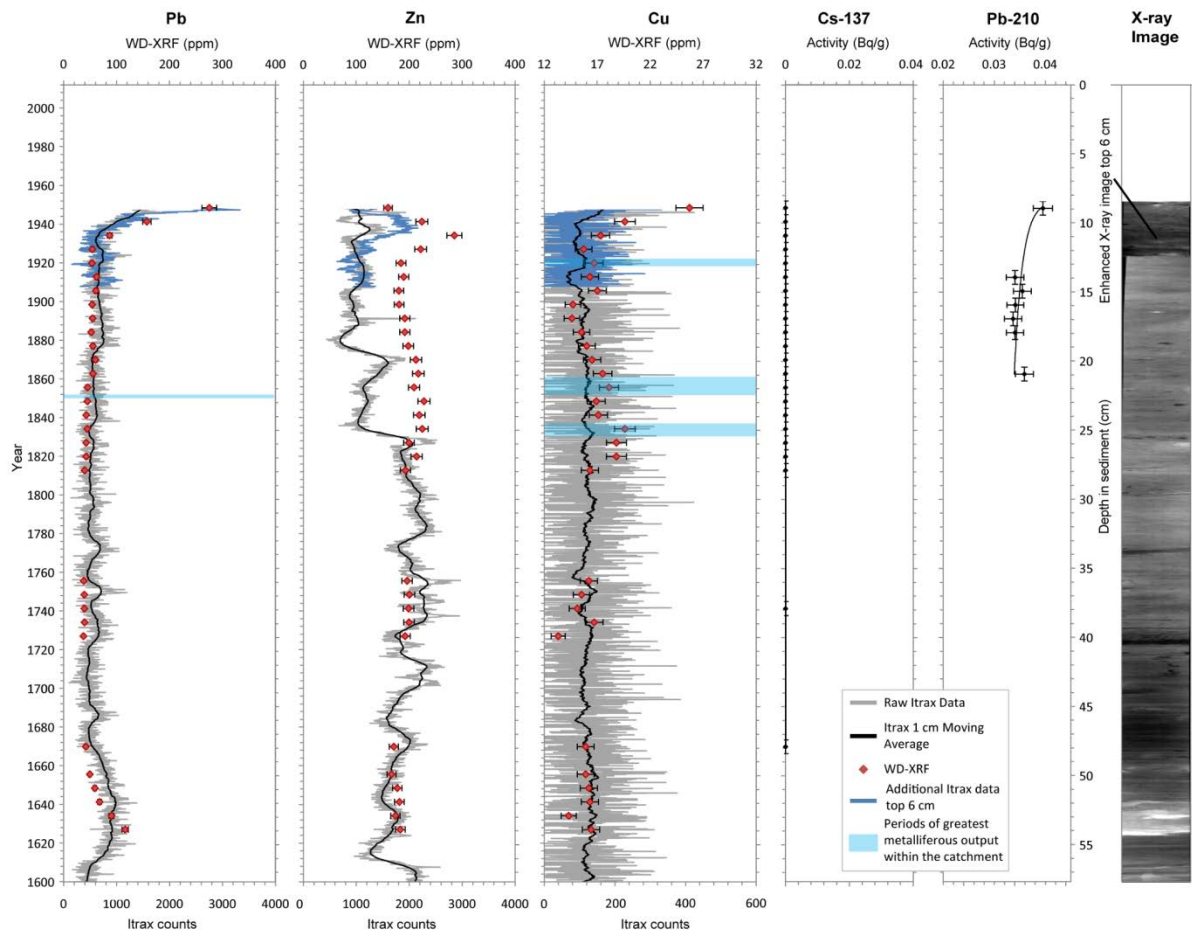


Fig 4: Elemental profiles, ^{137}Cs activity and total ^{210}Pb activity in core +54-03/57 PC (South Basin). Periods of metalliferous output are highlighted, continuous lines show Itrax peak areas, points show concentrations determined from sub-samples using WD-XRF and the X-ray image is from the Itrax core scanner. 8.4 cm is added to the sample depth to compensate for loss of sediment in the top of the core.

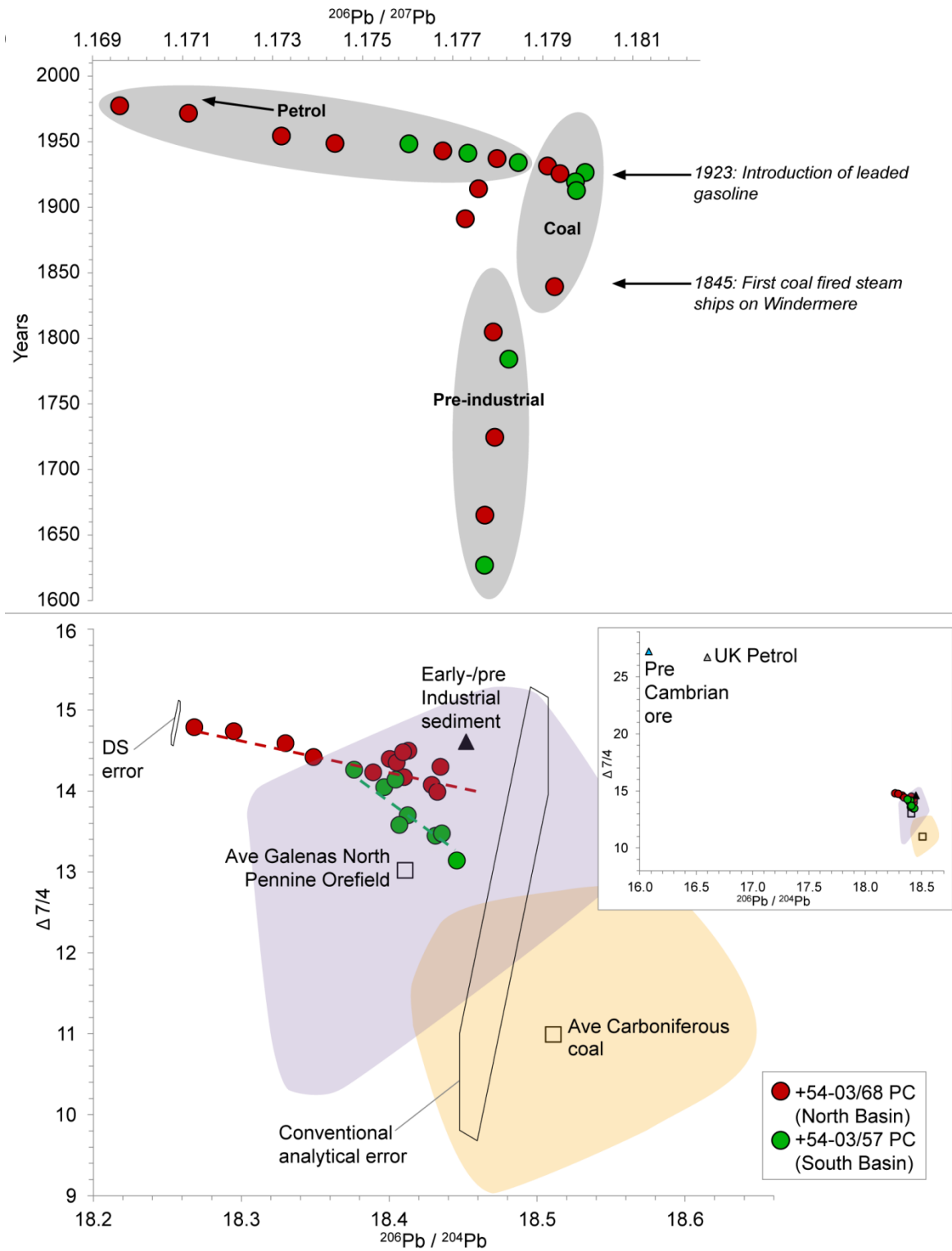


Fig 5: Upper panel: lead isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$) over time. Lower panel: $\Delta 7/4$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ with double-spike and conventional analytical errors for comparison, average (mean) end-member ratio for pre-/early industrial sediment and Carboniferous coal and galena ratios (derived by conventional lead isotope measurement techniques). Insert shows Pre-Cambrian ore ratios and UK gasoline end-member ratio. See Table 2 for details.

Core	Depth in core (cm)	$^{206}\text{Pb}/^{204}\text{Pb}$	\pm	$^{207}\text{Pb}/^{204}\text{Pb}$	\pm	$^{208}\text{Pb}/^{204}\text{Pb}$	\pm
+54-03/68 PC North Basin	6.02	18.2682	12	15.6192	11	38.2692	35
	7.02	18.2949	39	15.6216	38	38.3002	117
	10.02	18.3299	9	15.6239	9	38.3364	27
	11.02	18.3488	12	15.6242	12	38.3578	37
	12.02	18.3892	20	15.6267	19	38.4011	60
	13.02	18.4100	27	15.6283	25	38.4247	79
	14.02	18.4288	13	15.6294	13	38.4484	39
	15.02	18.4325	12	15.6290	12	38.4501	37
	17.02	18.4051	20	15.6296	19	38.4174	61
	21.02	18.4004	11	15.6296	11	38.4097	33
	30.02	18.4346	11	15.6323	10	38.4747	32
	36.02	18.4129	10	15.6319	10	38.4303	30
	45.02	18.3226	10	15.5548	9	38.2214	28
	60.02	18.4094	19	15.6314	18	38.4289	57
+54-03/57 PC South Basin	8.9	18.3762	12	15.6256	11	38.3754	35
	9.9	18.3968	9	15.6257	8	38.3906	25
	10.9	18.4121	18	15.6239	17	38.4089	54
	11.9	18.4356	22	15.6242	21	38.4394	66
	12.9	18.4453	42	15.6218	14	38.4388	42
	13.9	18.4313	37	15.6234	35	38.4311	109
	31.9	18.4067	15	15.6221	15	38.4125	45
	53.9	18.4042	29	15.6274	28	38.4025	87
	74.9	18.3075	9	15.5236	9	38.1420	28
End Member	Source	Isotopic composition of lead		Reference			
		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$				
Carboniferous coal	Durham Northumberland coalfield (n = 11)	18.51	15.60	Shepherd et al., (2009)			
Galenas (Pb-Zn mineralisation)	North Pennine Orefield (n = 26)	18.41	15.61	Shepherd et al., (2009)			
Pre Cambrian (ores in UK lead-alkyls)	Australia: Mt Isla	16.08	15.50	Chow et al., (1975)			
Pre-/early industrial sediments	Swansea Bay	18.45	15.63	Hamilton and Clifton (1979)			
	Southampton Water	18.45	15.63	Croudace and Cundy (1995)			
Gasoline	Southampton 1994-95 (n = 7)	16.60	15.55	Monna et al., (1997)			

Table 2: Lead isotope ratios in Windermere samples, major ore deposits and contemporary environmental materials. Errors are within measurement precision and represent 2 S.E. quoted as the last two d.p. of the isotope ratio. Details of the external standard reproducibility are given in the text. Windermere samples have been depth shifted to compensate for loss of sediment in the top of the cores (see discussion section). Ratios are displayed in Fig. 5.

Discussion

A number of studies have dated recent sediments in Windermere and other lakes in the catchment (Aston et al., 1973; Pennington et al., 1973; Pennington et al., 1976; Appleby et al., 1991; Appleby et al., 2003; Barker et al., 2005). In the North Basin, ^{210}Pb dates from a 1997 mini-core (located c. 600 m SW of core +54-03/68 PC) suggest a mean accumulation rate of approximately 0.18 cm/yr (Appleby, 2008). This is in agreement (within the estimated uncertainty) with the accumulation rate of 0.17 cm/yr determined for core +54-03/68 PC. Appleby (2008) also identified two peaks in the ^{137}Cs record at 4.5 cm and 10.5 cm related to the 1986 Chernobyl incident and the 1963 bomb maximum. In core +54-03/68 PC, two peaks in ^{137}Cs activity are also identified: at the top of the core (related to the 1986 Chernobyl incident) and at 4.5 ± 0.5 cm. This suggests a loss of at least 4.52 cm (0.17 cm/yr over 26 years) of sediment from the top of the core (Fig. 3). In the South Basin, outlier ^{210}Pb values and the absence of ^{137}Cs suggests a loss of at least 60 years of accumulation (initial input of ^{137}Cs estimated to be 1952, related to atmospheric nuclear weapons testing). This suggests a loss of at least 8.4 cm (0.14 cm/yr over 60 years) of sediment from the top of the core (Fig. 4). The ^{210}Pb accumulation rates are valid in the surface sediments; however, it is important to note that the accumulation rate may not be representative at depth, and therefore the depth in the core and the extrapolated chronology are displayed for comparison (Figs. 3 and 4).

In the North Basin, Itrax elemental profiles and WD-XRF concentrations identify an increase in lead concentration from 1935 to 1960, and a significant increase from 1960 to 1968. A similar increase is observed in the South Basin from 1935 to 1950 (Figs. 3 and 4). These increases are most likely the result of increased industrialisation, urbanisation and road traffic following the introduction and use of (^{206}Pb -depleted) leaded gasoline post-1923. Within the UK, this led to a dramatic increase in atmospheric lead emissions, particularly during the 1960s and 1970s (Farmer et al., 1996; Komárek et al., 2008; Shepherd et al., 2009). High-precision lead isotopes (measured by double spike, errors $< \pm 0.002\%$) also reveal a significant decline in $^{206}\text{Pb}/^{207}\text{Pb}$ from the 1920s to 1980 (attributable to the use of alkyl-leaded fuel), demonstrating a significant anthropogenic input of lead in recent sediments (Fig. 5). In addition, $\Delta 7/4$ (calculated relative to the Northern Hemisphere Reference Line; Hart, 1984) trends towards the UK gasoline end-member ratio which suggests leaded gasoline is a common source of lead in recent sediments (Fig. 5, lower panel).

The isotopic character of lead changes with depth, and samples ranging in age from the 1840s to the 1920s trend towards the end-member ratio for Carboniferous coal (Shepherd et al., 2009) (Fig. 5). In Windermere, the most likely source of Carboniferous coal is coal-fired steam ships, which operated on the lake from 1845 onwards (Pattinson, 1981; Pickering, 2001; McGowan et al., 2012). Expansion in the use of these boats took place following arrival of the railway in Windermere in 1847 and Lakeside in 1869, and also the introduction of a steam cargo service in 1872 (Pattinson, 1981). From the 1920s onwards, motor vehicles were common and the age of steam on Windermere gradually came to a close. The decline observed in $^{206}\text{Pb}/^{207}\text{Pb}$ from the 1920s to 1980 is most likely due to the end of coal-fired steamer operation on the lake and the introduction and use of leaded gasoline. Coal combustion (associated with the Industrial Revolution) also represents another possible source of Carboniferous coal.

Analysis of $\Delta 7/4$ also identifies components of natural lead and galena ore from mineral veins, most likely derived from the discharge of lead-rich waste from abandoned mines (Carboniferous Pb-Zn mineralisation) (Fig. 5, lower panel). Natural lead is derived from surface weathering (particularly in headwater regions not influenced by mining activities), soil erosion and Pb-Zn mineralisation. The elevated levels of lead in Windermere are therefore considered to be a mixture of natural lead, and three major components of anthropogenic lead (gasoline lead, coal combustion lead and lead derived from Carboniferous Pb-Zn mineralisation).

Copper concentrations also show an increase from 1960 to 1968 and 1978 to 1984 in the North Basin and from 1940 to 1950 in the South Basin (Figs. 3 and 4). Lead and zinc concentrations (particularly in the North Basin) show similar variations, suggesting a co-variance of these contaminants and a common source. To the north of Windermere, a number of up-system sediment traps (e.g. Grasmere, Elterwater and Langdale Tarn) (Fig. 2) have

limited the amount of mining related heavy metals entering Windermere. As a result, periods of metal workings do not correlate with peaks in mining related heavy metals due to the trapping efficiency of these up-system lakes. For example, at Elterwater (downstream from Greenburn Mine), copper contamination is recorded in sediments (Pickering, 2001), demonstrating the effectiveness of up-system sediment traps. Copper increases in the 1940s and 1960s could also be due to flood-induced metal inwash after the cessation of mining (similar to findings in other upland regions of Britain; Kelly, 1991), or weathering of bedrock in the catchment. Increases in zinc could also be due to anthropogenic activity within the catchment, in the form of processed waste and human sewage inputs. In particular, an increase in direct discharge of treated sewage effluents in the 1960s corresponds with an increase in zinc at this time.

Conclusions

This study investigates the pollutant deposition of Windermere and the surrounding catchment using high-resolution Itrax analysis (validated against WD-XRF), radiochronology (^{210}Pb and ^{137}Cs) and double spike lead isotopes (offering ten times the precision of the conventional single spike method). Application of these non-destructive and high precision analytical techniques has enabled determination of the timing and scale of anthropogenic inputs to Windermere, and demonstrates the effectiveness of an integrated approach when investigating pollution signals in lacustrine environments.

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