



This document is with a copy of the following article published by the Mining Heritage Trust of Ireland. It is provided for non-commercial research and educational use.

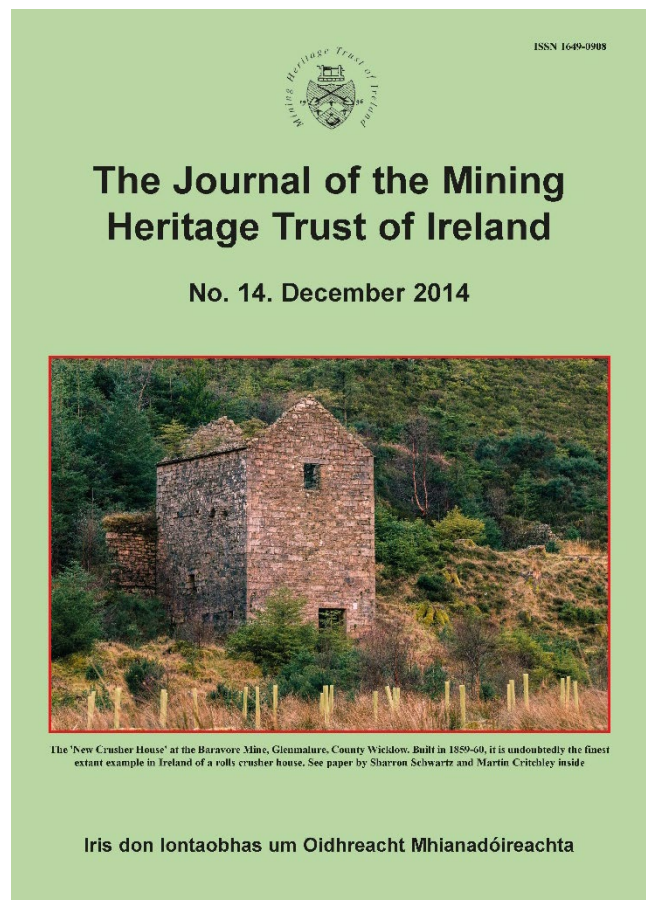
The Mining Heritage Trust of Ireland formally ceased its existence in 2019 but has provided a continuing website of resources with free access for those interested in the activities of the organisation in its various formats from 1996-2019, and in Irish mining heritage in a broader sense.

Callaghan, S. (2014) 'A Comparison of the Sedimentary Record of the Upper Lake Glendalough, County Wicklow, with the Historic Lead Mining Records of the Area' *Journal of the Mining Heritage Trust of Ireland*, **14**, pp. 87-102

Copyright of this article remains with the Mining Heritage Trust of Ireland whose archives, intellectual assets and library have been transferred to the Natural History Division of the National Museum of Ireland. Please contact naturalhistory@museum.ie for any enquiries relating to the MHTI.

This cover page must be included as an integral part of any copies of this document.

Please visit www.mhti.com for more information.





A COMPARISON OF THE SEDIMENTARY RECORD OF THE UPPER LAKE GLENDALOUGH, COUNTY WICKLOW, WITH THE HISTORIC LEAD MINING RECORDS OF THE AREA

Stephen Callaghan

Abstract: This article is the first to compare the sedimentary record of the Upper Lake at Glendalough with the known geology and mining history of the area. The tailings pond at the Glendalough mine site, constructed in the 1870s to prevent lead (Pb) entering the Upper Lake, was also investigated to determine whether it had any affect in reducing Pb contamination of the lake. Two sediment cores were collected from the lake, processed, dry weight and loss on ignition percents calculated, and then sediment samples were analysed by ICP-AES to determine the concentrations of the heavy metals: Pb, Zn, Cd, Cu and Ni. The results showed that the lake sediment is highly contaminated with Pb and Zn, concentrations are as high as 6.19mg/g for Pb and as high as 3.19mg/g for Zn. Of the two cores, GDL3 is thought to reflect most of the historic Pb mining at Glendalough, while it is thought that GDL1 only shows the end period of mining. The investigation of the cores also shows that the tailings pond made little impact on reducing the contamination of the lake by Pb and other heavy metals. *Journal of the Mining Heritage Trust of Ireland* 14, 2014, 87-102.

INTRODUCTION

Lake sediments can be significantly impacted by industrial activities (von Gunten, *et al.* 1997). Research by Grayson and Plater (2008) has demonstrated with respect to Ullswater in the English Lake District, that lead mining had a important impact on its lake sediments. Significant amounts of lead and zinc were produced during the 150 years of mining activity in the Glendalough valley and the aim of this research paper, the first of its kind for Glendalough, is to investigate whether the lake sediment in the Upper Lake at Glendalough holds an accurate environmental record of the contamination of the lake using the known historical records of the mining activity as a frame of reference. Lake sediment core samples were processed by acid digestion and analysed for lead, zinc, cadmium, copper and nickel by inductively coupled plasma atomic emission spectrometry (ICP-AES). The affects of the construction of a tailings pond were also investigated using the results of this analysis, to see whether its construction reduced the amount of lead that entered the lake.

SITE DESCRIPTION

The Upper Lake at Glendalough located in Glendalough valley, County Wicklow (Irish grid reference T105 963) is the focus of this study. The valley is drained by the Glenealo River which enters the lake at T097 962. The Upper Lake at Glendalough is less than 1.5km long and just under 0.5km at its widest point. According to a bathymetric survey carried out in 1915 (Seymour 1939), the lake is 29 metres at its deepest

point. The remains of the mining operations are located at the western end of the lake and between the lake and the mining remains, there is a naturally occurring wetland. There are significant remains at the mine site, including spoils heaps, mining buildings and a rolls crusher (see Schwartz and Critchley 2012).

GEOLOGY AND MINING

Glendalough sits near the edge of the Leinster batholith, an intrusive granitic body which formed during the Caledonian orogeny (O'Connor and Brück, 1978). This was a mountain building event, which resulted in the closure of the Iapetus Ocean. The older sedimentary rocks surrounding the batholith were metamorphosed into mica schists. Hydrothermal fluid convection systems leached metals from the surrounding aureole rock during the intrusion of the granite. These metal rich fluids mineralised fractures transecting the Leinster granite (Kennan *et al.* 1986). The veins varied in width from several inches to several feet (Smyth 1853).

The deposits in Glendalough primarily consisted of the sulphide minerals galena (PbS) and sphalerite (ZnS) with minor copper in the form of chalcopyrite (CuFeS₂) hosted in quartz veins. Other gangue minerals occurred with the deposit such as fluorite (CaF₂), calcite (CaCO₃) and barite (BaSO₄). It is of interest to note that the mineral assemblage at Glendalough lacks any minerals containing arsenic; research has also shown that the manganese oxides which occur in the Wicklow lead mines are quite As poor (Moreton *et al.* 2006).



Fig. 1: The Glendalough dressing floors. The square tailings pond (centre) and the Upper Lake in the background

Mining is currently believed to have begun in the adjacent valley of Glendasan in around 1798 or just after. This was a consequence of the army constructing a route into the Wicklow Mountains to suppress the Irish rebellion of 1798 which became known as the Military Road. As a result, lead was found in the valley and mining commenced shortly afterwards. Thomas Weaver, a mining engineer who was already involved in copper mining in Avoca, was responsible for the discovery and subsequent development of the newly discovered Luganure Lode in Glendasan, forming a company to work it (Smyth, 1853).

Weaver sold his shares in the Luganure Mines to the Mining Company of Ireland (MCI) in 1824 and this company were responsible for the mining operations in Glendalough. A MCI mining captain, John Clemes, discovered veins of ore in Glendalough in around 1852 which resulted in the advancement of mines there (Cole, 1922). Development of the Glendalough Mines was undoubtedly stimulated by a welcome rise in lead prices which led to the construction of improved infrastructure, including new dressing floors in 1855 (see Schwartz and Critchley 2012). During the 1850s and 60s the MCI planted approximately one million conifer trees in Glendalough valley to be used as timber supports in the mines (Cowman, 2007).

Once the ore was taken from the mines, it was processed on site: washed, crushed and concentrated, then sent off to be smelted into lead metal at the MCI's Ballycorus smelter near Dublin (Cole 1922; Schwartz and Critchley 2012). It was sometime between 1868–1873 that a tailings pond was

constructed (Schwartz and Critchley, 2012) in an attempt to prevent lead from entering the lake. The tailings pond has a small artificial levee surrounding it, possibly to prevent overflows. From the 1870s onwards, the MCI were challenged by declining lead prices that were sorely affecting their profit margins. Eventually in 1890, the Luganure Mines, including Glendalough, were sold to the Wynne family for £3,450 (FJ, 1890).

The working of the mines by the Wynnes was nowhere near as large scale as the operation by the Mining Company of Ireland and the bulk of their attention was initially focussed on the Whiterocks Adit in Glendalough. Aided by a grant from the British government, the Foxrock Lode in neighbouring Glendasan was reopened and at Glendalough, a small treatment plant was erected to rework the spoil heaps from the MCI era rich in ZnS and PbS, as lead and zinc were in demand by the munitions industry during the First World War (Schwartz and Critchley 2012). The plant operated from 1913–23, but was forced to close when the British government terminated the wartime grant, thus ending mining activity in Glendalough.

METHODOLOGY

Introduction

This section lists and details the various methodologies carried out from the initial coring and collection of the lake sediment cores, to the final inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

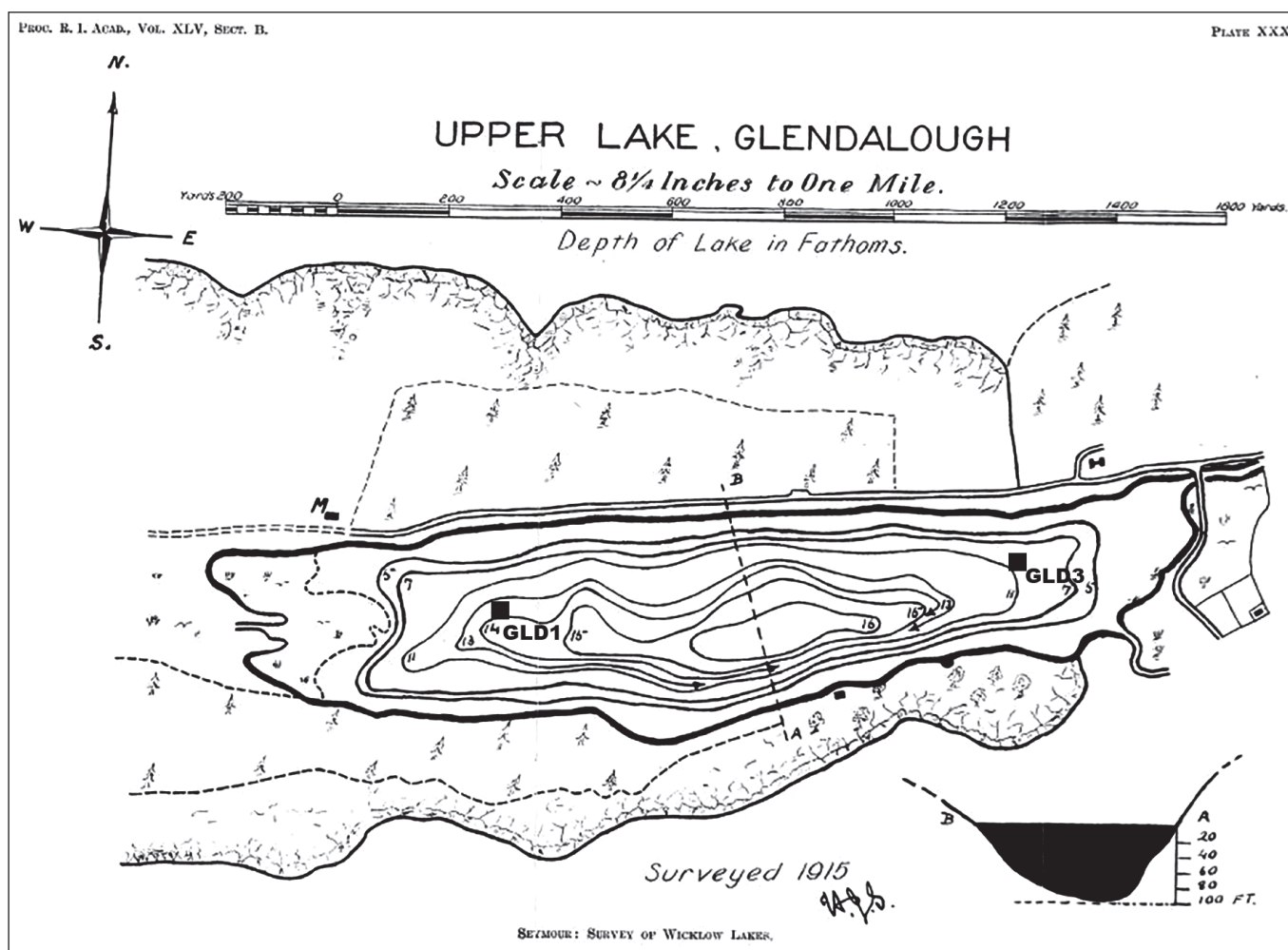


Fig. 2: Bathymetric survey of the Upper Lake, Glendalough, conducted in 1915 (Seymour, 1939). Coring sites are shown by the black boxes. Grid coordinates for the sites are: GLD1 - T09920/96140 GLD3 - T10730/96241

Collecting the Cores

Possibly the single most important part of this project or any paleolimnology project are the cores (Glew *et al.* 2001). These were the sole basis of lab work for this project, and therefore care was needed during their collection. It was very important to carefully choose the collection sites in the Upper Lake. With the help of a bathymetric survey conducted in 1915 (Seymour 1939), two sites were chosen. The first was at the western end of the lake between the deepest point of the lake and the inflow. The second location was in the eastern end of the lake, between the deepest point in the lake and the outflow (Figure 2). It was noted during a site investigation, that the western end of the lake has experienced a lot of sedimentation over the past decades. A sediment plume could be seen accumulating where the Glenealo River enters the Upper Lake. With this in mind it was considered that a sediment core from this side of the lake may not produce cores of an old enough age that would encompass all of the documented mining history at the site.

Equipment

- Modified Kajak-Brinkhurst corer
- Core tubes – 2 x 70cm, 4 x 50cm
- Echo sounder
- Rope
- Boat

Procedure

A boat was kindly provided by the National Parks and Wildlife Service. Once out on the lake, an echo sounder was used to gauge the depth of the water. Cores were not taken beyond a 30 metre depth.

The first stop was the first preselected coring site. The anchor was dropped and the boat was allowed to drift into the direction of the breeze. This was done to keep the boat as steady as possible and to provide a stable platform from which to take the core. The rope was attached to the corer, a modified Kajak-Brinkhurst model, to which heavy weights had been attached in the hope that it would provide better sediment penetration.

A modified Kajak-Brinkhurst (Figure 4) was used because they are reliable for soft sediment sampling (Brinkhurst *et al.* 1969). The corer was then carefully lowered off the side of the boat and allowed to reach and penetrate the bottom of the lake bed. The line was tugged to allow the corer to close, then the line was marked where the corer contacted the lake bed. The line was then pulled up and the corer retrieved. The first core was a practice run, to ascertain the nature of the lake sediment.

The first proper core was collected in a similar manner. This core was capped at the bottom of the core tube with a rubber



Fig. 3: Sediment plume clearly visible where the Glenealo River discharges into the Upper Lake, Glendalough



Fig. 4: GDL core after collection via modified Kajak-Brinkhurst corer

bung. The core tube was then unscrewed from the modified Kajak-Brinkhurst corer and the top of the core capped with a rubber bung. The core tube was then placed into a core tray and labelled GDL1. A replicate core labelled GDL2, was collected from the same location. This was to act as a back up core should anything go wrong with the processing of the first core. The next core to be taken was from a new site, towards the eastern end of the lake. Again, an echo sounder was used to gauge the depth of the water. Once at a suitable site, the boat was allowed to drift into the breeze. A test core was taken first. The next core was taken in a similar manner to GDL1 and GDL2. The core and its replicate were labelled GDL3 and GDL4.

EXTRUDING AND SECTIONING A SEDIMENT CORE AND DRY WEIGHT PERCENT

Introduction

After collection, extruding the core is the next step in the lengthy process of processing the sediment core (Glew *et al.* 2001).

Equipment

- Polypropylene pots
- Retort stands – to hold the core tube

- Perspex ring
- Aluminium slide
- Rubber bung and pole to extrude core
- Oven set to 105°C
- Paster pipettes and rubber tubing to remove top section of water

Procedure

The method described below was used to process both core GDL1 and GDL3. Before sectioning began, polypropylene pots were gathered and labelled with a unique number. Each labelled pot was then weighed without its lid on a weighing balance. This was the initial weight (W1) before drying. Retort stands were used to hold the core tube in position for extrusion. The top bung of the core tube was then removed. The top water section of the core was carefully removed by using a rubber tube filled with water to siphon off the water. A plastic paster pipette was used in addition to remove the top water section of the core.

The top bung was then replaced and the bottom bung was removed (this was done so the core did not slide out of the bottom). The rubber bung for extruding the core was then placed into the bottom of the core tube. The top bung was then removed from the core tube. A Perspex ring for sectioning the core was then placed onto the top of the core tube. Using a pole, the rubber bung was pushed up through the core tube and the top 1cm of the core was extruded into the Perspex ring. The aluminium slide was then used to separate the extruded 1cm of core, this was then carefully placed into a polypropylene pot.

The Perspex ring and aluminium slide were washed in between each sectioning, to prevent contamination of the samples. The entire core was sectioned using the same method. However for GDL3, the first 10cm were sectioned into 1cm intervals, then the rest was sectioned into 0.5cm sections, in the hope of producing a finer time resolution. The polypropylene pots with the wet sediment samples were then weighted on a balance without their lids. This was weight W2. The pots were then placed in an oven with their lids ajar, overnight at 105°C to dry. After drying, the pots were reweighed with their lids removed, weight post drying were W3.

The dry weight % was calculated using the following formula:

$$\text{Dry weight \%} = ((W3 - W1) / (W2 - W1)) \times 100$$

LOSS ON IGNITION

Introduction

Ignition of sediment samples takes place at 550°C, after ignition the loss in weight is proportional to the organic carbon content of the sample (Dean, 1974).

Equipment:

- Pestle and mortar
- Numbered crucibles
- Oven set at 105°C
- Muffle furnace programmed to 550°C

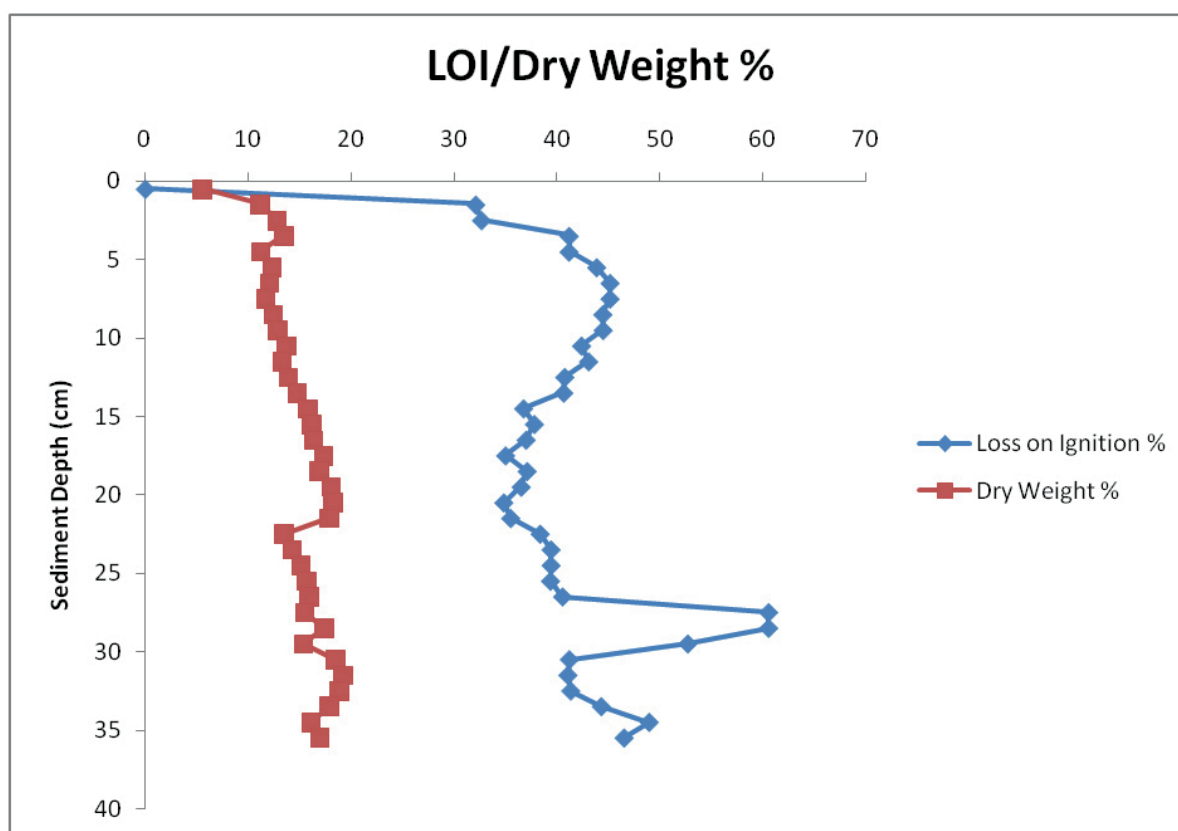


Fig. 5: GDL1 Loss on Ignition and Dry Weight %

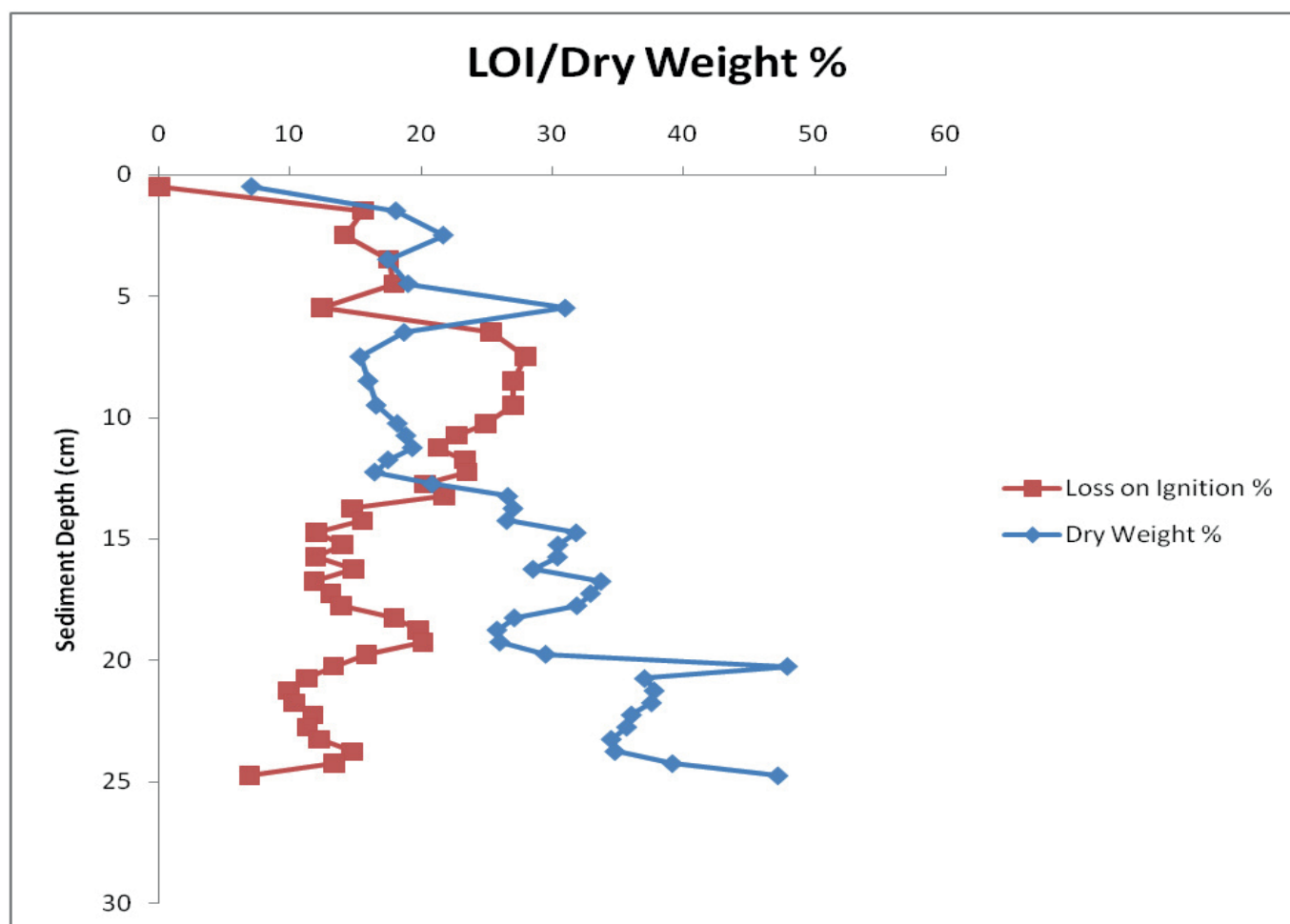


Fig. 6: GDL3 Loss on Ignition and Dry Weight %

Procedure

Sediment samples were dried in an oven at 105°C for 24 hours before they were examined. The dried sediment core samples were individually ground into a fine powder using a pestle and mortar. Tissue cloth was used to clean the pestle and mortar in between each grinding to remove excess material, and to prevent cross contamination of samples. A numbered crucible was placed onto a weighing balance and the weight was recorded to 3 decimal places (W1). One gram of the powdered core sediment was carefully added to the crucible (W2), this was done to within 0.1g accuracy. A muffle furnace was used to ignite the samples. The furnace was programmed to 550°C. Crucibles were placed into the furnace for one hour. After this the crucibles were removed and allowed to sit and cool. They were re-weighed immediately after cooling (W3); this was done to prevent the sample absorbing moisture from the atmosphere.

Loss on ignition %: $((W3-W2) / (W2-W1)) \times 100$

ACID DIGESTION

Introduction

Determining the concentrations of heavy metal in sediments is a two step process; the first process is the digestion of the sediments, by sequential addition of hydrofluoric acid, to

break down silicates, nitric and perchloric acids to oxidise the organic material, to open Teflon pots.

The second step is the analysis of the samples by inductively coupled plasma atomic emission spectroscopy (ICP-AES). For this project the ICP-AES analysis was carried out by Agri-Food and Biosciences Institute (AFBI).

Equipment

- Reagents;
 - 40% hydrofluoric acid,
 - 69% nitric acid,
 - 60% perchloric acid,
 - 35% hydrochloric acid,
 - Millipore Milli-Q water
- Teflon beakers
- 25ml volumetric flask – grade A
- Polypropylene pot – for sample storage
- Hot plate
- Fume hood
- Oven set at 105°C

It was very important to thoroughly wash out and clean the Teflon beakers and polypropylene pots before the lab work was carried out (Mester and Sturgeon, 2003). This was done to remove any material or residue from previous use of the equipment.

Procedure

The core samples were placed in an oven at 105°C for one hour before processing, this was done to ensure the samples were dry for weighting. Cleaned Teflon pots were gathered and numbered in sequence. Each Teflon pot was individually placed on a balance and 0.5g (+/-0.001g) of dried sediment core was added. A blank Teflon beaker was included for every 10 samples, this was done to test for potential contamination of samples.

The next step was the careful addition of 10ml of hydrofluoric acid (HF) to the samples. The Teflon pots were then placed on a hot plate with a low to medium setting, in a fume hood, the pots were the swirled every 30 minutes. This was done to prevent a ring of material building up in the pots. Once the HF acid evaporated off, 10ml of nitric acid (HNO₃) was added. The heat setting on the hot plate was increased. Similarly with the HF, the pots were swirled every 30 minutes to prevent a ring forming in the pots.

After the nitric acid had evaporated, 5ml of perchloric acid (HClO₄) was added. The heat of the hot plate was increased and the acid was allowed to reflux. This was done so any remaining organic material would be oxidised. The pots were swirled every 30 minutes to prevent a ring building up within.

For the final step the pots were allowed to cool and 5ml of hydrochloric acid (HCl) was added to each pot and swirled. Next 10ml of Millipore Milli-Q water was added and again swirled to assist with the dissolution of the salts. The pots were then left to stand for 5 minutes to allow the remaining salts to dissolve. The solution in the Teflon pots was carefully poured into a 25ml volumetric flask, the pot was then washed with Millipore Milli-Q water, this was then poured into the flask. The remainder of flask was made up with Millipore Milli-Q water. This was then poured into a polypropylene sample pot. It was important for the volumetric flask to be washed after making up each solution to prevent contamination of samples.

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

The second step of determining the heavy metal concentrations in the lake sediment core samples is analytical analysis. For this project inductively coupled plasma atomic emission spectrometry (ICP-AES) was used. As the ICP-AES analysis was not carried out by the author, a brief description of how ICP-AES works is given below. This method provides quick analysis and can detect minor to trace levels of different elements (USGS, 2013).

The liquid sample is introduced into a nebuliser; a mist of the sample is then sprayed into the inductively coupled plasma (ionised argon). The plasma is at a temperature between 6,000 – 10,000°C. This excites the outer shell electrons in the sample; when the electrons return to their ground state, a photon of light is emitted (USGS, 2013). A photomultiplier tube detector detects the different elements present in the sample.

RESULTS

Core	GDL1	GDL3
Irish Grid Ref	T 0992 9614	T 10730 96241
Water depth	22m	19m

Table 1: Irish grid references for core collection sites

Sample Collection Date	08/11/2013
Water Sample Depth	5m
Collection Location	T 10730 96241
Secchi depth	2.5m
pH	6.2
Alkalinity meq/L	0.131
Hazen Mg/L Pt	58

Table 2: Glendalough water quality results

LOSS ON IGNITION (LOI) AND DRY WEIGHT PERCENT

Loss on ignition was not carried out for the first 1cm of sample of both cores due to the limited nature of material available. As seen in figure 5 (GDL1) dry weight percent shows a general trend of incremental decrease with a few peaks of increasing dry weight percent. Dry weight increases at 29cm to 17% from 15% at 30cm, and at 23cm dry weight percent increase to 17% from 13% at 24cm depth. After this increase, a decline is seen for the rest of the core. Loss on ignition shows a large spike to 60% at 30cm depth. After this huge spike, LOI drops down to 40%. A slight increase is seen for the res of the core until 4cm depth when LOI decrease. These results will be expanded on in the discussion.

The top 10cm of GDL3 was sectioned into 1cm segments; the rest of the core was then segmented into 0.5cm in the hope of gaining a finer time resolution. The dry weight percents (Figure 6) show an overall trend of decreasing dry weight with a reduction in sediment depth. The loss on ignition results show an opposite trend, they increase gradually until 7cm depth when they begin to decrease. The deeper in the sediment core the more organic it is. Results are expanded upon further in the discussion section.

HEAVY METAL CONCENTRATIONS IN LAKE SEDIMENT

Above average levels of zinc were found in the procedural blanks, this was corrected by subtracting the average of the concentrations of the 3 procedural blanks from each GDL1 core sample (-6.02mg/L). The Pb/Zn concentrations for GDL1 are expressed in mg/g of dry sediment. The graph (Figure 7) shows high concentrations of Pb/Zn at a depth of 36cm (6.19 mg/g Pb, 3.19 mg/g Zn). These concentrations drastically drop until 27cm depth, and then there are slight peaks and troughs

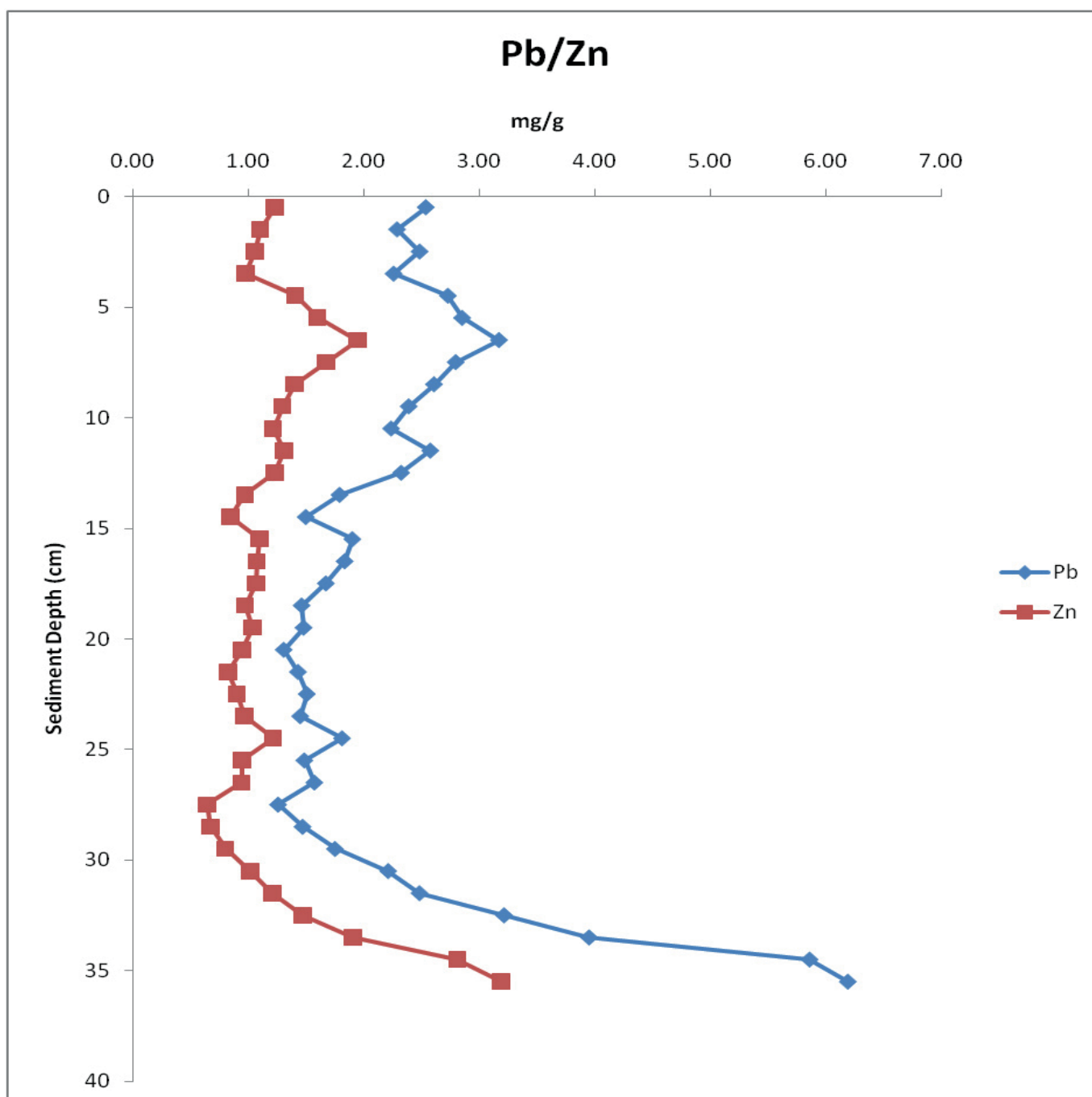


Fig. 7: GDL1, Lead and Zinc concentrations

for the rest of the core. These results are expanded upon in the discussion. Concentrations of Cd/Cu/Ni are expressed in $\mu\text{g/g}$ of dry sediment (see Figure 8). Copper shows the highest concentrations of all 3 metals.

The results for GDL3 are depicted in Figures 9 and 10. Above average levels of zinc were found in the procedural blanks, this was corrected by subtracting the average concentration of the 3 procedural blanks from each GDL1 core sample (-3.47mg/L). There is a major spike in Pb/Zn concentrations between 6 – 15cm depth (see Fig. 9). Nickel and copper are the most prevalent, with similar concentrations in the core, cadmium is at much lower concentrations (see Figure 10). All the metals can be seen increasing between a depth of 6 – 15cm

depth. Nickel shows a huge peak at 23.7cm depth and copper at 0.5cm depth. The mineral statistics for the Glendalough and Luganure mines were obtained from Morris *et al.* (2008) and are depicted in Figure 12. It is important to note that the years 1864-1865 only account for the ore from Luganure Mine; 1878 and 1880-1881 includes ore from Foxrock and Ruplagh Mines, Glendasan, Co. Wicklow.

DISCUSSION AND CONCLUSIONS

Water Quality

Insufficient data was collected to determine a trophic index for Glendalough Upper Lake. However from the data that was collected, a brief summary can be ascertained on the water

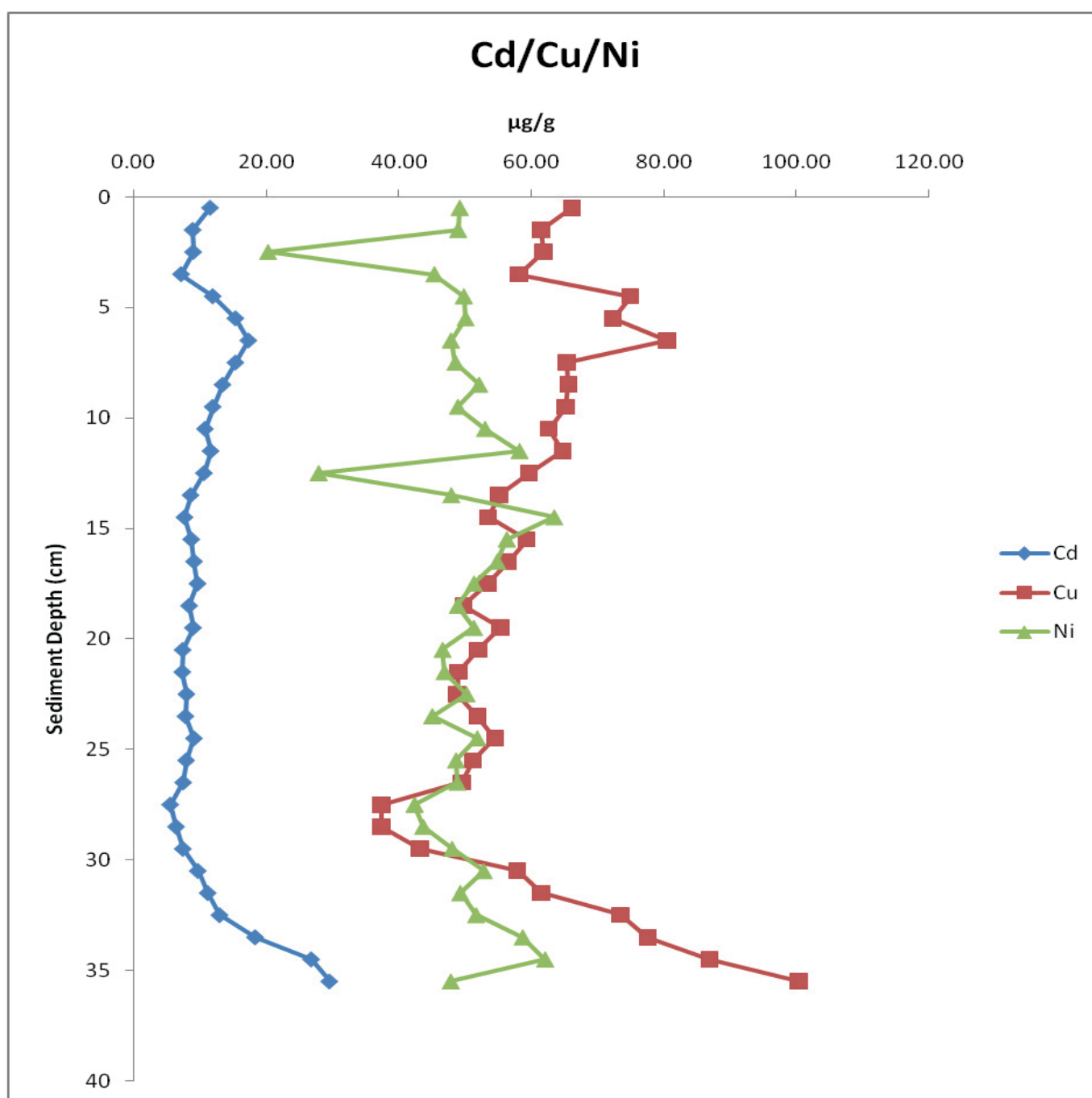


Fig. 8: GDL1, Cadmium, Copper and Nickle concentrations

quality of the lake. The low pH of 6.2 indicates low acidity of the lake water. Other previous studies have shown a similarly low pH of 5.8-5.9 over the period of 2004-2006 (EPA, 2008). The low acidity of lake would suggest that re-mobilisation of metals such as Zn and Fe is unlikely as this process requires acidic lake water conditions (Schindler *et al.* 1980). The low alkalinity of 0.131 meq/L reflects the limited to almost nonexistent carbonate rock geology in the region. As discussed in the introduction, Glendalough valley is chiefly comprised of granite and mica schist (O'Connor and Brück, 1978) with little or no carbonate rocks. This means that the lake has a low buffering effect against acidification.

While extruding the cores, it was noted that the only organisms

present were Chironomids. This widely distributed group of insects act as an indicator organism and in cases of highly polluted water they may be the only organisms present (Armitage *et al.* 1995). The lack of organisms present in the lake was also supported while speaking with park ranger, Damien Clarke, of the NPWS (National Parks and Wildlife Service), who mentioned that only small fish are present in the lake (D. Clarke 2013, pers. comms., 8 Nov).

Lake Sedimentation

A brief discussion of lake sedimentation is required in order to better understand and interpret the sediment core results. As mentioned in the methodology section, a sediment plume was noticed at the western end of the lake where the River

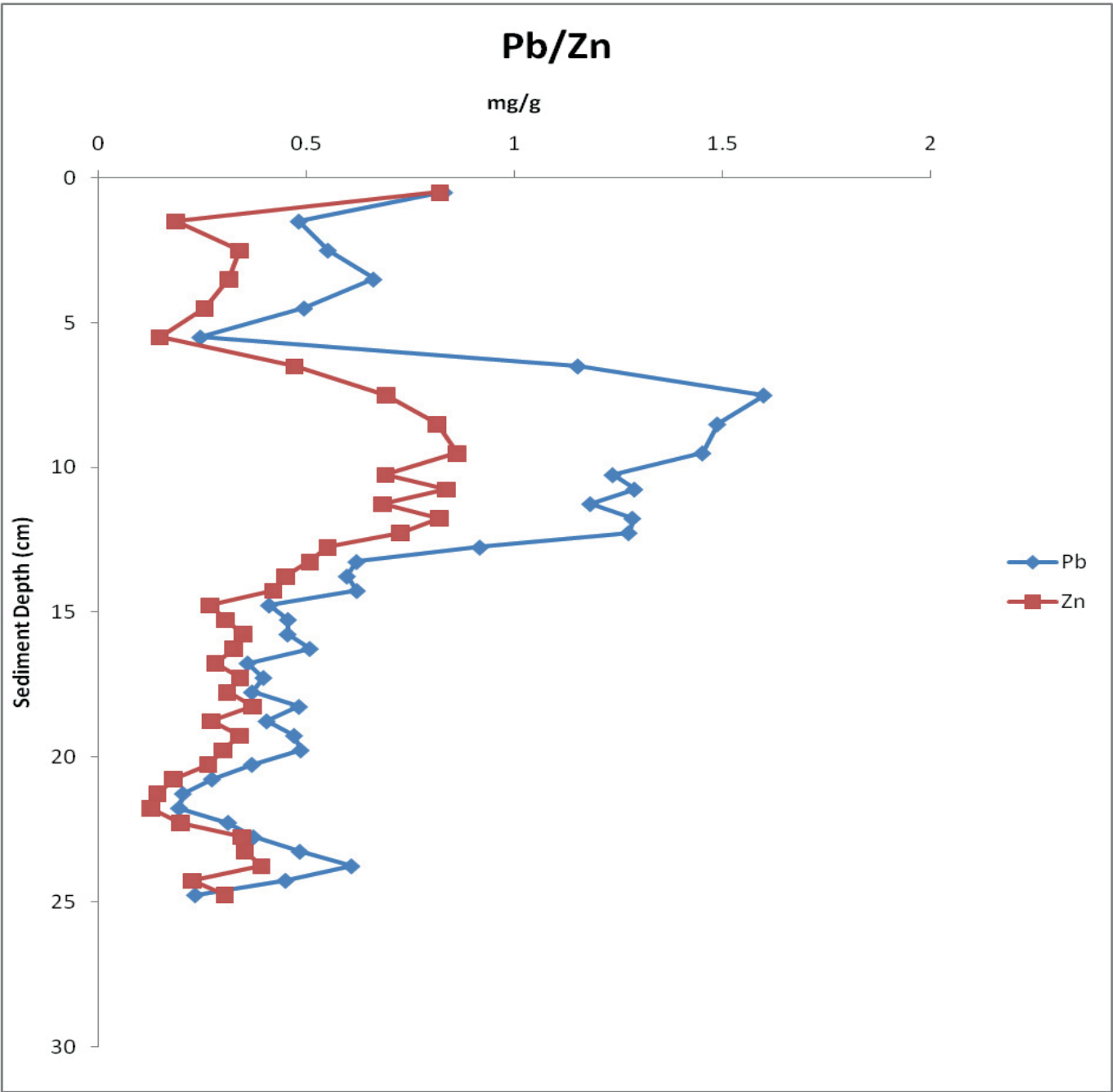


Fig. 9: GDL3, Lead and Zinc concentrations

Glenealo enters the Upper Lake. Further investigation of sedimentation in the lake has shown a dramatic change in the morphology of the western end of the lake (see Figure 11). As seen in Figure 11, the western end of the Upper Lake has experienced a great deal of sedimentation in the past 150 years. It is highly likely that mining was responsible for the increased rate of sedimentation, as the ore from the mines was crushed on site, which produced fine sediment. As seen on the 1838 6-inch map, there are two small inlets at the western end of the lake near the inflow. By 2005 both of these have been completely filled in with sediment; a sandy beach can also be seen.

It is probable that the natural sedimentation rate for the lake, especially at the western end of the lake has been artificially sped up by mining and mineral processing. This could

potentially limit the use of the first sediment core GDL1, as this was collected from between the deepest point of the lake and the inflow. The core was 41cm long (36cm after extrusion). The typical sediment depth to reach the year 1900 in similar upland lakes varies. Table 3 illustrates several examples.

Lake Name	Depth to 1900 (cm)
Lough Veagh	10.25
Lough Muck	16.25
Lough Mauwee	19.25
Lough Maam	10.25

Table 3: Lake Sediment Depth to 1900 (cm) (Rippey and Douglas, 2004)

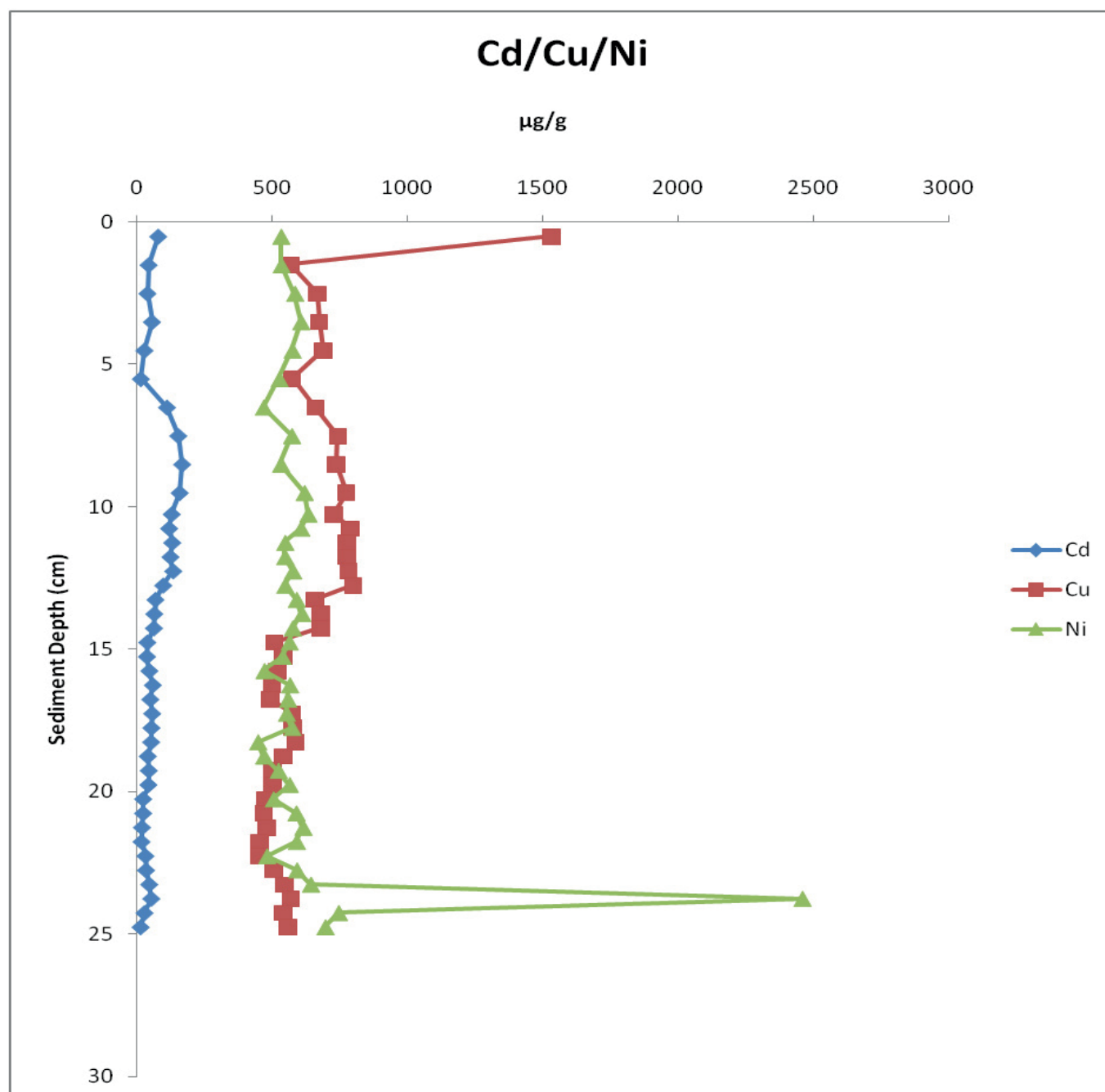


Fig. 10: GDL3, Cadmium, Copper and Nickel concentrations

Sediment Core Interpretation

Each core will be interpreted individually, drawing upon dry weight and loss on ignition percents, in addition to the heavy metal concentrations. Without further work, it is likely that no one answer will fully explain each core. A series of logical ideas will be put forward in the hope of explaining what is happening in each core, with an overall interpretation at the end of the paper.

GDL1 was 41cm in length when collected. However, due to compaction it was reduced to 36cm length after it was extruded from the core tube. Due to the relatively close nature to the Upper Lake's inflow, it is possible that GDL1 does not predate the desired date of 1850 (documented mining started around the 1850s). Assuming the year 1900 is at a depth of 10cm and taking into consideration a possibly increased

sedimentation rate, it would be fair to assume the year 1900 is at a greater depth than 10cm in core GDL1. The evidence in this core, discussed in greater detail below suggests that this core is only picking up the period before mining terminated in the valley: between the late-nineteenth century and the early-twentieth century.

Dry weight percents in GDL1 show a gradual decrease of from 17% at 36cm depth to 13.4% at 23cm depth; LOI shows a slight decrease from 46% organic material at 36cm depth to 41% at 30cm depth when there is a huge increase to 60% organic material. There is a slight correlating decrease peak in dry weight percent at 30cm when dry weight decreases from 18.5 to 15.3%. This may represent a period of time where fine material was being deposited into the lake. This is possibly a result of mining activity as the ore was crushed on site

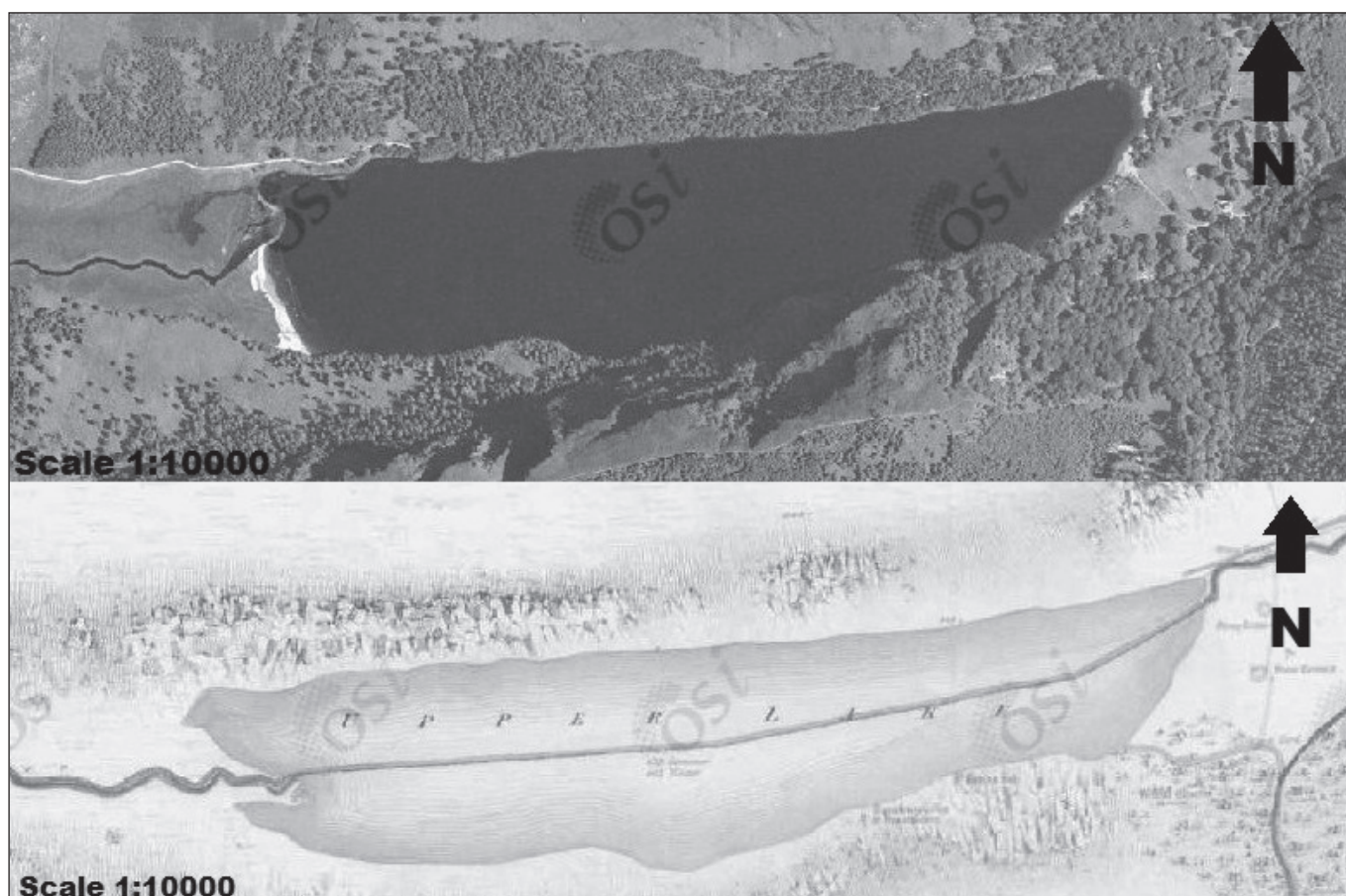


Fig. 11: Comparison over time, above: image taken 2005, below: 6" map dating from 1838 (after www.osi.ie)

producing a fine sandy material.

Pb/Zn concentrations for this possible period of fine sediment entering the lake are declining from very high concentrations of 6.19mg/g of Pb and 3.19mg/g at 36cm depth to 1.74mg/g of Pb and 0.80mg/g of Zn at 30cm depth, which are still considerably high concentrations. The average background levels of Pb and Zn for Eurasian lakes is 0.047mg/g for Pb and 0.122mg/g for Zn (Forstner, 1977). Background levels at Lough Dan, County Wicklow, the analogue site for the study carried out by Beining and Otte (1996), showed even lower levels of Pb and Zn. Pb was found to be 0.0041mg/g (in samples taken from the marsh) and Zn was undetectable.

The Pb/Zn decline may represent mining coming towards an end in the valley. After the possible period of fine sediment entering the lake, dry weight percent decreases gradually and LOI increases. This suggests that the material entering the lake is becoming courser. Pb/Zn slightly peak throughout the rest of the core increasing at 6.5cm to 3.16mg/g of Pb and 1.94mg/g of Zn. This peak could possibly reflect work carried out in the early- to mid-twentieth century by the Wynnes.

The close proximity of the workings to the Glenealo River would make contamination of the river quite easy, and it is likely that even after the mines stopped working, Pb/Zn was still contaminating the river and entering the lake, resulting in higher than average concentrations. The river sediment is still highly contaminated with Pb. Above the mine workings the Pb

in the river sediment is between 0.041-0.494mg/g, adjacent to the mine workings Pb concentrations are as high as 1.93mg/g and where the river enters the lake the concentrations of lead are as high as 10.2mg/g (EPA, 2007). This may explain why there are slight fluxes in Pb/Zn concentrations towards the top several cm of the core. It is almost impossible that these fluxes in Pb/Zn concentrations are from mining, as mining stopped in Glendalough valley in the early 20th century.

The concentrations of Cd/Cu/Ni show a somewhat similar trend to Pb/Zn concentrations. Cd declines from 30µg/g at 36cm depth to 10 µg/g at 30cm depth. Cu declines from 100µg/g at 36cm depth to 40µg/g at 30cm depth. Ni stays around 50µg/g at these depths in the core. The average concentrations of Cd present in Eurasian lakes is 0.53µg/g (Forstner, 1977). The high levels of Cd in the Upper Lake sediment can be explained due to mining activity as Cd is often associated with Zn deposits, and can comprise from 0.02 to 1.5% of the Zn mineral sphalerite (Salminen *et al.* 2005). An average Cu level in Eurasian lakes is 33µg/g (Forstner, 1977).

The high levels present in Glendalough Upper Lake are explained by mining, as there are noted Cu minerals present in the mineral assemblage at Glendalough. Cd/Cu/Ni do not increase beyond their originally high values between 36cm depth to 30cm depth. This is another possible indicator that their decline is possible evidence of mining coming to an end in the valley. Any slight additional increases in Cd/Cu/Ni

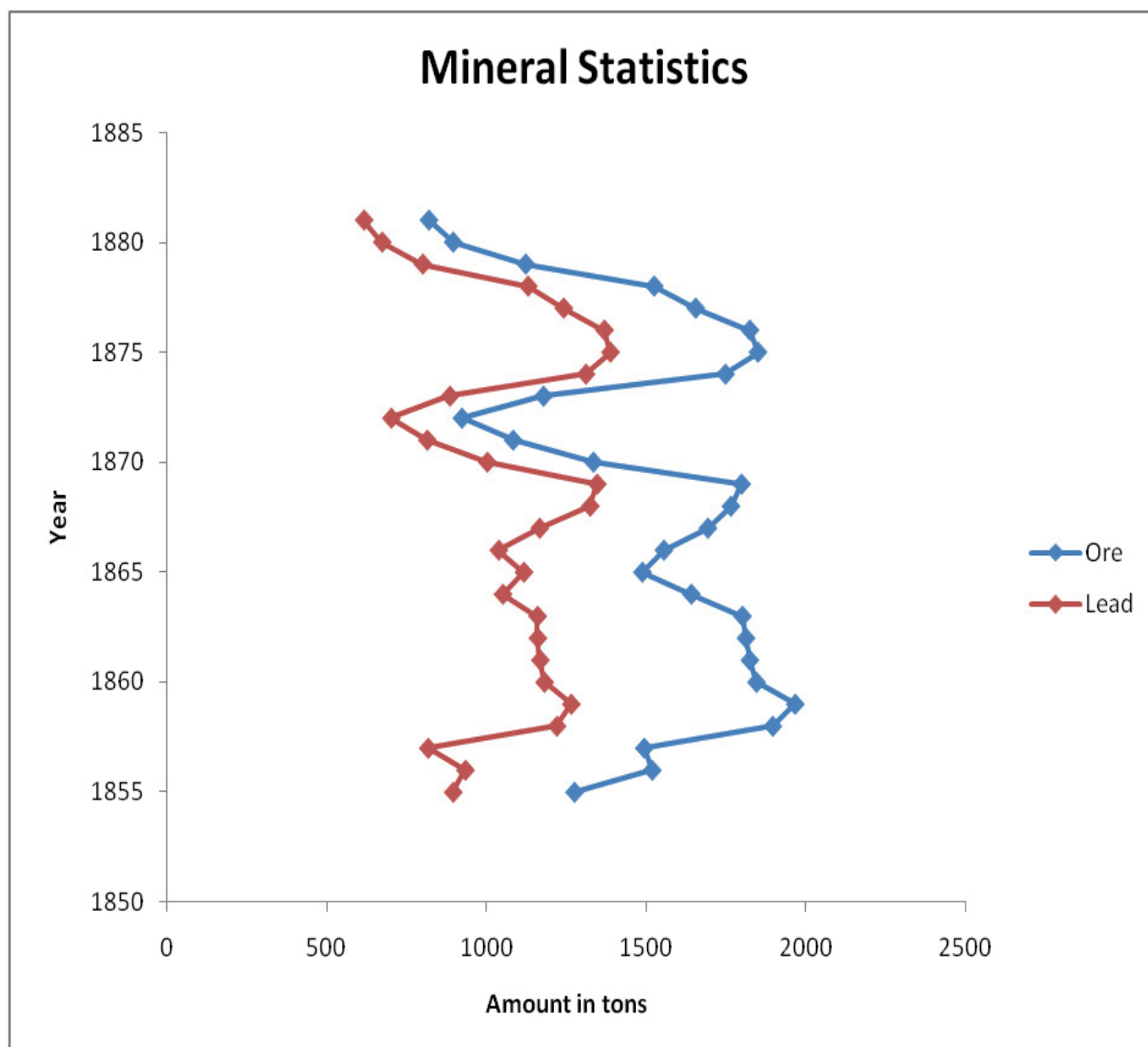


Fig. 12: Annual Mineral Statistics for the Glendalough and Luganure mines, obtained from Morris et al. (2008)

throughout the rest of the core may be a result from contamination of the Glenealo River or contaminated water draining from the mines.

GDL3 has potential to be a better core than GDL1 due to its collection site which was on the other side of the lake, away from the sediment plume. Assuming the sedimentation rate here has not been greatly affected, the year 1900 can be expected to be at around 10cm depth, give or take a few centimeters. The core was 30cm long after collection, but due to compaction of the core during extrusion it reduced in size to 25cm length. The first 10cm of the core was sectioned into 1cm segments and the rest into 0.5cm segments in the hope of getting a better time resolution for heavy metal contamination.

The dry weight and LOI percents for 25cm depth are 47.2% and 6.8% respectively. This would indicate towards a more coarse type of inorganic sediment being deposited in the Upper Lake. There is a decrease in dry weight percent and an

increase in LOI percent at around 19.5cm depth, dry weight decreases to 26% and LOI increases to 20%; this may infer that the sediment entering the lake is starting to become finer.

Pb/Zn concentrations are relatively high throughout the core. At 25cm depth, Pb is present at 0.23mg/g and Zn is present at 0.3mg/g. There is a peak in concentrations at 23.5cm depth, Pb rises to 0.6mg/g and Zn increases to 0.39mg/g. Although these concentrations are higher than the average Eurasian lake levels of 0.047mg/g for Pb and 0.122mg/g for Zn (Forstner, 1977), it is thought that these concentrations may not represent the start of mining in the 19th century. High levels of Pb naturally occurring in the rocks in the area, combined with erosion, has led to the lake being naturally contaminated even before mining began.

Moreover, recent analyses of peat cores taken from ombrotrophic bog on nearby Camaderry Mountain, hint at the intriguing possibility that mining may have been taking place



Fig. 13: L-R, the Glendalough mines and dressing floors, the square tailings pond above the Glenealo River which discharges into the Upper Lake where a sediment plume can be seen. Photograph, Martin Critchley, March 2012,

in the Glendalough area from the 11th century onwards, with a rapid growth from the 15th century (Mighall *et al.* 2013, 19). Things become very interesting at 13.75cm depth in the core. There is a dramatic change in dry weight and LOI percents. Dry weight decrease to 27.7% and LOI increases to 21.7%, this dry weight decreases and LOI increase continues until 6.5cm depth. Also for this period in the core, there is a huge Pb/Zn spike, concentrations of Pb/Zn increase dramatically from 0.59mg/g for Pb and 0.41mg/g for Zn at 13.75cm depth to 1.75mg/g for Pb and 0.72mg/g for Zn at 12.25cm depth. The decreasing dry weight percent and increase LOI suggests the sediment is becoming finer. Finer sediment generally has low concentrations of heavy metals, so the heavy metal spikes in the core are most certainly the result of mining. It is likely that the fine sediment entering the lake and the increase in Pb/Zn at 13.75cm depth signals mainstream production of Pb from the mines at Glendalough.

As seen in figure 15, Pb increases further at 7.5cm depth, the concentration here is 1.6mg/g. This is the highest peak in the core. Zn doesn't follow this high spike and remains in steady concentrations with minor peaks and troughs, the highest concentration reached being 0.86mg/g at 9.5cm depth. Cd concentrations increase between 12.75- 6.5cm depth. An increase in concentrations can also be observed for Cu and Ni over the same depth in the core. This again points towards the

idea that the main period of mining is represented from 13.75-6.5cm depth. It is intriguing that both cores contain Ni; GDL1 contains concentrations up to 60µg/g of Ni at 35cm depth and GDL3 has Ni concentrations up to 2459.038µg/g at 23.7cm depth. The study by Moreton and Green (2007) found no minerals in the Wicklow lead mines that contain Ni, and no other mineralogical descriptions of the region mention Ni being present.

However, Ni was also detected in the peat core samples taken from ombrotrophic bog on nearby Camaderry Mountain and has a profile similar to Cu (Mighall *et al.* 2013). While all rocks naturally contain a variety of different elements, the level of Ni in the lake sediment is substantially high. An average background level of Ni found in Eurasian lakes is recorded as being 61µg/g (Forstner, 1977). It is possible that the ore at Glendalough did contain minor traces of Ni, but further investigation is obviously required.

Overall it would appear that GDL1 does not record the entire history of mining in Glendalough but only catches the end of it in the late 19th century/early 20th century. GDL3 is more likely to have recorded most of the period of mining, if not all of it. There is a noticeable trend in both cores of steeply decreasing concentrations of Pb. In GDL1 Pb decreases from 6.19mg/g at 36cm to 1.25mg/g at 28cm depth. There is a

similar steep decline in Pb concentrations in GDL3. At 8cm depth Pb is at 1.6 µg/g, then at 6cm depth Pb decreases to 0.24µg/g. Both of these dramatic changes in Pb concentration probably represent the same period of time when mining is coming to an end. If these declines correlate, it supports the idea of a greater sedimentation rate at the western end of the lake.

In GDL3 between the depths of 5-15cm the spike in Pb concentrations has been attributed to mining activity. The slight decline in Pb between 11-13cm may represent the decline in mining experienced between 1870-1875. Mining picks up again after 1875, as does Pb in the sediment core. Deeper sediment cores, which could be taken with a mini mackereth corer are required to expand upon this interpretation.

Tailings Pond

Having examined the sediment cores, the tailings pond needs to be investigated as to whether its construction by the Mining Company of Ireland (MCI) around 1868 – 1873 (Schwartz and Critchley, 2012) had any affect at reducing the amount of Pb that entered the upper lake. Pb concentrations in the tailings pond are staggeringly high with concentrations up to 194mg/g (EPA, 2007). The tailings pond did likely help reduce the amount of fine material entering the lake, but the concentrations of Pb/Zn in the lake indicate that the lake is highly contaminated. It probably did not help that the tailings pond was located beside the Glenealo River. This would have made contamination of the river quite easy in periods of heavy rain or flooding. Also, the tremendous amount of spoil material so close to the Glenealo River meant that contamination was readily possible.

Assuming that the tailings pond was constructed sometime in the 1860s or early 1870s it can be assumed that a great deal of Pb would have already entered the lake as result of when mining first started in the 1850s. When the Wynne family took over mining in the valley, their operations were not as large as the MCI and the amount of ore they mined was not as much (Schwartz and Critchley, 2012). With all this in mind, if the tailings pond was retaining Pb it would be expected that Pb values in GDL3 would become increasingly less after an initial spike for the first 20 years of mining. However, this is not observed; Pb values spike for when mining is thought to have started, at around 13.75cm depth. However Pb values in the core continue to increase until a dramatic decrease between 6-5cm which likely signals the end of mining. The sharp decline of Pb at 6cm may represent the Wynne family's efforts at keeping the mines working.

Further Work

Further study could focus on cores recollected using a mini mackereth corer; this would allow for cores of up to 1 metre length and this could possibly help to refine the time line of mining. Also, longer cores could possibly collect medieval aged sediment. A recent study by Migall *et al.* (2013) has found indications of lead and other minerals in peat cores which could be evidence for mining activity in the Glendalough area from the 11th century onwards. If Pb can be found in lake sediment cores of a similar age, it would provide further evidence of possible medieval Pb mining in Glendalough, which would be a significant finding.

It might also be of interest to further investigate the source of the Ni in the lake sediment. The Ni concentrations are fairly high and there is no obvious source of where it is coming from. Additionally, the extent of contamination from mining in Glendalough and Glendasan could be examined. MacKenzie and Pulford (2002) showed that Pb and Zn was able to travel from the abandoned lead mines at Tyndrum, Scotland, to Lough Tay which is 25km away downstream. It would be interesting to determine how far Pb, Zn and other heavy metals migrate downstream from the Glendasan and Glenealo Rivers into the larger Avonmore River.

CONCLUSIONS

Similar to this study of the Upper Lake, Glendalough, that by Grayson and Plater (2008) attempted to reconstruct the chronological sequence of Pb input into Ullswater in the English Lake District, from mining which took place at Greenside Mine, Cumbria. In this case, the key dates for mining at Greenside could be observed in the lake sediment record, indicated by the start of large scale mining in 1840 which resulted in increased heavy metal concentrations in the sediment, and a reservoir dam failure at the mine in 1927. Both studies therefore demonstrate that it is possible to reconstruct contamination of lake sediment as a result of historic mining activity.

GDL1 shows a huge decline in Pb concentrations between 28-36cm which is attributed to mining ending in the valley around the early 20th century. The concentrations throughout the rest of the core never reach a similar high as the initial concentration of 6.19mg/g of Pb at 36cm depth. GDL3 is thought to reflect the start of mining between 13-15cm depth; the decline of mining in the 1870s is represented between 11-13cm depth and the ending of mining in the early 20th century is represented at 8cm depth. It is also thought that the decline in Pb which starts at 8cm depth correlates to the same sharp decrease of Pb in GDL1 28-36cm, with both declines in Pb representing the end of mining activities.

Finally, this study has demonstrated that the construction of the tailings pond seems to have been largely ineffectual at reducing Pb contamination of the Upper Lake. Despite the pond being built 20 years too late, it seems to have been unable or too inefficient to cope with the high concentrations of Pb that were being produced from the mines. The Mining Company of Ireland were forward in their thinking to try and prevent the migration of heavy metal into the lake by constructing the tailings pond, however they failed as the lake sediment is highly contaminated with Pb, Zn, Cd, Cu and Ni.

ACKNOWLEDGEMENTS

Thanks to my BSc supervisor Brian Rippey for all his help with this project and especially for going out of his way to collect core samples in Glendalough; also a big thanks to lab technicians, Pete Devlin and Hugo McGrogan, for their very helpful assistance. I am indebted to Gillian Nicholl of AFBI for analysing my samples by ICP-AES. The kind assistance of the National Parks and Wildlife Service of Ireland is also

much appreciated for permission to collect core samples from the Upper Lake of Glendalough; special mention and thanks to park ranger, Damian Clarke, for taking us out on the boat. Also thanks to Matthew Parkes, of the National Museum of Ireland, for providing useful information for this project.

REFERENCES

- Armitage, P. D., Cranston, P., and Pinder, L. C (1995). *The Chironomidae: Biology and Ecology of Non-Biting Midges*. Springer.
- Beining, B., Otte, M. (1996). 'Retention of Metals Originating from an Abandoned Lead: Zinc Mine by a Wetland at Glendalough, Co. Wicklow'. *Biology and Environment: Proceedings of the Royal Irish Academy*. 96B (2), 117-126.
- Brinkhurst, R. O., Chua, K. E. *et al.* (1969) 'Modifications in sampling procedures as applied to studies on the bacteria and tubificid oligochaetes inhabiting aquatic sediments', *Journal of the Fisheries Research Board of Canada*. 26, 2581-2593.
- Cole, A. J (1922). *Memoirs of a Geological Survey of Ireland*. 1st ed. Dublin: Stationary Office. 109-116.
- Cowman. (2007). 'The Mining Company of Ireland's Operations at Glendasan-Glendalough 1825-1895'. *The Journal of the Mining Heritage Trust of Ireland*. 7, 45-49.
- Dean, W. E. (1974). 'Determination of carbonate and organic matter in calcareous sediment and sedimentary rocks by loss on ignition: comparison with other methods'. *Journal of Sedimentary Petrology*. 41, 242-248.
- EPA, (2008). 'Water Quality of Lakes'. In: Clabby, K.J., Bradley, C., Craig, M., Daly, D., Lucey, J., McGarrigle, M., O'Boyle, S., Tierney, D. and Bowman, J. *Water Quality in Ireland*. Wexford: EPA. 3.1-3.18.
- Forstner, U. (1977). 'Metal concentrations in recent lacustrine sediments'. *Archiv fuer Hydrobiologie*. 80 (2), 172-191.
- Glew, J. R., Smol, J. P., Last, W. M. (2001). 'Sediment Core Collection and Extrusion'. *Developments in Paleoenvironmental Research*. 1, 73-105.
- Grayson, R.P., Plater, A.J. (2008). 'A lake sediment record of Pb mining from Ullswater, English Lake District, UK'. *Journal of Paleolimnology*. 42, 183-197.
- Gunten, H. R. von, Sturm, M. and Moser, R. N. (1997). '200-Year Record of Metals in Lake Sediments and Natural Background Concentrations'. *Environ. Sci. Technol.*, 31(8), 2193-2197.
- Kennan, P. S., McArdle, P., Williams, F. M., Doyle, E. (1986). 'A review of metal deposits associated with the Leinster Granite, SE Ireland and a model for their genesis'. In: Andrew, C. J., Crowe, R. W. A., Finlay, S., Pennell, W. M., Pyne, J. F. *Geology and Genesis of Mineral Deposits in Ireland*. Dublin: Irish Association for Economic Geology. 201-210.
- MacKenzie, A.B., Pulford, I.D. (2002). 'Investigation of contaminant metal dispersal from a disused mine site at Tyndrum, Scotland, using concentration gradients and stable Pb isotope ratios'. *Applied Geochemistry*. 17, 1093-1103.
- Mester, Z., Sturgeon, R. E. (2003). 'Sample preparation for trace element analysis'. *Elsevier*. 43, 1066.
- Migall, T. M., Timpany, S., Critchley, M. F., Cortizas, A. M., Sanchez, N. S. (2013). 'A Palaeoecological Assessment of the Impact of Former Metal Mining at Glendalough, County Wicklow Ireland'. *The Journal of the Mining Heritage Trust of Ireland*. 13, 9-22.
- Moreton, S., Green, D. (2007). 'The Mineralogy of the Wicklow Lead Mines'. *The Journal of the Mining Heritage Trust of Ireland*. 7, 19-32.
- Moreton, S., Green, D. and Tindle, A.G. (2006). 'Manganese oxide minerals from veins in the Leinster Granite'. *Irish Journal of Earth Sciences*, 24, 29-36.
- Morris, J., Cowman, D., Burt, R., Gill, M., Cox, W. (2008). *The Mineral Statistics for Ireland 1806-1920*. Unpublished book. 281-283.
- O'Connor, P. J., Brück, P. M. (1978). 'Age and Origin of the Leinster Granite'. *Journal of Earth Science*. 1 (2), 105-113.
- Riphey, B., Douglas, R. W. (2004). 'Reconstructing regional-scale lead contamination of the atmosphere (1850-1980) in the United Kingdom and Ireland using lake sediments'. *Global Biogeochemical Cycles*. 18, 1-14.
- Salminen, R. *et al.* (2005). *Geochemical Atlas of Europe: Part 2. Finland*: Geological Survey of Finland. 103-110.
- Seymour, H. J. (1939). 'Bathymetric Survey of Three Lakes in Co. Wicklow'. *Proceedings of the Royal Irish Academy*. 45, 297-299.
- Schindler, D. W., Hesslein, R. H., Wagemann, R., Broecker, W. S. (1980). 'Effects of Acidification on Mobilization of Heavy Metals and Radionuclides from the Sediments of a Freshwater Lake'. *Canadian Journal of Fisheries and Aquatic Sciences*. 37 (3), 373-377.
- Schwartz, S. P., Critchley, M. F. (2012). 'The Lead Ore Dressing Floors at Glendalough and Glendasan, County Wicklow 1825-1923: A History, Survey and Interpretation of Extant Remains'. *The Journal of the Mining Heritage Trust of Ireland*. 12, 5-52.
- Smyth, W.W. (1853). *On the Mines of Wicklow and Wexford*. London: Longman, Brown, Green and Longmans. 349-365.

Newspapers and Periodicals

- FJ *Freeman's Journal*, 30 July 1890, p. 3.

Internet Resources

- EPA, (2007). Glendalough-VanDiemen's Site Report. Available: <http://gis.epa.ie/EnvisionMines/Reports/Appendix%205%20Site%20Reports/Glendalough/Glendalough-VanDiemen%27s%20Site%20Report.pdf>. Last accessed 24th Oct 2013.
- USGS, (2013). ICP-AES Technique Description. Available: <http://minerals.cr.usgs.gov/gips/na/5process.html>. Last accessed 24th Apr 2014.