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Palaeoecological study of Llyn Padarn

H. Bennion, A. Burgess, K. Roe, H. Yang, R. Thomas

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Mae'r data ynghylch diatomau'n awgrymu y gallai crynodiadau maetholion fod wedi gostwng rhyw ychydig ers yr 1980au, ac yn fwyaf nodedig ers canol yr 1990au, gan fod *Fragilaria crotonensis* wedi dirywio o gymharu â *Tabellaria flocculosa* (math hir), gan fod yr ail yn gysylltiedig yn gyffredinol â lefelau is o faetholion. Gallai'r gostyngiad, y deuir i gasgliad yn ei gylch, mewn maetholion fod yn gysylltiedig â chyflwyno prosesau tynnu ffosfforws yng ngwaith trin carthion Llanberis yn 1995. Fodd bynnag, nid yw'r data'n darparu tystiolaeth o adferiad dramatig sy'n gysylltiedig â thrin carthion yn well. Yn wir, mae *Asterionella formosa* yn parhau'n amlwg iawn ymhlith fflora'r diatomau, ac mae canrannau cymharol *C.* aff. *comensis* yn parhau'n isel iawn. Felly, mae'r casgliadau presennol yn wahanol iawn i'r rhai a welwyd yn y samplau cyfeirio. O gofio i'r newidiadau diweddar, tuag at dacsonau sy'n dangos crynodiadau is o faetholion, gael eu gweld mewn tri sampl yn unig, argymhellir y dylid ailddadansoddi craidd gwaddod mewn pum mlynedd, a pharhau i fonitro’r ffytoplancton hefyd er mwyn asesu a yw’r newidiadau a welwyd yn y gymuned ddiatomau’n dal i ddigwydd.

Mae’r defnydd a wnaed o’r model diatomau-ffosfforws cyflawn yn dangos cynnydd a gostyngiad dilynol mewn crynodiadau ffosfforws cyflawn y deuir i gasgliadau yn ei gylch yn sgîl diatomau (DI-TP), sy’n arwain at y dehongliad ecolegol o’r data ynghylch diatomau. Roedd y crynodiadau DI-TP ar eu huchaf yn yr 1960au a’r 1970au, gyda gwerthoedd a oedd yn cyfateb i ~13 µg L^{-1} o’u cymharu â < 10 µg L^{-1} ar waelod y craidd, ac roeddent yn gostwng ar frig y craidd, gan ddychwelyd i werthoedd a oedd yn cyfateb i ~10 µg L^{-1}. Fodd bynnag, mae’r newidiadau y deuir i gasgliadau yn eu cylch yn fach, ac nid ydynt yn fwy na’r amrywiad rhyngflynyddol mewn crynodiadau ffosfforws cyflawn a fesurwyd yn y llyn. Rhaid dehongli’r canlyniadau DI-TP yn ofalus, oherwydd nad oedd y model yn cynnwys cynrychiolaeth dda o rai o’r tacsonau yng nghraidd Llyn Padarn. Yng ngoleuni cyfyngiadau allbwn y model, rhoddir mwy o bwyslais ar ddehongli newidiadau mewn rhywogaethau na’r gwerthoedd y deuir i gasgliadau yn eu cylch yng nghyswllt ffosfforws. Er hynny, caiff y data ei ategu gan y ffosfforws yn y gwaddod, sydd hefyd yn dangos i’r crynodiadau uchaf gael eu gweld yn yr 1960au-1970au, gyda gostyngiad bach mewn crynodiadau ffosfforws dros oddeutu’r degawd diwethaf.

Ni cheir tystiolaeth o asideiddio yn Llyn Padarn dros y 200 mlynedd diwethaf, oherwydd mae fflora’r diatomau’n gyson yn cynnwys tacsonau sy’n nodweddiadol o ddyfroedd amniwtral. Fodd bynnag, ceir tystiolaeth o halogi oherwydd metelau rhwng dechrau a chanol yr 1800au, a ddatgelwyd gan grynodiadau uchel o gopr, sinc a phlwm, a allai fod wedi deillio o waith mwyngloddio cynnar neu weithgareddau diwydiannol eraill yn y dalgylch. Er enghraifft, roedd safleoedd mwyngloddio copr yn gweithredu rhwng 1750 ac 1850, gyda’r gwaith ar ei anterth yn yr 1830au. Gwelwyd gostyngiad amlwg yng nghrynodiadau’r metelau hyn ers canol y bedwaredd ganrif ar bymtheg, pan ddaeth gwaith mwyngloddio i ben yn y dalgylch. Mae’n fwy na thebyg bod cynnydd mewn lefelau haearn ac arsenig, a welwyd yn ychydig gentimetrau uchaf y craidd, a oedd yn dyddio o adeg ar ôl 1998, yn deillio o newidiadau mewn potensial rhydocs yn y rhyngwyneb rhwng y gwaddod a’r dŵr. Mae hefyd yn bosibl bod y cynnydd mewn haearn yn gysylltiedig â dosio fferrig, a gyflwynwyd yng ngwaith trin carthion Llanberis yn 1995.

EXECUTIVE SUMMARY

This report summarises the findings of a study that was carried out to assess environmental change over the last 200 years in Llyn Padarn. The lake is designated as a Site of Special Scientific Interest (SSSI) for several reasons including its populations of Arctic charr and floating water-plantain. However, there have been growing concerns about the water quality of Llyn Padarn in recent years owing to a decline in the adult charr population and occurrence of the blue-green algal bloom in 2009. Enrichment of the lake is a particular concern as the lake receives effluent from the Llanberis sewage treatment works (STW). In the light of the high conservation interest of Llyn Padarn, an understanding of recent environmental change is required.

The study involves the analysis of a dated sediment core collected from Llyn Padarn in 2009 in order to assess environmental change over the last few centuries. The study focuses on diatom remains in the sediment core and also includes the application of an existing diatom-total phosphorus (TP) model to reconstruct the nutrient history of the lake. Additionally, X-ray fluorescence analysis was carried out to assess downcore changes in chemical composition with a particular focus on iron, copper and P.

The palaeolimnological work has provided some new insights into the ecology of Llyn Padarn. The results indicate that prior to ~1950 the diatom assemblages of Llyn Padarn comprised nutrient-poor taxa from the "*Cyclotella-Achnanthidium minutissimum*" complex, typically observed in the reference samples of low alkalinity, deep lakes in the UK. This assemblage was replaced by one dominated by *Asterionella formosa* in the late 1950s-early 1960s, a species associated with richer waters and, therefore, indicates enrichment of the lake from this time. However, the abundance of *C.* aff *comensis* had started to decline relative to the mesotrophic taxa in the mid to late 1800s, suggesting gradual enrichment from this time. This early enrichment likely reflects the large population of labourers associated with the slate quarry, and subsequent tourist development around Llanberis. The timing of the more pronounced phase of enrichment is coincident with the start of operations at the Llanberis STW in the 1950s. From the 1970s further mesotrophic taxa appeared in the lake, notably *Aulacoseira subarctica*, *Fragilaria crotonensis* and *Synedra rumpens* var. *familiaris*. These shifts may be linked to the increasing tourist population in the catchment in the late 1970s which would have put greater strain on the Llanberis STW.

The diatom data suggest that there may have been a slight reduction in nutrient concentrations since the 1980s and, most notably, since the mid-1990s as *Fragilaria crotonensis* has declined relative to *Tabellaria flocculosa* (long form), the latter generally being associated with lower nutrient levels. The inferred reduction in nutrient concentrations could be associated with the introduction of P-stripping at the Llanberis STW in 1995. However, the data do not provide evidence of a dramatic recovery linked to improved sewage treatment. Indeed *Asterionella formosa* continues to dominate the diatom flora and relative percentages of *C.* aff. *comensis* remain very low and, therefore, the present assemblages are far removed from those observed in the reference samples. Given that the recent changes towards taxa indicative of lower nutrient concentrations were seen in only three samples, repeat coring in five years time alongside continued monitoring of the phytoplankton is recommended to assess whether the observed shifts in the diatom community are sustained.

Application of the diatom-TP model indicates an increase and subsequent decrease in diatom-inferred TP (DI-TP) concentrations and thereby follows the ecological interpretation of the diatom data. The DI-TP concentrations were at their highest in the 1960s and 1970s with values of ~13 µg L^{-1} compared to < 10 µg L^{-1} at the bottom of the core and decreased at the top of the core, returning to values of ~10 µg L^{-1}. However, the magnitude of the inferred changes is small and is no greater than the inter-annual variation in measured TP concentrations of the lake. The DI-TP results must be interpreted with caution owing to poor representation in the model of some of the taxa in the Llyn Padarn core. In light of the limitations of the model output, greater emphasis is placed on interpretation of the species shifts rather than the inferred P values. Nonetheless the data are supported by the P content of the sediment which also exhibits maximum concentrations in the 1960s-1970s and a small decline in P concentrations over the last decade or so.

There is no evidence of acidification at Llyn Padarn over the last 200 years as the diatom flora is comprised of taxa typical of circumneutral waters throughout. However, there is evidence of metal contamination in the early to mid-1800s as revealed by high concentrations of copper, zinc and lead which could derive from early mining or other industrial activities in the catchment. For example, copper mines operated from 1750-1850 with peak mining activity in the 1830s. There has been a marked decline in concentrations of these metals since the mid-19th century when mining activity ceased in the catchment. Increases in iron and arsenic seen in the upper few centimetres of the core, dated to post-1998, are most likely to be derived from changes in redox potential at the sediment-water interface. It is also possible that the iron increase is associated with ferric dosing, which was introduced at the Llanberis STW in 1995.

1 INTRODUCTION

1.1 Background

Llyn Padarn is a large (97.6 ha), lowland (105 m a.s.l.) lake situated at the lower end of the Llanberis Pass in Gwynedd, North Wales (SH569614). The town of Llanberis is located towards the south-west and on the north-east shore there is a slate tip from the now disused Dinorwic slate quarry; a tourist railway also runs along this side of the lake (Map 1). Llyn Padarn was formerly connected to Llyn Peris via the Afon-y-Bala. However, in 1978 Llyn Peris became the lower reservoir for the Dinorwic power station, and the introduction of the Dinorwic pumped storage scheme in the 1980s resulted in the Afon Nant Peris (the inflow to Llyn Peris) being diverted and channeled through a tunnel so that it now by-passes Llyn Peris and flows into Afon-y-Bala which then flows into Llyn Padarn.

Map 1 Location of Llyn Padarn (area highlighted in red represents the SSSI boundary).

The Llanberis Sewage Treatment Works (STW) was constructed in the mid-1950s and discharges into the slow flowing Afon-y-Bala less than 200 metres upstream of Llyn Padarn. The STW was first consented in 1967 and the consent was last updated in March 2010, when consent limits were set at the following; 95 percentile look up table limits for Biological Oxygen Demand (BOD) of 40 mg L^{-1}, Suspended Solids 60 mg $L^{-1}$and Total Phosphorus (TP) 3.5 mg L^{-1}, and maximum limits for BOD of 80 mg L^{-1}, Suspended Solids 120 mg L^{-1}, iron 5 mg $L^{-1}$and aluminium 1 mg L^{-1}. There is also a rolling annual mean limit for TP of 1.6 mg L^{-1} (Environment Agency Wales 2009). Prior to construction of the Llanberis STW it is likely that sewage was discharged directly into Llyn Padarn (Katherine Griffiths, EAW, pers. comm.). The Nant Peris STW also eventually flows into the lake. This STW is small (People Equivalent of 111) and has a descriptive consent so there are no numeric limits and no chemical sampling is carried out at this works. Consent compliance at the works is determined through a programme of site inspections (Katherine Griffiths, EAW, pers. comm.).

Although small-scale mining activity was widespread in Snowdonia since at least Roman times, larger scale operations around the time of the Industrial Revolution are likely to have had a much more significant effect. The Llanberis and Clogwyn Goch copper (Cu) mines operated between about 1750 and 1850 (Crew 1976), and the Llanberis mine, which was sited at Glan-Llyn on the southern shore of Llyn Peris, was likely to have been responsible for significant pollution including the fish kills reported by contemporary literature (Forrest 1919). Peak mining activity was during the 1830s, when up to 11,000 tons of ore were extracted, although the operation was never very profitable (Crew 1976). By 1850 the mines had largely been abandoned. The Dinorwig slate mine in Llanberis operated in the 19th and 20th centuries. A railway was constructed on the shore of Llyn Padarn to transport slate to sea at Port Dinorwig. At its peak during the 1870s the mine employed 3,500 men but eventually closed in 1969 (National Slate Museum, Llanberis, pers. comm.).

Llyn Padarn is designated as a Site of Special Scientific Interest (SSSI) for several reasons including its rare, genetically distinct Arctic charr (*Salvelinus alpinus*) population, the presence of the nationally scarce Annex II aquatic macrophyte taxon, *Luronium natans* L. (Floating Water-plantain) and the exposure of geologically important Cambrian rock sequences. The Countryside Council for Wales (CCW) is responsible for the monitoring and management of SSSIs in Wales. The lake is one of only three remaining sites in Wales for natural populations of Arctic charr and the Llyn Padarn population is genetically distinct from populations in Llyn Cwellyn and Llyn Bodlyn. Monitoring using hydroacoustic techniques has shown a gradual decline in the fish population in the adult charr size range in comparison to surveys conducted in 2002 and 2003 (Davies 2007).

In a review of the status of Arctic charr in Britain and Ireland, Maitland *et al.* (2007) outlined a number of reasons for declining Arctic charr stocks. These included acidification, eutrophication, species introductions and climate change. There have been no known recent introductions of new species to Llyn Padarn and since there have been reductions in atmospheric sulphur levels in recent years, it is unlikely that the lake has become more acidic. Water chemistry data collected monthly in 2008 and fortnightly in 2009 by the Environment Agency Wales (EAW) also indicate that Llyn Padarn is unlikely to be affected by acidification because it is well-buffered, having a circumneutral pH (mean pH for 2008 = 7.3 and 2009 = 7.5) (Environment Agency Wales 2009).

Eutrophication is of concern due to the Llanberis STW. Low hypolimnetic dissolved oxygen concentrations found in Llyn Padarn could be indicative of a deteriorating trophic status within the lake (Davies 2007). Cyanobacterial algal blooms have recently been reported in Llyn Padarn (Environment Agency Wales 2009). A bloom of *Anabaena flos-aquae* lasted from May 2009 to October 2009. A previous bloom of *Staurastrun* in 1992 resulted in a 1993 court case involving the local angling club bringing proceedings against Welsh Water for the decline of Llyn Padarn as a fishery. This led to the introduction in 1995 of phosphate stripping at the Llanberis STW to reduce the phosphate concentration entering the lake and a new consent was issued by the EAW to reduce permitted phosphate discharges into the Afon-y-Bala. Monitoring of P levels in the STW effluent and Afon-y-Bala is ongoing. The current EAW Water Framework Directive classification for TP based on data collected in 2008 classes the lake in Good Ecological Status as the annual mean for this year was 9 µg L^{-1}. However this is very close to the Good-Moderate Ecological Status boundary of 10 µg L^{-1}. The mean TP concentration for 2009 was a little higher at 13 µg L^{-1} and hence the lake would be classed as Moderate Ecological Status based on the more recent data. In 2008 the mean annual chlorophyll a concentration was 4.37 µg L^{-1} with a maximum concentration of 7.5 µg L^{-1} in September. However, in 2009 the mean chlorophyll concentration was somewhat higher at 9.16 µg L^{-1} with the maximum value recorded at 25.2 µg L^{-1} during August. Nitrogen (N) concentrations in the lake are low with mean annual total N (TN) values of 0.28 mg L^{-1} and 0.25 mg L^{-1} in 2008 and 2009, respectively. The data suggest that N enrichment is not a problem in Llyn Padarn, probably because little agricultural land lies within the lake catchment. It should be noted that the EAW samples are collected at the outflow which is at the opposite end of the lake to the Llanberis STW and from where the core was taken (see Map 2).

A site condition assessment carried out in 2005 using Common Standards Monitoring (CSM) methods determined that Llyn Padarn was in overall ‘unfavourable’ condition (Burgess *et al*. 2006). It passed the attribute targets for macrophyte species composition and structure, supporting a Type 2 “oligotrophic” assemblage comprising *Littorelletea* taxa including *Littorella uniflora*, *Isoetes lacustris*, *Subularia aquatica* and *Luronium natans*. Seddon (1972) produced a similar macrophyte species list. The submerged vegetation zonation was fairly typical of an oligotrophic lake, although no *Lobelia dortmanna* was present. Kay *et al*. (1999) note the first record of *L. natans* from Llyn Padarn in 1848 and the last record in 1997. Although *L. natans* currently grows in Llyn Padarn, it was recorded only as ‘Rare’ (DAFOR scale) during macrophyte surveys undertaken for CSM condition assessment in both 2003 and 2005, growing in limited areas at depths of between 2 and 3 m (see Burgess *et al*. 2006 for further details). Llyn Padarn is also notified for *Isoetes echinospora*, but this taxon was not recorded in surveys conducted in 2003 and 2005, nor most recently in 2009. Water clarity was lower than expected for an oligotrophic lake and the non-native invasive Nuttall’s water-thyme, *Elodea nuttallii,* was recorded as locally abundant in the deeper water areas of the lake in 2003, another feature indicating unfavourable condition. Burgess *et al.* (2006) did not have access to dissolved oxygen (DO) profile data, but subsequent recovery of DO data from this period indicates that the lake’s hypolimnion was also deoxygenated in summer. The 2009 August oxygen depth profile showed a decrease from 10 mg L^{-1} at the surface to 3 mg L^{-1} at the deepest point in the lake. In comparison the nearby and deeper Llyn Cwellyn, had DO levels of 11 mg L^{-1} at the surface compared with 8 mg L^{-1} at its deepest point (Environment Agency 2009).

Based on diatom phytobenthos assemblages collected from stones in Llyn Padarn between 2003 and 2004 (five samples), Llyn Padarn’s ecological status was classified as ‘Good’, with a mean Ecological Quality Ratio (EQR) of 0.89 (Kelly *et al*. 2007). The phytobenthos samples were dominated by *Achnanthidium minutissimum*, with representatives from the *Synedra rumpens* complex and small *Nitzschia* spp. comprising most of the remainder. Phytobenthos samples collected in the spring and autumn of 2005 were also found to be composed largely of *A. minutissimum* and their sub-community was also found to be similar to the earlier samples. However, phytobenthos collected from the marginal zones of large, deep lakes may not always reflect conditions in the open water zone.

Diatom analysis of three samples from an undated sediment core taken from the lake in August 2004 showed that the diatom assemblage shifted from dominance of *Cyclotella comensis*, a species typically associated with nutrient-poor waters, towards co-dominance of other planktonic taxa such as *Aulacoseira subarctica*, *Asterionella formosa* and *Cyclotella pseudostelligera*, most commonly associated with more productive systems (Burgess *et al*. 2005). Analysis of a surface sediment sample taken from the lake in 2008 recorded a low floristic diversity (Hill's N2 = 6.41) and was similarly dominated by planktonic diatom taxa, with composition similar to that seen in the surface sample of the 2004 core with the exception that there was a higher relative abundance of *Tabellaria flocculosa* in the earlier sample (Burgess *et al*. 2009). This is most likely an artifact of the timing of core collection as the 2008 core was taken in early summer, whereas the 2004 core was taken in late summer when populations of the autumn-blooming *T. flocculosa* had increased.

There have been a number of previous studies carried out on Llyn Padarn and neighbouring Llyn Peris. Happey-Wood (1975) showed that the two lakes supported contrasting phytoplankton populations, and Pentecost and Happey-Wood (1978) demonstrated rates of primary production about five times greater in Llyn Padarn. At the time of these studies Llyn Peris was reported to be dominated by Chrysophyceae, whereas Llyn Padarn was dominated by Diatomaceae. Priddle and Happey-Wood (1983) described the seasonal periodicity in the algal assemblages of Llyn Padarn as being dominated by diatoms in spring, followed by the cyanobacterium *Oscillatoria limnetica* in summer, with a further diatom growth in autumn, whilst small Chlorophyta were present throughout the year.

Elner and Happey-Wood (1978) and Elner *et al*. (1980) determined the history of these two lakes from the pollen, diatom, chrysophyte and chemical stratigraphy of long, dated sediment cores (4.75 m core representing 6000 years from Llyn Padarn and 2.1 m core representing 900 years from Llyn Peris). Principal changes in the diatom communities in Llyn Padarn were concluded to have occurred as a result of vegetational changes in the catchment area. From ~ 6000 until 2200 years B.P., Llyn Padarn was an acid oligotrophic lake dominated by *Aulacoseira distans* (formerly *Melosira distans*). *Pinus* deforestation appears to have ended the *A. distans* zone, increased nutrient status and initiated dominance of small *Cyclotella* spp. in the deciduous forest zone. It appears that ~ 2200 years B.P., Llyn Padarn became more enriched, with *Asterionella formosa* being the most numerous diatom. This appears to coincide with a period of rapid deforestation and an increased rate of catchment erosion. Reversion to oligotrophic conditions and dominance of *Cyclotella* spp. then occurred at ~ 2000 years B.P. as dominant catchment land cover changed from deciduous forest to a heath and grassland community. From 1972, *A. formosa* was the major component of Llyn Padarn's phytoplankton community.

In contrast, the diatom communities of Llyn Peris were influenced to a large extent by mining and quarrying within the catchment. The oldest material from the Llyn Peris core was characterized by centric diatoms similar to those found in the Llyn Padarn sediment, dating from 2000 years B.P. However, by 200 years B.P. the chemistry of the sediment core from Llyn Peris showed evidence of extensive copper and slate mining. At this time the species of siliceous algae preserved in the Llyn Peris core changed and the current differences in algal communities in the two lakes appear to originate from this point in history. *Rhizosolenia eriensis* was dominant in the Llyn Peris sediments at the time when copper influx from mining was at a peak (100-200 years B.P.) This zone also exhibited an increase in *Synedra rumpens*. Interestingly, the authors noted many distorted frustules of this diatom taxon from this period.

This review of the literature, catchment history and recent monitoring data has shown that Llyn Padarn has been subject to several pressures over a range of timescales, not least metal pollution and nutrient loading. In light of the lake's high conservation interest and concerns regarding the Arctic charr populations, hypolimnetic deoxygenation and recent occurrences of blue-green algae, a fuller understanding of environmental change over the last century or so is required.

1.2 Objectives

The aim of this project is to sample and analyse a lake sediment core from Llyn Padarn and relate the findings to chemical and nutrient changes over time and known events in the lake's history. Palaeolimnological methods offer a means of reconstructing the environmental history of standing waters by studying subfossil fragments of the biota preserved in the lake sediments. The project aims to reconstruct the environmental history of Llyn Padarn over approximately the last century using diatoms, with particular attention to the eutrophication history of the site.

Diatom analysis of only three samples from an undated core taken from the lake in August 2004 showed that the diatom assemblage shifted from dominance of *Cyclotella comensis*, a species typically associated with nutrient-poor waters, towards co-dominance of other planktonic taxa such as *Tabellaria flocculosa*, *Aulacoseira subarctica*, *Asterionella formosa* and *Cyclotella pseudostelligera,* commonly associated with more productive systems (Burgess *et al*. 2005). This study aims to build on this earlier work and to analyse a new sediment core at a higher resolution and to provide a chronology in order to determine the timing and rates of change. This will enable shifts in the diatom assemblages over time to be much better understood and matched to known events in the lake's history, such as construction of the Llanberis STW. An existing diatom-TP transfer function will be applied to the diatom data in order to infer the trophic history of the lake. Additionally, X-ray fluorescence analysis will be carried out to assess downcore changes in chemical composition with a particular focus on Fe, Cu and P.

Specifically the aims are to:

- Undertake a brief literature review of the history of the lake;
- Collect an open water core from the deep basin;
- Sub-sample the core and perform lithostratigraphic analyses;
- Date the core using radiometric dating methods (^{210}Pb and ^{137}Cs);
- Conduct a quantitative reconstruction of water chemistry by analysing twelve samples in the core for diatom remains
- Calculate and present any changes in diatom-inferred total P (DI-TP) and diatom-inferred pH (DI-pH) over time;
- Analyse the core using X-Ray Fluorescence (XRF) to track changes in Fe, Cu and P; and
- Produce a report detailing methods, results and discussion.

2 METHODOLOGY

2.1 Core collection

A single sediment core was collected from the deep basin of the lake using a Glew gravity coring device. The coring location was located by a hand-held echo sounder and recorded by GPS.

2.2 Extrusion and core description

The core was extruded in the field at 0.5 cm intervals to a depth of 20 cm and at 1 cm intervals thereafter. Any visible stratigraphic changes were noted and the core was photographed. The percentage dry weight (%DW) which gives a measure of the water content of the sediment, percentage loss on ignition (%LOI) which gives a measure of the organic matter content, and percentage carbonate were determined in the laboratory on every sample by standard techniques (Dean 1974). Wet density was measured on selected samples by filling and weighing a 2 cm^3 brass vial with sediment.

2.3 Radiometric dating

A reliable method of establishing a chronology for sediment cores is to use radiometric dating techniques (Appleby 2001). ^{210}Pb occurs naturally in lake sediments as one of the radioisotopes in the ^{238}U decay series. It has a half-life of 22.26 years, making it suitable for dating sediments laid down over the past 200 years. The total ^{210}Pb activity in sediments comprises supported and unsupported ^{210}Pb. ^{210}Pb settles out of the atmosphere and is then bound by organic matter and deposited in the lake. Once in the sediment it is assumed to be immobile and spontaneously decays and is referred to as supported ^{210}Pb. In most samples the supported ^{210}Pb can be assumed to be in radioactive equilibrium with ^{226}Ra and the unsupported activity at any level of a core is obtained by subtracting the ^{226}Ra activity from the total ^{210}Pb (Appleby *et al*. 1986).

^{210}Pb dates for sediment cores can be calculated using both the constant rate of ^{210}Pb supply (CRS) model and the constant initial ^{210}Pb concentration (CIC) model (Appleby and Oldfield 1978). The CRS model is most widely accepted; it assumes that the ^{210}Pb supply is dominated by direct atmospheric fallout, resulting in a constant rate of supply of ^{210}Pb from the lake waters to the sediments irrespective of net dry mass accumulation rate changes. If there are interruptions to the ^{210}Pb supply, for example sediment focusing, dates are calculated either by the CIC model or by using a composite of both models. The factors controlling the choice of model are described in full in Appleby and Oldfield (1983).

^{137}Cs (half-life 30 years) and ^{241}Am are artificially produced radionuclides, introduced to the study area by atmospheric fallout from nuclear weapons testing and nuclear reactor accidents. ^{137}Cs activity in sediments prior to the 1986 Chernobyl nuclear accident derives mainly from nuclear weapons testing fallout. Where this isotope is strongly adsorbed on to sediments, the activity versus depth profile is presumed to reflect varying fallout rate and useful chronological markers are provided by the onset of ^{137}Cs fallout in 1954, and peak fallout in 1963.

Sediment samples from the Llyn Padarn core (coded PADA2) were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay in the Bloomsbury Environmental Isotope Facility (BEIF) at University College London using either an ORTEC HPGe GWL series well-type, or an ORTEC HPGe LOAX series planar-type, coaxial low background intrinsic germanium detector. ^{210}Pb was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope ^{214}Pb following three weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662kev and 59.5kev. The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy gamma rays within the sample (Appleby *et al.* 1992).

2.4 X-Ray Fluorescence (XRF) analysis

X-Ray Fluorescence (XRF) analysis is a method that measures the abundance of chemical elements in a material in order to determine its composition. Here, XRF analyses were carried out to track downcore changes in chemical composition with a particular focus on Fe, Cu and P. High sensitivity energy dispersive X-ray fluorescence analysis was performed using a Spectro X-Lab 2000 instrument in the Department of Geography at UCL which covers all elements from Na-U. Sub-samples (every 3rd cm) from each core were run under helium, as a fine powder, using an internal calibration. Standards were run alongside the samples to check for accuracy and precision. The major elements such as P and Fe are presented as % data and the trace elements such as Cu are presented as concentrations expressed as $\mu g\ g^{-1}$. These are the standard units of measurements output by the XRF analysis.

2.5 Diatom analysis

Diatom slides were prepared from 22 sub-samples of the core using standard techniques (Battarbee *et al.* 2001). These were screened for preservation and to assess points of change in the core, following which 12 samples were selected for counting. Sub-samples were counted and identified using a Leitz research microscope with a 100x oil immersion objective and phase contrast. Principal floras used in identification were Krammer and Lange-Bertalot (1986-1991). A minimum of 300 valves were identified in each sample. All diatom data are expressed as percentage relative abundance.

A quantitative approach to reconstruction of environments has been developed over the last few decades based on a predictive equation, or transfer function, that models the relationship between species composition and water chemistry (Birks 1998). The transfer function is generated using a calibration, or training, set of modern surface-sediment samples and a contemporary, water chemistry dataset from a large number of water bodies spanning the environmental gradient of interest. Once calibrated, it is then applied to the fossil diatom assemblages in a sediment core to provide quantitative inferences of past water chemistry. The technique of weighted averaging (WA) regression and calibration, developed by ter Braak (e.g. ter Braak and van Dam 1989), and its extension to a method called WA partial least squares (WAPLS) (ter Braak and Juggins 1993), have become standard techniques in palaeolimnology for reconstructing past environmental variables. Modern environmental optima are calculated for each taxon based on their distribution in the training set whereby the environmental variable measured at each sample is weighted by a measure of species abundance so that samples with high abundance of a species are given more weight. The past chemical conditions are then derived from the weighted average of the optima of all taxa present in a given fossil sample. The methodology and the advantages of WA over other methods of regression and calibration are well documented (e.g. ter Braak and van Dam 1989; Line *et al.* 1994).

Prior to interpretation of diatom reconstructions, it is important to assess the performance of the model being used. The strength of the relationship between the inferred and measured values is described by the coefficient of determination known as r^2. This is calculated for the original training set of lakes in the model (the apparent r^2) and also by a computer intensive cross-validation procedure, such as jack-knifing or boot-strapping, which is based on a test set of lakes generated from the original training set and provides a more realistic estimate (the predicted r^2). The r^2 value can range from 0 (no fit) to 1 (perfect fit) and, therefore, the higher the value the better the model is considered to be. The errors of the models are described by the root mean square error (RMSE) which essentially summarises the differences between the measured values for the training set of lakes and the diatom inferred values generated by the model. As for the r^2 values, these can be calculated based on the original training set (the apparent RMSE) and more realistically on the cross-validated test set (the RMSE of prediction or RMSEP). The lower the error, the better the model performs.

Transfer functions were applied to the diatom data, following taxonomic harmonisation between the training set and the fossil data. The reconstruction of diatom-inferred TP (DI-TP) was produced using a training set of 56 relatively large, deep lakes (> 10 m maximum depth) from Scotland, Northern Ireland, Cumbria, southern Norway and central Europe (Bennion *et al*. 2004). The training set has annual mean TP concentrations ranging from 1-73 µg TP L^{-1} and a median value of 22 µg TP L^{-1}. The model is based on simple WA and inverse deshrinking (ter Braak and van Dam 1989). The r^2 between observed and inferred values was 0.75 and the RMSEP based on the jack-knifing cross validation method was 0.25 $\log_{10}$ µg TP L^{-1}. The performance of this model is slightly poorer than that of the diatom-TP model based on 152 lakes in Northwest Europe which has an r^2 of 0.91 and an RMSEP based on the jack-knifing cross validation method of 0.21 $\log_{10}$ µg TP L^{-1} (Bennion *et al.* 1996). This is most likely because of the relatively fewer number of lakes in the deep lake model. However, the Northwest Europe model is comprised of relatively small, shallow (< 10 m maximum depth), productive lochs with annual mean TP concentrations ranging from 5-1200 µg TP L^{-1}, and a median value for the dataset of 104 µg TP L^{-1} and, therefore, is not suitable for Llyn Padarn as it contains different types of lakes and would considerably overestimate TP concentrations for a nutrient-poor lake.

The reconstruction of diatom-inferred pH (DI-pH) was produced using the Surface Water Acidification Programme (SWAP) training set of 167 lakes from largely acid-sensitive, upland regions of the UK, Norway and Sweden (Stevenson *et al*. 1991). The model is based on simple WA with classical deshrinking (Line *et al*. 1994). The median value for the dataset is pH 5.3 and the model has a RMSEP of 0.32 pH units. All reconstructions were implemented in C^2 (Juggins 2003).

2.6 Data analysis

Summary statistics of the diatom data were calculated for each sample in the core including the number of taxa observed and the Hill’s N2 diversity score which is an estimate of the effective number of taxa (Hill and Gauch 1980). The results of the analyses were plotted as a stratigraphic diagram using C2 (Juggins 2003). Cluster analysis was performed on the core data to identify the major zones in the diatom record using ZONE v.1.2 (Juggins 1991). ZONE is an MS-DOS program which employs a variety of constrained clustering techniques (ConsLink, ConISS, SplitLSQ and SplitINF) from which common splits can be identified. Zones are illustrated on the stratigraphic plot in order to facilitate description of the major compositional changes.

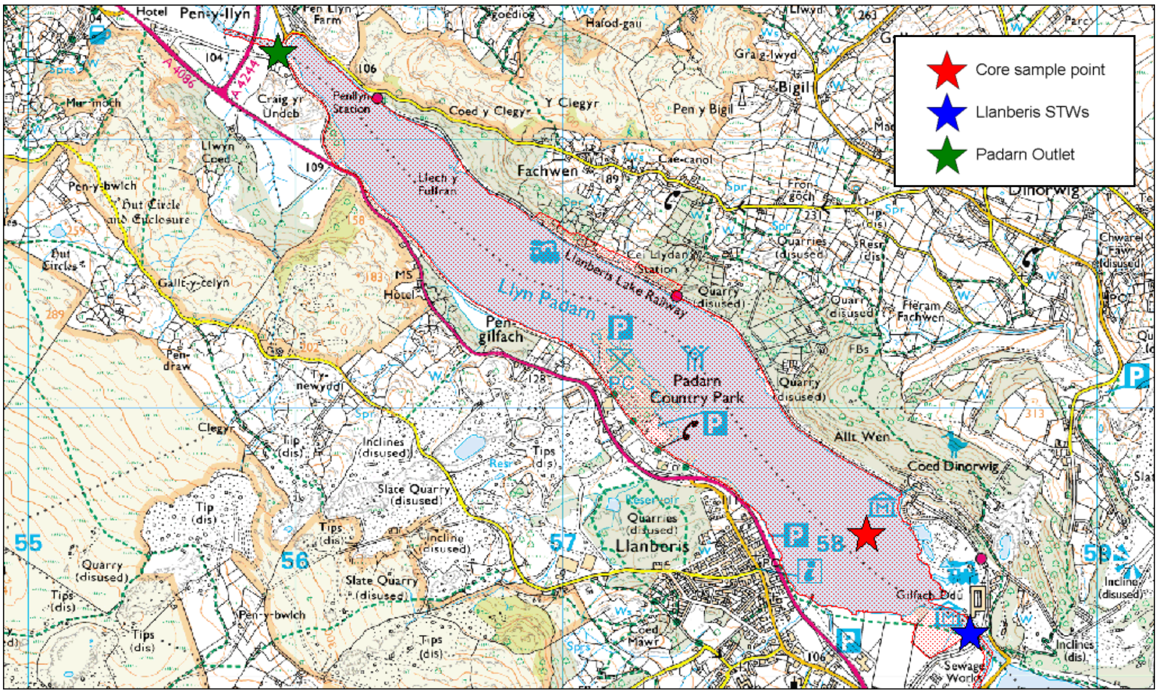
The degree of floristic change in the diatom assemblages between the bottom sample and every other sample in the core was assessed using the squared chord distance (SCD) dissimilarity coefficient (Overpeck *et al*. 1985) implemented in C2 (Juggins 2003). This is preferred to other dissimilarity measures as it maximises the signal to noise ratio, it performs well with percentage data and has sound mathematical properties (Overpeck *et al*. 1985). The scores range from 0 to 2 whereby 0 indicates that two samples are exactly the same and 2 that they are completely different. The method has been used in a number of studies to assess degree of change in diatom assemblages with respect to acidification (e.g. Simpson 2005; Simpson *et al*. 2005) and eutrophication (e.g. Bennion *et al.* 2004).

Principal components analysis (PCA), an indirect ordination technique (ter Braak and Prentice 1988), was used to analyse the variance downcore within the diatom assemblages using C2 (Juggins 2003). The technique summarises the main changes in the data and helps to identify zones of change within complex species-rich data sets. The sample scores for PCA axis 1 are given. Where scores between two neighbouring samples in the core differ markedly this indicates that the assemblages have undergone substantial change between these two points in the core. The scores are also plotted in the stratigraphic diagram to illustrate the timing of any shifts and whether these were gradual or abrupt.

3 RESULTS

3.1 Core description

A 33 cm sediment core (PADA2) was collected on 1st September 2009 from the deep basin of the lake at SH 58136, 60534 in a water depth of 27 m, using a Glew corer (see Map 2). The Secchi depth at the time of sampling was 3 m and there was a visible bloom of *Anabaena*.



Map 2 Location map of the coring site, Llanberis STWs and the EAW outlet sampling point.

The core had an undisturbed surface and chironomid tubes were evident. The core was homogeneous and dark brown in colour throughout (Figure 3.1). The core was relatively organic with %LOI values of ~ 15% in the lower core, rising to ~20% at the surface (Figure 3.2b). The core was denser in the lower section with both wet density and %DW values decreasing towards the surface of the core. %DW declined from ~25% to 6% (Figure 3.2a). The core had low carbonate content with values of < 6% throughout (Figure 3.2c).

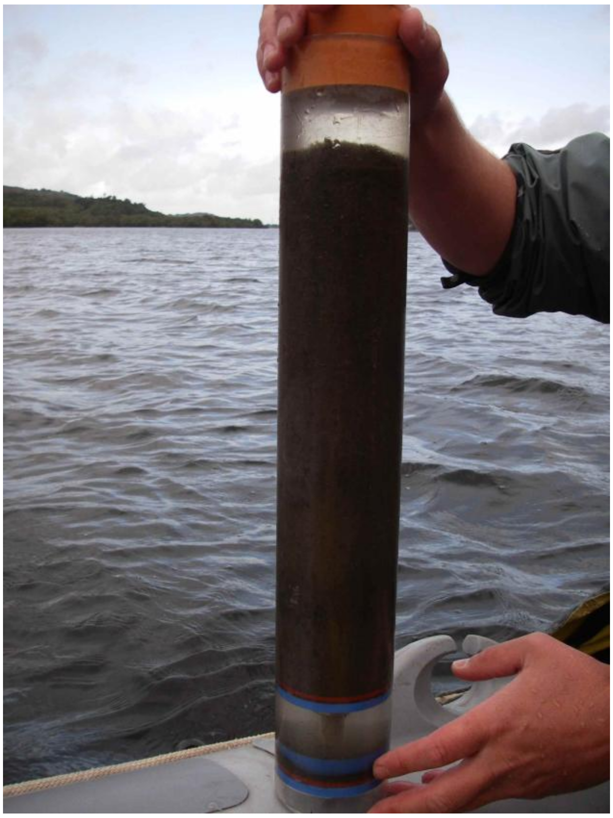


Figure 3.1 Photograph of the core from Llyn Padarn (PADA2)

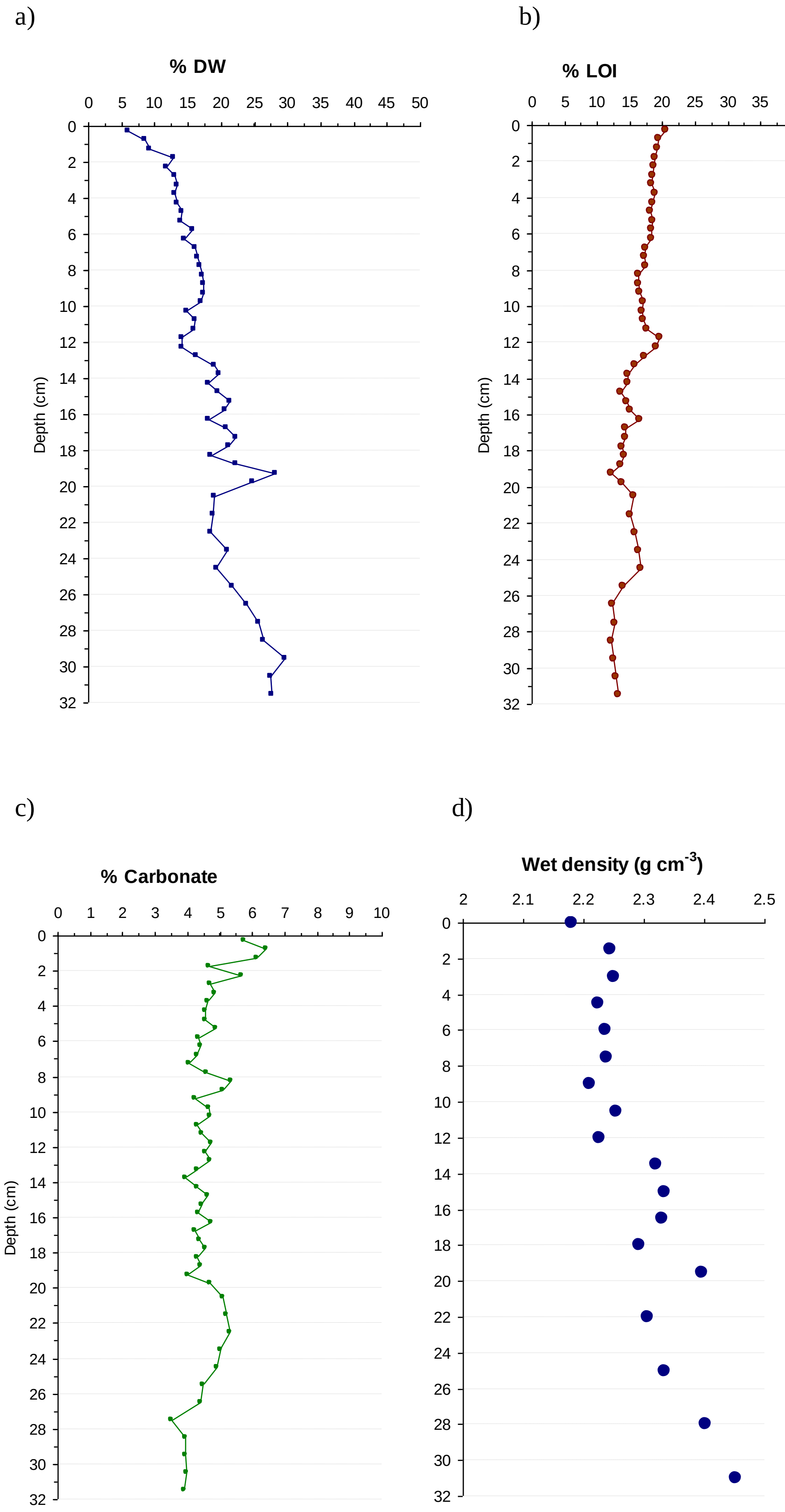


Figure 3.2 Profiles for a) Percentage dry weight (DW), b) organic matter (LOI), c) carbonate and d) wet density profiles of PADA2

3.2 Radiometric dating

Equilibrium depth of total ^{210}Pb activity with the supporting ^{226}Ra is at ~26 cm of the core (Table 3.1). The trends of unsupported ^{210}Pb activities, calculated by subtracting ^{226}Ra activity from total ^{210}Pb activity (Figure 3.3a), decline irregularly with depth (Figure 3.3b). Changes in unsupported ^{210}Pb suggest that sedimentation rates have generally increased over time. The unsupported ^{210}Pb inventory in the core is 9300 Bq m^{-2}, which yields an unsupported ^{210}Pb flux to the sediment of 289 Bq m^{-2} yr^{-1}. This implies that the coring location might have been subject to slight sediment focusing, a process whereby water turbulence moves sedimented material from shallower to deeper zones of the lake.

The ^{137}Cs activity versus depth shows a relatively well-resolved peak at 14.25 cm (Table 3.2, Figure 3.3c). This peak is likely to be derived from the 1963/4 fallout maximum of the atmospheric testing of nuclear weapons.

The use of the CIC model was precluded by irregular changes in unsupported ^{210}Pb activities in the core. Therefore, the core chronology was calculated using the CRS dating model (Appleby 2001). The raw CRS model puts the 1963 layer just below 14.25 cm, which is in good agreement with the corresponding layer suggested by the ^{137}Cs record. The chronology of the core is shown in Table 3.3. ^{210}Pb calculated sedimentation rates show that there is a gradual increase in sedimentation from the mid-19th century to the 1960s, followed by fluctuating rates with a slower increase in rate over the last 50 years or so (Figure 3.4).

Table 3.1 ^{210}Pb concentrations in core PADA2

Depth	Dry Mass	Pb-210						Cum Unsupported Pb-210	
		Total		supported		Unsupp			
cm	g cm^{-2}	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq Kg^{-1}	±	Bq m^{-2}	±
0.25	0.0158	484.43	22.99	54.44	4.68	429.99	23.46	68.2	4.3
2.25	0.2456	428.22	21.2	58.93	4.19	369.29	21.61	984.8	59.8
5.25	0.6965	413.94	19.41	60.12	4.02	353.82	19.82	2614.8	130.4
7.25	1.0275	335.38	21.91	67.45	4.92	267.93	22.46	3637.2	158.2
10.25	1.587	324.31	19.29	56.26	4.21	268.05	19.74	5136.6	205.7
14.25	2.342	195.29	15.99	61.69	3.73	133.6	16.42	6594.5	256.3
16.25	2.8248	203.73	9.5	64.07	2.33	139.66	9.78	7254	271.7
18.25	3.287	169.37	9.2	63.92	2.37	105.45	9.5	7816.7	276.9
20.5	3.8596	183.22	13.55	68.89	3.57	114.33	14.01	8445.6	285
22.5	4.3691	143.72	8.94	59.49	2.43	84.23	9.26	8947.5	294.2
24.5	4.898	94.82	12.31	64.89	3.6	29.93	12.83	9225.1	299.5
26.5	5.4269	82.77	8.54	78.66	2.66	4.11	8.94	9293.9	306.2
28.5	5.9558	73.11	7.73	70.37	2.18	2.74	8.03	9311.7	309.6

Table 3.2 Artificial fallout radionuclide concentrations in sediment core PADA2

Depth	**Cs-137**	
cm	**Bq Kg^{-1}**	**±**
0.25	82.87	4.08
2.25	90.53	4.08
5.25	136.06	4.27
7.25	155.02	5.62
10.25	157.02	4.86
14.25	195.61	4.9
16.25	81.25	2.05
18.25	72.05	2.09
20.5	74.7	2.74
22.5	51.48	1.78
24.5	10.46	1.86
26.5	3.09	1.06
28.5	4.54	0.93

Table 3.3 ^{210}Pb chronology of core PADA2

Depth	**Drymass**	**Chronology**			**Sedimentation Rate**		
		Date	**Age**				
cm	**g cm^{-2}**	**AD**	**yr**	**±**	**g cm^{-2} yr^{-1}**	**cm yr^{-1}**	**± %**
0	0	2009	0				
0.25	0.0158	2009	0	2	0.0668	0.612	6.4
2.25	0.2456	2005	4	2	0.07	0.514	6.9
5.25	0.6965	1998	11	2	0.0587	0.375	7
7.25	1.0275	1993	16	2	0.0656	0.369	9.5
10.25	1.587	1983	26	2	0.0482	0.257	9
14.25	2.342	1969	40	2	0.0627	0.304	13.8
16.25	2.8248	1960	49	3	0.0453	0.192	10.7
18.25	3.287	1950	59	4	0.0434	0.178	13.8
20.5	3.8596	1932	77	5	0.0229	0.09	19.9
22.5	4.3691	1903	106	12	0.0125	0.048	37.1
23.5	4.6336	1875	134	13	0.0094	0.036	41.4
24.5	4.898	1848	161	15	0.0063	0.024	45.8

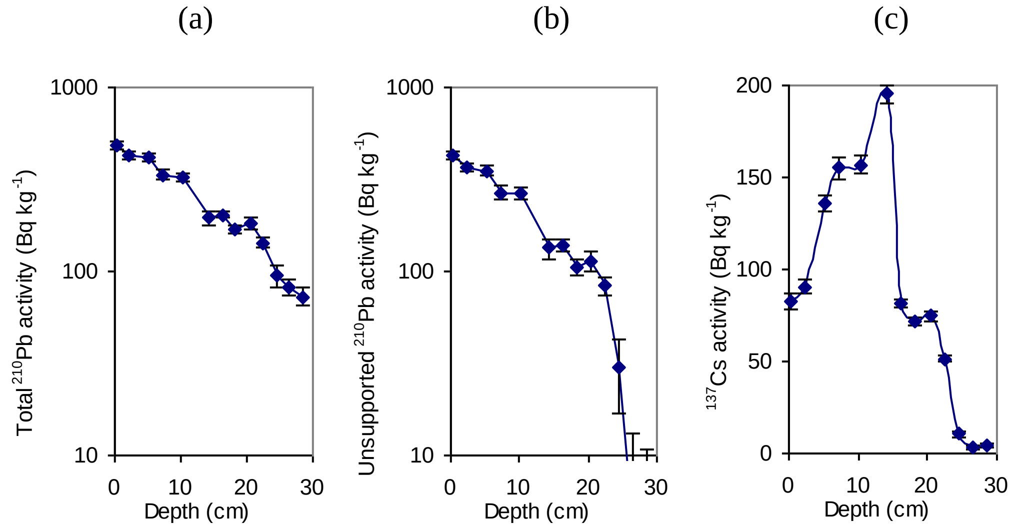


Figure 3.3 Fallout radionuclide concentrations in core PADA2 showing (a) total ^{210}Pb, (b) unsupported ^{210}Pb, and (c) ^{137}Cs concentrations versus depth

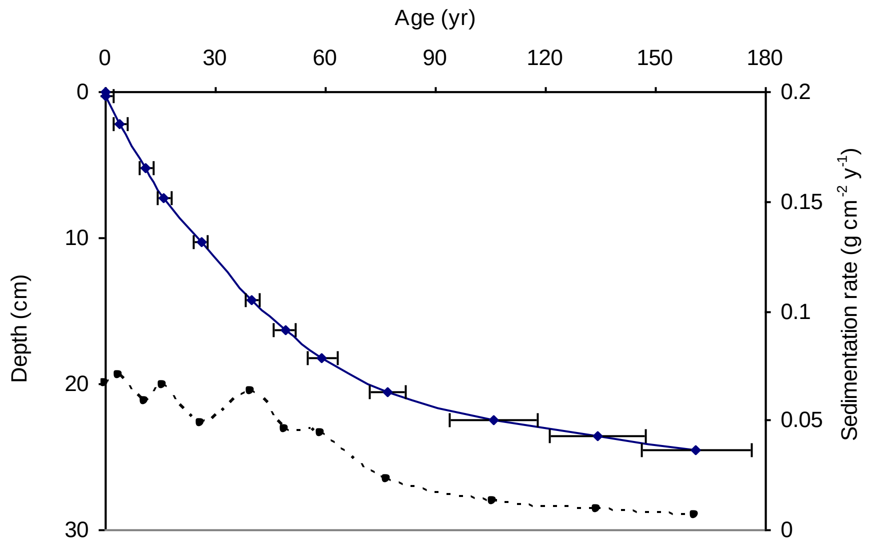


Figure 3.4 Radiometric chronology and sedimentation rates of core PADA2 (the age-depth curve is shown by the solid line and the sedimentation rate is shown by the dotted line)

3.3 XRF analysis

3.3.1 Distribution of Aluminium (Al), Silica (Si), Titanium (Ti) and Potassium (K)

The Al, Si, Ti, and K profiles show that concentrations of these geochemical elements in the sediment core are relatively stable but with a slight decrease towards the core surface (Figure 3.5). The decrease is likely to be a result of the increase in organic content in the upper part of the core (Figure 3.6a), suggesting that the main source of sediments was relatively stable.

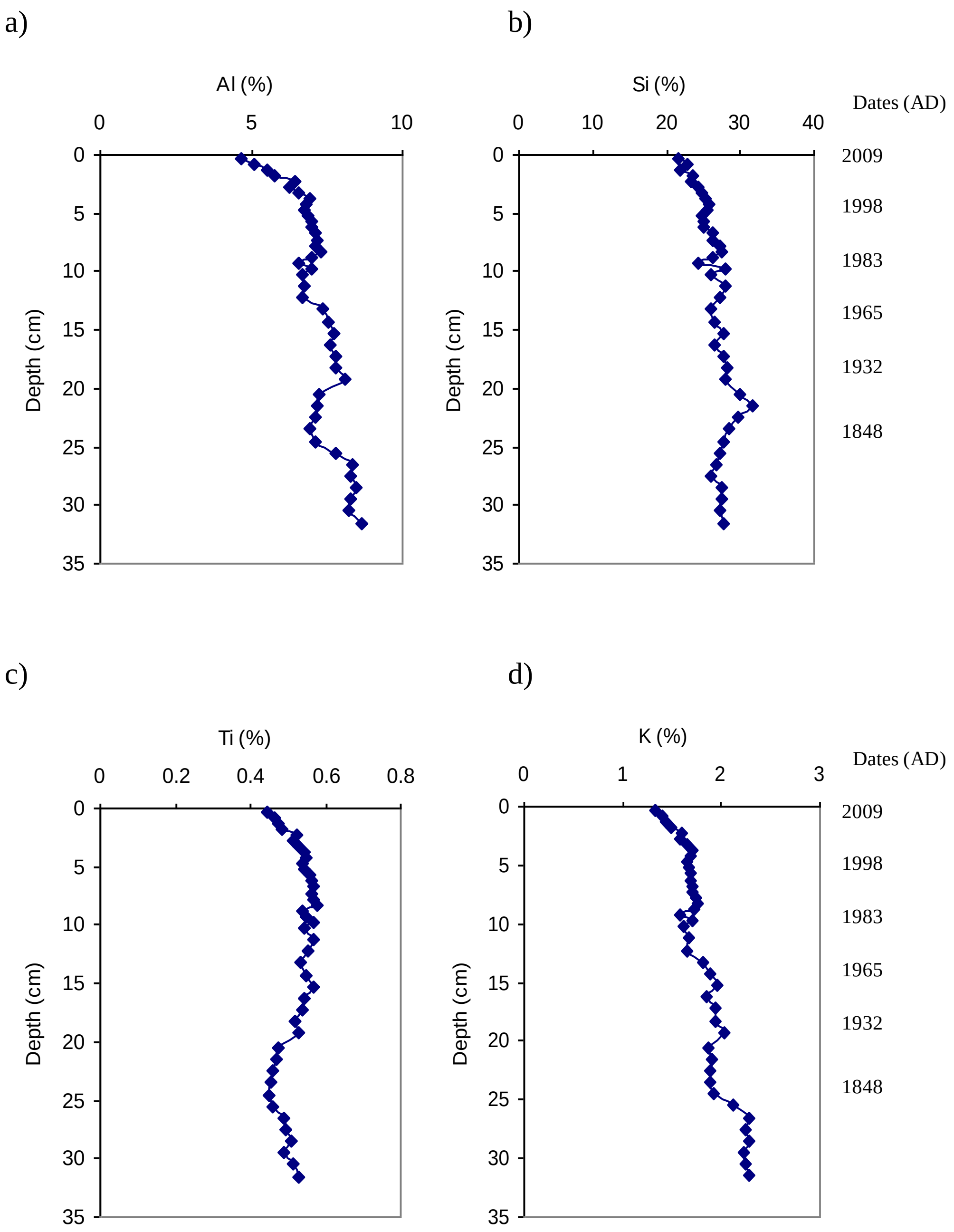


Figure 3.5 The Al, Si, Ti and K concentration profiles in the PADA2 core

3.3.2 Distribution of Phosphorus (P)

There is an increase in P concentrations from ~0.2% at the bottom of the core to ~0.4% at ~ 10 cm depth, dated to 1983. This is followed by a slight decline towards the surface to values of ~0.35% (Figure 3.6b). It appears that the general trends in %LOI and P concentrations below ~10 cm in the core are similar, suggesting that P concentrations are associated with organic matter. The slight decline in P in the upper ~10 cm may be due to the introduction of P-stripping at the Llanberis STW in the last decade or so but this interpretation is tentative as factors controlling P in lake sediments are complex, being affected by geochemical, physical and biological processes. Thus, sedimentary P profiles may have only a vague relationship to the timing of increased P inputs (Anderson *et al.* 1993). Current sedimentary P concentrations are still considerably higher than those in the lower part of the core.

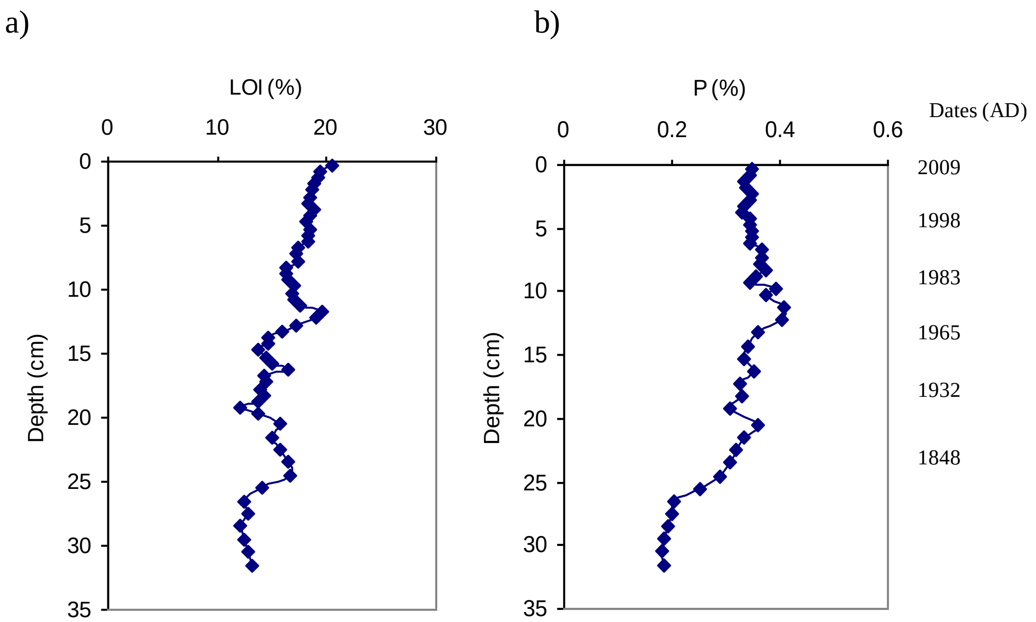


Figure 3.6 The LOI and P profiles in the PADA2 core

3.3.3 Distribution of Manganese (Mn) and Iron (Fe)

Concentrations of Mn and Fe are relatively stable (Figure 3.7) except for an increase in Fe in the upper 5 cm of the core, dated to post-1998 (Figure 3.7b). The Fe increase could be related to the introduction of ferric dosing at the Llanberis STW in 1995. However, it is more likely to be derived from changes in redox potential (Eh) at the sediment-water interface, which frequently results in enrichment of Fe in the surface sediments, and has been observed in numerous cores (e.g. Couture *et al.* 2010). Fe concentrations in the core are relatively high being in the range of 6.4 to 8.4%. These values are slightly higher than the median concentration of Fe in Scottish stream sediments of ~5%, for example, but are not a cause for concern (H. Yang, pers. comm.). Mn concentrations are ~0.2% and appear to reflect the local geology.

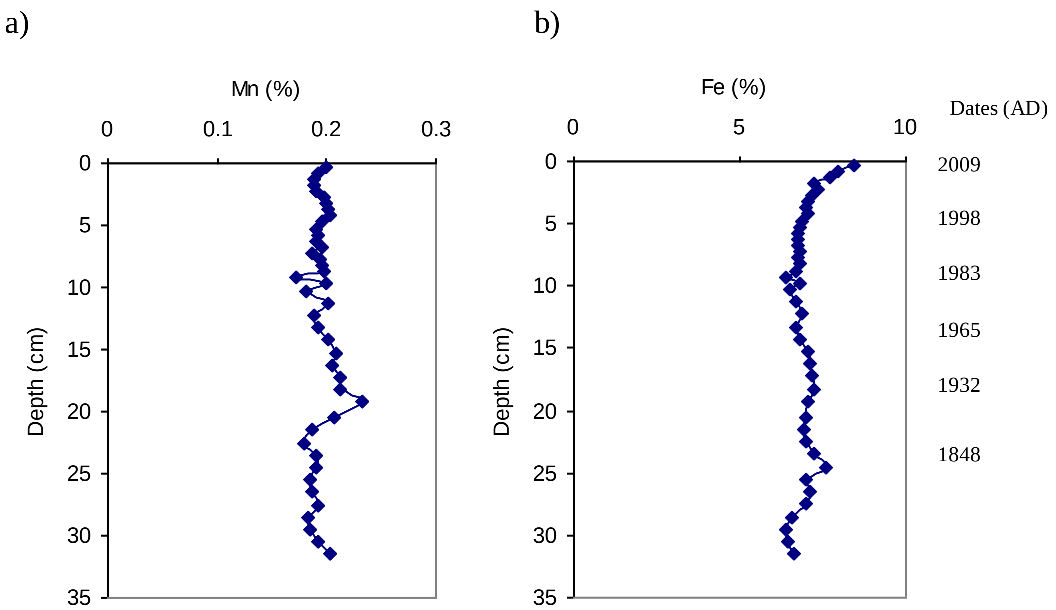


Figure 3.7 The Mn and Fe concentration profiles in the PADA2 core

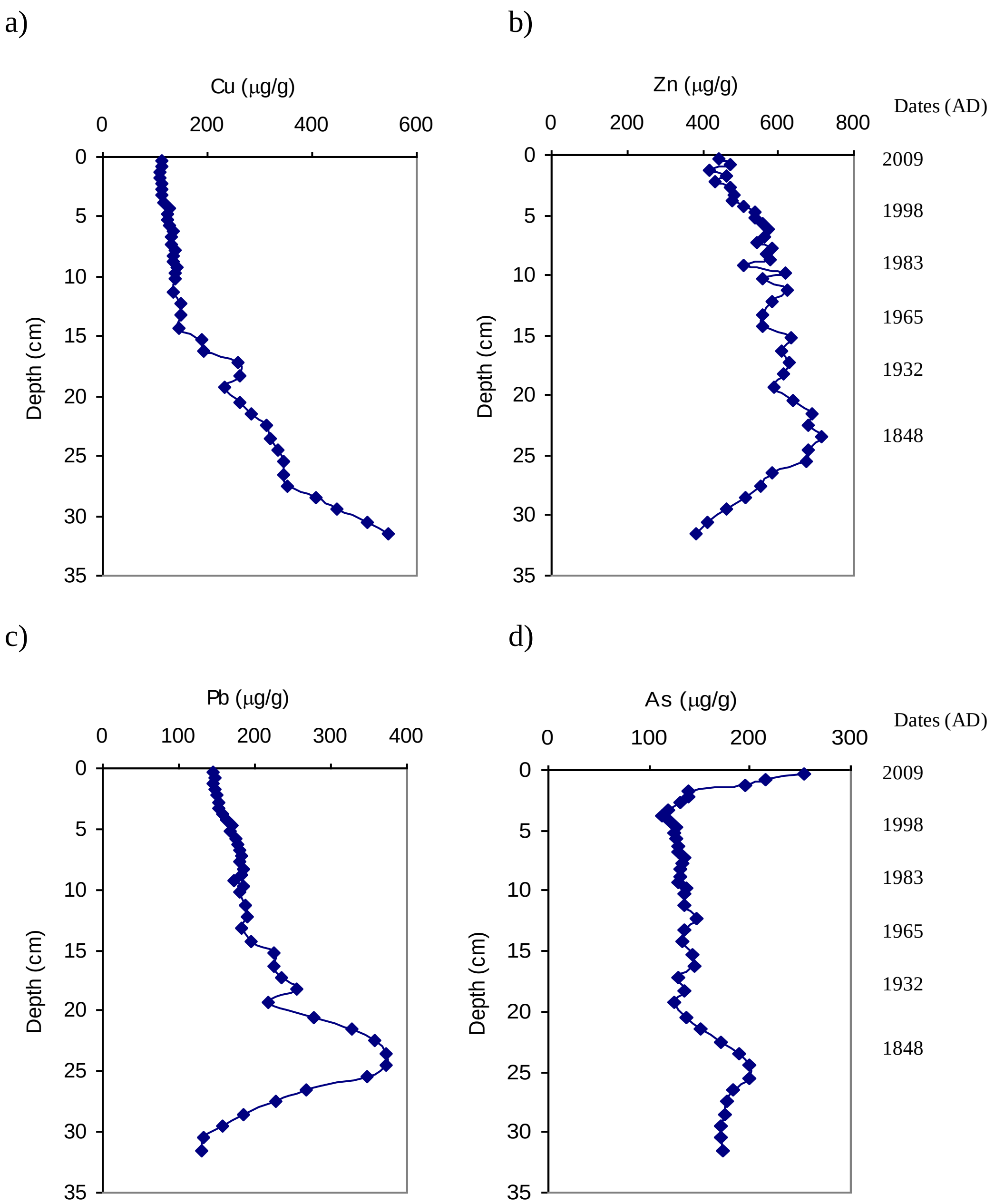


Figure 3.8 The Cu, Zn, Pb and As concentration profiles in the PADA2 core

3.3.4 Distribution of Copper (Cu), Zinc (Zn), Lead (Pb) and Arsenic (As)

The concentration profiles of Cu, Zn, Pb and As are shown in Figure 3.8. There is a marked gradual decline in Cu concentrations from 546 µg g^{-1} at the core base, dated to pre-1850, to 113 µg g^{-1} at the surface (Figure 3.8a). Comparing the Cu profile with the geochemical element profiles in Figure 3.5, it can be concluded that high Cu concentrations in the lower part of the core were derived from outside of the lake system. Hence, the lake has been contaminated by Cu since before the mid-19th century and has been in recovery from Cu pollution from that time to the present day. Cu pollution in the sediments most likely derives from the impact of the Llanberis and Clogwyn Goch copper mines. There is a peak at ~25 cm in the Zn, Pb and As profiles, suggesting that there was relatively heavy contamination of Zn, Pb and As during the mid-19th century (Figure 3.8b, c, d). This agrees very well with the historic record of activity in the Llanberis mine (Crew 1976). Similarly to Cu, declines in Zn and Pb concentrations from 25 cm upwards imply a gradual recovery of the lake from Zn and Pb pollution. An increase in As in the upper 3 cm of the core is likely to be a result of changes in redox potential at the sediment-water interface and has been seen in numerous sediment cores from other sites (Yang and Rose 2005; Couture *et al.* 2010). With the exception of Cu concentrations in the lower part of the core, which are relatively high, the concentrations of the other metals in the Llyn Padarn core are typical for the UK (Yang and Rose 2005).

3.4 Diatom analysis

Twelve samples were analysed for diatoms from the core PADA2 (Table 3.4). Diatoms were abundant and generally well preserved, with no evidence of dissolution. A total of 94 diatom taxa were observed in the core with between 26 and 44 taxa per sample. The samples were not particularly diverse, N2 values being < 8 reflecting the relatively high percentage abundances of only a small number of taxa. The samples were dominated by planktonic diatoms, varying from 55 to 72% of the total count. The results for the major taxa (occurring at >2% relative abundance) are shown in Figure 3.9 and the full dataset is presented in Appendix 1. Most of the taxa were present in the diatom TP and pH training sets with over 90% of the assemblage being represented in all of the Llyn Padarn samples. Nevertheless, some of the taxa in the Llyn Padarn core, whilst being present in the diatom-TP training set, occurred in fewer than 15 of the 56 training set lakes and, therefore, the optima for these taxa are not very robust. Furthermore the errors associated with the DI-TP values are quite large (see Table 3.4 and Figure 3.10). Hence, a degree of caution should be exercised when interpreting the DI-TP results and greater emphasis in the results and discussion is placed on the species shifts rather than the DI-TP values.

There were marked changes in the assemblages during the period represented by the core with three main zones and two sub-zones identified by cluster analysis. The chronology produced by radiometric dating was used to assign dates to the upper 25 cm of the core.

Zone 1 (32-16.25 cm); pre-1850-1956

Zone 1 was divided into two sub-zones: 1a (32-21.5 cm) and 1b (21.5-16.25 cm). Zone 1a was dominated by *Cyclotella* aff. *comensis* (~40-50%), a planktonic taxon typically associated with deep lakes of low productivity. Occurring alongside at moderate abundances were the periphytic taxa *Fragilaria capucina* var. *gracilis* (10-20%) and *Achnanthidium minutissimum* (~10%), also associated with low to moderate nutrient concentrations. *Cyclotella pseudostelligera* and *Synedra rumpens*, taxa more commonly found in slightly richer lakes, were also present, albeit at low abundances. It is interesting to note that a number of valves of *S. rumpens* in this zone (in particular between ~1900 and 1950) were distorted, being bent in two or three places. This phenomenon has been observed by other authors, and notably by Elner and Happey-Wood (1978) from the copper-rich zone of a sediment core from Llyn Peris. However, it is noteworthy that the period of peak mining activity and therefore expected maximum contamination was during the 1830s whereas the period containing the most distorted valves in core PADA2 was somewhat later than this. The bottom sample (30.5 cm) recorded low abundances of acid-tolerant taxa including *Nitzschia perminuta* and *Brachysira vitrea*.

The planktonic taxon, *Asterionella formosa*, associated with moderate nutrient concentrations was recorded throughout Zone 1, accounting for only a low percentage of the diatom assemblage in Zone 1a, but a rapidly increasing percentage of the diatom assemblage throughout Zone1b. This shift in the species assemblage is reflected in the gradual decrease in PCA axis 1 scores and an increase in dissimilarity (SCD) scores throughout Zone 1, as the diatom species assemblage deviates from that found in the bottom sample of the core. The DI-TP concentrations increased throughout this zone from ~9 $\mu g\ L^{-1}$ in Zone 1a to ~13 $\mu g\ L^{-1}$ by the top of Zone 1b, largely as a result of the increasing relative percentage abundance of *A. formosa*, which has a TP optimum of 15 µg L^{-1} in the dataset and concomitant decrease in *C.* aff. *comensis*, a taxon with a low TP optimum in the dataset (8 µg L^{-1}). Figure 3.9 gives further information on the TP optimum of the diatoms recorded in the core.

Zone 2 (16.25-12.25 cm); 1956-1976

Zone 2 contained only one sample. The diatom species recorded in this sample were broadly similar to those recorded in Zone 1, however there were notable shifts in the relative abundances of key taxa; *C.* aff. *comensis* decreased markedly to <10% and that of *A. formosa* increased significantly to >40%. This compositional change is typically associated with lakes experiencing eutrophication e.g. Lake Windermere (Sabater and Haworth 1995). There was a small, but notable peak of the eutrophic taxon, *C. pseudostelligera* in Zone 2 and *Fragilaria crotonensis,* a taxon of mesotrophic waters, appeared at low abundance, providing further evidence of nutrient enrichment. The shift in the species assemblage at the Zone 1/2 boundary was reflected in a sharp decrease in PCA axis 1 scores (>1), and an increase in SCD scores to 0.85. The DI-TP concentration reached its highest value of 13.4 µg L^{-1} in this zone, reflecting the increase in relative abundance of meso-eutrophic taxa and the decrease in abundance of *C.* aff. *comensis*.

Zone 3 (12.25-0 cm); 1976-2009

A further significant decrease in PCA axis 1 scores (~0.5) and an increase in SCD scores to ~1.2 was recorded at the Zone 2/3 boundary, reflecting the appearance or increasing importance of a number of mesotrophic planktonic taxa, most notably *Aulacoseira subarctica*, *F. crotonensis* and *Synedra rumpens* var. *familiaris*. However, Zone 3 was dominated by *A. formosa* (30-45%). The assemblage in Zone 3a was relatively stable with only minor fluctuations in the relative percentage abundances. This stability is reflected in the PCA axis 1 scores which show only small changes. Zone 3b was characterised by an increase in *Tabellaria flocculosa* (long) and a concomitant decline in *F. crotonensis*. The DI-TP concentrations decreased slightly throughout Zone 3 from ~13 to 10 µg L^{-1}, most likely reflecting the increase in relative percentage abundance of *T. flocculosa* (long) (optimum = 7 µg L^{-1}) and the decreasing abundance of *F. crotonensis* (optimum = 19 µg L^{-1}) over the last decade, as well as the slight decline in *A. formosa*. The reconstructed TP concentration for the surface sediment sample is ~10 µg L^{-1} and is therefore similar to the inferred values in the lower part of the core. However, the dissimilarity scores between the bottom sample and the samples in Zone 3 were high (SCD >1) indicating significant floristic change from the pre-1850 assemblages and an assemblage today that is markedly different from that in the past.

The DI-pH values ranged from 7.21 to 7.57 in Zones 1 to 3 thereby indicating circumneutral conditions throughout the period represented by the core. There is no evidence of acidification. The trends in DI-pH largely follow those of DI-TP suggesting that the slight decline in inferred pH values in Zone 3 reflects the reduced productivity of the lake in recent years.

Table 3.4 Summary diatom data for PADA2

Depth (cm)	No. of taxa	N2	DI-TP µg L^{-1}	Lower error DI-TP µg L^{-1}	Upper error DI-TP µg L^{-1}	DI-pH	SCD	PCA axis 1 scores
0	31	6.4	10.3	5.8	18.3	7.21	1.27	-0.69
2	41	6.9	10.4	5.8	18.4	7.27	1.13	-0.65
4	34	5.5	10.1	5.7	18.0	7.30	1.32	-0.89
6	44	7.3	12.0	6.7	21.3	7.31	1.16	-0.63
8	35	5.7	11.9	6.7	21.1	7.51	1.18	-0.75
10	32	4.0	13.0	7.3	23.2	7.51	1.24	-0.96
14	35	4.3	13.4	7.5	23.8	7.57	0.85	-0.48
18	30	4.8	12.0	6.8	21.4	7.53	0.39	0.73
20	27	4.5	11.2	6.3	19.8	7.53	0.46	0.43
22	33	5.2	10.4	5.8	18.5	7.49	0.25	1.02
24	28	3.6	8.6	4.8	15.2	7.49	0.21	1.48
30	26	4.7	9.1	5.1	16.3	7.38	0.00	1.40

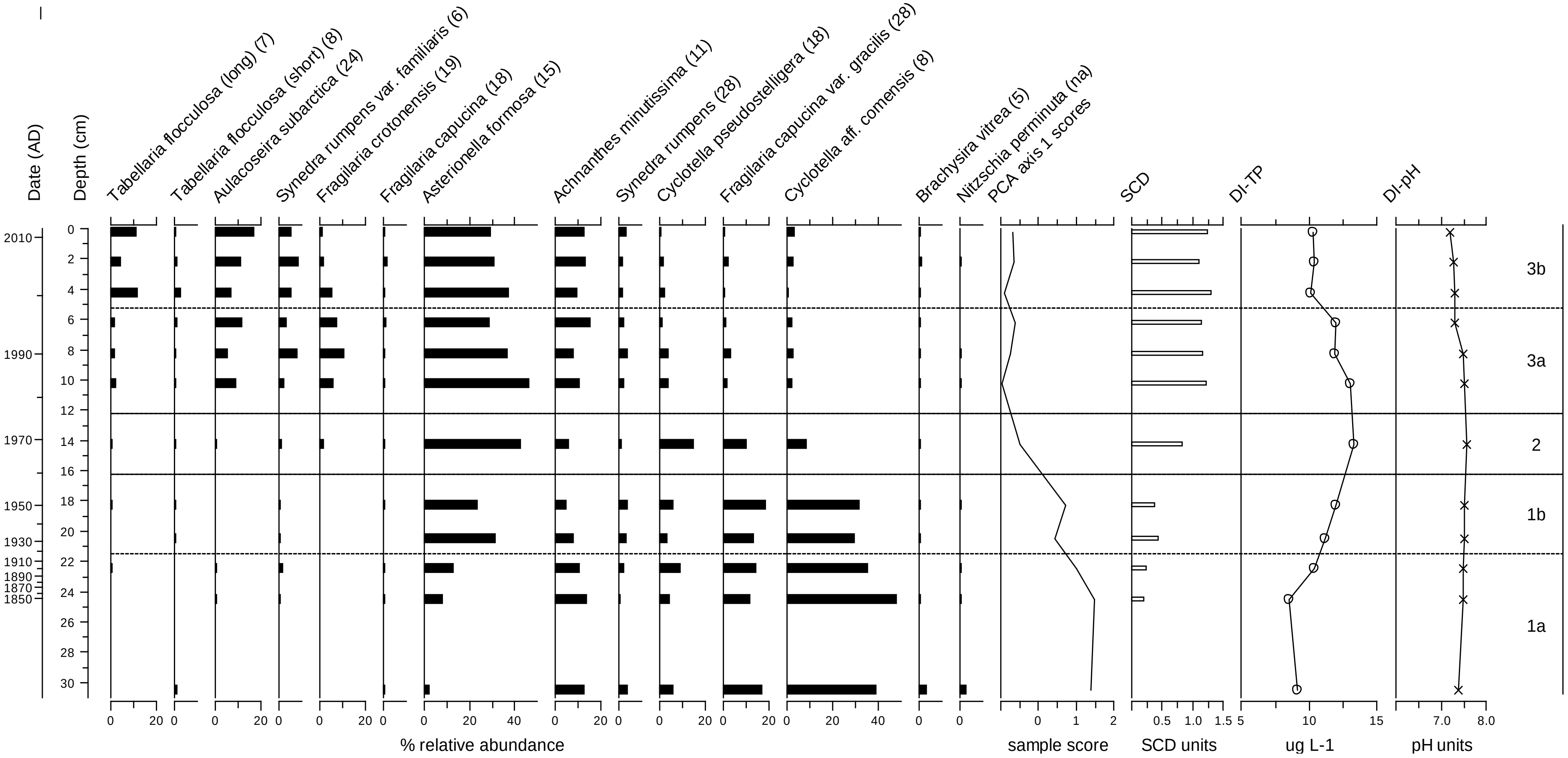


Figure 3.9 Summary diatom diagram for Llyn Padarn (core PADA2) (DI-TP optima in µg L^{-1} are given in brackets for each species)

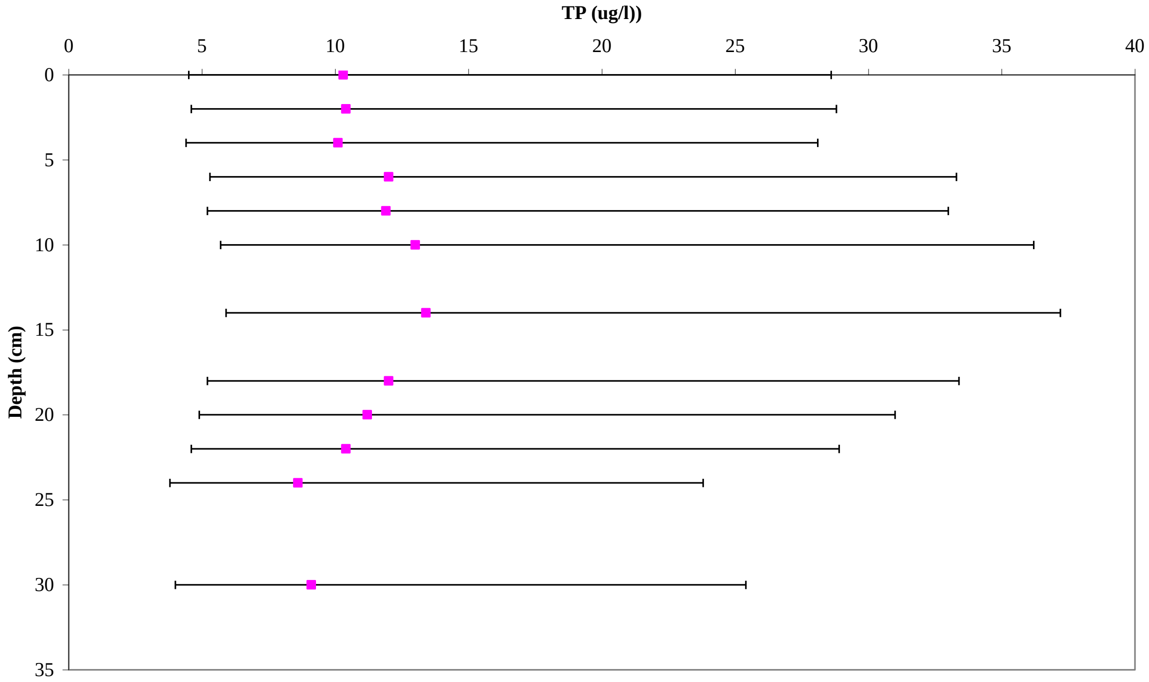


Figure 3.10 Errors associated with the DI-TP model results

4 DISCUSSION

The palaeoecological study indicates that Llyn Padarn has experienced significant shifts in its diatom assemblages indicative of eutrophication over the last few centuries. The association of shifts in the diatom record with events in the catchment is summarized in Table 4.1. The discussion is divided into the three main phases in the trophic history of the lake as identified by the study. A separate section focuses on interpretation of the diatom-inferred TP history and the limitations associated with the model. The evidence for acidification and metal pollution are also briefly discussed.

4.1 The pre-enrichment period

The dominant diatom species in Llyn Padarn until ~1960 was *Cyclotella* aff. *comensis,* a taxon typically associated with nutrient-poor waters. The "*Cyclotella-Achnanthidium minutissimum*" complex observed in the basal assemblages of the Llyn Padarn core has been observed in the reference samples of low alkalinity, deep lakes elsewhere in the UK (Bennion *et al.* 2004) and, therefore, appears to characterise the pre-enrichment diatom community for this lake type. Indeed Elner *et al.* (1980), in their study of diatoms in a core from the lake representing the last ~6000 years, showed that whilst there were early shifts in the diatom flora associated with major land cover changes, oligotrophic conditions and dominance of *Cyclotella* spp. prevailed from ~ 2000 years B.P. as dominant catchment land cover changed from deciduous forest to a heath and grassland community.

4.2 The enrichment period

There was a marked decline in *Cyclotella* aff. *comensis* relative to *Asterionella formosa* from the late 1950s-early 1960s in the Llyn Padarn core. The increasing importance of *Asterionella formosa* from ~1970 was also recorded by Elner *et al.* (1980). The species shift was coincident with the start of operations at the Llanberis STW. However, the abundance of *C.* aff *comensis* had started to decline relative to the mesotrophic taxa in the mid to late 1800s, suggesting gradual enrichment from this time. This early enrichment likely reflects the large population of labourers associated with the slate quarry. From the 1970s further mesotrophic taxa appeared in the lake. The isolation of Llyn Peris from Llyn Padarn and the probable increasing tourist population in the late 1970s, which would have placed greater pressure on Llanberis STW, may have contributed to the observed enrichment. Whatever the cause of eutrophication, the study suggests that nutrient concentrations were at their highest in the 1960s and 1970s. At this time the DI-TP concentrations were ~13 µg L^{-1} compared to 9 µg L^{-1} at the bottom of the core (although see section 4.4) and the sedimentary P profile also exhibits maximum concentrations in the 1960s-1970s. The increase in sedimentary P concentrations from the core base to the 1970s mirrors the shifts in the diatom record and may be related to increased external nutrient loads and enhanced algal production within the lake.

A similar suite of diatom species shifts have been observed in the sediment records of other lakes receiving sewage effluent. In Bassenthwaite Lake, Cumbria, Bennion *et al.* (2000) noted a shift from a *Cyclotella-Achnanthes minutissima* (now *Achnanthidium minutissimum*) flora prior to the mid-1880s to one dominated by *Asterionella formosa* and *Synedra nana* through the late 1800s and first half of the twentieth century, to one comprised of *Aulacoseira subarctica, Fragilaria crotonensis* and *Cyclotella pseudostelligera* from the 1960s. Similarly, in a core from Esthwaite Water, Cumbria, Bennion *et al.* (2000) reported the expansion of *A. formosa* and *F. crotonensis,* and the replacement of *Cyclotella comensis*, *C. radiosa* and *A. minutissima* by species more commonly associated with nutrient-rich water from ~1950. Likewise in Windermere South Basin, Sabater and Haworth (1995) recorded major shifts from a nutrient-poor assemblage of *C. comensis*, *C. radiosa*, *Tabellaria flocculosa* and *Achnanthes minutissima* to *Asterionella formosa* and *T. flocculosa* var *asterionelloides* in the mid-1800s, followed by expansion of *Fragilaria crotonensis* and *A. subarctica* from ~1950. In all cases cited above the shifts were reported to signal the progressive enrichment of the lake and, in particular, the expansion of *Asterionella formosa* and *Fragilaria crotonensis*, as also seen in Llyn Padarn, was thought to be related to enrichment resulting from increased sewage entering the systems.

Species shifts similar to those seen in the Llyn Padarn core were also seen in a palaeoecological study of Llyn Tegid (Bennion *et al.* 2003). The study revealed a clear shift in the diatom community in ~1985 marked by a significant decline in the oligotrophic *Cyclotella* taxa and an increase in *Asterionella formosa*. There was greater inter-annual variability in the diatom assemblages towards the top of the core with peaks of *Tabellaria flocculosa* in ~1992 and *Fragilaria crotonensis* in ~1994. The DI-TP data identified a recent phase of eutrophication in Llyn Tegid with values increasing from ~10 µg TP L^{-1} to ~30 µg TP L^{-1} over the period 1980-1996. In the case of Llyn Tegid, the exact cause of enrichment was not established owing to limited documentary data on land use changes and historical events in the catchment. Given that there are only three small sewage treatment works in the catchment, which are estimated to contribute only 13% of the total phosphate entering the lake (Millband 1996), it was thought unlikely that these were the main cause of increased in-lake TP levels, and diffuse, agricultural sources were likely to be more important.

In summary, the species succession seen in the Llyn Padarn core has been observed in numerous large, deep lakes and clearly signals enrichment of the lake starting in the late 1800s with a second more pronounced phase since the late 1950s.

4.3 Recent changes since ~1980

The diatom shifts towards the upper part of the core suggest that there has been a small degree of recovery since the 1980s and most notably since the mid-1990s as *Fragilaria crotonensis* has declined relative to *Tabellaria flocculosa* (long form). The former taxon is generally associated with higher nutrient concentrations than the latter. Consequently the DI-TP reconstruction indicates that concentrations have returned to ~10 µg L^{-1}. The sedimentary P profile also suggests that there has been a decline in P concentrations in the last decade or so, which could be related to reduced external loading or a decrease in algal production within the lake, although factors controlling P in lake sediments are complex and therefore this interpretation is somewhat tentative. It should be noted, however, that *A. formosa* continues to dominate the diatom flora, *Aulacoseira subarctica* is still present in high percentages and relative percentages of *C.* aff. *comensis* remain very low and, therefore, the present assemblages are far removed from those observed in the pre-enrichment period. Hence, the lake is still far from reference condition.

The causes of the recent changes in the diatom record are uncertain but could be related to the introduction of P-stripping at the Llanberis STW in 1995. However, the data do not provide evidence of a dramatic recovery linked to improved sewage treatment and this could be partly due to the likely increased loading to the STW since the mid-1990s. Furthermore the recent increase in *Tabellaria flocculosa* could be related to factors in addition to nutrient concentrations such as weather patterns and competition with other algae. For example, Macan (1984) identified a relationship between a decline in *Tabellaria* var *asterionelloides* and drier, milder summers in Lake Windermere, and Talling and Heaney (1988) suggested that its decrease could be related to competition from the Cyanobacteria *Anabaena* spp. and the dinoflagellate *Ceratium*. The increase observed in *Tabellaria flocculosa* in the Llyn Padarn record could, therefore, be related to wetter summers although this is entirely speculative in the absence of long term climate data. Moreover the changes were seen in a relatively small number of samples (the upper three samples of the core) and further sampling is recommended in future to ascertain whether this shift is sustained (see below).

4.4 The diatom-inferred phosphorus history

The marked enrichment signal exhibited by the diatom shifts in the core is more muted in the DI-TP reconstructed values. Whilst the increase and subsequent decrease in DI-TP concentrations follows the ecological interpretation of the diatom data, the magnitude of the increase is rather small and is within both the error of the model and the natural inter-annual range of TP concentrations in the lake. For example the DI-TP values increase from 9 µg L^{-1} at the bottom of the core to a maximum of only 13 µg L^{-1} in the 1960s-1970s, and the annual mean TP concentration measured by the Environment Agency sampling programme at the lake outflow was 9 µg L^{-1} in 2008 and 13 µg L^{-1} in 2009. In many applications of diatom-P transfer functions the inferred increase is often considerably larger. For example, in Llyn Tegid DI-TP values increased from 10 to 30 µg TP L^{-1} (Bennion *et al.* 2003) and in Windermere South Basin the DI-TP trends closely followed long term nutrient measurements with inferred values increasing from 5 to 50 µg TP L^{-1} (Bennion *et al.* 2005).

Diatom-P reconstructions have been validated against long-term monitoring data with encouraging results (e.g. Bennion *et al.* 1995, 2000, 2005; Rippey *et al.* 1997). In the majority of cases, the transfer functions appear to give reliable results in that DI-TP for the surface samples correspond closely with current measured TP, and the inferred trends are supported by other historical data where available. The models can, therefore, in most instances, be used with confidence for establishing reference nutrient conditions. Few models, however, are entirely error free and diatom transfer functions are no exception. Potential error sources include poor estimates of species optima for some taxa, inherent bias in inverse deshrinking techniques which results in over-estimation at the low end of the environmental gradient and under-estimation at the high end, and natural high variability in TP concentrations (e.g. Anderson *et al.* 1993; Bennion *et al.* 2001; Bradshaw and Anderson 2001). The species optima errors are primarily due to the complexity of lake ecosystems and the fact that factors controlling algal abundance in lakes are multivariate. Light, temperature, flushing rate, substrate and grazing pressure have all been shown to influence diatom distributions in lakes (e.g. Anderson *et al.* 1993; Bennion 1994). Weather-dependent factors such as the timing of the onset of stratification and the variation in flushing rate from year to year are important in controlling the numbers and composition of the phytoplankton (e.g. Reynolds and Irish 2000).

The predictive ability of the model used here for inferring TP concentrations for Llyn Padarn is weaker than the Northwest European model developed by Bennion *et al.* (1996), largely due to the relatively low number of lakes in the training set (56 compared to 152 sites). The errors associated with the reconstructed values are shown in Table 3.4 and Figure 3.10. However, the 56 lake model was considered to be more appropriate for Llyn Padarn than the Northwest European model as the latter includes mostly small, shallow lakes with much higher TP concentrations than those of Llyn Padarn and it would most certainly over-estimate values for this lake. Furthermore when applied to a set of Scottish lochs the 56 lake model appeared to produce reliable results (Bennion *et al.* 2004). It should be noted, however, that there are several taxa in the Llyn Padarn core that, whilst present in the 56 lake training set, do not occur in many of the training set lakes and therefore their optima may be less accurate than those of taxa which occur in large numbers of lakes. For example, *Synedra rumpens* and its variety *familiaris* were present in only 3 lakes, *Tabellaria flocculosa* forms, short and long, occur in only 15 and 14 lakes respectively, and *Fragilaria capucina* var. *gracilis* occurs in only 17 lakes in the training set. Further expansion of the 56 lake model to include more lakes should allow species optima to be better estimated and may result in improved performance.

In light of the model limitations, it is advised that greater emphasis is placed on interpretation of the species shifts themselves rather than the TP changes inferred by the transfer function. Nonetheless whilst the actual values inferred by the model may be questionable, there is no reason to believe that the inferred increase and subsequent decrease is unreliable.

4.5 Evidence of acidification

The palaeoecological data provide no evidence of acidification of Llyn Padarn over the last 200 years as the diatom flora remains one typical of circumneutral lakes throughout. This is in contrast to Llyn Cwellyn where the diatom record showed that the lake had acidified by ~0.7 pH units since the late 1800s but there was no evidence of change in the trophic status of the site (Bennion 1996). While the early assemblages of Llyn Cwellyn were similar to those seen in the bottom part of the Llyn Padarn core, being dominated by circumneutral, planktonic *Cyclotella,* these shifted to an acidophilous, periphytic assemblage (e.g. *Peronia fibula*, *Eunotia exigua*) towards the core surface, reflecting acidification. Meanwhile, the DI-TP values for Llyn Cwellyn were uniform at 6-8 μg TP L^{-1}, indicating stable, oligotrophic conditions throughout the period represented by the core.

The contrasting nature of the changes in the diatom assemblages of these two sites clearly shows the power of the diatom record for assessing the drivers of change. In Llyn Cwellyn, an acid sensitive lake, the diatom shifts are clearly indicative of acidification, whereas in Llyn Padarn which lies in a reasonably well buffered catchment, the shifts are indicative of enrichment.

4.6 Evidence of metal pollution

There is evidence of metal contamination in the mid-1800s as revealed by the high concentrations of Cu, Zn and Pb. Copper pollution in the sediments could derive from early mining or other industrial activities in the catchment as copper mines operated from 1750-1850 with peak mining activity in the 1830s. There has been a marked decline in concentrations of these metals since the mid-19th century when mining activity ceased in the catchment.

Increases in Fe and As were seen in the upper 3-5 cm of the core, dated to post-1998. These are most likely to be derived from changes in redox potential at the sediment-water interface. Fe and As are typically enriched at the interface of oxic and anoxic zones and increased concentrations are, therefore, commonly seen in the upper few centimetres of sediment cores (e.g. Yang and Rose 2005; Couture *et al.* 2010). Ferric dosing was introduced at the Llanberis STW in 1995 and it is possible that the Fe increase could be attributed to this source but this explanation is entirely speculative.

Table 4.1 Timeline of events in the recent history of Llyn Padarn and possible diatom evidence

Date	Event	Diatom evidence
2010	STWs consent updated	N/A
2009	*Anabaena flos-aquae* (cyanobacteria) bloom from May to October 2009	None to note
1995	P-stripping became operational at the Llanberis STW. Phosphate limit of 3.5 mg L^{-1} added to consent.	Post 1995 - increase in *Tabellaria flocculosa* and decrease in *Fragilaria crotonensis*; suggesting reduced nutrient concentrations.
1992	Record of an algal bloom	None to note
1984	Dinorwic pumped storage scheme opened	See comment for 1970s
1970s Early 1970s 1974	Isolation of Llyn Peris from Llyn Padarn by diversion of Afon Nant Peris as part of the Dinorwic pumped storage scheme. Tourist railway (Llanberis Lake Railway) opened 1971 and extended 1972. Potentially linked with increase in tourist population STW extended	Continued decline of *Cyclotella* aff. *comensis* and decline of *Fragilaria capucina* var. *gracilis*. Appearance and /or increase in relative abundance of mesotrophic taxa including *Aulacoseira subarctica*, *Fragilaria crotonensis* and *Synedra rumpens* var. *familiaris*, suggesting further eutrophication.
1969	Closure of Dinorwic slate quarry	See comment for 1967
1967	STW consent first formally documented	See comment for 1953/4. Increase in eutrophic *Cyclotella pseudostelligera* around this time.
1953/4	Llanberis STW started operating	Decrease in relative abundance of oligotrophic *Cyclotella* aff. *comensis* and increase in mesotrophic *Asterionella formosa* around 1960, indicating eutrophication.
Pre-1950s	Likely that raw sewage discharge to Llyn Padarn prior to construction of Llanberis STW	
~late 1800s-1950s	Elner *et al.* (1980) report that the influx of copper to Llyn Peris' sediments was very high ~ 150 years ago	Bent / distorted *Synedra rumpens* valves recorded –probably linked with high concentrations of copper; valves probably originated from Llyn Peris.
1840	Original Llanberis railway constructed – steam locomotives – slate & passengers	
Pre-1800s	Llanberis copper mine opened ~ 1750. The first commercial attempts at slate mining took place in 1787	Slightly higher relative abundances of acid-tolerant / low nutrient diatom taxa e.g. *Brachysira vitrea* and *Nitzschia perminuta* than in rest of the core.

5 CONCLUSIONS AND RECOMMENDATIONS

The palaeolimnological work has provided some new insights into the ecology of Llyn Padarn. In particular:

- There have been marked changes in the diatom flora of Llyn Padarn over the last 200 years. In particular, there has been a switch from *Cyclotella-Achnanthidium minutissimum* domination, a typical pre-enrichment community for this lake type, to a community comprising *Asterionella formosa*, *Aulacoseira subarctica, Fragilaria crotonensis* and *Tabellaria flocculosa,* indicating nutrient enrichment.
- The diatom data indicate that an early phase of enrichment occurred in Llyn Padarn in the late 19th century, likely reflecting the large population of labourers associated with the slate quarry, and subsequent tourist development around Llanberis. The data suggest that a second, more pronounced, enrichment phase occurred from the late 1950s with the most nutrient-rich conditions in the 1960s and 1970s. This is coincident with the start of operations at the Llanberis sewage treatment works.
- Diatom shifts in the upper core towards species indicative of slightly lower nutrient concentrations suggest small recent improvements in nutrient status that may be linked to improved sewage treatment since 1995. However, the data do not provide evidence of a dramatic recovery.
- In spite of the large observed community shifts, changes in nutrients as inferred by the diatom-TP model are relatively small. This is most likely due to poor representation of some of the Llyn Padarn diatom species in the training set of the 56 lake model. In light of the model limitations, greater emphasis is placed on interpretation of the species shifts rather than the inferred phosphorus values.
- There is no evidence of an acidification problem in Llyn Padarn either now or in the past, with circumneutral diatoms present throughout the core.
- There is evidence of metal contamination in the mid-1800s most likely associated with mining activity in the catchment at that time. There has been a marked decline in metal concentrations since the mid-19th century coincident with the cessation of local mining activity.
- Increases in Fe and As were seen in the upper few centimetres of the core, dated to post-1998. These are most likely to be derived from changes in redox potential at the sediment-water interface. While it is possible that the Fe increase could be associated with ferric dosing, which was introduced at the Llanberis STW in 1995, this explanation must be treated as entirely speculative.

Given that the recent changes towards taxa indicative of lower nutrient concentrations were seen in only three samples, repeat coring in five years time alongside continued monitoring of the phytoplankton is recommended to assess whether the observed shifts in the diatom community are sustained.

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APPENDIX 1: DIATOM DATA FOR LLYN PADARN CORE, PADA2 (% RELATIVE ABUNDANCE)

Percentage data			**Depth (cm)**											
Full name (new)	**Full name (old)**	**Code (old)**	**0.25**	**2.25**	**4.25**	**6.25**	**8.25**	**10.25**	**14.25**	**18.25**	**20.5**	**22.5**	**24.5**	**30.5**
Psammothidium helveticum	*Achnanthes helvetica*	AC134A	1.90	1.67	0.61	1.47	0.59	0.53	0.53	0.00	0.00	0.00	0.00	0.58
Eucocconeis laevis	*Achnanthes laevis*	AC083A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	0.00
Planothidium lanceolatum	*Achnanthes lanceolata*	AC001A	0.00	0.00	0.30	0.00	0.29	0.00	0.26	0.00	0.00	0.00	0.00	0.00
Achnanthes marginulata	*Achnanthes marginulata*	AC022A	0.00	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Achnanthidium minutissimum	*Achnanthes minutissima*	AC013A	13.28	13.63	10.02	15.63	8.26	10.96	6.32	5.10	8.34	11.21	14.04	13.39
Karayevia oblongella	*Achnanthes oblongella*	AC143A	0.81	0.00	0.00	0.49	0.44	0.27	0.00	0.00	0.00	0.00	0.14	0.00
Rossithidium pusillum	*Achnanthes pusilla*	AC035A	0.00	0.00	0.91	0.24	0.00	0.00	1.19	0.00	0.26	0.70	0.84	0.73
Achnanthes sp.	*Achnanthes* sp.	AC9999	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.57	0.52	0.23	0.00	0.00
Psammothidium subatomoides	*Achnanthes subatomoides*	AC136A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.56	0.00
Amphora inariensis	*Amphora inariensis*	AM013A	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00
Amphora pediculus	*Amphora pediculus*	AM012A	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.00
Asterionella formosa	*Asterionella formosa*	AS001A	29.54	31.15	37.63	29.30	37.17	46.79	43.21	24.08	32.07	13.32	8.71	2.62
Aulacoseira subarctica	*Aulacoseira subarctica*	AU020A	17.34	11.68	7.28	12.21	5.60	9.36	0.53	0.00	0.00	0.47	0.28	0.00
Brachysira brebissonii	*Brachysira brebissonii*	BR006A	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Brachysira vitrea	*Brachysira vitrea*	BR001A	0.27	1.39	0.61	0.73	0.29	0.53	0.53	0.28	0.52	0.23	0.28	3.78
Caloneis sp.	*Caloneis* sp.	CA9999	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	0.00
Cocconeis placentula	*Cocconeis placentula*	CO001A	0.00	0.00	0.61	0.61	0.00	0.27	0.13	0.00	0.00	0.00	0.28	0.00
Cyclotella aff. comensis	*Cyclotella aff. comensis*	CY010A	3.52	3.06	0.30	2.69	2.95	2.67	8.96	32.29	29.99	35.98	48.31	39.59
Cyclotella cf. *krammeri*	*Cyclotella* cf. *krammeri*	CY054A	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyclotella cf. *distinguenda* var. *unipunctata*	*Cyclotella* cf. *distinguenda* var. *unipunctata*	CY028B	0.00	0.00	0.00	0.00	0.29	0.27	0.00	0.00	0.00	0.00	0.56	0.29
Cyclotella pseudostelligera	*Cyclotella pseudostelligera*	CY002A	0.81	2.23	2.43	1.71	4.42	4.01	15.02	6.23	3.65	9.58	4.49	6.40
Encyonopsis cesattii	*Cymbella cesattii*	CM015A	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.28	0.00	0.00	0.28	0.87
Encyonema gracile	*Cymbella gracilis*	CM018A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.87
Encyonopsis microcephala	*Cymbella microcephala*	CM004A	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Encyonema minutum	*Cymbella minuta*	CM031A	0.00	0.00	0.61	0.00	0.00	0.80	0.26	0.57	0.52	0.93	0.56	0.00
Cymbella perpusilla	*Cymbella perpusilla*	CM010A	0.00	0.00	0.30	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.28	0.00
Encyonema silesiacum	*Cymbella silesiaca*	CM103A	0.27	0.00	0.30	0.24	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.29
Cymbella sp.	*Cymbella* sp.	CM9999	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Denticula tenuis	*Denticula tenuis*	DE001A	0.00	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.12	0.00
Diatoma tenue	*Diatoma tenue*	DT004A	0.00	0.42	0.30	1.59	0.59	0.67	0.92	0.28	0.00	0.00	0.00	0.00

Counts data			**Depth (cm)**											
Full name (new)	**Full name (old)**	**Code (old)**	**0.25**	**2.25**	**4.25**	**6.25**	**8.25**	**10.25**	**14.25**	**18.25**	**20.5**	**22.5**	**24.5**	**30.5**
Diatoma mesodon	*Diatoma mesodon*	DT021A	0.54	0.70	0.30	1.22	0.00	0.00	0.00	0.28	0.65	0.47	0.56	1.16
Eunotia bilunaris var. *mucophila*	*Eunotia bilunaris* var. *mucophila*	EU070B	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Eunotia exigua	*Eunotia exigua*	EU009A	0.27	0.00	0.30	0.98	0.59	0.27	0.53	0.28	0.00	0.00	0.00	0.00
Eunotia implicata	*Eunotia implicata*	EU107A	0.00	0.00	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.23	0.00	0.00
Eunotia incisa	*Eunotia incisa*	EU047A	0.27	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Eunotia intermedia	*Eunotia intermedia*	EU108A	0.00	0.28	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.44
Eunotia minor	*Eunotia minor*	EU110A	0.27	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Eunotia sp.	*Eunotia* sp.	EU9999	0.00	0.83	0.46	1.10	0.44	0.80	0.26	0.42	0.26	0.00	0.00	0.00
Eunotia tenella	*Eunotia tenella*	EU004A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00
Pseudostaurosira brevistriata	*Fragilaria brevistriata*	FR006A	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00
Fragilaria capucina	*Fragilaria capucina*	FR009A	1.08	2.23	1.06	1.34	0.59	0.27	1.05	0.28	0.00	0.70	0.56	0.58
Fragilaria capucina var. *gracilis*	*Fragilaria capucina* var. *gracilis*	FR009H	0.81	2.78	1.21	1.83	3.54	1.87	10.28	18.84	13.43	14.60	12.08	17.18
Fragilaria capucina var. *mesolepta*	*Fragilaria capucina* var. *mesolepta*	FR009B	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fragilaria constricta	*Fragilaria constricta*	FR010A	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	0.00
Staurosira construens var. *venter*	*Fragilaria construens* var. *venter*	FR002C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.28	0.00
Fragilaria crotonensis	*Fragilaria crotonensis*	FR008A	1.63	1.95	5.61	7.69	11.06	6.55	2.11	0.00	0.26	0.00	0.00	0.00
Fragilariforma exigua	*Fragilaria exigua*	FR064A	0.00	0.00	0.91	1.22	0.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pseudostaurosira pseudoconstruens	*Fragilaria pseudoconstruens*	FR056A	0.00	0.00	0.00	0.00	0.00	0.80	0.00	0.00	0.00	0.00	0.00	0.00
Fragilaria vaucheriae	*Fragilaria vaucheriae*	FR007A	0.00	0.28	0.30	0.49	0.29	0.53	0.26	0.28	0.52	0.35	0.56	0.29
Fragilariforma virescens	*Fragilaria virescens*	FR005A	0.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Frustulia rhomboides	*Frustulia rhomboides*	FU002A	0.00	0.56	0.00	0.00	0.00	0.27	0.53	0.00	0.00	0.00	0.00	0.00
Gomphonema gracile	*Gomphonema gracile*	GO004A	0.27	0.00	0.00	0.00	0.00	0.00	0.26	0.28	0.00	0.70	1.12	0.00
Gomphoneis olivaceum	*Gomphonema olivaceum*	GO001A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.29
Gomphonema parvulum	*Gomphonema parvulum*	GO013A	0.54	1.11	1.52	1.71	0.00	1.07	0.26	0.28	0.00	0.47	0.56	0.58
Gomphonema pumilum	*Gomphonema pumilum*	GO080A	0.00	0.56	0.00	0.24	1.47	0.00	0.00	0.57	0.00	0.00	0.00	0.00
Gomphonema truncatum	*Gomphonema truncatum*	GO023A	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Meridion circulare	*Meridion circulare*	MR001A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.29
Navicula angusta	*Navicula angusta*	NA037A	0.00	0.28	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00
Mayamaea atomus	*Navicula atomus*	NA084A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.52	0.00	0.00	0.00
Navicula cryptocephala	*Navicula cryptocephala*	NA007A	0.00	0.56	0.61	0.24	0.00	0.00	0.26	0.28	0.26	0.00	0.00	0.00
Navicula leptostriata	*Navicula leptostriata*	NA156A	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Navicula mediocris	*Navicula mediocris*	NA006A	0.00	0.28	0.30	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Navicula menisculus	*Navicula menisculus*	NA030A	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Eolimnia minima	*Navicula minima*	NA042A	0.81	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00

Counts data			**Depth (cm)**											
Full name (new)	**Full name (old)**	**Code (old)**	**0.25**	**2.25**	**4.25**	**6.25**	**8.25**	**10.25**	**14.25**	**18.25**	**20.5**	**22.5**	**24.5**	**30.5**
Navicula pseudoscutiformis	*Navicula pseudoscutiformis*	NA013A	0.00	0.28	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Navicula radiosa	*Navicula radiosa*	NA003A	0.00	0.28	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Navicula rhyncocephala	*Navicula rhyncocephala*	NA008A	0.00	0.28	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.00
Navicula sp.	*Navicula* sp.	NA9999	0.00	0.00	0.00	0.24	0.59	1.07	0.53	0.85	0.26	0.23	0.00	0.00
Navicula veneta	*Navicula veneta*	NA054A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00
Neidium bisulcatum	*Neidium bisulcatum*	NE004A	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitzschia angustata	*Nitzschia angustata*	NI020B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00
Nitzschia dissipata	*Nitzschia dissipata*	NI015A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.29
Nitzschia fonticola	*Nitzschia fonticola*	NI002A	0.00	0.14	0.00	0.00	0.59	0.00	0.26	0.00	0.52	0.00	0.00	0.00
Nitzschia palea	*Nitzschia palea*	NI009A	1.08	0.00	0.00	0.98	0.59	0.00	0.00	0.00	0.52	0.00	0.00	0.00
Nitzschia perminuta	*Nitzschia perminuta*	NI193A	0.00	0.28	0.00	0.24	0.29	0.27	0.13	0.57	0.00	0.93	1.12	2.91
Nitzschia cf. *tubicola*	*Nitzschia* cf. *tubicola*	NI048A	0.00	0.00	0.00	0.24	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00
Nitzschia sp.	*Nitzschia* sp.	NI9999	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.23	0.00	0.00
Nitzschia sublinearis	*Nitzschia sublinearis*	NI024A	0.00	0.00	0.46	0.00	0.29	0.00	0.40	0.00	0.13	0.23	0.28	0.29
Peronia fibula	*Peronia fibula*	PE002A	0.27	0.83	0.61	0.49	0.59	0.00	0.00	0.00	0.52	0.00	0.00	0.00
Pinnularia appendiculata	*Pinnularia appendiculata*	PI014A	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00
Pinnularia microstauron	*Pinnularia microstauron*	PI011A	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pinnularia sp.	*Pinnularia* sp.	PI9999	0.00	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00
Pinnularia subcapitata	*Pinnularia subcapitata*	PI022A	0.27	0.56	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rhopalodia sp.	*Rhopalodia* sp.	RH9999	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00
Stephanodiscus parvus	*Stephanodiscus parvus*	ST010A	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Surirella angusta	*Surirella angusta*	SU001A	0.00	0.00	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00
Surirella brebisonii	*Surirella brebisonii*	SU073A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	0.00
Synedra acus var. *angustissima*	*Synedra acus* var. *angustissima*	SY003C	0.00	0.00	0.00	0.12	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00
Synedra pulchella	*Synedra pulchella*	SY008A	0.00	0.00	0.00	0.37	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Synedra rumpens	*Synedra rumpens*	SY002A	3.52	2.23	2.12	2.44	4.13	2.41	1.32	4.25	3.91	2.80	1.26	4.37
Synedra rumpens var. *familiaris*	*Synedra rumpens* var. *familiaris*	SY002B	5.96	8.76	5.77	3.66	8.41	2.67	1.58	0.85	0.52	2.34	0.28	0.15
Synedra ulna	*Synedra ulna*	SY001A	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.23	0.00	0.15
Tabellaria [*flocculosa* (long)]	*Tabellaria* [*flocculosa* (long)]	TA9998	11.65	4.59	12.29	1.95	2.21	2.41	0.40	0.28	0.26	0.47	0.00	0.00
Tabellaria [*flocculosa* (short)]	*Tabellaria* [*flocculosa* (short)]	TA9997	0.81	1.39	3.03	1.47	1.18	0.27	0.53	0.28	0.78	0.00	0.00	1.60

APPENDIX 2: DATA ARCHIVE APPENDIX

Data outputs associated with this project are archived as Project No. 269 and Media No. 980 on server–based storage at the Countryside Council for Wales

The data archive contains:

[A] The final report in Microsoft Word and Adobe PDF formats.

[B] Spreadsheet of diatom counts and percentages in excel format (PADA2_diatom data_for CCW.xls) and chemical analysis (PADA2-data_XRF.xls)

Metadata for this project is publicly accessible through Countryside Council for Wales' Library Catalogue http://www-library.ccw.gov.uk/olibcgi/w24.cgi by searching 'Dataset Titles'. The metadata is held as record no 112214.

Date: 21st April 2010