

Peat erosion and atmospheric deposition impacts on an oligotrophic lake in eastern Ireland

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Abstract

The Holocene diatom and pollen records from Kelly's Lough have been analysed to determine the timing and extent of the acidification in this upland lake. The pollen data during the early Holocene reflect the typical vegetation changes that occur in sediments throughout Ireland during this period. The diatom record begins by being dominated by circumneutral and acidophilous benthic forms. Later tychoplanktonic *Aulacoseira* species begin to expand and dominate indicating increased water transparency following the stabilization of catchment soils. Peatland development in the catchment is evident from approximately 6450 cal yrs BP. The main change in the diatom assemblages at this time is the decline of *Aulacoseira* species and expansion of periphytic species. At around 1450 cal yrs BP, loss-on-ignition (LOI) values, *Calluna* pollen and microscopic charcoal all increase suggesting the initiation of a major phase of peat erosion and an increased inwash of organic matter to the lake. Lake acidity changed significantly although the initial acidification is very subtle as indicated by the diatom-inferred pH record. Changes in the diatom assemblages might be largely the result of increasing erosion and inwash of organic matter from the catchment to the lake leading to reduced water transparency and more acidic conditions. The diatom flora remains relatively stable until the mid-twentieth century when more acidibiontic species increase. These diatom changes result in the reconstructed pH curve showing a moderate recent acidification from pH 5.7 to 5.1. About half of the total change in pH took place by around the late 1960s. The lowest diatom-inferred pH value occurs in the late 1970s, and parallels the peak in SO₂ emissions in Ireland. Acidic conditions seem to have prevailed in Kelly's Lough throughout its entire history and alkalinity has been low or absent for much of the time. However, soil acidification and inwash of organic acids from peatlands are not a sufficiently effective mechanism to explain the low pH levels found today in Kelly's Lough. The effect of acid deposition on the waters of Kelly's Lough is clear and it has probably caused these already naturally acid waters to acidify further.

Introduction

Over the last three decades extensive research has been carried out on the acidification of surface waters in Europe and North America. Interest in the relative importance of each of the possible causes for recent acidification led to extensive research on the many mechanisms of acidification. Long-range transport of industrial emissions of sulphur was suggested as the cause of increases in lake water acidity (Odén 1968; Brakke et al. 1987). Other hypotheses of possible causes included post-glacial natural acidification and land-use change. The tendency of certain lakes lying in catchments on base-poor or slow-weathering bedrock to become gradually more acidic during the postglacial time period has been recognised for many decades (Mackereth 1966; Pennington 1984). Long-term acidification has been reported from many countries and has been ascribed to both base cation leaching and the paludification of catchment soils (e.g. Seppä and Weckström 1999; Prather and Hickman 2000). In addition, acidity arising from *Sphagnum* dominated peatlands in the surrounding catchments of acid sensitive lakes, i.e. alkalinities below 10 mg l⁻¹, has been found to be a primary factor responsible for their acidification in Alberta (Canada) (Hasley et al. 1997). Human modification of catchment or soils may alter the relationships and it was suggested that the recent acidification of lakes owes more to catchment soil acidification than to acid deposition (Rosenqvist 1978; Krug and Frink 1983).

It was not until the application of palaeolimnological techniques using lake sediments that the timing of acidification was established (Flower and Battarbee 1983; Battarbee 1984; Battarbee et al. 1985; Jones et al. 1986). Factors such as catchment geology, soils, vegetation and hydrology all have influential roles in the susceptibility of lake waters to acidification. A slow rate of natural acidification occurred in some lakes (Renberg 1990a). There is also evidence of alternating acidification-alkalinization periods associated with land-use changes (Renberg et al. 1993). However, these processes are not strong enough to cause significant acidification (Battarbee 1984; Jones et al. 1986). The cause-effect relationship between acid deposition of anthropogenic origin and lake acidity is now well established and it has been confirmed that deposition of atmospheric pollutants is the main cause of acidification in recent decades (Battarbee 1990; Renberg et al. 1990; Jones et al. 1993). Such pollutants have caused major changes in the phytoplankton composition of acid sensitive lakes in recent years (Brettum 1996; Arts 2002). The ultimate test of this relation is the

number of studies that have revealed recovery trends in low acid neutralizing capacity (ANC) lakes following significant reductions in deposition and concentrations of inorganic acids in the last few decades (Battarbee et al. 1988; Juggins et al. 1996; Tipping et al. 1998).

In Ireland, following the emerging interest in acid deposition and its effects on surface waters, long-term biological and chemical monitoring of acid-sensitive lakes and their inflowing streams has been carried out twice yearly since 1991 (EPA 2004) showing that the artificial acidification of surface waters is not widespread. Nevertheless, evidence of acidification has been reported for Ireland (Flower et al. 1994) and increased concentrations of acidic substances were recorded notably in the run-off waters from acid-sensitive catchments where coniferous afforestations occurred (EPA 2004). Acid sensitive water bodies in Ireland occur in areas with slowly weathering bedrock formations along the western seaboard and in the East in Co. Wicklow. In these areas, the surface waters are characterised by their low alkalinity and hence, poor capacity to neutralise acid inputs. Bulk deposition of sulphur from anthropogenic sources remains low over the western part of Ireland but is significant in eastern areas, where it is associated with rain bearing easterly winds. This highlights the significant influence of anthropogenic acidification (Kelly-Quinn et al. 2000, Aherne et al. 2002). However, there are uncertainties associated with the critical load calculations due to the interference of sea salts and organic acids (Aherne et al. 2002). Without long-term monitoring data only palaeolimnological investigations can supply unequivocal evidence of atmospheric deposition in such regions. Accordingly, this study focuses on long-term acidification processes to test the hypothesis that the present low pH values in an oligotrophic upland lake in the Wicklow Mountains is not due to long-term processes but to recent acid deposition. We have used pollen analysis to investigate the vegetation history in the catchment of the lake and then diatom analysis to assess the effect of vegetation dynamics and other terrestrial changes on the lake. Compositional changes in the diatom remains found in sediment cores have been shown to represent a valuable indicator of past changes on lacustrine ecosystems and their catchment area (Prather and Hickman, 2000; Smol and Cumming, 2000). pH is usually one of the most important parameters determining the diatom assemblage composition in freshwaters, and diatom-inferred pH reconstructions have been shown to be generally reliable (Birks et al. 1990; Birks, 1995). Consequently, in this paper, we use diatom-inferred pH reconstructions as estimates of timing, rate and magnitude of pH changes in Kelly's Lough.

Site description

Kelly's Lough (52.57.17N-6.25.45W) is situated in the east of Ireland within the Lugnaquilla Complex, an extensive upland area located near the centre of the Wicklow Mountains (Figure 1). Lugnaquilla stands in the middle of the complex and at 925 m is the highest mountain in Wicklow. The bedrock of the area is predominantly granite surrounded by schist and slates and the most extensive soil types are dominated by peat with blanket peat bog covering the uplands. The area shows considerable peat erosion although it is not as extensive as in the uplands of western Ireland. Kelly's Lough is an elliptical, small, dark water, cirque lake. It has a maximum depth of 8.6 m and is located at 585 m above sea level. Its catchment is covered by blanket bog with peat depths up to 2 m and bare rock surfaces. One of the most important side effects of peat erosion is the siltation of waters fed by peatlands causing a decrease of pH (Oliver et al. 1983). Clear indications of surface water acidification have been found in several rivers and lakes in the Wicklow Uplands (Kelly-Quinn et al. 1996). This upland region is the origin of several rivers such as the Slaney, Avonbeg and Glenealo rivers as well as numerous smaller rivers and streams. These are typical oligotrophic upland water bodies on acid substrata.

Sheep grazing and afforestation are the main form of land-use, although there is no afforestation above the lake. The vegetation is a mix of heath, blanket bog and upland grassland dominated by *Calluna vulgaris*, *Nardus stricta* and *Eriophorum* species. The climate in the Wicklow Mountains is mild with mean daily temperature estimates ranging from averages of 1 °C in January to 13 °C in July. Average annual rainfall in these upland areas ranges from 1300 to 2400 mm and increases with altitude. The number of rain days varies between 175 and 200 (> 0.2 mm) per year. Precipitation is highly influenced by airborne sea salts, but their proportion decreases eastwards (Aherne and Farrell 2002). In contrast, concentrations of NO₃⁻ and the proportion of non marine SO₄²⁻ increase towards the east reflecting the influence of easterly winds and closer proximity of major emission sources (Bowman and McGettigan 1994, Aherne and Farrell 2002). This is reflected in the average deposition rates for hydrogen ions, non-marine sulphate and oxidised nitrogen which are significantly higher at the east coast of Ireland compared with the rest of the country (Bowman and

McGettigan 1994). The weighted mean volume (1994-1998) pH of rainfall was 4.90 and mean annual concentration of sulphate was $29.9 \mu\text{mol} \text{ l}^{-1}$ (Aherne and Farrell 2002).

Methods

Three piston cores were retrieved from the deepest part of Kelly's Lough in order to obtain a good integration of all different sediment sources within the lake. One short core (110 cm) was taken with a rod operated modified plexiglass piston corer retaining the undisturbed sediment/water interface. Two other overlapping cores of the lower sediments were extracted using a Livingstone corer (Livingstone 1955) driven through casing down to 507 cm depth. The whole length of the plexiglass core was extruded vertically at 1cm intervals in the field. The remaining cores sections were wrapped in the field and stored at $4 \text{ }^{\circ}\text{C}$ until subsampled subsequently in the laboratory. Sediment description followed Troels-Smith (1955), and dry weight, wet density and loss-on-ignition determinations (LOI) were determined using standard procedures (Dean 1974).

Chronology was determined through radiometric dating. The uppermost part of the core was dated using the natural fallout radionuclide ^{210}Pb by the Department of Experimental Physics in University College Dublin using the constant rate of supply (CRS) (Appleby and Oldfield 1978). Contiguous 1cm samples were taken down to a depth of 20cm, dried overnight at $60 \text{ }^{\circ}\text{C}$ and then ground to less than $\sim 1 \text{ mm}$. Lower sediments were dated using the radiocarbon method. Subsamples 1cm thick were dried and submitted to Beta Analytic Inc. for AMS dating. Radiocarbon dates were calibrated to calendar years (Stuiver and Reimer 1993) and were rounded to the nearest 50 years. Linear interpolation was used to determine the chronology of the sequence.

Samples for the analysis of water chemistry were collected four-monthly between June 2001 and April 2002 from the central part of the lake from 0.5 m depth and analysed using standard methods (APHA 1992). The lake is nutrient poor (total phosphorus $8.3 \mu\text{g l}^{-1}$; total nitrogen $1.6 \mu\text{g l}^{-1}$; calcium 0.26 mg l^{-1} ; magnesium 0.35 mg l^{-1}), pH is acidic (mean annual pH 5.1), and conductivity is low ($25 \mu\text{S cm}^{-1}$). More details on selected chemical and physical characteristics are presented in Table 1.

Diatom analysis

Samples for diatom analysis were taken at 5 cm intervals from 20 cm depth to the bottom of the core and at 2 cm intervals for the upper levels. Diatom slides were prepared using 30% H₂O₂ and 10% HCl following standard procedures (Renberg 1990b), and aliquoted evaporated suspensions were embedded in Naphrax (R.i. = 1.74). At least 500 valves were counted per slide on random transects on a light microscope (Olympus BX40) using phase-contrast oil immersion objectives with a magnification of 1000x. Diatom taxonomy followed standard floras (Krammer and Lange-Bertalot 1986-1991). Other taxonomic and floristic works were also used (Foged 1977; Flower and Battarbee 1985; Hartley 1996; Lange-Bertalot and Metzeltin 1996; Camburn and Charles 2000).

Chrysophycean stomatocysts were counted along with diatoms, and the diatom:cyst ratio was calculated for each analysed sample. The proportion of diatom frustules to chrysophyte cysts can be a useful index of trophic status in temperate lakes (Smol 1985). Chrysophytes are generally associated with low total phytoplankton biomass and trophic status and oligotrophic phases in temperate lakes.

Diatom stratigraphical diagrams were prepared using the PSIMPOLL computer program (Bennett 1992). The main zones of change in the diatom data were identified by stratigraphically constrained agglomerative analyses; the method applied was constrained incremental sum of squares cluster analysis (CONISS) (Grimm 1987), as implemented in the PSIMPOLL program. Square root transformation was used in order to optimise the signal to noise ratio. The 'broken-stick' model was used to assess the significance of diatom assemblage zones (Bennett 1996).

Numerical analysis and pH reconstruction

Multivariate ordination techniques were performed on the diatom data using CANOCO (version 4.0) (ter Braak and Šmilauer 1998). The initial detrended correspondence analysis (DCA) indicated a gradient longer than 2 s.d. units (2.963 s.d.) so unimodal methods were applied (ter Braak 1987; ter Braak and Prentice

1988). DCA was used to determine the species variation and the underlying gradients in the fossil assemblages because correspondence analysis (CA) showed an evident arch effect (Hill and Gauch 1980). Only those taxa with more than 2% abundance observed in at least two samples were included in analyses of species abundances, to minimize the influence of rare species. Species abundance data were square root transformed to reduce the effect of highly variable population densities on ordination scores.

Quantitative palaeolimnological reconstructions were applied to the downcore samples. Diatom-inferred pH (DI-pH) was estimated using a weighted averaging (WA) model (Birks et al. 1990; ter Braak and Juggins 1993; ter Braak et al. 1993) based on the IN-SIGHT modern diatom-water chemistry data set (Leira et al. in press). This is a representative data set of 35 lakes from Ireland ranging from upland acid lakes to lowland alkaline lakes with a median value of 6.5 pH units. The transfer function has a good agreement between measured and diatom-inferred pH ($r^2 = 0.93$) and the model had a low RMSE of 0.30. After leave-one-out cross validation, WA with classical deshrinking provided the best estimate, as this model had the lowest errors of prediction (RMSEP) of 0.40 pH units and the highest r^2 (0.86). The calculations were made using the program C2 (Juggins 2003). As the pH scale is not linear, tests have been also carried out using H^+ concentrations ($\mu\text{eq l}^{-1}$) derived from the diatom-inferred pH values to permit a realistic comparison of the rate of natural acidification with the recent rates of acidification (Laxen 1984).

The rate of pH and $[H^+]$ change per 100 calibrated yrs was estimated from the slope coefficient of linear regressions of diatom-inferred pH and $[H^+]$ on calibrated ages for the time intervals defined by the diatom assemblage zones (Bradshaw et al. 2000). The statistical significance of the difference between the slopes of the regression lines of two adjacent zones was assessed with a two-tailed t test.

Pollen analysis

Samples for pollen analysis were prepared from the same levels as for diatoms at 5cm resolution throughout the profile. Pollen preparation followed the standard acetolysis treatment (Faegri and Iversen 1989). Mineral material in the subsamples was removed by HF treatment. Precise volumetric subsamples were prepared to which a known number of *Lycopodium clavatum* spores in suspension were added to enable the calculation of pollen concentration (Stockmarr 1971). Pollen samples were suspended in silicone oil (2000

cs) and were counted using a Leitz Ortholux binocular microscope. The identification of pollen grains was aided by the use of the key and illustrations of Moore et al. (1991), illustrations from Reille (1992) and reference material held in the Department of Botany, Trinity College Dublin. Pollen and spore nomenclature follows Bennett et al. (1994). The pollen sum (minimum number of 350 grains) included all identifiable pollen and fern spores with the exception of obligate aquatic taxa, pre-Quaternary spores and *Sphagnum*. The pollen diagrams were prepared using TILIA 2.0.b.4 (Grimm 1991). Constrained Sum of Squares Cluster Analysis (CONISS) was used to determine the position of zone lines within the pollen data of each site (Grimm 1987). The number of statistically significant pollen assemblage zones in each pollen sequence was determined by the 'broken-stick' model (Bennett 1996). The 'point count' method developed by Clark (1982) was used to estimate the microscopic charcoal concentration.

Results

Sediment stratigraphy and Chronology

Sediment in the lower part of the Kelly's Lough core consisted of an inorganic sequence (500 – 485 cm) overlain by more organic sediment above 485 cm. ^{210}Pb analysis showed a typical exponential decay profile as would be expected if accumulation rates remained fairly constant which suggests that the sedimentary profiles are relatively undisturbed. Radiocarbon dates from the sediment also indicated a consistent sequence of sediment accumulation, in which, the long-term sedimentation rate has been rather constant at 0.05 cm yr^{-1} (Table 2). From 165 cm to the top of the core the sediment accumulation rates increases from $0.0563 \text{ cm yr}^{-1}$ to approximately $0.1240 \text{ cm yr}^{-1}$ and is accompanied by a ^{14}C inversion (Table 2). The oldest date gives an age of 10 900 cal years BP at 485cm at the clay-organic sediment transition and the start of the diatom record.

Dry weight and Loss on Ignition

The sediment shows a sharp transition from late-glacial clays to post-glacial muds, with organic matter increasing from about 3% to >18% within 10 cm (Figure 2). Dry weight was highest in the basal 50 cm of the core, sharply decreasing to lower values above this which were maintained for the rest of the record. The organic matter content estimated from LOI showed greater variation over the core. Organic matter was lowest at the base and increased gradually to higher values. For most of the record, the post-glacial sediments were relatively uniform, with LOI values ranging between 25-45%. Above 140 cm the organic matter content increased rapidly, reaching its highest values at 60cm (84%) and is associated with a ¹⁴C inversion (Table 2; Figure 2). LOI values declined to 52% over the uppermost 20 cm of the core with a slight increase to 60% in the core top sample (Figure 2).

Diatom results

Diatom stratigraphy

A total of 104 diatom samples were analysed with 224 diatom taxa identified. Figure 3 shows only those taxa that were observed in more than 5% of the samples, and therefore, summarises the more commonly occurring and abundant taxa found in the Kelly's Lough core. The lowermost three samples did not contain any diatom remains. The most abundant diatoms include *Aulacoseira* Thwaites species. While *Fragilaria exigua* Grunow, *Anomoeoneis exilis* (Kutz.) Cleve, *Anomoeoneis brachysira* (Brebisson in Rabenhorst) Grunow in Cleve, *Eunotia incisa* Gregory and *Cymbella gracilis* (Ehr.) Kutzing are consistently present throughout. The Kelly's Lough diatom sequence was divided into six diatom assemblage zones (DAZ) in order to facilitate description on selected taxa that reached 2% abundance in at least 2 samples (Table 3).

Ordination of the diatom data

DCA axis 1 ($\lambda_1 = 0.291$; 43.1%) and DCA axis 2 ($\lambda_2 = 0.049$; 7.4%) explained a total of 50.5% of the diatom species variance (Figure 4a). The second DCA axis represented a much smaller amount of the variation in the diatom data, and the ratio between the eigenvalues for the first and second axis was greater than 1.4. This illustrates that the floristic structure of the diatom assemblages was dominated by a single gradient, with other underlying gradients of variation being relatively unimportant. Underlying environmental gradients can be inferred from the distribution of diatom assemblages along both axes. The data infer that axis 1 represented a gradient of pH with decreasing pH to the left. Circumneutral and alkaliphilic species occur on the right (e.g., *Navicula arvensis*, *Cymbella gaeumannii* and *Aulacoseira perglabra*), while acidophilic and acidobiontic species (*Eunotia tenella* and *Tabellaria quadrisepata*) occur on the left. The inferred underlying gradient for axis 2 appears to correlate well with the LOI profile with increasing organic matter towards the top of the Figure 4b. Two main groups were easily identified in the DCA ordination. Samples between 475 cm and 480 cm depth were grouped together and were characterised by the highest values on DCA axis 1. There was a large degree of similarity between samples from 145 cm to 470 cm depth, and hence they were inferred to be similar along both underlying environmental gradients. The samples from the upper 140 cm were clearly distinct from the rest of the core and large difference occurred between 140 cm and 145 cm depth with increases in *Tabellaria flocculosa*, *Eunotia tenella* and *Pinnularia irrorata*. These samples showed much more separation along DCA axis 2, therefore indicating an important response to the environmental gradient represented by this axis. The increase in *T. flocculosa*, *E. tenella* and *P. irrorata* also separated the samples in the direction of DCA axis 1 and were characterised by low values on DCA axis 1. This indicated that both groups of samples had sufficiently different species assemblages to form distinct groups and represented a higher species turnover. Samples from the top of the core plotted together at the lower left corner. These samples were characterised by the presence of the acidobiontic *Tabellaria quadrisepata* and acidophilous *Navicula leptostriata*.

pH reconstruction

The present day pH measured at Kelly's Lough is c. 5.1 (Table 1) which is in good agreement with the diatom-inferred pH value of 5.2 for the surface sediment sample. The diatom-inferred pH values range between 6.6 and 5.1 during the history of the lake.

The inferred pH for the early Holocene samples was the highest of the whole record. All estimated values for DAZ 1 were above 6.5 (Figure 3). The inferred pH decreased slowly over the record as the community changed from planktonic to benthic. There was an inferred drop in pH between 465 cm and 155 cm to less than 6.0, which corresponded with the disappearance of *Aulacoseira* species and the increase in *Eunotia tenella* and *Pinnularia irrorata*. The underlying gradients along DCA axis 1 and 2 also suggested a large floristic change at this depth.

A more rapid pH decrease was seen in DAZ 6. The lowest pH value of this zone was 5.5 between 40 cm and 60 cm depth and has been dated to between 1677 and 1516 AD. This decrease is characterised by an increase in *Navicula leptostriata* and the appearance of *Tabellaria quadrisepata*. Both species were either absent or present in very low abundances in all the previous samples. At the top of DAZ 6, reconstructed pH recovered a little and averaged at about 5.6 above 40 cm depth. This recovery corresponds to the disappearance of *Navicula leptostriata* and *Tabellaria quadrisepata*.

The lowest inferred pH values of the entire record occurred in DAZ 7 with a sharp drop at the uppermost part of the core to 5.1; these data have been redrawn at larger scale to facilitate interpretation (Figure 5). This large decrease at 4 cm reflects a rapid increase in *Tabellaria quadrisepata*, which brings the percentage of acidobiontic taxa above 20%. All inferred values for DAZ 7 were less than 5.2.

Overall, samples scores along DCA axis 1 follow the diatom-inferred pH trends with higher reconstructed pH at the base of the record, and steadily decreasing values continuing to the top of the core. The differences in the slope of pH decline and $[H^+]$ increase between the diatom assemblage zones is only significant for the last 1000 yrs BP (Table 4). The rate of pH change in the first four zones is below 0.001 pH units per 100 yrs and is not significant. The most rapid rate of pH decline and the most rapid rate of increase in $[H^+]$ take place over the last 50 yrs BP, in the uppermost zone. Both, pH and $[H^+]$ rate of change are statistically significant, but not highly significant (p values = 0.09 and 0.045 respectively; Table 4). The

rates of pH decline and $[H^+]$ increase in DAZ 6 are both highly significant. The zone of more prolonged pH decline appears to be DAZ 5, between 4400 and 1100 yrs BP where pH and $[H^+]$ regressions were statistically significant, although there is no statistically significant difference between the slopes of the regression line when compared to the previous zones (Table 4).

Pollen results

A summary pollen percentage diagram (Figure 6) has been divided into six pollen assemblage zones (PAZ) as determined by the 'broken-stick' model (Bennett 1996). The pollen assemblage zones are described in Table 5.

Microscopic charcoal

The microscopic charcoal counted on the same slides as the pollen is presented in Figure 7. Microscopic charcoal was present in almost all samples analysed. Its concentration is quite low in the lower half of the profile but begins to increase from 185 cm onwards and reaches its highest value at 75 cm. The upper half of the profile is dominated by high values of microscopic charcoal – over 60% of samples have values of $0.8 \text{ cm}^2 \text{ cm}^{-3}$ or over.

Discussion

The pollen data indicate that the entire Holocene record was retrieved from Kelly's Lough although the diatom record does not span the whole period. The basal pollen samples (PAZ KL-1) capture the termination of the Younger Dryas and subsequent expansion of more thermophilous taxa such as *Juniperus* and *Betula* in the early Holocene. The absence of sediments of Late-glacial age at this site is consistent with data from other cirque lakes in Ireland which indicate that they accumulated ice during the Younger Dryas (Gray and Coxon 1991).

The diatom species found in this lake are fairly typical of upland, soft-water lakes. During the early Holocene, Kelly's Lough was characterised by a moderate pH and low sediment LOI values. The pollen

data (Figure 6) reflect the typical vegetation changes that can be seen from sediments throughout Ireland for the same time period (Mitchell et al. 1996). Diatom assemblages were dominated by circumneutral and acidophilous forms. Common diatoms during this period included *Cymbella gaeumannii*, *Navicula arvensis* and *Fragilaria exigua* inferring a pH between 6.5 and 6.7. This type of community is in contrast to diatom floras of similar age at many other upland sites in Britain and Europe where small alkaliphilous forms of *Fragilaria* species are often dominant. The most frequent diatoms in Kelly's Lough during this period were also common in studies carried out in upland lakes from Scotland (Jones et al. 1989). This assemblage composition suggests that the acidity of Kelly's Lough might relate to its location on slow weathering granite bedrock.

Later *Aulacoseira perglabra* appeared followed by *Aulacoseira lirata*, and the values of circumneutral forms fell. These changes suggested some alteration in the lake but there is little change in the inferred pH. The expansion of *Aulacoseira* species, which are tychoplanktonic diatoms, might be related to an increase in water transparency following the stabilization of catchment soils. The inwash of materials may have created turbid conditions that restricted the development of diatom phytoplankton during the previous period. The inferred pH values are 6.3-6.6. Except for the increases of *Aulacoseira alpigena* and *A. distans* var. *nivalis*, the diatom flora is remarkably constant over the next two zones (DAZs KL4 & KL5). The proportion of acidobiontic species is still low (< 5%), and inferred pH values range between 6.0 - 6.3.

Peatland development in the Kelly's Lough catchment is evident from approximately 6450 cal yrs BP (340 cm). There is a continued decline in tree taxa and an expansion of peatland indicator taxa, particularly *Calluna* and *Sphagnum* (Figure 6). After 4400 cal yrs BP diatom-inferred pH values decrease slowly but steadily in parallel with these fundamental changes in the character of the catchment. These changes in the diatom assemblages may have due to the natural long-term soil leaching and peatland development or possibly in response to climate change. There are, however, no significant changes in the pollen data at this time, which would rule out any dramatic climate change perturbation as the direct cause for the water lake pH reduction. Nevertheless, these changes might be indirectly related to climate, though mediated by the catchment dynamics.

Both *Calluna* and *Sphagnum* steadily increase in values up to c. 1050 cal yrs BP (135 cm) when they both become fairly constant, and remain so to the present day. After around 1450 cal yrs BP, radiocarbon

dates indicate a much higher rate in sediment accumulation compared to the preceding millennia. Sedimentation rate rises from 0.0563 cm yr⁻¹ before 1900 yrs BP to 0.1240 cm yr⁻¹ (Figure 7). This faster accumulation of sediment is indicative of dynamic changes in the catchment. It coincides with further declines in trees and a rise in *Calluna* pollen. The *Calluna* curve also appears to correlate with the LOI and the microscopic charcoal curves (Figure 7). Ericaceous species sprout vigorously after burning (Mallik and Gimingham 1985) and so the vegetation communities in the Kelly's Lough catchment were strongly influenced by frequent fires over the last 1500 years. Most, if not all of these fires are considered to be anthropogenic in origin. A similar trend was seen from Liffey Head Bog (which is also in the Wicklow Mountains 25 km to the north) over the same time period (Cole 2000). Other typical peatland taxa were present during the past 6000 years such as *Erica*, *Narthecium*, *Menyanthes* and *Potentilla*-type, confirming peatland establishment and continual presence in the Kelly's Lough catchment during the latter half of the Holocene. These features support the initiation of a relatively major phase of peat erosion and an increased transport of organic matter from the peatlands to the lake.

Increased sedimentation rates have been reported from other small lakes but at earlier ages (e.g., O'Connell et al. 1987; Bradshaw and McGee 1988; Dalton 1999). Upland peat erosion is a widely recognised process in Ireland and has been reported since at least 3000 BP (Bradshaw and McGee 1988). The overall changes in LOI at Kelly's Lough are very similar to these other sites but the ¹⁴C and ²¹⁰Pb dates of the Kelly's core suggest different timing of peat erosion. The cause of the LOI increase in this acidic, unproductive lake is almost certainly due to increase peat erosion, a supposition supported by the clear ¹⁴C dating inversion at this level. We therefore assume that the rapid rise in LOI values at 145 cm depth reflects the onset of peat erosion. Although, dating this rise might be problematic due to contamination by 'older carbon', it is possible to calculate a date using a combination of ²¹⁰Pb and ¹⁴C chronologies. In this case there is good agreement between both for a date around *c* 1150 BP (*c* 800 AD). These results appear to be in conflict with data from Arts Lough which lies 2 km north of Kelly's Lough at a similar altitude (490 m) where that peat erosion is thought to have commenced at 3200 cal yrs BP and this was associated with a significant increase in LOI as well (Bradshaw and McGee 1988). Poor dating control at Arts Lough has prompted the suggestion that this date for the onset of peat erosion might be too old (Stevenson et al. 1990). Our data suggest that the onset of a first phase of peat erosion in eastern Ireland took place at some time *c.*

AD 800, a more recent date than the one suggested by Bradshaw and McGee (1988) but still older than the date of *c.* AD 1500-1700 given by Stevenson et al. (1990). These results are, however, consistent with the timing of the significant changes in the Holocene records from Lochnagar in north-east Scotland (Dalton et al. 2005) and in Lough Nabrackbaddy in north-west Ireland (Bradshaw and McGee 1988) suggesting that peat erosion in those catchments started after 1500 cal. yrs BP.

These changes are coincident with the shift to a periphytic dominated diatom assemblage with the decline and eventually total disappearance of *Aulacoseira* species, and expansion of *Tabellaria flocculosa* and *Eunotia exigua*. The phytoplankton community of lakes undergoes dramatic changes during the course of acidification and, as pH decreases, the species richness also decreases as the community composition and structure changes (Beauchamp and Kerekes 1989; Ilmavirta and Huttunen 1989; Stenson et al. 1993; Brettum 1996). This decrease in diversity is more apparent in clear-water lakes than in humic lakes (Stenson et al. 1993). Large inputs of allochthonous organic material from peatlands can be an important contributor of humic acids and acidification (Kullberg et al. 1993). Diatoms are very sensitive to this kind of disturbance, but despite the clear increase in the organic matter content, this was not sufficient to cause a strong drop in lake water pH in Kelly's Lough, which only fell from *c.* 5.9 to 5.7. Nor was it sufficient to cause the expansion of acidobiontic taxa. This finding appears to be consistent with other studies of long-term acidification on lakes situated on slow weathering granitic bedrock in the United Kingdom (Jones et al. 1986) suggesting that the inwash of organic acids is unlikely to create intense acidification. Previous studies in Finland appear to be in conflict with these findings as they show stronger decreases in pH values, up to 3.3 pH units, due to the spread of peatlands (Tolonen et al. 1986; Seppä and Weckström 1999; Prather and Hickman 2000). However, these clear-water lakes had an alkaliphilous diatom flora after formation and in none of these cases was the initial post-glacial diatom-inferred pH as low as at Kelly's Lough. Furthermore, the small catchment to lake area ratio in Kelly's Lough may have been an important constraint in the concentration values of organic acids in the lake water. Not only can humic substances alter the pH of lake water, they can also affect biological communities and processes, either directly through interfering with metabolic processes or indirectly by altering the bioavailability of nutrient and toxicants (Kullberg et al. 1993). Humic substances can depress primary productivity of phytoplankton by binding with phosphorus or forming iron-phosphate complexes (Jackson and Hecky 1980). So although the changes in the diatom

community may be related to inwash of organic material from peat erosion, there might be other factors involved apart from acidification. In particular, changes in the organic carbon concentrations in water have an important effect on diatom assemblages (Fallu et al. 2002). There are strong relationships between diatom community structure and organic matter concentrations and its effect on water light regime (Fallu and Pienitz 1999; Pienitz and Vincent 2000). More specifically, losses in planktonic assemblages have been associated with peat inwash (Jones et al. 1986; Jones et al. 1989) and this is also evident at Kelly's Lough.

A further pH drop took place between 400 and 220 cal yrs BP (Figures 3 and 5). Research carried out in Norway (Stabell 1990) associated rapid early pre-industrial acidification with a reduction in the base status of local soils and establishment of forests on the catchment. Forests were not established around Kelly's Lough at this time but a similar pH decrease was also found in the recent sediments from the Upper Lake, Glendalough, which lies a few kilometres north of Kelly's Lough (Cox and Murray 1991). Although the two cores show very similar pH profiles, the inferred timing of the pH decrease is anomalous. The pH decrease in the Upper Lake was considered by Cox and Murray (1991) to have been caused by nineteenth century mining in the catchment. The top 30 cm of the Upper Lake core is dated by ^{210}Pb covering the period from 1889 to 1987. Extrapolation of this sedimentation rate (1.4 mm yr^{-1}) down core suggests a date of *c.* AD 1650 for the centre of the period of pre-industrial acidification, at 65 cm, which is in good agreement with the age obtained for the Kelly's Lough profile, but certainly outside the nineteenth century date proposed by the authors and predating the onset of copper mining, which is reported to have begun in the Avoca River valley, Co. Wicklow, around 1720 (Gallagher and O'Connor, 1999). This is also coincident with the onset of a second major phase of peat erosion which occurred at some time between 300 and 400 years ago in UK (Tallis 1985, 1987; Stevenson et al. 1990).

Since the dates show that this drop in pH probably took place between AD 1600 and AD 1700 we cannot discount the influence of the cold period known as the Little Ice Age (LIA). Similar changes in water quality, involving slight acidification, are also apparent at Round Loch of Glenhead (Flower and Battarbee 1983) and at Lochnagar (Jones et al. 1993; Dalton et al. 2005) about 400 years ago. The LIA is known to have been characterized by increases in frequency and severity of storms (Manley 1974; Sweeney 2000). Under these conditions erosion might have been accelerated, especially if burning also occurred during this

period (Shimwell 1974). The extent of human impact on the landscape prior to 1800 is poorly known but recent studies from the Wicklow Mountains area concluded that the imprint of human activity on the landscape over the last 1200 years appears to have overwhelmed the impacts that could be attributed solely to climatic change associated with the Little Ice Age (Cole and Mitchell 2002). It is important to note however that inwash of organic substances has been shown to be an insufficient explanation to lead to significant water acidification. So, even if this change is climate induced, local features, probably involving hydrology, could account for this acidification period. Well humified peat has very low hydraulic conductivity, and little run-off flows through the peat itself (Kullberg et al. 1993; Halsey et al. 1997). Thus, although the acidity of peatlands is high, the down-stream effects of bogs might not be very important. However, acidic lake systems occurring in peat environments can reach lower pH levels when they are subject to acid pulses during major precipitation events or during periods of drought due to the greater flow-through (Halsey et al. 1997). In these cases, discharges of hydrogen ions and mobilised toxic metals occur to streams and lakes (Gorham et al. 1985).

After this acidification event there is little change in the diatom flora of the lake until the mid-twentieth century when diatoms characteristic of circumneutral water such as *Anomoeoneis exilis* begin to decline and are replaced by more acidiphilous species. By the early 1970s the acid tolerant diatom species *Tabellaria quadrisepitata* reaches its highest abundance in the sediment record. The diatom-inferred pH shows a moderate acidification from pH 5.7 to pH 5.1. About half of the total change in pH took place by the late 1960s (Figure 5). A similar rate of change had taken place by 1970 with very little change after 1980 (Figure 7). However, in terms of H⁺ ion concentration most of the total change took place between 1970 and 1980. The period between 1960 and 1970 represents an increase in the H⁺ concentration of some 2 µeq l⁻¹, while an increase around 4 µeq l⁻¹ occurs between 1970 and 1980. The lowest diatom-inferred pH value occurs in the late 1970s, and parallels the peak in SO₂ emissions in Ireland (Mylona 1996). This is important information for establishing the relationship between industrial emissions and subsequent acidification and suggests that these changes may be the result of an increase in the deposition of strong acids from the atmosphere rather than a response to catchment change. In humic lakes like Kelly's Lough the effect of strong mineral acids is superimposed on the contribution of organic acids to acidity (Gorham et al. 1986;

Brakke et al. 1987) and, as a consequence, organic acids make humic lakes generally more sensitive to acidification than clear water lakes (Brakke et al. 1987). Recent analysis of spheroidal carbonaceous particles (SCP) from Kelly's Lough shows that the rapid increase in their concentration is coincident with the drop in inferred pH (B. O'Dwyer, work in progress). SCPs are a product of incomplete combustion formed during the high-temperature burning of fossil fuels and they readily accumulate in lake sediments (Rose and Appleby 2005). SCPs first appear in Ireland from the 1850s through to 1910, with rapid increases associated with increased coal consumption between 1940 and 1970 (Rose and Appleby 2005). A sub-surface peak in SCP concentrations has been dated to the early 1980s at a number of sites in western and northern Ireland, followed by a subsequent decline reflecting the implementation of more rigorous pollution control legislation (Rose and Appleby 2005). A number of studies in Scotland and Wales have described similar diatom changes in the recent sediments (Jones et al. 1986; Jones et al. 1989; Jones et al. 1993; Flower et al. 1994; Jones et al. 1997). They concluded that the changes were the result of an increase in the deposition of strong acid from the atmosphere rather than a response to catchment dynamics.

Conclusions

Acidic conditions seem to have prevailed in Kelly's Lough throughout its entire history. The timing of changes of all proxies is closely correlated suggesting that the lake system is responding to catchment dynamics from the development and erosion of peatlands, which have had an effect in the aquatic environment causing important changes in the diatom assemblages. The results presented in this paper provide evidence of two major phases of peat erosion. The onset of a first phase in eastern Ireland took place at some time c. AD 800, while a more recent phase has been dated between AD 1600 and AD 1700. Despite the fact that the lake is acid sensitive, the data presented here indicate that these processes are not a sufficiently effective mechanism to explain the low pH levels found in Kelly's Lough today. Although the influence of coloured organic acids from natural sources is clear, there is no evidence for a significant recent increase over time in the contribution to the acidity in Kelly's Lough that would explain further decreases in pH. This implies that the effect of acid deposition on the waters of Kelly's Lough is clear and it has probably caused these already naturally acidified waters to acidify further.

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Table 1 Chemical and physical characteristics of Kelly's Lough from surface water samples. The limnological values refer to epilimnetic measurements carried out in the lake during 2001 (four-monthly sampling between June 2001–April 2002; $n = 4$)

Variable	Units	Surface water value
Silicates	mg l ⁻¹	0.82
pH		5.1
Alkalinity	mg l ⁻¹ CaCO ₃	0.46
Conductivity	μS cm ⁻¹	25
Colour	mgPtCo l ⁻¹	29
Chloride	mg l ⁻¹	4.23
Sulphate	mg l ⁻¹	1.91
Sodium	mg l ⁻¹	0.51
Potassium	mg l ⁻¹	0.34
Magnesium	mg l ⁻¹	0.35
Calcium	mg l ⁻¹	0.26
Dissolved Oxygen	mg l ⁻¹	1.76
Nitrates	mg l ⁻¹	0.14
Total Nitrogen	μg l ⁻¹	1.58
Total Phosphorus	μg l ⁻¹	8.32
Secchi Depth	m	1.80

Table 2 Radiocarbon dates from the Kelly's Lough sequence. The calibrated age range (Stuiver and Reimer 1993) was calculated with a probability of 95.4% (two sigma)

Depth (cm)	Laboratory reference	yrs ¹⁴ C (BP)	yrs cal. (BP)	yrs cal. AD(+) BC (-)	δ13 C (‰)
100-101	β-173462	1620±40	1550-1390	560, 400	-27.0
164-165	β-165539	1360±40	1320-1240	630, 170	-26.8
245-246	β-173462	2520±40	2750-2460	- 800, - 520	-26.7
			5460-5070	3510, 3420	
294-295	β-165540	4600±50	5340-5270	3390, 3320	-26.6
			5170-5070	3220, 3120	
334-335	β-165541	5430±50	6300-6170	4350, 4220	-26.3
369-370	β-165542	6480±50	7460-7290	5510, 5340	-26.1
410-411	β-173463	8220±50	9400-9360	7450, 7400	-25.7
459-460	β-165543	8970±60	10230-9920	8280, 7970	-24.8
485-486	β-173464	9610±40	11160-10750	9210, 8800	-24.7

Table 3 Description of diatom assemblage zones (DAZ) from Kelly's Lough

Zone Depth (cm) Age (cal yrs BP)	Principal taxa	Overall trends
DAZ 1: KL1 485 - 462.5 10 850 – 10 350	Characterised by <i>Navicula arvensis</i> Hustedt, <i>Cymbella gaeumannii</i> Meister and <i>Fragilaria exigua</i> . <i>Cymbella gaeumannii</i> and <i>Fragilaria exigua</i> decreased as <i>Achnanthes minutissima</i> Kutzing and <i>Aulacoseira</i> spp appeared and increased	Initial diatom flora dominated by benthic assemblages.
DAZ 2: KL2 462.5 - 412.5 10 350 – 9200	Planktonic <i>Aulacoseira perglabra</i> (Østrup) Haworth and the increase of the periphytic <i>Achnanthes minutissima</i> marked the beginning of this zone. <i>Aulacoseira perglabra</i> appeared and increased to ca. 25%.	Shift from a benthic dominated flora to an open water dominated one
DAZ 3: KL3 412.5 - 357.5 9200 – 7050	Fluctuations in the relative abundances of <i>Aulacoseira</i> spp. <i>A. lirata</i> (Ehr.) Ross in Hartley appeared and increased rapidly (27%). <i>A. perglabra</i> declined.	Planktonic species are the major components of this zone
DAZ 4: KL4 357.5 - 277.5 7050 – 4400	<i>Aulacoseira alpigena</i> (Grunow) Krammer gradually increased to reach its maximum abundance at the top of the zone (15%). Typical benthic taxa were <i>Cymbella perpusilla</i> A.Cleve and <i>Eunotia rhynchocephala</i> Hustedt .	Overall decrease in dominance of planktonic species although they continued to be abundant. Benthic species continued to maintain a small population in this part of the core.
DAZ 5: KL5 277.5 - 142.5 4400 – 1100	Planktonic species <i>Aulacoseira alpigena</i> , <i>A. distans</i> (Ehr.) Simonsen var. <i>nivalis</i> (Wm.Sm.) Haworth, and <i>A. lirata</i> were still common in this zone. Steady and gradual increase of <i>Tabellaria flocculosa</i> (Roth) Kutzing. The heavily silicified centric <i>A. perglabra</i> disappeared.	Steady decline of the planktonic component of diatom community.
DAZ 6: KL6 142.5 – 13 1100 – 50	<i>Aulacoseira</i> spp decreased in importance and disappeared whereas other benthic species, <i>Pinnularia irrorata</i> (Grunow) Hustedt and <i>Eunotia tenella</i> (Grunow) gHustedt, rose in abundance. <i>Tabellaria flocculosa</i> dominated this zone followed by <i>Anomoeoneis exilis</i> (Kutz.) Cleve. Small occurrences of <i>Navicula leptostriata</i> Jorgensen and the acidobiontic <i>Tabellaria quadrisepitata</i> Knudson.	Rapid important changes in dominant species. Final decline and disappearance of planktonic assemblage.
DAZ 7: KL7 13 -0 50 – present	Dominated by high values of <i>Navicula leptostriata</i> (15%) and <i>Tabellaria quadrisepitata</i> (24%). <i>Tabellaria flocculosa</i> , <i>Anomoeoneis garrensis</i> , <i>Pinnularia irrorata</i> and <i>Eunotia tenella</i> declined towards the top of the zone. <i>Anomoeoneis brachysira</i> and <i>Fragilaria exigua</i> declined in the uppermost levels.	Increase in acidobiontic taxon <i>Tabellaria quadrisepitata</i> .

Table 4 Results of regression analysis of diatom-inferred pH and [H⁺] in relation to calibrated ages for the different diatom assemblage zones (r = correlation coefficient, p = probability value). Bold numbers in italics indicate that the difference between slopes was statistically significant when compared with the previous zone

Diatom Assemblage Zone	DI-pH			DI-[H ⁺]		
	Rate of Change per 100 yr	r	p-value	Rate of Change per 100 yr	r	p-value
7	<i>0.9100</i>	0.855	0.014	<i>-9.2000</i>	0.864	0.012
6	<i>0.0300</i>	0.756	0.000	<i>-0.1300</i>	0.682	0.000
5	0.0030	0.333	0.090	-0.0062	0.389	0.045
4	-0.0010	0.146	0.589	-0.0020	0.183	0.499
3	0.0006	0.134	0.694	-0.0002	0.031	0.928
2	0.0010	0.123	0.734	-0.0014	0.119	0.743
1	-0.0009	0.058	0.926	0.0015	0.128	0.837

Table 5 Description of pollen assemblage zones (PAZ) from Kelly's Lough

Zone Depth (cm) Age (cal yrs BP)	Principal taxa	Overall trends
PAZ 1: KL-1 500 – 472.5 >10 900 – 10 550	Initial <i>Huperzia</i> peak is followed by peaks in <i>Rumex</i> and <i>Juniperus</i> . Both <i>Salix</i> and <i>Betula</i> increase in abundance towards the top of the zone. Poaceae and Cyperaceae decline towards the top of the zone.	Zone characterised by a succession of replacements by more thermophylous taxa.
PAZ 2: KL-2 472.5 – 457.5 10 550 – 10 150	This zone is dominated <i>Corylus</i> -type pollen (> 60%). <i>Salix</i> and <i>Betula</i> decline while <i>Quercus</i> and <i>Ulmus</i> become established.	Thermophylous trees become established.
PAZ 3: KL-3 457.5 – 427.5 10 150 – 9550	<i>Corylus</i> -type pollen continues to dominate while <i>Pinus</i> , <i>Quercus</i> and <i>Ulmus</i> expand. Poaceae and other herbaceous taxa decline.	Temperate woodland becomes established at the expense of shrub and herbaceous taxa.
PAZ 4: KL-4 427.5 – 342.5 9550 – 6550	Tree pollen dominates (80-90%) with a significant expansion of <i>Pinus</i> (20-30%). Other tree taxa maintain abundance with <i>Alnus</i> establishing at c. 7650 cal yrs BP. This coincides with a decline in <i>Pinus</i> and small increases in <i>Calluna</i> and <i>Sphagnum</i> .	Temperate woodland dominates but its composition changes throughout the zone
PAZ 5: KL-5 342.5 – 247.5 6550 – 2850	With the exception of <i>Alnus</i> , tree pollen declines. Significant declines in <i>Pinus</i> and <i>Ulmus</i> . <i>Calluna</i> , Poaceae and <i>Sphagnum</i> expand.	Declines in woodland associated with expansion of heath/bog taxa.
PAZ 6: KL-6 247.5 – 5 2850 – present	Further declines in tree taxa, especially <i>Pinus</i> , <i>Quercus</i> , <i>Ulmus</i> and <i>Alnus</i> . Further expansion of <i>Calluna</i> , Poaceae and <i>Sphagnum</i> but also <i>Potentilla</i> and Cyperaceae.	Tree taxa continue to decline with further expansion of bog taxa.

FIGURE CAPTIONS

Figure 1 Location map of Kelly's Lough and its catchment. Bathymetry and location of the coring site are also shown

Figure 2 Diagram of Kelly's Lough sediment lithology including bulk density (BD g cc⁻¹), dry matter (% DW) and organic matter (% LOI)

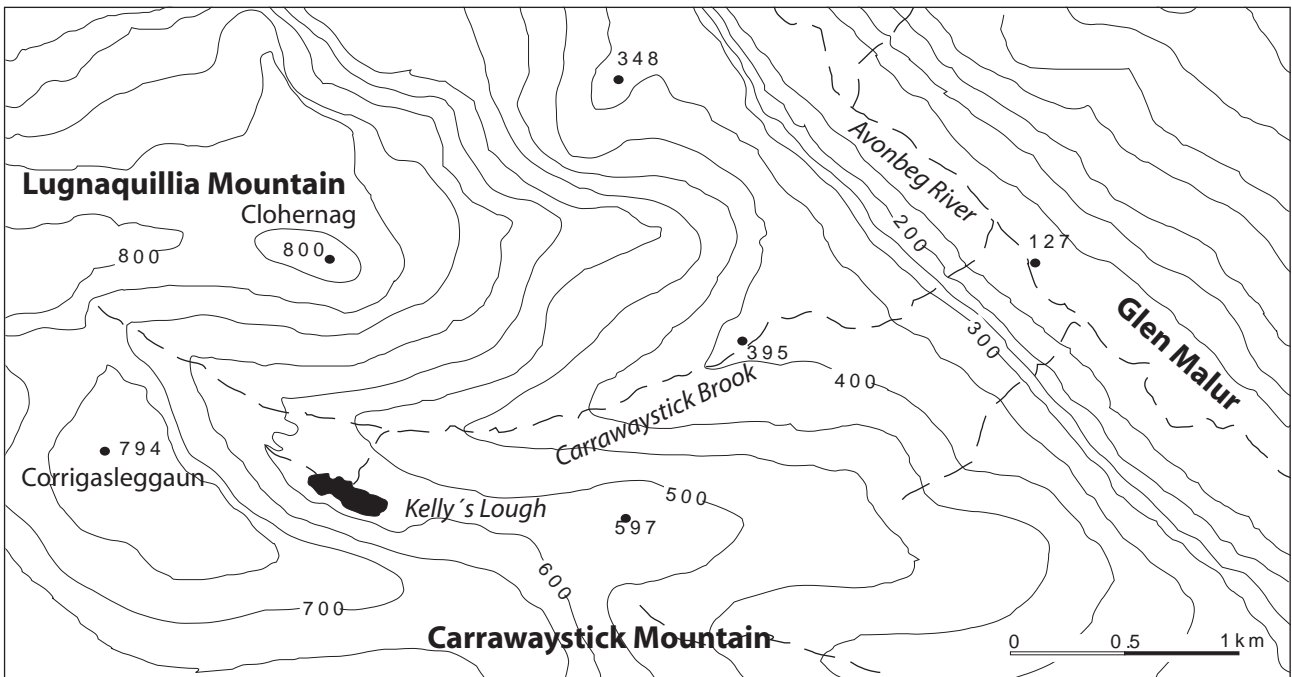
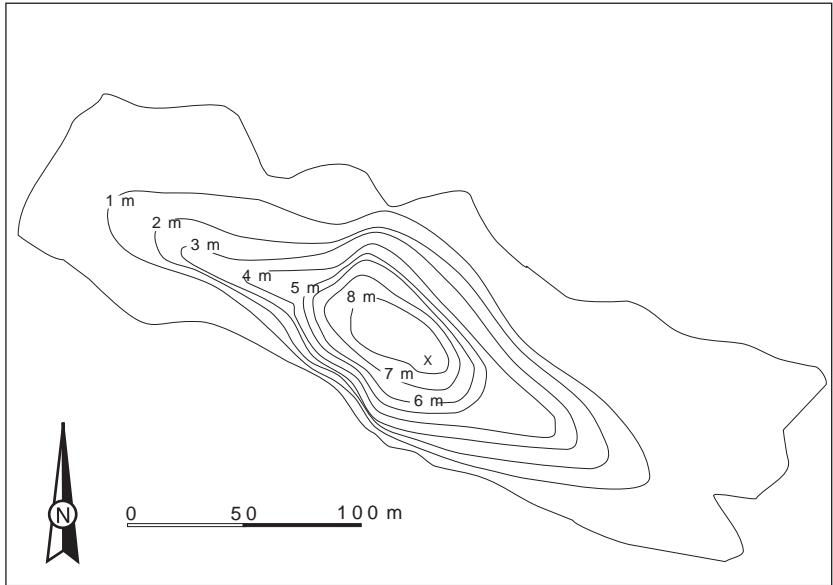
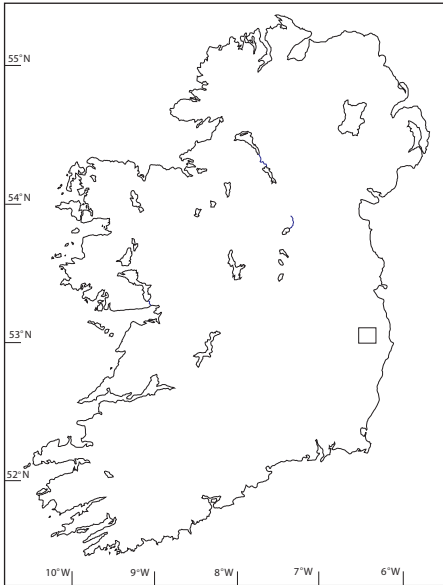
Figure 3 Summary diatom diagram for Kelly's Lough indicating the CONISS biostratigraphic zones and plotted on a depth scale along with age scale (C:V = chrysophyte cyst to diatom valve ratio). Only selected taxa are shown

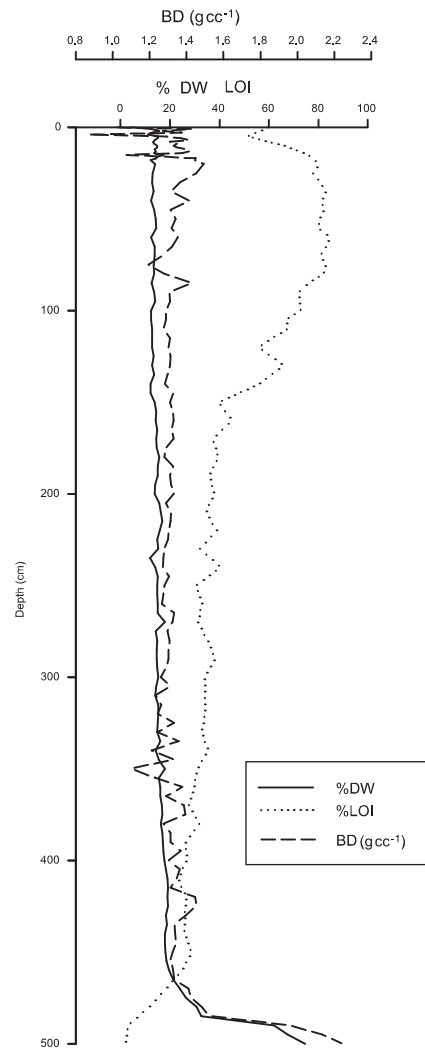
Figure 4 Plot of the DCA of the first two ordination axes for the Kelly's Lough diatom taxa (a) and samples (b)

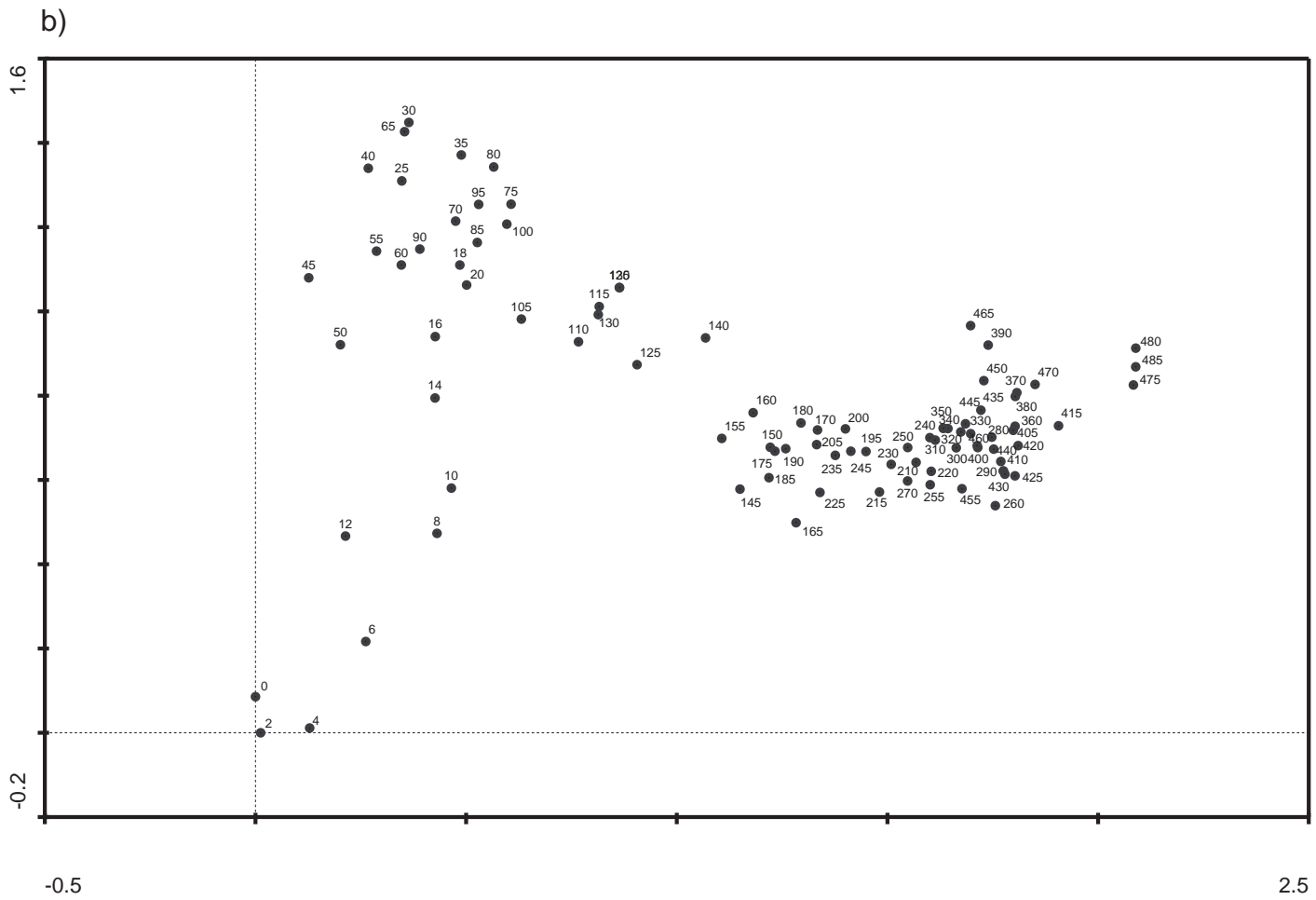
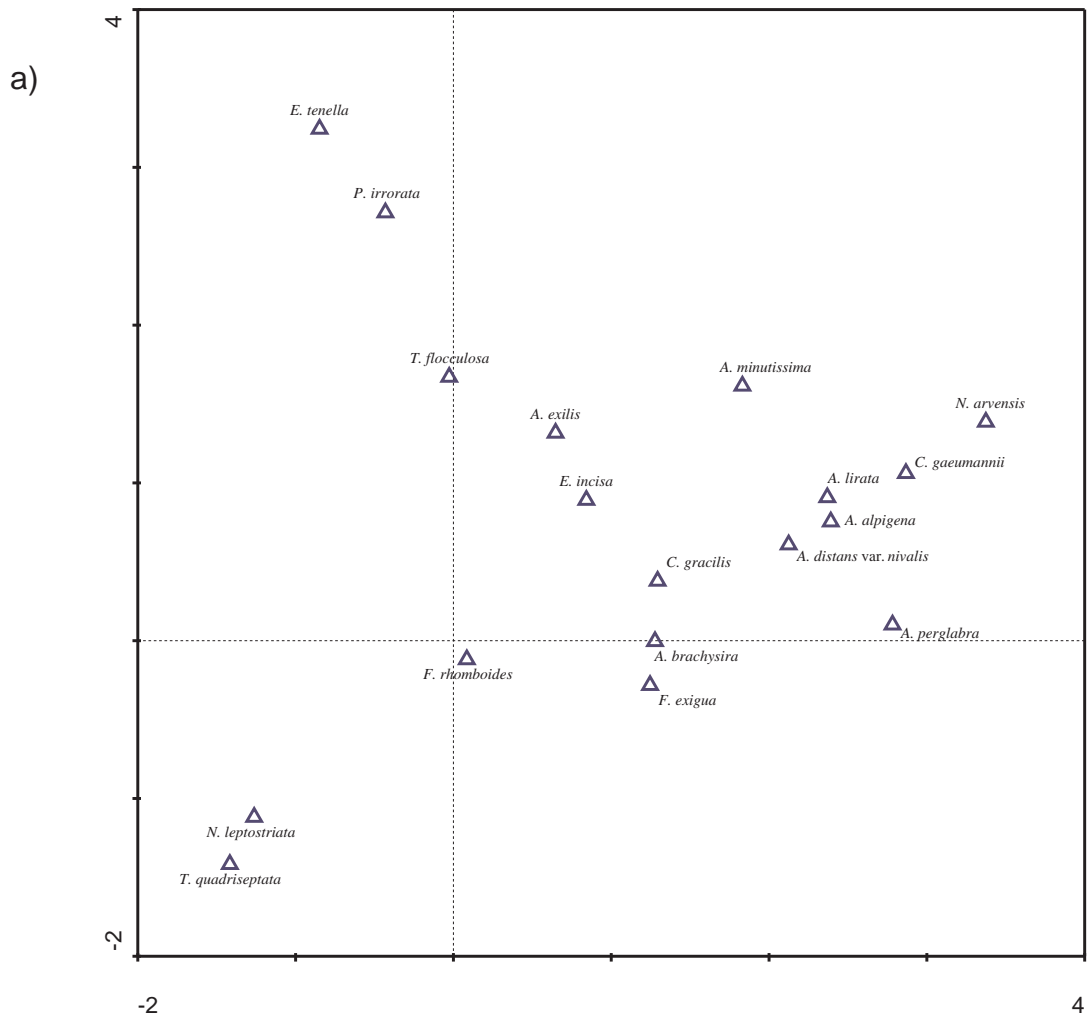
Figure 5 Summary diatom diagram for the top 100 cm of Kelly's Lough sediment core and estimated ²¹⁰Pb dates (C:V = Chrysophyte cyst to diatom valve ratio)

Figure 6 Summary pollen diagram for Kelly's Lough. Pollen data are expressed as percentages of the calculation sum and plotted on estimated age scale

Figure 7 Summary diagram of Kelly's Lough including sediment accumulation rate (SAR), dry matter (% dry weight), organic matter (% LOI), diatom-inferred pH, [H⁺] µequivalent litre⁻¹, DCA scores for the first two axes, microcharcoal concentrations and percentage of *Calluna* against depth and calendar years BP







Kelly's Lough

