Assessing the ecological status of candidate reference lakes in Ireland using palaeolimnology

MANEL LEIRA[♦1], PHIL JORDAN[♦♦], DAVID TAYLOR[♦], CATHERINE DALTON[*], HELEN BENNION[^], NEIL ROSE[^] and KENNETH IRVINE[♦]

[♦] *School of Natural Sciences, Trinity College, University of Dublin, Ireland;* [♦♦] *School of Environmental Sciences, University of Ulster, Coleraine, Northern Ireland;* [*] *Department of Geography, University of Limerick, Ireland; and* [^] *Environmental Change Research Centre, University College London, England*

[1] corresponding author: email leiram@tcd.ie

Summary

(1) The EU Water Framework Directive (WFD) requires that member states establish type-specific reference conditions for all water bodies, including freshwater lakes. This presents a problem in those locations where human activity has resulted in significant changes to the biological, chemical and physical characteristics of water bodies.

(2) Seventy-six oligotrophic and meso-oligotrophic lakes (0-19 μg TP L^{-1}) thought to be relatively unimpacted by human activity have been identified in Ireland and nominated as candidate reference lakes (CRLs) by the Environmental Protection Agency (EPA). The research presented here used palaeolimnological (lake sediment-based) techniques to test the actual and historical ecological site-specific status of a representative selection of these CRLs. In line with similar work in the UK, and where the temporal record of sedimentation was sufficiently long, the study adopted *c.* 1850 as the primary baseline date for reference conditions.

(3) Short sediment cores were obtained from the deepest parts of 35 CRLs during fieldwork in 2003, and chronologies were established from profiles of spheroidal carbonaceous particles (SCP). Twenty-two cores of sediment appeared, on the basis of SCP concentrations, to date back to *c.* 1850. Sediment in the remaining 13 cores appeared to post-date this reference baseline. Unless the SCP chronologies suggested otherwise, diatom assemblages present in top and bottom samples from the cores were used as proxies of, respectively, present-day and reference conditions. Lake water pH (DI-pH) and TP concentration (DI-TP) were inferred from the diatom data. Higher resolution sampling (up to five sediment samples per core) was adopted at seven sites where the SCP-based chronology was more robust and for at least one core from each of the most common types of CRLs. Sediment chemistry data were determined to identify possible anthropogenic drivers of the observed changes in the diatom assemblages.

(4) Ordination and dissimilarity measures identified the main patterns of variation in the diatom data and the directions and magnitude of change between samples from the same core. Eleven of 34 CRLs for which diatom data were available showed little or no change in biological status between core top and bottom samples. Core bottom samples in six of these dated back to pre- or *c.* 1850 and reference (and high ecological) status could therefore be confirmed in these cases. The estimated age of core

bottom samples in the remaining five cores was in the period just after c. 1850 to *c.* 1950 (4 cores) or was impossible to determine (1 core). Twenty-three (68 %) of the CRLs sampled showed biologically important deviation from reference condition, with acidification and nutrient enrichment seemingly the main causes of change. Catchment disturbance, notably peat erosion possibly linked to recent afforestation (largely in the form of conifer plantations), also appeared to have been a factor in some cases.

(5) *Synthesis and application.* The study provides the first systematic examination for Ireland of changes to water quality in (perceived) pristine lakes over the last *c.* 150 years, and demonstrates the potential of palaeolimnology to support the implementation of the WFD. Results indicate that diatom communities in low alkalinity lakes have been particularly altered and for some acidification and nutrient enrichment appear to have been important drivers. Furthermore, higher resolution results call into question the validity of applying *c.* 1850 as the date for reference conditions across Ireland.

Key words: acidification, diatoms, eutrophication, palaeolimnology, reference conditions, sediment chemistry, Water Framework Directive

Introduction

The *EU Water Framework Directive* (WFD, Directive 2000/60/EC) aims to maintain or improve the ecological status of the range of water resources in Europe by 2015. Accordingly, EU states are required to identify, delimit and differentiate surface water bodies and to establish hydromorphological, physiochemical and biological type-specific reference conditions (OJEC 2000: L327/27). Biological reference conditions, equating to high ecological status and showing no or very minor distortion as a result of human activity, can be established in several ways (Andersen, Conley & Hedal 2004). In Ireland, where parts of the country have relatively low levels of human activity, it is possible that some surface water bodies show no more than minor deviations from reference state, therefore allowing, at least in part, a spatial approach to the determination of biological reference conditions.

The Environmental Protection Agency (EPA) in Ireland nominated 76 lakes as candidate reference lakes (CRLs), or lakes that possibly represent type-specific reference conditions, based largely on current levels of human activity in their catchments. The research presented here tested the status of a representative selection of these 76 CRLs using palaeolimnological techniques, and examined the influence of a range of potential drivers of ecological change. Because of the large number of lakes involved in the current study, a 'top and bottom' approach was applied to the analysis of sediment cores. This approach involves the analysis of two samples per sediment core per site (Smol 2002) and assumes that the top and bottom samples in a sediment core integrate, respectively, conditions at the time of coring and site-specific reference conditions, although the latter is dependent on the rate of sediment accumulation. The remains of diatoms were used as the main proxy of aquatic biological conditions, because of their sensitivity to a wide variety of aquatic variables, including acidity and nutrient availability, and their often abundant preservation in lake sediments (Stoermer & Smol 1999; Battarbee et al. 2001).

It has been generally agreed in the UK that *c.* 1850 is a suitable reference date for the assessment of anthropogenically-driven aquatic impacts (Moss, Johnes & Phillips 1996; Battarbee 1999; Bennion, Fluin & Simpson 2004), and the research presented here uses this date as the primary reference baseline, where it could be established. In many parts of northwestern Europe, however, profound human impacts pre-date the mid 19th century (see, for example, the work of Bradshaw (2001) in Denmark), and this was certainly the case in parts of Ireland, where rural population densities were often far greater than current levels during the early to mid 19th century (Huang & O'Connel 2000; Donnelly, 2001). High levels of fertilizer applications were not a feature of agriculture in Ireland until intensification commenced in the 1950s (Tunney 1990), however, and *c.* 1950 is probably an appropriate secondary reference baseline in those locations where nutrient enrichment is potentially a significant problem.

Methods

Fieldwork and coring

Sediment cores were collected from a representative selection of CRLs from the most populated CRL typology classes. The CRL typology, which was in effect a working typology specific to Ireland, was based upon measurements of alkalinity (< 20 mg L^{-1} $CaCO_3$, 20-100 mg L^{-1} $CaCO_3$, > 100 mg L^{-1} $CaCO_3$), average water depth (< > 4 m) and lake area (< > 50 ha). Thirty-five CRLs were selected for coring: all are oligotrophic or meso-oligotrophic and most are located in the western part of Ireland at altitudes of less than 300m asl (Figure 1; Table 1). The 35 CRLs cored were divided amongst seven of the total of 12 typology classes: 1) low alkalinity, shallow, small lakes; 2) low alkalinity, shallow, large; 3) low alkalinity, deep, small; 4) low alkalinity, deep, large; 6) moderate alkalinity, shallow, large; 8) moderate alkalinity, deep, large; 10) high alkalinity, shallow, small; and 12) high alkalinity, deep, large lakes.

Sediment cores were collected during the period June-September 2003 from the deepest part of each of the 35 CRLs using a 0.5 m Renberg gravity corer (Renberg 1991), with coring usually following an extensive bathymetric survey. Water samples were also obtained at each coring site for subsequent chemical and biological characterisation, and any obvious signs of human impact noted. Information on lake water quality and land cover in the catchment for each CRL sampled, in the form of 1990 CORINE data, was also obtained from the EPA.

Laboratory analyses

Sediment cores were subsampled in the field at 0.5 cm intervals for the upper 5 cm and at 1 cm intervals thereafter, and bagged in labeled zip-lock bags.

Concentrations of spheroidal carbonaceous particles (SCP) in samples of lake sediments provide a record of the impact of fossil fuel combustion in the region, and down-core variations in these have been shown to provide a reliable dating method (Rose & Appleby 2005). The start of the SCP record in lake sediments at many sites across Europe is *c.* 1850, while *c.*1950 marks the start of a rapid increase in concentrations, resulting from increased electricity generation and the widespread availability of cheap oil (Rose et al. 1995), which peaked some two to three decades later. There is some uncertainty attached to the precise dating of peaks in SCP concentrations in Ireland, because few studies have been carried out locally. However, separate studies in the northwest and north of Ireland dated the peak in SCP concentrations to 1981 ± 2 and 1980 ± 3 (Rose 2001). In the current study, the estimation of SCP concentrations in five sediment samples per core followed the method of Rose (1994). SCP were counted at x400 magnification under a light microscope and concentrations expressed as numbers of SCP per gram dry mass of sediment (g DM^{-1}). Although estimates of sediment age and accumulation rates based on such coarsely resolved analyses have to be treated with caution, there was some evidence to validate the approach. Thus, the estimated accumulation rate for Dan, one of the CRLs sampled in the current study, corresponds closely with published ^{210}Pb-based data for the same site (Nowlan et al. 2000), while the accuracy of the SCP-based chronology for Nambrackkeagh was confirmed using newly available ^{210}Pb-based accumulation rate data (McGee unpublished data). Chronological control in the current study was based on: the start of the SCP record, 1850±25 years (*c.* 1850); the rapid increase in SCP concentrations, 1950±10 (*c.* 1950); and the peak in SCP concentrations, 1980±3 (*c.* 1980) (Rose et al. 1995). In addition, the top 0.5 cm thick slice of sediment in a core (the core top sample) was assumed to date to the year of coring (i.e., 2003).

Samples were prepared and analysed for diatoms using standard methods (Battarbee et al. 2001). At least 300 valves were counted for each sample using oil immersion objective and phase contrast microscopy. The relative abundance of all species (including unidentified forms) was determined as the percentage of the total count (Battarbee et al. 2001). Diatoms were identified using standard floras (Krammer & Lange-Bertalot 1986-91).

Two levels of resolution were employed: two samples (top and bottom) per core were analysed for 28 of the cores; a higher resolution (4 or 5 samples per core, including top and bottom samples) was adopted for cores where there was particular interest in the magnitude, rate and direction of change from the reference sample and where the SCP-based chronology was most robust (seven sites in total). At least one example from each of the main types of CRLs was analysed at higher resolution. Generally, core samples contained abundant, well-preserved diatoms, although poor preservation and low concentrations of diatom frustules characterised core samples from the higher alkalinity lakes Bane, Cullaun, Lene, McNean and Rea. In those cases where a sample was found to contain insufficient abundances of well-preserved diatoms, the stratigraphically contiguous sample was analysed in its place. Only in one case (Fad East, Donegal) were fossil diatoms absent throughout the core from below the upper 2 cm.

Dry weight, density and the concentrations of a range of elements, including total phosphorus (TP), sodium (Na), potassium (K), calcium (Ca), iron (Fe), and manganese (Mn), were determined on core samples from all 35 CRLs. Dry weight and density measurements are important for the interpretation of sediment chemistry data, aiding the development of areal sediment and chemical accumulation rates, and were obtained for all core samples. Levels of sedimentary TP are used in the interpretation of nutrient enrichment as inferred from biological analyses (Rippey & Anderson 1996), while those of Na, K and Ca could indicate periods of catchment erosion. Fe and Mn in sediments are indicators of fine sediment ingress to lakes but can also be vectors for mobilisation of TP in anoxic sediments (Mackereth 1966).

In the majority of cases, wet density was determined from the final weight of extruded sediments of known volume. Dry weight was determined on each whole extruded sediment slice (105 °C for 24 hours) (Hilton, Lishman & Millington 1986). Sediment chemistry in each core was determined in the majority of cases on the top five 0.5 cm- and the bottom five 1 cm-thick slices. Additional sediment samples were analysed between the uppermost and lowermost sets of samples in cores of sediment that had relatively robust SCP-based chronological control and that represented the most common types of CRLs encountered (32 CRLs in total).

Following Boyle (2001), dried sediments were disaggregated by pestle and mortar and, after further drying, 0.3 g of the dried sediment was added to Teflon beakers. Sediment samples were sequentially digested with concentrated hydrofluoric (HF), nitric (HNO_3) and perchloric ($HClO_4$) acids at temperatures from 40-60 °C and preserved as acidified 25 ml solutions; 30 samples were digested at a time and a blank, certified reference material (CRM) and repeat digest were included for quality control in each run of measurements. Chemical concentrations (mg g^{-1}) were determined on 20 x dilutions in diluted HNO_3 using an ICP-OES, and were also transformed to an accumulation rate (mg cm^{-2} yr^{-1}) form using SCP-based estimates of sediment accumulation rate and measurements of sediment dry density.

Data analyses

Analyses of diatom data involved samples from 34 CRLs, because of the poor preservation of diatoms in samples from Fad East. As reliable chronologies could not be established for Lene, O'Flynn and Tay on the basis of SCP concentrations, discussions concerning down-core variations in sediment chemistry are therefore restricted to the 32 CRLs for which there was relatively tight chronological control.

The degree of floristic change between diatom assemblages in core top and bottom sediment samples was assessed using the squared chord distance dissimilarity index (SCD). SCD emphasises the pattern in the data at the expense of the random variation in species abundances and has been shown theoretically to perform better than other types of coefficients for determining ecological resemblance amongst samples (Overpeck, Webb & Prentice 1985). The SCD technique was recently used as a basis for quantifying the degree of floristic change between reference and surface diatom assemblages in a palaeolimnological study of 26 lochs in Scotland (Bennion, Fluin & Simpson 2004) and for defining reference conditions for acidified waters in the UK (Simpson et al., 2005). SCD scores range from 0 to 2, with 0 indicating that two samples have exactly the same species composition, and 2 that their compositions are entirely different. A SCD score < 0.4 (approximating to the 2.5 percentile) was used in the current research to define sites with low floristic change between the bottom and top sample. This is more stringent than the 5th percentile used by Bennion, Fluin & Simpson (2004) and reflects revised thinking about what constitutes biologically important change at a site following closer examination of sediment sample data from over 200 UK lake cores held in the AMPHORA database (Environmental Change Research Centre, UCL). Unimpacted lakes in this database typically have SCD scores of <0.4.

Detrended Correspondence Analysis (DCA; Hill & Gauch 1980) was used to identify the main patterns of variation in the diatom data, and to establish the directions and magnitude of changes in biological conditions at each coring location. Version 4.5 of CANOCO was employed in the DCA-based ordination of diatom data (ter Braak & Šmilauer 2002). Prior to all analyses, diatom abundances were square root transformed in order to stabilise variance, and rare species were down-weighted.

Diatom-inferred pH and TP (DI-pH and DI-TP) were established using standard weighted averaging (Birks, Juggins & Line 1990; Birks et al. 1990; Korsman & Birks 1996; Koster, Racca & Pienitz 2004) in order to quantify any changes in nutrient status and acidity. All diatom-inferred values were established using the computer software package C2 (Juggins 2003). In the absence of a diatom assemblage-water quality training set specific to Ireland, DI-pH and DI-TP were determined using a preliminary training set that comprised diatom counts for surface sediment samples and several years of measurements of lake water quality made by the EPA. The training set for pH comprised information from the 35 CRLs studied in the current research; pH values ranged between 5.11 and 8.54 and had a median value of 6.5 pH units. The resultant weighted averaging partial least squares two-component (WA-PLS2) model ($r^2 = 0.84$) had a root mean squared error of prediction (RMSEP) of 0.43 pH units. The training set for TP included additional information from 10 nutrient-enriched lakes in Ireland so as to extend the TP gradient. TP values in the training set were in the range 0 to 2.55 log10 µg TP L^{-1}, and had a median value of 0.90 log10 µg (8.0 µg) TP L^{-1}. The resultant WA-PLS2 model ($r^2 = 0.64$) generated a RMSEP = 0.202 log10 µg TP L^{-1}. The difference between current DI-TP and reference DI-TP was used to derive a qualitative estimate of degree of change, with a difference in DI-TP greater than the RMSEP deemed biologically important.

A comparison of the models used in the current research to derive pH and TP from diatom assemblages with other transfer functions recently developed for Northern Ireland and for Europe is presented in Table 2. In general, the statistical performance of the predictive models used in the current work compares well with other diatom-TP and pH transfer functions.

Results

Approximate sediment chronologies for CRLs

Down-core variations in SCP concentrations (Appendix S1; see Supplementary material) permitted allocation of each of the 35 sediment cores analysed to one of three categories, based on the apparent completeness of the SCP profile: (1) complete, where the start of the SCP record was within the length of the core, and depths for *c.* 1950 and *c.* 1980 were extrapolated assuming a constant sediment accumulation rate (13 cores in total); (2) curtailed, where SCP were only present in the uppermost part of the core, presumed to be due to slow sediment accumulation rates rather than a loss of sediments (11 cores in total); and (3) incomplete, where SCP were present in all samples and an estimate for *c.* 1850 was extrapolated to a sediment depth below the base of the core (11 cores in total). It was thus possible to estimate the age of the bottom sediment core sample in 18 cases, with rates of sediment accumulation in these 18 cores varying widely, from a low of 0.09 cm yr^{-1} (Dunglow) to a high of 0.58 cm yr^{-1} (Kiltooris) (Table 3).

Down-core variations in sediment chemistry and diatom data

Sediment chemistry data, in concentration form, together with density and dry weight measurements are presented in Appendix S2 and S3 respectively (see Supplementary material). Differences in accumulation rates between mean reference and mean present-day samples for the three cations Ca, K and Na are shown in Figure 2. In general, the results do not indicate increasing exogenic inputs, with only Talt showing increases in Ca, Na and K accumulation rates, which is consistent with increased sediment dry weight towards the top of the core. Stable or falling exogeic inputs of sediment to the CRLs studied are also evident when the sediment chemistry data are expressed in concentration form. Changes in Mn and Fe accumulation rates are shown in Figure 3. Manganese accumulation rates increase in some lakes where there are no other cation increases, which is indicative of mobilisation and accretion at a redox boundary (Davison 1993). Increases in Mn are also apparent when the data are expressed in concentration form. Again, Talt is an exception where Mn and Fe increases are also likely to be dependent on exogenic inputs consistent with increased dry weights. Total P accumulation rates (Figure 4) indicate a decrease from reference rates for all lakes, with the exception of Talt and Cullaun. It is likely that increased TP accumulation rates at Talt are linked to evidence of inwash, while a link between increased Ca and TP accumulation rates at Cullaun may be due to co-precipitation of TP with $CaCO_3$ (Jager & Rohrs 1990). There is, however, a caveat on the interpretation of these sediment chemistry data. First, the calculation of dry mass sediment accumulation rates using SCP chronologies may introduce an error because the model assumes a linear accumulation rate between dated horizons. The level of error, however, is likely to be minimized in the current research because of the relatively low levels of human activity (and therefore rates of erosion) in the catchments for many of the CRLs cored. Second, and especially with regard to the sedimentary P profiles, chemicals may become concentrated at the sediment-water interface due to diagenesis and mobility. According to the concentration data, this does not appear to be a problem, however. Even in the low alkalinity lakes, where diagenetic mobilisation would be expected to occur (as a result of exogenic Fe and Mn inputs from acid soils) and where changes in the Fe and Mn profiles indicate mobilisation, only a minor concurrent increase in the sedimentary P concentration profiles is evident. Except for Arderry and Fee, by far the largest increases in sedimentary P concentration are in the high alkalinity lakes, where there are no indications of Fe and Mn mobilisation and where these would be supply-limited from calcareous catchment soils.

The main down-core differences in diatom assemblages are tabulated in Appendix S4 (see Supplementary material). SCD scores between diatom assemblages in present-day and bottom core samples ranged from 0.046 to 1.769 (Table 4). In order to facilitate assessment of the departure from reference conditions, core bottom, present-day and, in some cases, mid-core samples from each lake were combined on the same DCA ordination biplot (Figure 5). Eleven (32 %) of the 34 sites for which top-bottom comparisons in diatom assemblages were possible generated SCD scores < 0.4, indicating little or no change in biological status when compared to the reference benchmark. These 11 cases were distributed among the different CRL typology classes, although none were in typology class 12 (deep, large, high alkalinity). Aside from CRLs in typology class 12, where differential preservation of diatom frustules may have been a factor influencing the results, large, deep, low alkalinity lakes (typology class 4) were most consistent in showing biologically important changes when compared to reference conditions. Eighty-two percent of CRLs within this class generated SCD scores > 0.4. Many of the moderate to high alkalinity CRLs (typology classes 6 to 12) studied have also experienced important biological changes, based on the SCD scores, although at some of these differential preservation of diatom frustules may have been an important factor.

Down-core differences in DI-pH and DI-TP are given in Table 4. These results must be viewed in the context of limitations in the models used to infer pH and TP based on diatom and environmental data for lakes in Ireland. Note that because of the known deficiencies in the model used, differences in DI-TP between core top and bottom samples are also reported in Table 4 as proportional change. Present-day reconstructions of pH at 12 of the CRLs sampled show higher pHs and 22 show lower pHs when compared with core bottom samples, although only four lakes (Dan, Easky, Kylemore and Tay, all low alkalinity CRLs) show a decline in pH > RMSEP. Ten CRLs appear to have experienced a reduction in DI-TP, while DI-TP increased at 24 sites. However, only in Tay does the reduction in DI-TP appear important (> RMSEP). By comparison, two low alkalinity CRLs show an increase in DI-TP > RMSEP between core bottom and present-day conditions: Fee and Feeagh (both EPA typology class 4). Arderry and Cloonaghlin also exhibited a change in DI-TP, although no relevant and concurrent increases in TP accumulation rate were evident.

Of the seven cores studied at higher resolution, low alkalinity lakes showed the most striking changes in DI-pH and DI-TP (e.g., Easky, Keel and Fee, Figures 6 and 7). Keel and Fee exhibit increases in DI-TP up to c. 9 μg L^{-1} TP, while at Keel the increase in DI-TP occurred before *c.* 1850 and shows some stability since the reference date. Ballynakill (typology class 6, moderate alkalinity) and Annaghmore and Muckanagh (respectively, typology classes 10 and 12, high alkalinity) show only relatively small changes in DI-pH and DI-TP between the reference and present-day samples.

Discussion

Insignificant differences between core top and bottom diatom assemblages were found in 11 CRLs (32 % of those studied) providing support for largely stable ecological conditions at these sites. Sedimentary P accumulation rates largely show a decrease from reference. Reduced rates of P accumulation when compared with reference rates may be an artifact of the data. However, they may also reflect changes in land use and human population levels following the famines in Ireland of the early to mid 19th century, which had their most profound impact (rural depopulation on a massive scale) in the west of the country (Donnelly, 2001). The core bottom sample in six of the lakes represent *c.* 1850 AD reference conditions, or before, and therefore reference (and high ecological) status could be verified in these cases. Core bottom samples for the other five CRLs dated to the period between the primary and secondary reference baselines (i.e. *c.* 1850 to *c.* 1950). As this period was prior to agricultural intensification and afforestation in much of Ireland, the reference status of these sites would also appear justified

Biologically important changes were evident between reference and present-day conditions for 68 % of the CRLs studied. The main drivers of change appear to be either nutrient enrichment or increased acidity in these oligotrophic and meso-oligotrophic lakes. Phosphorus transfer to freshwaters is a major cause of nutrient enrichment in Ireland at present, although no link was found in the current research between indicators of the mass transfer of exogenic soil material and those lakes with increasing TP accumulation. Increased TP transfer is not necessarily linked directly to increased soil loss, however, and both increased discrete point sources, such as those associated with rural dwellings and septic tanks, and diffuse soluble P losses from P-saturated soils or inappropriate slurry spreading (during wet weather) (Jordan et al. 2005) are possible drivers of changes in the diatom assemblages recorded here.

Peat inwash could have influenced the composition at several lakes that have experienced biologically important changes in diatom assemblages, but show no major change in the DI-pH and DI-TP profiles. CRLs appearing to have been impacted by peat inwash experienced a shift to a benthic diatom assemblage characterised by *Fragilaria* taxa and, in some cases, the loss of planktonic assemblages. Small, benthic

Fragilaria are considered pioneering assemblages and have been related to rapidly changing environmental conditions (e.g., increased turbidity in the water column). Furthermore, diatom-community changes associated with peat inwash that has had a tangible impact on lake sediments are usually characterized by the loss of planktonic assemblages (Jones, Stevenson & Battarbee 1989). Peat erosion could have been linked to afforestation, as conifer plantation, many dating to the period post-1950, accounts for a substantial proportion of the land cover in the catchments for CRLs that may have experienced peat erosion.

Of particular note is the comparatively high incidence of important alterations in biological conditions among the low alkalinity, large deep lakes (82 % of CRLs in typology class 4 generated SCD scores > 0.4). Nutrient enrichment does not appear to have been the driver here as increases in DI-TP are relatively minor and are not generally supported in the sedimentary TP data. It could be, however, that biologically important TP concentrations in lake water are not in balance with sediment-based TP. Moreover, relatively small increases in TP concentrations in P-limited lakes may impact diatom populations before any increases are evident in sediment chemistry: rapid DI-TP change has been found in some historically oligotrophic lakes in Northern Ireland prior to increases in sediment TP (P. Jordan & N.J. Anderson unpublished data). Acidification appears to have been a factor at several of these lakes, however, notably Dan, Kylemore and Tay.

The more finely resolved sediment chemistry and diatom data from Keel (low alkalinity) and Talt (moderate alkalinity) are of particular interest. The sedimentary data for Keel indicate relatively little change between *c.* 1850 and the present-day. The rate of sedimentation at Keel was, however, low (0.19 cm yr^{-1}) and the base of the 41cm-long core of sediment obtained dated to the late 18th century, based on an extrapolation of the SCP chronology. Comparisons of diatom assemblages and DI-TP between the core bottom and present-day samples from this site indicate much more important changes than those between *c.* 1850 and present-day, due to increased abundances of *Asterionella ralfsii* (a taxon that was not recorded in pre-*c.* 1850 sediments). The ecology of this taxon is not well known but appears to be indicative of peatland disturbance and nutrient enrichment (Liehu, Sandman & Simola 1986). It could therefore be argued that *c.* 1850 is not an appropriate reference date for Keel and this may also be the case for several other lakes in catchments that until the mid

19th century supported far higher population densities than today. The results from Talt indicate a pattern of change that may be hidden in some of the less finely resolved core datasets. The sediment chemistry for this site indicates catchment disturbance in the form of increases in sediment dry weight and in Ca, Fe, K, Mn, Na and TP accumulation rates between *c.* 1950 and the present-day samples. According to the dry weight and sediment chemistry data, the catchment has stabilised since this disturbance event although diatom communities and pH levels have yet to recover fully.

Analysis of the moderate and high alkalinity lakes (typology classes 6, 8, 10 and 12), where dissolution of silica diatom frustules has caused preservation and therefore interpretation problems, highlights the difficulties of using diatoms to assess floristic change in these systems. As the sedimentary data that are available for sites within these classes show some deviation from reference conditions may have occurred, a separate study should focus specifically on these typology classes using biological indicators other than diatoms (e.g. chironomids, cladocera, ostracods, pigments) should be implemented. A further limitation of this investigation was that it was only possible to consider in any detail a restricted range of potential causes of variability, despite the potential role of other important influencing factors, notably climate change (e.g., Smol & Cumming 2000; Lotter et al. 2002; Sorvari, Korhola & Thompson 2002; Hudson, Dillon & Somers 2003; Michelutti, Douglas & Smol 2003; Rühland, Priesnitz & Smol 2003; Smol et al. 2005). A number of lakes in this study have experienced a rise in *Cyclotella* taxa when compared with reference conditions, which could not be related directly to human activities. Increased abundances of various *Cyclotella* species have been linked to climate change throughout the Canadian arctic (Karst-Riddoch, Pisaric & Smol 2005) as well as in temperate regions (Wolin & Stoermer 2005) and climate change since *c.* 1850 is likely to have impacted oligotrophic and meso-oligotrophic lakes in Ireland.

To conclude, results generated from the first, systematic palaeolimnology-based examination of the recent ecological histories of oligotrophic and meso-oligotrophic lakes in Ireland and presented in this paper:

- highlight the potential of palaeolimnological studies to assess reference conditions in aquatic ecosystems;

- indicate that 32 % of CRLs studied show relatively little deviation from reference conditions, thus confirming the reference status of these 11 lakes;
- demonstrate that large, deep, low alkalinity lakes in particular (82 % of this type of CRL studied) show biologically important deviation from reference conditions,
- confirm acidification and nutrient enrichment as important drivers of recent changes, but do not exclude other natural factors such as climate change; and
- suggest that *c*. 1850 may not be an appropriate reference baseline in all cases, especially when viewed in the context of the history of rural Ireland since the mid-19th century.

Acknowledgements

The research presented here would not have been possible without the support of the EPA (project # 2002-W-LS/7) and we would like to thank in particular Jim Bowman of the EPA. Thanks are also due to Eddie McGee for the ^{210}Pb data from Lough Nambrackkeagh, to Sheila McMorrow for assistance with the figures, and to several staff and postgraduate research students from UU Coleraine, Trinity College, University of Dublin and University of Limerick, most notably Richard McFaul and Guangjie Chen, for assistance with fieldwork. Finally, thanks are owed to the numerous landowners who facilitated access to CRLs and to the reviewers of an earlier version of this paper for their very helpful and constructive comments.

References

Andersen, J.H., Conley, D.J. & Hedal, S. (2004) Palaeoecology, reference conditions and classification of ecological status: the EU Water Framework Directive in practice. *Marine Pollution Bulletin*, **49**, 283-290.

Anderson, N.J., Rippey, B. & Gibson, C.E. (1993) A comparison of sedimentary and diatom-inferred phosphorus profiles: implications for defining pre-disturbance nutrient conditions. *Hydrobiologia,* **253**, 357-366.

Battarbee, R.W. (1999) The importance of palaeolimnology to lake restoration. *Hydrobiologia*, **395/396**, 149-159.

Battarbee, R.W., Jones, V.J., Flower, R.J., Cameron, N.G., Bennion, H., Carvalho, L. & Juggins, S. (2001) Diatoms. *Tracking Environmental Change Using Lake Sediments Vol. 3: Terrestrial, Algal, and Siliceous Indicators* (eds J.P. Smol, H.J.B. Birks and W.M. Last), pp. 155-202. Kluwer Academic Publishers, Dordrecht.

Bennion, H. (1994) A diatom-phosphorous transfer function for shallow, eutrophic ponds in southeast England. *Hydrobiologia*, **275/276**, 391-410.

Bennion, H., Juggins, S., & Anderson, N.J. (1996) Predicting epilimnetic phosphorous concentrations using and improved diatom-based transfer function and its application to lake eutrophication management. *Environmental Science & Technology*, **30**, 2004-2007.

Bennion, H., Fluin, J. & Simpson, G.L. (2004) Assessing eutrophication and reference conditions for Scottish freshwater lochs using subfossil diatoms. *Journal of Applied Ecology*, **41**, 124-138.

Birks, H.J.B., Juggins, S. & Line, J.M. (1990) Lake surface-water chemistry reconstructions from palaeolimnological data. *The Surface Waters Acidification Programme* (ed B.J. Mason), pp. 301-313. Cambridge University Press, Cambridge.

Birks, H.J.B., Line, J.M., Juggins, S., Stevenson, A.C. & ter Braak, C.J.F. (1990) Diatoms and pH reconstruction. *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences*, **327**, 263-278.

Boyle, J.F. (2001) Inorganic geochemical methods in palaeolimnology. *Tracking Environmental Change Using Lake Sediments Volume 2 Physical and Geochemical Methods* (eds W.M. Last and J.P. Smol), pp 83-141. Kluwer Academic Publishers, Amsterdam.

Bradshaw, E.G. (2001) *Linking land and lake. The response of lake nutrient regimes and diatoms to long-term land-use change in Denmark*. PhD Thesis, University of Copenhagen.

Cameron, N.G., Birks, H.J.B., Jones, V.J., Berge, F., Catalan, J., Flower, R., Garcia, J., Kawecka, B., Koinig, K.A., Marchetto, A., Sánchez-Castillo, P., Schmidt, R., Šiško, M., Solovieva, N., Štefková, E., & Toro, M. (1999) Surface-sediment and epilithic diatom pH calibration sets for remote European mountain lakes (AL:PE project) and their comparison to the Surface Waters Acidification Programme (SWAP) calibration set. *Journal of Paleolimnology*, **22**, 291-317.

Davison, W. (1993) Iron and manganese in lakes. *Earth-Science Reviews*, **34**, 119-163.

Donnelly, J.S. (2001) *The Great Irish Potato Famine*. Boston Publishing, Stroud.

Hill, M.O. & Gauch, H.G. (1980) Detrended Correspondence Analysis, an improved ordination technique. *Vegetatio*, **42**, 47-58.

Hilton, J., Lishman, J.P. & Millington, A. (1986) A comparison of some rapid techniques for the measurement of density in soft sediments. *Sedimentology*, **33**, 777-781.

Huang, C.C. & O'Connel, M. (2000) Recent land-use and soil-erosion history within a small catchment in Connemara, western Ireland: evidence from lake sediments and documentary sources. *Catena*, **41**, 293-335.

Hudson, J.J., Dillon, P.J. & Somers, K.M. (2003) Long-term patterns in dissolved organic carbon in boreal lakes: the role of incident radiation, precipitation, air temperature, southern oscillation and acid deposition. *Hydrology and Earth System Sciences*, **7**, 390-398.

Jager, P. & Rohrs, J. (1990) Coprecipitation of phosphorus with calcite in the eutrophic Wallersee (alpine foreland of Salzburg, Austria). *Internationale Revue der Gesamten Hydrobiologie*, **75**, 153-173.

Jones, D.S., Stevenson, A.C., & Battarbee, R.W. (1989) Acidification of lakes in Galloway, South West Scotland: a diatom and pollen study of the post-glacial history of the Round Louch of Glenhead. *Journal of Ecology*, **77**, 1-23.

Jordan, P., Menary, W., Daly, K., Kiely, G., Morgan, G., Byrne, P. & Moles, R. (2005) Patterns and processes of phosphorus transfer from Irish grassland soils to rivers - integration of laboratory and catchment studies. *Journal of Hydrology*, **304**, 20-34.

Juggins, S. (2003) *C2 Software for ecological and palaeoecological data analysis and visualisation. User guide Version 1.3*, pp. 69. Newcastle University, Newcastle upon Tyne.

Karst-Riddoch, T.L., Pisaric, M.F.J. & Smol, J.P. (2005) Diatom responses to 20th century climate-related environmental changes in high-elevation mountain lakes of the northern Canadian Cordillera. *Journal of Paleolimnology*, **33**, 265-282.

Korsman, T. & Birks, H.J.B. (1996) Diatom-based water chemistry reconstructions from northern Sweden: A comparison of reconstruction techniques. *Journal of Paleolimnology*, **15**, 65-77.

Köster, D., Racca, J.M.J. & Pienitz, R. (2004) Diatom-based inference models and reconstructions revisited: methods and transformations. *Journal of Paleolimnology*, **32**, 233–246

Krammer, K. & Lange-Bertalot, H. (1986-91) Bacillariophyceae. 1-4 Teil. *Süßwasserflora von Mitteleuropa* (eds H. Ettl, J. Gerloff, H. Heynig and D. Mollenhauer). Gustav Fischer-Verlag, Stuttgart.

Liehu, A., Sandman, O. & Simola, H. (1986) Effects of peatbog ditching in lakes: problems in palaeolimnological interpretation. *Hydrobiologia*, **143**, 417-424.

Lotter, A.F., Appleby, B.G., Bindler, R., Dearing, J.A., Grytnes, J.A., Hofmann, W., Kamenik, C., Lami, A., Livingstone, D. M., Ohlendorf, C., Rose, N. & Sturm, M. (2002) The sediment record of the past 200 years in a Swiss high-alpine lake: Hagelseewli (2339 m.a.s.l). *Journal of Palaeolimnology*, **28**, 111-127.

Mackereth, F.J. (1966) Some Chemical Observations of Post-Glacial Lake Sediments. *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences*, **250**, 165-and.

Michelutti, N., Douglas, M.S.V. & Smol, J.P.. (2003) Diatom response to recent climate change in a high arctic lake (Char Lake, Cornwallis Island, Nunavut). *Global and Planetary Change*, **38**, 257-271.

Moss, B., Johnes, P. & Phillips, G. (1996) The monitoring of ecological quality and the classification of standing waters in temperate regions: a review and proposal based on a worked scheme for British waters. *Biological Reviews*, **71**, 301-339.

Nowlan, N.V., Mitchell, P.I., Murray, D.A., Leon Vintro, L. & Seymore, E. (2000) Measurement and interpretation of lead-210 and caseium-137 profiles in relation to recent sedimentation in some Irish lakes. *Verhandlungen Internationale Vereinigung fiir Theoretische und Angewandte limnologie*, **27**, 2303-2306.

OJEC (2000) Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal of the European Communities*, 1-327.

Overpeck, J.T., Webb, T. & Prentice, I.C. (1985) Quantitative Interpretation of Fossil Pollen Spectra - Dissimilarity Coefficients and the Method of Modern Analogs. *Quaternary Research*, **23**, 87-108.

Renberg, I. (1991) The HON-Kajak sediment corer. *Journal of Paleolimnology,* **6**, 167-170.

Rippey, B. & Anderson, N.J. (1996) Reconstruction of lake phosphorus loading and dynamics using the sedimentary record. *Environmental Science and Technology*, **30**, 1786-1788.

Rose, N.L. (1994) A note on further refinements to a procedure for the extraction of carbonaceous fly-ash particles from sediments. *Journal of Paleolimnology*, **11**, 201-204.

Rose, N.L. (2001). Fly-ash particles. *Tracking Environmental Change Using Lake Sediments Vol. 2 Physical and Geochemical Methods* (eds W.M. Last and J.P. Smol), pp. 319-349. Kluwer Academic Publishers, Amsterdam.

Rose, N.L. & Appleby, P.G. (2005) Regional Applications of Lake Sediment Dating by Spheroidal Carbonaceous Particle Analysis I: United Kingdom. *Journal of Paleolimnology*, **34**, 349-361.

Rose, N.L., Harlock, S., Appleby, P.G. & Battarbee, R.W. (1995) Dating of recent lake sediments in the United Kingdom and Ireland using spheroidal carbonaceous particle (SCP) concentration. *The Holocene*, **5**, 328-335.

Rühland, K., Priesnitz, A. & Smol, J.P. (2003) Palaeolimnological evidence from diatoms for recent environmental changes in 50 lakes across Canadian arctic treeline. *Arctic, Antarctic and Alpine Research*, **35**, 110-123.

Simpson, G. L., Shilland, E. M., Winterbottom, J. M. & Keay, J. (2005). Defining reference conditions for acidified waters using a modern analogue approach. *Environmental Pollution*, **137**, 119-133.

Smol, J.P. (2002) *Pollution of Lakes and Rivers: A Paleoenvironmental Perspective*. Arnold Publishers, London; Co-published by Oxford University Press, New York.

Smol, J.P. & Cumming, B.F. (2000) Tracking long-term changes in climate using algal indicators in lake sediments. *Journal of Phycology,* **36**, 986-1011.

Smol, J.P., Wolfe, A.P., Birks, H.J.B., Douglas, M.S.V., Jones, V.J., Korhola, A., Pienitz, R., Rühland, K., Sorvari, S., Antoniades, D., Brooks, S.J., Fallu, M-A., Hughes, M., Keatley, B., Laing, T., Michelutti, N., Nazarova, L., Nyman, M., Paterson, A.M., Perren, B., Quinlan, R., Rautio, M., Saulnier-Talbot, E., Siitonen, S., Solovieva, N. & Weckström, J. (2005) Climate-Driven Regime Shifts in Arctic Lake Ecosystems. *Proceedings of the National Academy of Sciences*, **102**, 4397-4402.

Sorvari, S. Korhola, A. & Thompson, R. (2002) Lake diatom response to recent Arctic warming in Finnish Lapland. *Global Change Biology*, **8**, 153-163.

Stoermer, E.F. & Smol, J.P. (1999) *The Diatoms. Applications for the Environmental and Earth Sciences*. Cambridge University Press, Cambridge, UK.

ter Braak, C.J.F. & Šmilauer, P. (2002) *CANOCO 4.5*. Biometris, Wagenigen.

Tunney, H. (1990) A note on a balance sheet approach to estimating the phosphorus fertiliser needs in agriculture. *Irish Journal of Agricultural Research*, **29**, 149-154.

Wolin, J.A. & Stoermer, E.F. (2005) Response of a Lake Michigan coastal lake to anthropogenic catchment disturbance. *Journal of Paleolimnology*, **33**, 73-94.

Table and Figure captions

Table 1: *Summary of locational information and chemical-physical characteristics for 35 CRLs cored in the present study. Water quality data were provided by the EPA and are annual means.*

Table 2: *Summary performance statistics of published diatom-TP and pH transfer functions, showing the statistics of the Irish models for comparison*

Table 3: *Approximate chronologies and estimated sediment accumulation rates, based on down-core variations in SCP abundances*

Table 4: *Summary of down-core variations in biological and inferred parameters for the 35 CRLs studied (full names and lake codes shown). Data comprise Squared chord distance (SCD) scores for pairs of reference and surface samples from 34 of the 35 CRLs, along with Hill's SD units and diatom inferred TP and pH changes (DI-pH and DI-TP). 'Prop change in DI-TP' = the proportion of change in DI-TP in the c.2003 sample compared to reference, where for example 0.8 = 20% decrease, 1.2 = 20% increase etc. CRLs that appear on the basis of their SCD scores (i.e., SCD scores < 0.4) to have had their CRL status verified in this study are shaded. NB no SCD score based on an intra-core comparison was calculated for Fad Inishowen East [Fad East] (County Donegal, Lake code = FAD) because of an absence of well-preserved diatoms throughout the core (see text for further details).*

Figure 1: *Location of the 35 CRLs discussed in this paper*

Figure 2: *Sediment chemistry accumulation rates showing the reference and present-day (c. 2003) samples and the mean of the top 5 samples (0-2.5cm) for the 32 CRLs sampled for which there is tightest chronological control. 'Mean REF' refers to the mean of the samples encompassed by the SCP dating limits.*

Figure 2a: *Sodium accumulation rates.* **Figure 2b:** *Calcium accumulation rate. Calcium in the six high-alkalinity lakes is an order-of-magnitude higher than other lakes and reflects the predominance of calcareous soils in lake catchments.* **Figure 2c:** *Potassium accumulation rates.*

Figure 3: *Sediment chemistry accumulation rates showing the reference and present-day (c. 2003) samples and the mean of the top 5 samples (0-2.5cm) for the 32 CRLs sampled for which there is tightest*

chronological control. 'Mean REF' refers to the mean of the samples encompassed by the SCP dating limits.

Figure 3a: *Manganese accumulation rates.* **Figure 3b:** *Iron accumulation rate.*

Figure 4: *Total phosphorus accumulation rates showing the reference and present-day (c.2003) samples and the mean of the top 5 samples (0-2.5cm) for the 32 CRLs sampled for which there is tightest chronological control*

Figure 5: *DCA plot combining reference and present-day (c. 2003) sediment samples, as well as mid-core samples where available. Lines connect the reference and present-day samples for each core. The direction is the direction of floristic change and its length is a measure of floristic difference (units=Hill's SD). See Table 4 for explanation of lake codes.*

Figure 6: *DI-TP reconstructions and sediment TP percentage for seven cores that were analysed at relatively high resolution.*

Figure 7: *DI-pH reconstructions and percentage changes in Fe and Ca accumulation rates for seven cores that were analysed at relatively high resolution.*

Lake name	Irish Grid Ref.	Lake code	Typology class	Altitude (m amsl)	Lake area (ha)	Max. depth (m)	pH	Conductivity (µS cm^{-1})	Alkalinity (mg $L^{-1}CaCO_3$)	TP µg L^{-1}	% land cover in catchment					
											URBAN	FORESTRY	PASTURE	AGRICULT	BOGS	OTHER
Annaghmore	M 900 837	ANN	10	46	53.1	5.7	8.46	351	159.4	6	0.00	0.00	91.44	0.00	0.00	8.56
Arderry	L 995 457	ARD	4	37	81.1	11.6	6.33	84	6.14	6	0.00	9.51	0.00	0.00	90.49	0.00
Ballynakill (Gorumna)	L 856 225	BAL	6	13	23.9	16.4	7.1	244	20.02	5	-	-	-	-	-	-
Bane	N 550 712	BAN	12	112	75.4	16.9	8.43	297	132.5	5	0.00	0.00	94.94	4.68	0.00	0.39
Barfinnihy	V 850 768	BAF	3	249	13.6	16.7	6.84	56	4.2	4	0.00	0.00	0.00	0.00	95.30	4.70
Barra	B 935 120	BAR	2	90	62.6	6.0	6.31	54	3.80	5	0.00	0.00	1.78	0.00	62.04	36.18
Bunny	R 375 967	BUN	10	17	102.9	11.6	8.47	361	156.2	5	0.00	0.00	36.70	0.74	1.22	61.33
Cloonaghlin	V 610 709	CLO	4	109	127.7	29.4	6.82	62	2.0	5	0.00	0.00	0.00	0.00	70.41	29.59
Cullaun	R 315 905	CUL	12	16	49.7	20.1	8.40	393	172.0	6	0.00	0.00	72.15	5.44	0.41	22.01
Dan	O 150 40	DAN	4	200	102.9	33.5	5.11	42	-0.1	6	0.00	8.75	1.01	0.00	51.79	38.45
Doo	C 359 394	DOO	3	283	9.0	6.8	5.88	78.1	2.05	12	0.00	0.00	0.00	0.00	100.00	0.00
Dunglow	B 782 117	DUN	2	13	61.2	6.1	5.73	100	59.63	6	0.00	0.00	1.31	4.37	93.83	0.49
Easky	G 442 225	EAS	2	180	119.2	11.0	6.53	48	4.04	7	0.00	0.00	0.00	0.00	100.00	0.00
Fad Inishowen East	C 539 439	FAD	3	233	12.3	13.6	6.35	80.9	5.02	7	0.00	0.00	0.00	0.00	49.08	50.92
Fee	L 790 613	FEE	4	47	173.7	31.5	6.55	62	3.06	9	0.00	14.02	0.00	0.00	72.46	13.51
Feeagh	F 965 000	FEA	4	11	394.8	43.0	7.39	86	9.60	8	0.00	22.69	0.10	1.62	63.95	11.65
Keel (Rosses)	B 847 162	KEE	1	136	11.4	10.5	5.3	135	2.4	8	0.00	0.00	0.00	0.00	99.91	0.09
Kiltooris	G 676 972	KIL	6	7	43.5	13.5	7.18	205	27.43	14	0.00	0.00	47.87	10.73	17.97	23.42
Kindrum	C 185 430	KIN	8	8	60.8	11.0	8.27	318	69.47	11	0.00	0.00	18.49	22.16	59.34	0.00
Kylemore	L 770 552	KYL	4	35	132.2	25.1	6.59	72	6.99	6	0.00	11.87	0.00	0.24	66.61	21.28
Lene	N 510 685	LEN	12	93	416.2	19.7	8.46	250	104.9	6	0.00	0.00	78.92	11.62	0.00	9.46
McNean	H 040 400	MCN	8	50	977.8	16.9	7.60	116	23.6	17	0.00	13.39	26.36	20.64	22.72	16.89
Muckanagh	R 370 925	MUC	12	17	96.1	17.8	8.53	462	208.6	5	0.00	0.00	55.29	9.18	21.74	13.79
Nahasleam	L 971 244	NAH	1	33	28.1	1.4	6.5	100.8	9.59	7	0.00	5.86	0.00	0.00	92.75	1.39
Nambrackkeagh	L 821 603	NAB	1	65	6.7	8.8	5.98	101	2.26	10	0.00	44.21	0.00	0.00	53.32	2.47
Naminn	C 396 419	NAM	1	150	15.0	7.8	6.55	112	7.0	10	0.00	0.00	0.00	0.00	100.00	0.00
Naminna	R 176 710	NAN	1	169	20.2	8.4	6.02	77	0.7	8	0.00	36.55	0.00	0.00	63.45	0.00
O'Flynn	M 585 795	OFL	10	77	137.5	3.4	8.51	333	138.9	10	0.52	0.00	54.12	0.00	42.04	3.32
Oorid	L 930 460	OOR	4	45	60.5	12.0	6.40	65	8.06	7	0.00	3.10	0.00	4.73	92.17	0.00
Rea	M 615 155	REA	12	81	301.1	20.9	8.54	308	128.5	6	3.07	0.00	86.73	10.20	0.00	0.00
Shindilla	L 960 460	SHI	4	38	70.2	23.0	6.45	73	6.17	4	0.00	5.69	0.00	0.00	94.31	0.00
Talt	G 398 150	TAL	8	130	97.3	23.0	8.01	190	85.09	8	0.00	0.81	26.12	0.00	73.07	0.00
Tay	O 160 75	TAY	4	250	50.0	32.8	5.12	40	-0.3	8	0.00	0.58	0.00	0.00	59.09	40.34
Upper	V 900 817	UPE	4	18	169.9	36.1	6.41	58	2.8	5	0.00	6.30	0.44	2.50	83.72	7.04
Veagh	C 022 215	VEA	4	40	260.9	28.0	6.30	33	2.16	0	0.25	3.15	0.00	0.00	65.19	31.41

Table 1

Training set reference	Number of lakes	Estimation		Prediction	
		RMSE	r^2	RMSEP	r^2
Irish lakes pH	35	0.282	0.93	0.427	0.86
(this paper)				(jack)	
Irish lakes TP	45	0.174	0.84	0.202	0.64
(this paper)				(jack)	
SWAP pH	167	0.230	0.91	0.290	0.86
Birks et al. (1990)				(jack)	
ALPE pH	118	0.133	0.97	0.326	0.82
Cameron et al. (1999)				(jack)	
NW Europe TP	152	0.150	0.91	0.210	na
Bennion, Juggins & Anderson (1996)				(jack)	
N Irish TP	43	0.172	0.75	Na	na
Anderson, Rippey & Gibson (1993)					
SE England TP	30	0.160	0.79	0.280	na
Bennion (1994)				(boot)	

Table 2

Lake	Typology class	Length of core (cm)	Estimated depth 1850 ± 25 (cm)	Estimated depth 1950 ± 10 (cm)	Estimated depth 1980 ± 5 (cm)	Estimated age of bottom diatom sample	Estimated sediment accumulation rate (cm yr^{-1})
Annaghmore	10	20	17-19	5-7	2-3	1834	0.12
Arderry	4	36	>9?				
Ballynakill	6	36	29-35	10-13	4-5.5	1831	0.21
Bane	12	17	4.5-8?	1.5-3?	0.5-1?		
Barfinnihy	3	40	>9?				
Barra	2	36	50-63	17-22	7.5-9	1905	0.37
Bunny	10	25	21-24	7-8.5	3-4	1833	0.15
Cloonaghlin	4	34	9-17?	3-6?	1-2.5?		
Cullaun	12	31	8-14?	2.5-5?	1-2.5?		
Dan	4	31	43-57	15-20	6.5-8.5	1909	0.33
Doo	3	31	72-86	25-30	10.5-13	1944	0.53
Dunglow	2	11	13-15	4-6	2-3	1885	0.09
Easky	2	27	23-27	8-9	3-4	1838	0.16
Fad	3	27	>27	6-7	2-4		
Fee	4	38	10-18?	3.5-6.5?	1.5-3?		
Feeagh	4	36	66-76	23-27	10-12	1926	0.47
Keel	1	41	28-30	11-15	3-4.5	1788	0.19
Kiltooris	6	34	66-110	23-40	10-19	1944	0.58
Kindrum	8	30	20-22	7-8	3-4	1776	0.13
Kylemore	4	40	>10?				
Lene	12	29	>29				
McNean	8	19	12-14	3.5-5	1.5-2.5	1950	0.36
Muckanagh	12	42	31-40?	10.5-14?	4.5-6?		
Nahasleam	1	27.5	8-14?	2.5-5?	1-2.5?		
Nambrackkeagh	1	26.5	17-21	6-7	2.5-3.5	1789	0.12
Naminn	1	30	22-24	6-7	2.5-3.5	1804	0.15
Naminna	1	26.5	8-15?	2.5-5.5?	1-2.5?		
O'Flynn	10	42	>42				
Oorid	4	39	>10?				
Rea	12	36	9-17?	3-6?	1-2.5?		
Shindilla	4	29	18-21	6-7	2.5-3.5	1775	0.13
Talt	8	22	18-21	5.5-7	2.5-3.5	1830	0.13
Tay	4	36	>36				
Upper	4	40.5	35-40	11-14	4.5-6	1840	0.25
Veagh	4	34	c. 60	c. 20	c. 9		

Table 3

Lakes	**Lake codes**	**Typology class**	**SCD**	**SD Hill's units**	**Change in DI-pH units**	**Prop. change in DI-TP**
Annaghmore	ANN	10	0.835	1.118	0.11	0.95
Arderry	ARD	4	0.859	1.797	-0.08	1.31
Ballynakill	BAL	6	0.509	1.24	-0.09	1.09
Bane	BAN	12	0.557	1.112	0.21	1.01
Barfinnihy	BAF	3	0.139	0.731	0.03	1.04
Barra	BAR	2	0.409	0.986	-0.01	1.01
Bunny	BUN	10	0.351	0.94	0.03	0.90
Cloonaghlin	CLO	4	1.599	1.416	0.39	1.31
Cullaun	CUL	12	1.302	1.376	-0.29	1.18
Dan	DAN	4	0.410	0.806	-0.43	0.96
Doo	DOO	3	0.259	1.139	-0.21	1.02
Dunglow	DUN	2	0.171	1.176	-0.08	0.97
Easky	EAS	2	1.034	1.1	-0.47	1.08
Fad	FAD	3	-	-	-	-
Fee	FEE	4	0.967	1.494	-0.09	2.05
Feeagh	FEA	4	1.769	1.822	-0.19	1.89
Keel	KEE	1	0.319	1.1	-0.14	1.31
Kiltooris	KIL	6	0.288	1.171	-0.02	1.03
Kindrum	KIN	8	0.423	1.26	0.25	1.25
Kylemore	KYL	4	1.044	1.551	-0.76	0.91
Lene	LEN	12	0.478	1.001	0.06	1.01
McNean	MCN	8	0.148	1.056	0.15	1.14
Muckanagh	MUC	12	0.458	0.884	-0.12	1.10
Nahasleam	NAH	1	0.296	0.787	-0.10	1.03
Nambrackkeagh	NAB	1	0.75	0.984	0.12	1.25
Naminn	NAM	1	0.562	1.205	-0.05	1.09
Naminna	NAN	1	0.735	1.123	-0.30	0.92
O'Flynn	OFL	10	0.327	1.045	0.19	0.83
Oorid	OOR	4	0.987	1.715	-0.19	1.08
Rea	REA	12	0.472	1.554	-0.25	1.02
Shindilla	SHI	4	0.416	1.039	0.10	1.20
Talt	TAL	8	0.96	1.508	-0.25	0.99
Tay	TAY	4	1.169	1.069	-0.58	0.58
Upper	UPE	4	0.046	1.019	-0.09	0.98
Veagh	VEA	4	0.245	0.923	0.05	1.01

Table 4

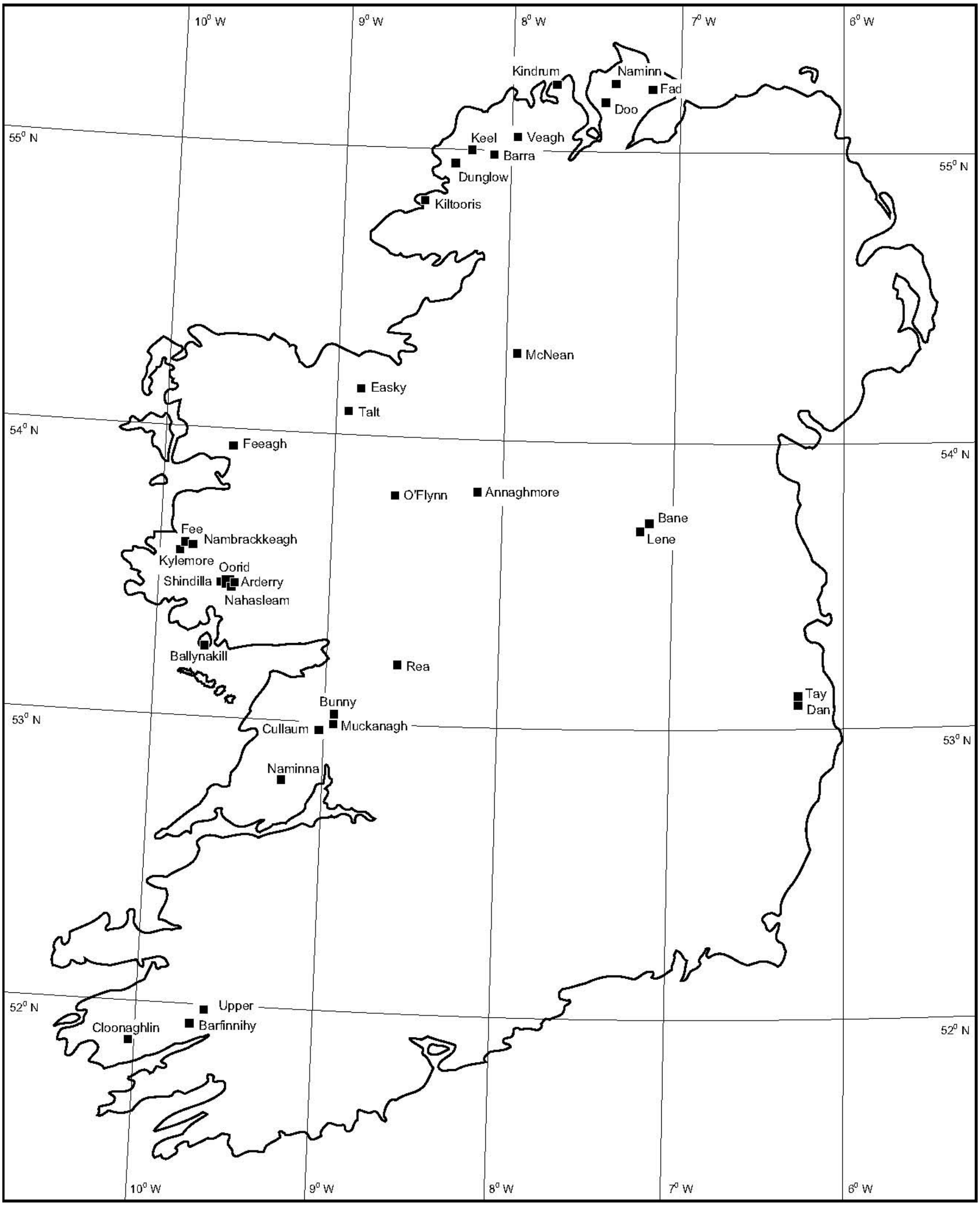
10° W
9° W
8° W
7° W
6° W
55° N
54° N
53° N
52° N
Kindrum
Naminn
Fad
Doo
Keel
Veagh
Barra
Dunglow
Kiltooris
McNean
Easky
Talt
Feeagh
O'Flynn
Annaghmore
Bane
Lene
Fee
Nambrackkeagh
Kylemore
Oorid
Shindilla
Arderry
Nahasleam
Ballynakill
Rea
Bunny
Tay
Dan
Cullaum
Muckanagh
Naminna
Upper
Barfinnihy
Cloonaghlin

Figure 1

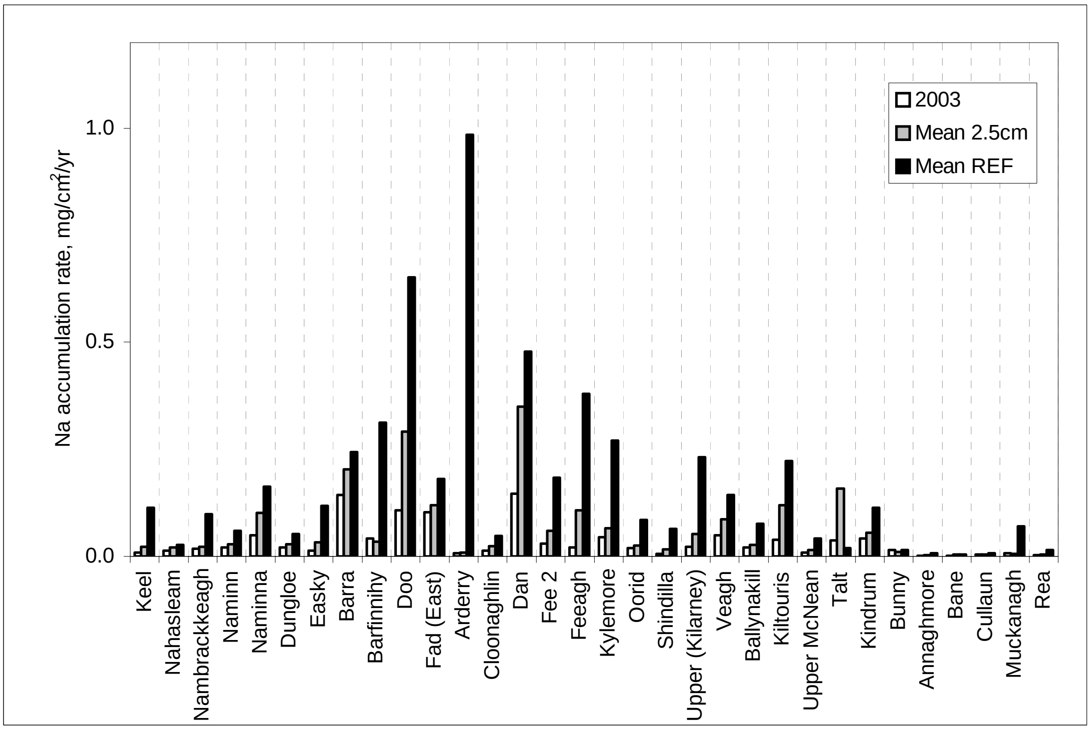

Figure 2a

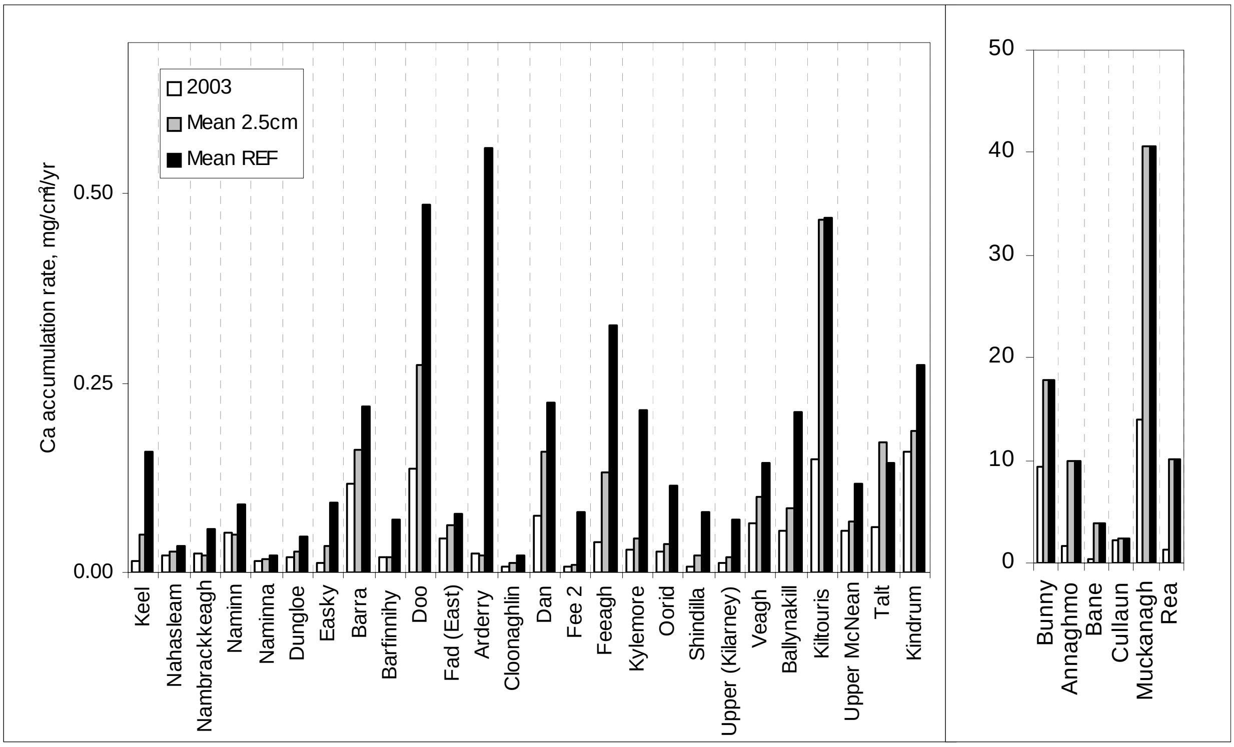

Figure 2b

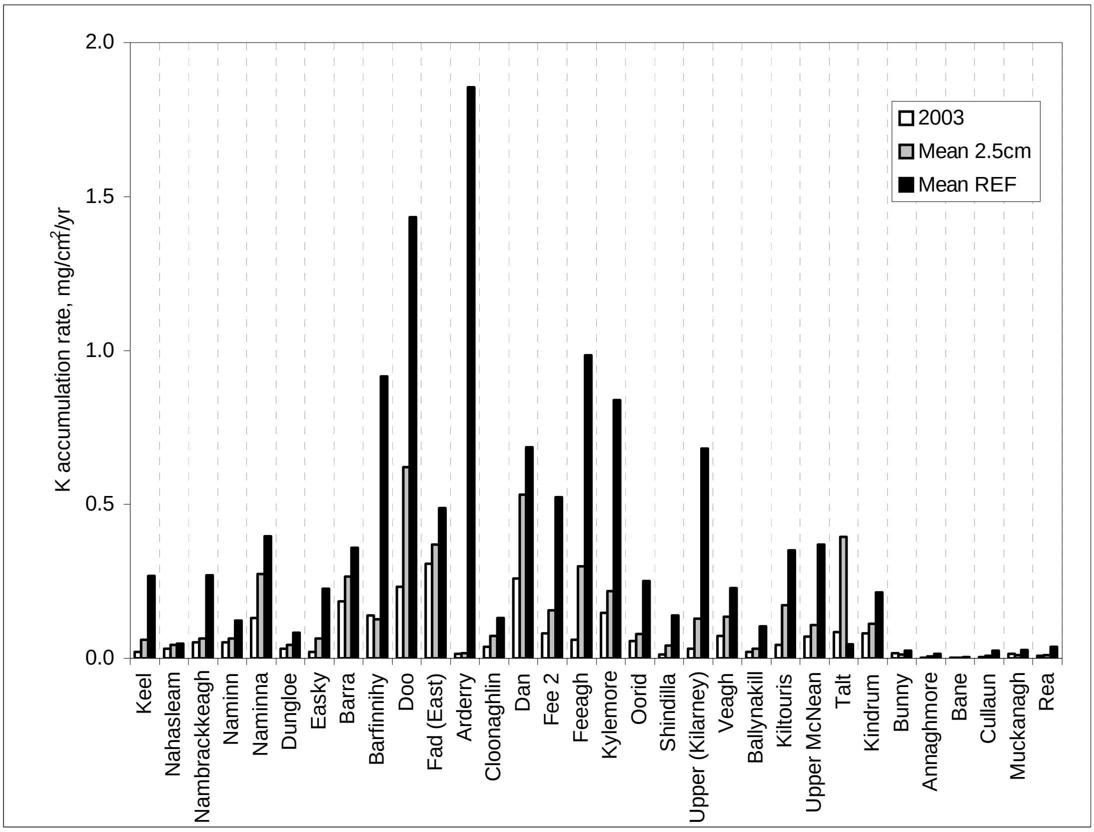
K accumulation rate, mg/cm^2/yr
2.0
1.5
1.0
0.5
0.0
2003
Mean 2.5cm
Mean REF
Keel
Nahasleam
Nambrackkeagh
Naminn
Naminna
Dungloe
Easky
Barra
Barfinnihy
Doo
Fad (East)
Arderry
Cloonaghlin
Dan
Fee 2
Feeagh
Kylemore
Oorid
Shindilla
Upper (Kilarney)
Veagh
Ballynakill
Kiltouris
Upper McNean
Talt
Kindrum
Bunny
Annaghmore
Bane
Cullaun
Muckanagh
Rea

Figure 2c

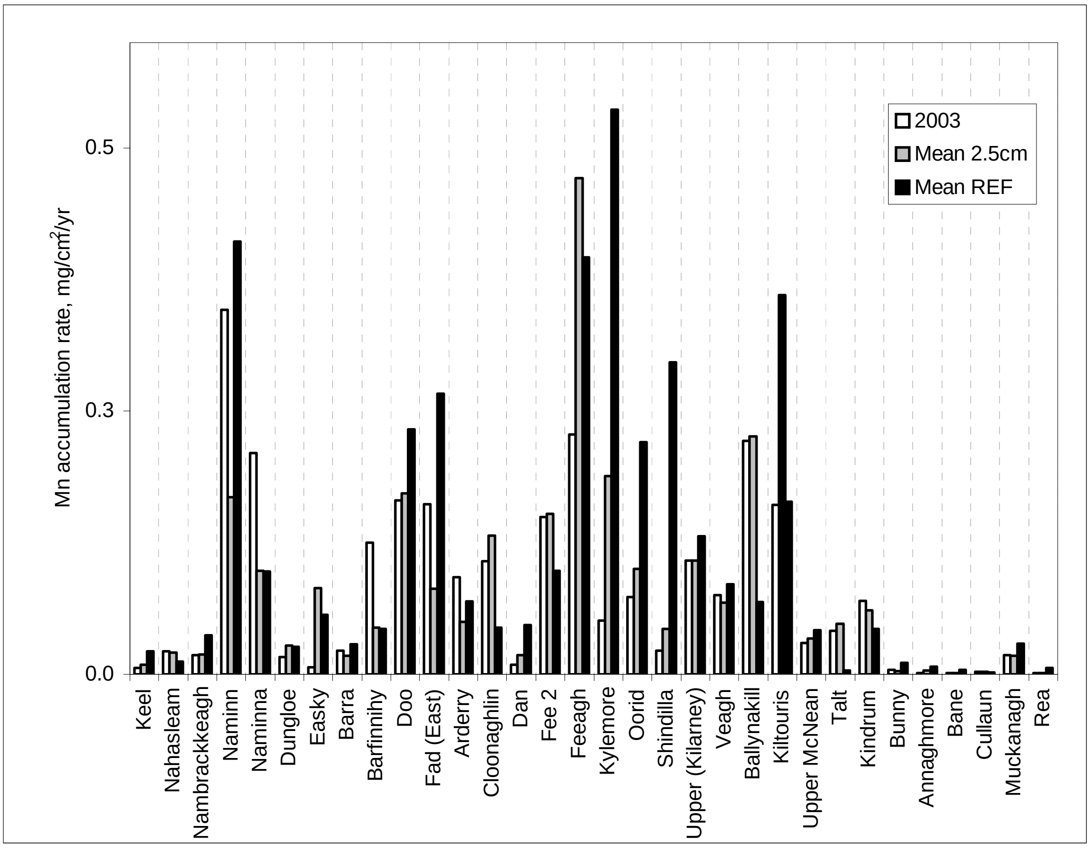

Figure 3a

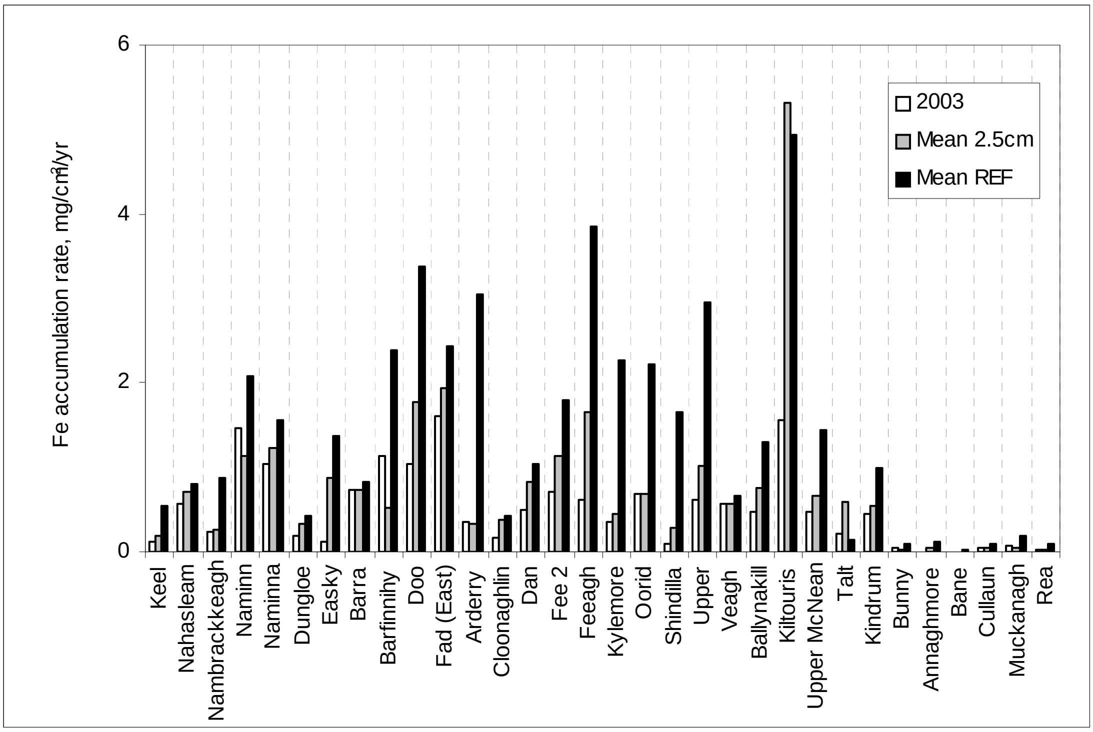

Figure 3b

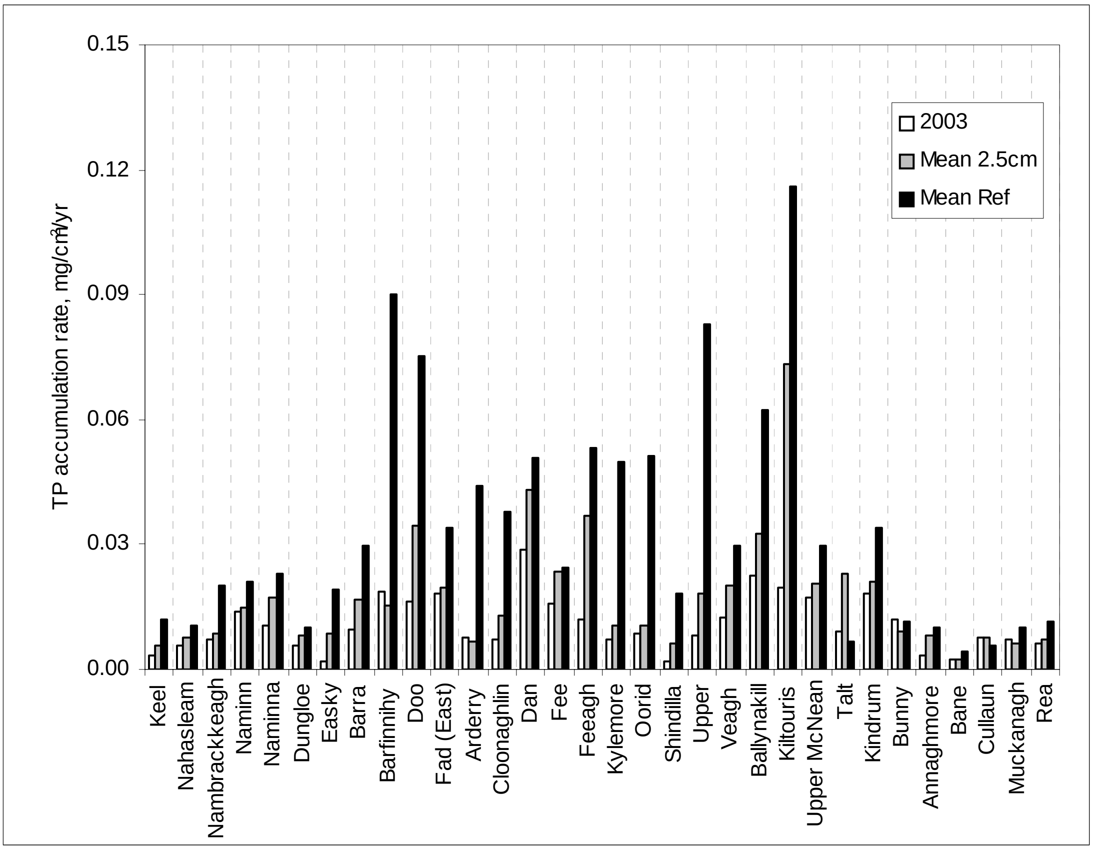
TP accumulation rate, mg/cm²/yr
0.15
0.12
0.09
0.06
0.03
0.00
□ 2003
▨ Mean 2.5cm
■ Mean Ref
Keel
Nahasleam
Nambrackkeagh
Naminn
Naminna
Dungloe
Easky
Barra
Barfinnihy
Doo
Fad (East)
Arderry
Cloonaghlin
Dan
Fee
Feeagh
Kylemore
Oorid
Shindilla
Upper
Veagh
Ballynakill
Kiltouris
Upper McNean
Talt
Kindrum
Bunny
Annaghmore
Bane
Cullaun
Muckanagh
Rea

Figure 4

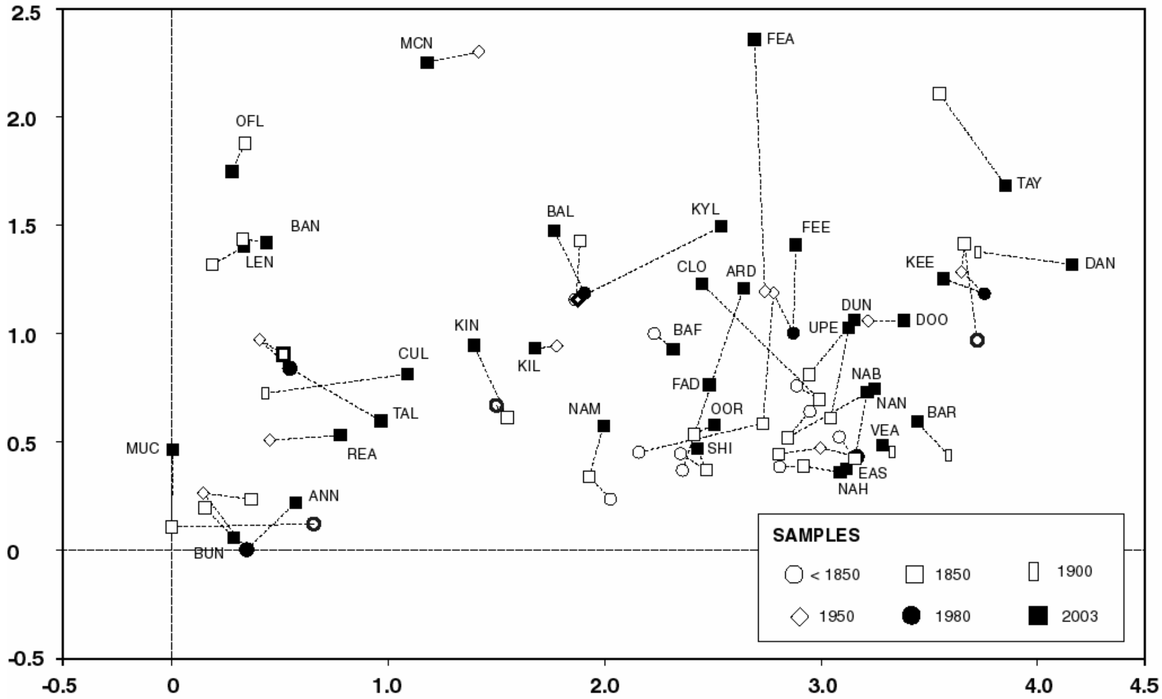
2.5
2.0
1.5
1.0
0.5
0
-0.5
-0.5
0
1.0
2.0
3.0
4.0
4.5
MCN
FEA
OFL
TAY
BAN
LEN
BAL
KYL
FEE
CLO
ARD
KEE
DAN
DUN
DOO
UPE
KIN
BAF
CUL
KIL
FAD
NAB
NAN
TAL
NAM
OOR
BAR
VEA
MUC
REA
SHI
EAS
NAH
ANN
BUN
SAMPLES
< 1850
1850
1900
1950
1980
2003

Figure 5

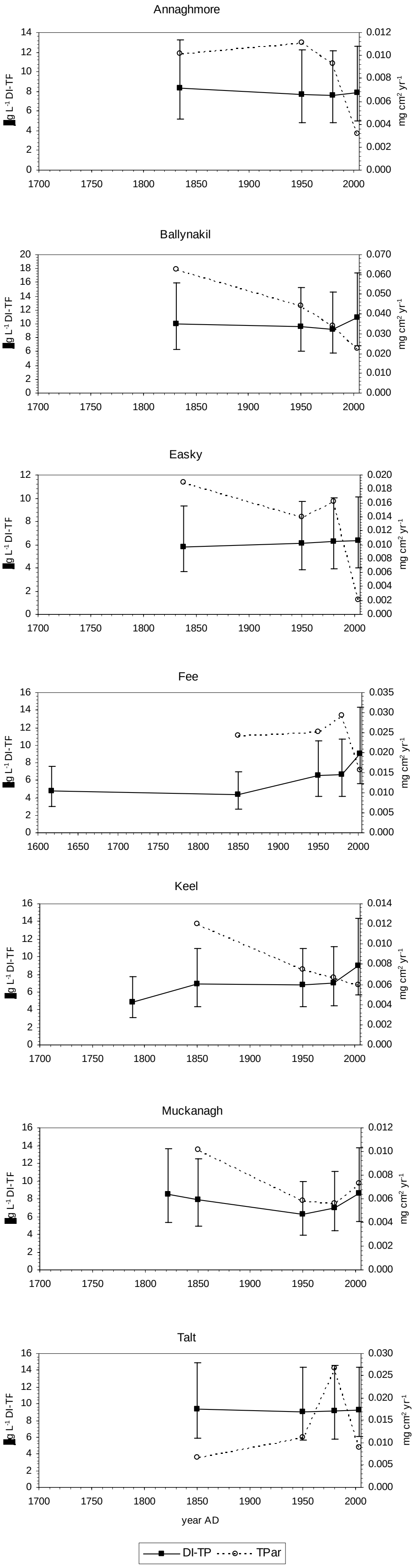
Annaghmore
0 2 4 6 8 10 12 14
0.000 0.002 0.004 0.006 0.008 0.010 0.012
Ballynakil
0 2 4 6 8 10 12 14 16 18 20
0.000 0.010 0.020 0.030 0.040 0.050 0.060 0.070
Easky
0 2 4 6 8 10 12
0.000 0.002 0.004 0.006 0.008 0.010 0.012 0.014 0.016 0.018 0.020
Fee
0 2 4 6 8 10 12 14 16
0.000 0.005 0.010 0.015 0.020 0.025 0.030 0.035
1600 1650 1700 1750 1800 1850 1900 1950 2000
Keel
0 2 4 6 8 10 12 14 16
0.000 0.002 0.004 0.006 0.008 0.010 0.012 0.014
Muckanagh
0 2 4 6 8 10 12 14 16
0.000 0.002 0.004 0.006 0.008 0.010 0.012
Talt
0 2 4 6 8 10 12 14 16
0.000 0.005 0.010 0.015 0.020 0.025 0.030
1700 1750 1800 1850 1900 1950 2000
µg L-1 DI-TF
mg cm2 yr-1
year AD
DI-TP
TPar

Figure 6

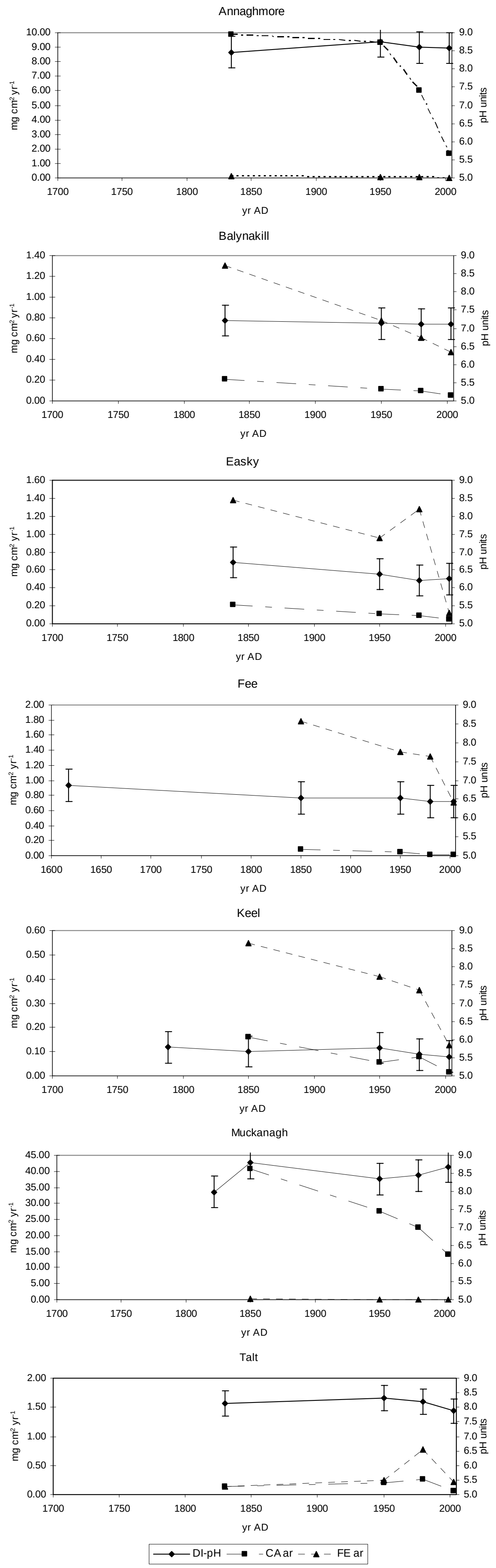
Annaghmore
Balynakill
Easky
Fee
Keel
Muckanagh
Talt
mg cm^2 yr^{-1}
pH units
yr AD
1600
1650
1700
1750
1800
1850
1900
1950
2000
DI-pH
CA ar
FE ar

Figure 7