A reference typology of upland lakes in the UK based on pre-acidification diatom assemblages from lake sediment cores

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Abstract

This paper has two aims: (i) to show for the first time how a natural typology can be established using palaeoecological methods; and (ii) to show how it can be used in lake restoration studies with respect to the definition of recovery targets for acidified lakes. By defining the characteristic reference assemblages for low alkalinity site types rather than for a specific site it allows success to be measured more broadly, unconstrained by the specific composition of the pre-acidification flora.

We analyse statistically the pre-acidification diatom assemblages of sediment cores from 121 low alkalinity lakes in the UK in order to assess whether a reference typology for such lakes can be defined on the basis of their diatom floras. We use samples dating to approximately 1850 AD to represent pre-acidification conditions. The results show that three main clusters can be identified, two dominated by benthic taxa (Clusters 1 and 3) and one dominated by planktonic taxa (Cluster 2). Cluster 1 is characterised by taxa such as *Brachysira vitrea*, *Cymbella microcephala* and *Fragilaria* spp., Cluster 2 by *Cyclotella comensis*, *C. radiosa*, *Asterionella formosa*, *Aulacoseira subarctica* and *Achnanthes minutissima* and Cluster 3 by *Eunotia incisa*, *Frustulia rhomboides* var. *saxonica*, *Fragilaria virescens* var. *exigua*, and *Cymbella perpusilla*. Although environmental data for 1850 AD are not available it is apparent from the contemporary distribution of the taxa in the different clusters that Cluster 2 represents the most alkaline pre-acidification conditions. Some sites in this cluster have been acidified, but some, especially the larger, deeper lakes have been enriched. Cluster 1 includes sites that contain diatoms with relatively high pH optima (pH 6.4-7.4 whereas Cluster 3 sites contain diatoms with the lowest pre-acidification pH conditions in the data-set. Sites in this cluster also have the lowest base cation concentrations at the present day and include the sites in the UK that have been most affected by acid deposition.

Keywords: diatoms, diatom-inferred pH, acidification, reference conditions, lake typology, low alkalinity lakes

Introduction

Surface water acidification became a prominent environmental issue in Europe and North America in the 1980s following observations of declining fish populations in rivers and lakes in Scandinavia (Jensen and Snekvik 1972; Almer et al. 1974) and Canada (Beamish and Harvey 1972). Major research programmes in both North America and Europe demonstrated conclusively that acidification was caused by sulphur (S) and nitrogen (N) gas emissions from the combustion of fossil fuel and that the effects of acidification were not limited to fish populations but included significant modification of all trophic levels in low alkalinity freshwater ecosystems in regions with high acid deposition. Following the decline in acid emissions in recent decades (Vestreng et al. 2007) many lakes and streams are showing signs of chemical and biological recovery. Key questions now are: (i) what was the status of low alkalinity water bodies prior to acidification by acid deposition? (ii) what is the current state of acidified water bodies in comparison to their pre-acidification (or reference state)? (iii) are acidified lakes and streams returning towards their pre-acidification state? (iv) how much progress has been made in reaching that state? and (v) to what extent is the recovery being deflected by other processes, e.g. as a result of the confounding influences of nitrogen deposition or climate change?

Here we address the first of these questions for UK lakes. The natural or reference state of low alkalinity lakes prior to acidification is a central issue relevant not only to an assessment of whether lakes are recovering from acidification but more specifically to an assessment of the degree and direction of recovery. The question can only be addressed using palaeoecological techniques as there are no instrumental records in the UK, or indeed globally, that are sufficiently long to document conditions in pre-acidification times. The oldest observations for pH and alkalinity are from the English Lake District from 1928 (Sutcliffe et al. 1982) but even these early records post-date the first palaeoecological evidence for the beginning of acidification by several decades. Palaeoecological research conducted over the last 30 years indicates that the onset of acidification in the UK occurred predominantly in the 19th century (Battarbee 1984, Battarbee et al. this volume). Diatom analysis has been the premier technique used as diatoms are well preserved in the sediments of acid lakes (cf. Cameron 1995) and provide a robust measure of acidity change (cf. Battarbee et al. 2008).

Until now most interest in the pre-acidification reference period has focussed on the use of diatoms in reconstructing pH, with the emphasis on establishing target pHs for recovery (Battarbee et al. 2008) or establishing pH histories for comparison with hindcasts from dynamic model output (e.g. Battarbee et al. 2005). In this paper we focus on the biological record *per se* and use the pre-acidification diatom assemblages from sediment cores not as indicators of pH but as a means of assessing the biological variability of low alkalinity lakes prior to the impact of acid deposition. Although low alkalinity lakes (defined as alk <0.2 meq/l in the lake typology for ecoregion 18 (Great Britain-GB) (Phillips 2003)) are regarded as a single type of lake within the context of this wider lake classification scheme, they vary considerably with respect to many biologically significant factors including catchment characteristics (geology, soils, vegetation, hydrology), lake characteristics (altitude, area, depth, shoreline extent) and water chemistry (e.g. base cations, pH, alkalinity, conductivity, colour). These properties vary in space and some vary in time. They act separately and in combination in influencing the structure and dynamics of diatom communities in low alkalinity lakes.

Future work will attempt to examine the relationship between environmental variables and diatom assemblage composition during the immediate pre-acidification time period. Such an analysis is precluded until we can assemble a plausible range of pre-acidification values for those potentially explanatory environmental variables, such as base cation concentration, DOC, temperature, that are likely to have changed as a result of the acidification process itself. Here, consequently, we base our analysis solely on the varying composition of the diatom assemblages preserved in the pre-acidification sediment record and use it to identify a natural classification or typology of low alkalinity lakes for the UK.

Sites

The database for this study includes diatom analyses that have been compiled over the last 30 years consisting of records from 121 sites, with alkalinity < 200 μeq/l, (Figure 1) and comprising data from many different research projects that have been conducted since 1980. Consequently there is some inconsistency in the data available. Chemical data are missing for some sites and in cases where measured alkalinity data were not available an alkalinity class (less than 200 μeq/l) was inferred from catchment geology following the method of Phillips (2003). For the same reason the sites are not ordered systematically along specific geographical or chemical gradients. They do, however, cover a wide range of the low alkalinity site-types found in the UK today as reflected by their distribution (Figure 1), their sensitivity to acidification, indicated by current alkalinity and by their degree of acidification (Table 1).

All sites contain diatom-rich early nineteenth-century sediments, and the samples used in the analysis were selected from each core to represent conditions occurring in the lakes during the pre-acidification period taken here as 1850 AD in cases where core chronologies were available, or the base of the core where there was no chronology. The core tops differ in date according to the date of sampling, varying from the late 1980s to 2003. In almost all cases the core-top assemblage can be assumed to represent the diatom populations growing in the lake at approximately the time of maximum acidity. For some sites, diatom analyses are available over the full length of the cores whereas only "top" and "bottom" records are available for others sites. Fourteen sites currently contain sediment traps that are emptied annually and eleven of these sites form part of the UK Acid Waters Monitoring Network and are used specifically to assess responses to the reduction in acid deposition that has taken place over the last 20 years or so in the UK (cf. Monteith and Evans 2005).

Methods

Although the diatom data used here were generated by different analysts at different times the slides were prepared according to the same standard techniques (e.g. Battarbee et al. 2001) and 300-500 individual valves were identified and counted using x 100 oil immersion objectives in either phase contrast, differential interference contrast or brightfield. The taxonomy and nomenclature used follows the protocol developed for the SWAP project (Stevenson et al. 1991). Problematic taxa were identified with the aid of a range of reference floras, especially those by Krammer and Lange-Bertalot (1986, 1988, 1991a,b). Observations for all taxa, expressed as proportions of the total sample count, were used in the data analysis.

Diatom reference assemblages were derived by cluster analysis of the diatom data. Pair-wise Euclidean distances between samples were computed on the Hellinger transformed (Legendre and Gallagher 2001) diatom data and then analysed using minimum variance clustering. The Hellinger transformation has been shown to be a good distance coefficient for closed compositional data of this kind (Overpeck et al. 1985). Analysis of the resulting dendrogram identified three broad groups of diatom assemblages. This hierarchical analysis was further optimised using *k*-means clustering starting from the *k*=3 solution of the minimum variance cluster analysis.

Principal components analysis (PCA) of the centred and standardised, Hellinger transformed diatom data was used to visualise relationships among samples and reference assemblages in terms of diatom species composition. Cluster centroids were superimposed upon ordination diagrams by predicting the locations in PCA axis 1 and 2 space for samples representing mean species composition for each cluster. All ordinations are displayed using symmetric scaling.

Indicator species analysis for the three reference assemblages was performed following the methodology of Dufresne and Legendre (1997). Significant indicator species values were determined via 1000 random permutations.

As there are no direct observations for lake water acidity for the early nineteenth century we use diatom-inferred pH values for core “bottoms” and “tops” to indicate the probable range of pH values for these low alkalinity lakes prior to the impact of acid deposition and to show the inferred change in pH that has taken place for the acidified sites in the data-set. The pH values for core “top” and “bottom” samples were calculated using simple weighted averaging (WA) with inverse deshrinking fitted to the EDDI combined pH data set (http://craticula.ncl.ac.uk/Eddi). EDDI was preferred over other training sets due to its good performance against measured pH at the Acid Waters Monitoring Network sites (Battarbee et al. 2008) and its greater size, potentially enabling better analogue matching between the pre-acidification samples and the training set samples. Bootstrap-derived root-mean-squared error of prediction ($\mathrm{RMSEP}_{\mathrm{boot}}$) for this model is 0.44 based on 1000 bootstrap samples. pH optima for indicator taxa were computed on the basis of the distribution of each taxon as a function of measured pH using abundance data from the EDDI combined-pH training set

The contemporary calcium values were obtained using standard water chemistry analytical techniques, and pre-acidification calcium values (Ca_{ref}) were calculated using the "F-factor" approach (Brakke et al. 1990) employed in critical loads modelling (Henriksen et al. 1992; Battarbee et al. 1996). Here we use F to estimate reference non-marine calcium concentration "Ca_{ref}" as follows:

$Ca^* = Ca - (0.037 \times Cl)$

$Ca_{ref} = Ca^* - F(SO_4^* + NO_3 - SO_{4ref})$

where F and SO_{4ref} are estimated empirically according to the methods in Battarbee et al. (1996) and Henriksen et al. (1992) respectively.

Calcium is used because it is generally the dominant base cation associated with alkalinity production (bicarbonate) in catchment soils and is usually highly correlated with alkalinity. Non-marine calcium (Ca^{*}), corrected using chloride concentrations to determine the marine component, is used because only this fraction of total Ca is associated with bicarbonate production; the remaining marine component is associated with neutral sea-salt inputs.

Results

Figure 2 shows a PCA ordination of the diatom assemblages for the core "bottom" samples by site. It also shows the percentage variance accounted for by the main axes. The minimum variance clustering analysis indicates that the assemblages can be divided into three clusters. The distribution of some of the principal indicator taxa in the clusters are shown in Figures 3 - 5.

Cluster 1

The indicative taxa for cluster 1 are listed in Table 2. All are benthic taxa and some, such as *Fragilaria construens* var. *venter* and *F. pinnata* (Figure 3a,b) are almost entirely restricted to this group. *Brachysira vitrea* on the other hand, is more widespread, and it occurs in some abundance across sites in all clusters (Figure 3c). The remaining taxa in the group are found only in low numbers, but at many sites. The weighted average pH optima for the different taxa of this cluster range from pH 6.4 – 7.4 (Table 2).

The sites in Cluster 1 are listed in Table 1 together with diatom-inferred pH values for the bottom and top samples and the contemporary measured water pH. Although these sites have relatively high pre-acidification pH levels they are sensitive to acidification. Full core analysis has been carried out for several sites including Llyn Irddyn (IRD), and Loch nan Eun (EUN) (Battarbee et al. 1988; Jones et al. 1993) both of which have been acidified due to their location in areas of high acid deposition. Other sites in this cluster for which core analysis has been carried out, such as Lough Maumwee (MWEE), Loch Uisge (UIS) and Loch Corrie nan Arr (ARR) still have relatively high pH levels at the present day (Table 1) and remain unacidified or only slightly acidified (Flower et al. 1993, 1994) due to their location in regions of low acid deposition in Ireland and North-west Scotland.

Cluster 2

The indicative taxa of Cluster 2 are listed in Table 2. They are dominated by planktonic taxa, especially *Cyclotella comensis*, *C. radiosa*, *Asterionella formosa* and *Aulacoseira subarctica,* all of which are more or less confined to this cluster (Figure 4a-d). All taxa have relatively high pH optima (Table 3). The only abundant non-planktonic taxon in this group is *Achnanthes minutissima* that co-occurs at the planktonic rich sites in Cluster 2 but is also very abundant in the benthic diatom dominated sites in Cluster 1 (Fig 4e).

There are few sites in this group (Table 1). One, Loch Dee (LDE) is known to have acidified and lost its planktonic diatom flora (Flower et al. 1987). Others, predominantly the larger, deeper sites, (e.g. Loch Lomond (LOMO), Wastwater (WAST), Lake Bala (BALA)) have not acidified although they have low alkalinity water and are located in areas of historically high acid deposition.

Cluster 3

The indicative taxa for cluster 3 are listed in Table 2. As for cluster 1 but unlike cluster 2 they are all benthic taxa but are characteristic of more acidic waters (pH optima from 4.9 – 6.4) than the taxa in either clusters 1 or 2. Many belong to the *Eunotia* genus that tend to be confined to acid waters, although *E. incisa* has a somewhat more widespread distribution (Figure 5a). *Fragilaria virescens* var. *exigua* is also an indicator of this group, but occurs also in some abundance in Group 1 (Figure 5b) reflecting its preference for less acidic waters. *Brachysira brebissonii*, *Frustulia rhomboides* var. *saxonica*, and *Cymbella perpusilla*, are more restricted to cluster 3 (Figure 5 c-e). *Tabellaria quadriseptata*, a taxon that has increased at many sites due to acidification also occurs in this cluster (Figure 5f) indicating that there were a number of naturally quite acidic sites in the UK before the beginning of the recent acidification period. These include Loch Enoch (ENO) and Loch Narroch (NARR) in the Galloway region. Many of the sites in this group, although beginning to recover, are now among the most acidified sites in the UK. Examples include Blue Lough (,BLU), Loch Enoch (ENO), the Round Loch of Glenhead (RLGH), Loch Grannoch (LGR), Loch Narroch (NARR), Loch Neldricken (NELD), Loch Valley (VAL), and Woolmer Pond (WOOL) (Battarbee et al. 1988; Flower & Beebee 1987).

Discussion

Low alkalinity lakes (< 0.2 meq/l) constitute a single type in the lake classification schemes used in the EU Water Framework Directive (Phillips 2003) but low alkalinity lakes can vary substantially with respect, for example, to pH, base cation concentration, marine influence, dissolved organic carbon (DOC) as well as altitude, depth, and habitat structure. Many of the sites, those with naturally low alkalinity in areas of high acid deposition have been acidified (cf. Battarbee et al. 1996) causing changes not only in pH, but also, for example, in base cation concentration (Henriksen 1979) and DOC (Monteith et al. 2007). As a result any lake typology based on contemporary chemistry and/or biology would predominantly reflect the impact of pollution over the last 150 years rather than define a natural classification. Consequently here we attempt to develop a natural typology based on the pre-acidification diatom records of UK low alkalinity lakes.

Diatoms are extremely abundant, diverse and well preserved in the sediments of low alkalinity lakes and the typology generated here can therefore be assumed to be unbiased by problems of diatom representativity. The typology itself is based only on biological criteria. No attempt has been made at this stage to relate the typology to environmental factors in any quantitative way, although such an analysis may be possible in future if reliable methods can be developed to reconstruct past water chemistry for this time period independent of the diatom data. We have, however, used the diatom-inferred pH data (Figure 6) and the contemporary and retrodicted Ca^{++} data (Figure 7) to provide some basic chemical characterisation of the three clusters that have been identified.

Each of the three clusters contains characteristic taxa that are either widespread across the range of sites, occurring in two or more clusters but most abundant in one cluster, or are restricted to a single cluster. Widespread abundant taxa include *Brachysira vitrea* (Figure 3) that is an indicator of Cluster 1 but occurs also in Cluster 3 and *Achnanthes minutissima* that is an indicator of Cluster 2 but also occurs in abundance in Cluster 1. The most distinctive cluster floristically is Cluster 2 that is characterised principally by planktonic taxa, e.g. *Cyclotella comensis*, *C. radiosa*, *Asterionella formosa* and *Aulacoseira subarctica,* that are more or less restricted to this group (Figure 4). The sites in this cluster are mainly large deep-water lakes that in some cases have subsequently acidified (e.g. Loch Dee (LDE)) and in other cases, e.g. Loch Lomond (LOMO), Lake Bala (BALA) and Loweswater (LOWS), have become more enriched. The latter sites have catchments that contain human settlements and agricultural land. As such, although due to their low alkalinity status they may have been sensitive to acid deposition they have been more influenced by nutrient loading over recent decades. These sites all show clear evidence of eutrophication from their diatom records (Bennion et al. 2000, 2003, 2004). Sites in Cluster 2 tend to have higher pre-acidification pH and Ca levels than other sites (Figure 6, 7), but it is possible that some of these sites have been also buffered from the effects of acid deposition as a result of alkalinity generation from nutrient-related increases in productivity (cf. Davison 1986).

Clusters 1 and 3 are both dominated by benthic diatoms with Cluster 1 being characterised by diatoms found in higher pH waters than those in Cluster 3 (Table 2).

Although Cluster 1 is characterised by taxa typically found in circumneutral waters and Cluster 3 by taxa typical of naturally acidic waters, some taxa occur in both clusters. For example, *Brachysira vitrea* is an indicator of cluster 1 and *Fragilaria virescens* var. *exigua* is an indicator of cluster 3 (Figure 5) but both occur in abundance at sites distributed across the interface between the clusters. Both are dominant in the pre-acidification period of lakes that are very sensitive to acidification and sediment core analysis has shown that both have declined at many sites including the Round Loch of Glenhead (Flower and Battarbee 1983).

Overall, and despite the clear overlap in species occurrences between the clusters, sites at the extremes of the clusters have few species in common and contain floras that represent significantly different water chemistry with respect to pH and base cation concentration (Figure 6, 7).

Cluster 3 contains the sites with the lowest calcium concentration both at the present day, and, it can be assumed, also during the pre-acidification period (Figure 7). The diatom floras of these sites in the past were not only naturally acidophilous but also mainly lacked a natural diatom plankton. Sites in this Cluster are the most sensitive to acidification and all those in the cluster situated in areas of high acid deposition have been acidified. There are however acidified sites also in the somewhat less sensitive Clusters 1 and 2, reflecting the location of those sites in areas of especially high acid deposition.

Today, as acid deposition decreases and lakes begin to recover from acidification it might be expected that the diatom floras of the acidified sites in each of the Clusters should return towards floras contained in these different reference groups even if they do not regain the exact species composition of their pre-acidification conditions. This is especially the case for moorland sites. Although there have been changes in land management in the catchments of moorland sites, especially with respect to grazing intensity and the proportion of cattle to sheep (cf. Patrick et al. 1990), there is little evidence from the sediment records of these sites that these changes have had a detectable influence on lake water chemistry over recent decades. In these cases the acidified sites in Cluster 1 should regain their populations of *Brachysira vitrea* and *Achnanthes minutissima*, those in Cluster 2 should also regain *A. minutissima,* together with their plankton populations, especially *Cyclotella comensis,* and those in Cluster 3 should regain communities dominated by one or more of *Eunotia incisa*, *Frustulia rhomboides* var. *saxonica*, *Fragilaira virescens* var. *exigua, Brachysira brebissonii, B. vitrea* and *Cymbella perpusilla*.

Some acidified sites have had significant parts of their catchments afforested during the last 50 years or so, but all had moorland catchments during the pre-acidification period represented by the samples in this analysis from the early 19th century. In all cases so far studied the acidification of sites that have afforested catchments at the present day began prior to afforestation (cf. Flower and Battarbee 1983; Kreiser et al. 1990) indicating that afforestation was not the primary cause of acidification. However, it is also apparent that catchment afforestation has had a major impact on water quality in many cases through changes to hydrology and soil erosion as well as enhancing the effects of acid deposition (Harriman and Morrison 1982; Kreiser et al. 1990). In these cases, catchment conditions are now significantly different from those in the early 19th century and a reduction in acid deposition may not lead to the restoration of diatom communities that characterised their pre-acidification floras. Sites of this kind occur in all clusters, for example, Loch Skerrow (SKE) in Cluster 1, Loch Dee (LDE) in Cluster 2 and Loch Grannoch (LGR), Llyn Berwyn (BER) and L. cwm Mynach (MYN) in Cluster 3.

There may be other reasons why sites may not regain pre-acidification diatom floras characteristic of these references conditions. It is apparent that at several monitored sites in the UK that nitrate levels are increasing, especially at sites with high historic N deposition where soils at the present day leach nitrate (Curtis et al. 2005), and at all sites it is probable that there have been increases in surface water temperature associated with recent trends in global warming (des Clers et al. 2008). However, the reference assemblages defined here describe the natural range of conditions for low alkalinity lakes before any changes due to acid deposition, catchment afforestation, nitrate leaching or greenhouse gas emissions occurred, and therefore serve as a benchmark that enables the extent and direction of recovery as a result of the reduction in acid deposition to be measured.

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Table 1.

Site	Name	Clu.	Long.	Lat.	EqAlk	pH (obs)	pH (t)	pH (b)	pH (b-t)
ARR	Loch Coire nan Arr	1	-5.65	57.42	49.06	6.3	5.88	5.91	0.03
BEIS	Loch na Beiste	1	-5.57	57.89	42	6.18	6.38	6.29	-0.09
BLWY	Llyn Bochlwyd	1	-4.01	53.11	na	5.45	5.25	6.35	1.1
CADH	Loch Dubh Cadhafuaraich	1	-4.24	58.13	-2	5.14	5.51	6.68	1.17
CE45A	Llynoedd Ieuan	1	-3.78	52.42	-11	6.72	5.08	6.09	1.01
CHON	Loch Chon	1	-4.55	56.21	na	5.6	5.37	6.28	0.91
CLYD	Llyn Clyd	1	-4.04	53.12	33.93	5.21	6.15	6.24	0.09
CON	Llyn Conwy	1	-3.82	53	0	5.68	5.63	6.3	0.67
CREI	Loch na Creige Duibhe	1	-5.38	58.05	6.5	4.83	6.17	6.24	0.07
CUAR	Loch nan Cuaran	1	-4.91	58.17	19	6.99	6.06	6.54	0.48
CULF	Loch Cul Fraioch	1	-5.37	58.24	5.25	6.2	5.95	6.35	0.4
CW018	Llyn Fach	1	-3.59	51.72	na	4.95	6.31	6.49	0.18
CW024	Lyn Alwen	1	-3.65	53.09	na	6.56	5.42	6.05	0.63
CW027	Llyn Mymbyr	1	-3.93	53.1	na	4.74	5.78	6.22	0.44
CW028	Gloyw Llyn	1	-4.01	52.85	na	5.49	5.56	6.39	0.83
DOI	Loch Doilet	1	-5.59	56.75	15.43	4.9	5.62	5.99	0.37
DUBH	Lochanan Dubha	1	-5.14	58	9	5.25	5.8	6.03	0.23
DUL	Llyn Dulyn	1	-3.99	52.8	1.04	5.18	5.78	6.09	0.31
EIB	Llyn Eiddew Bach	1	-4.01	52.89	na	4.95	6.41	6.89	0.48
EIDW	Llyn Eiddwen	1	-4.04	52.28	na	6.55	6.66	6.35	-0.31
ENN	Ennerdale Water	1	-3.38	54.52	na	7.05	6.02	6.76	0.74
EUN	Loch nan Eun	1	-3.27	56.95	0	4.54	5.55	5.87	0.32
FLEO	Loch Fleodach Coire	1	-4.93	58.18	20.75	4.97	6.4	6.72	0.32
FNOD	Llyn Fanod	1	-4.05	52.26	103	6.08	6.61	6.43	-0.18
FOEL	Llyn y Foel-frech	1	-4.01	53	na	6.71	6.32	6.28	-0.04
GAIN	Loch na Gaineimh	1	-4.11	58.24	59	5.4	6.49	6.55	0.06
GLAS	Llyn Glas	1	-4.09	53.07	33.45	6.76	6.61	6.64	0.03
GLFR	Llyn Glasfryn	1	-4.38	52.95	na	6.25	6.97	6.69	-0.28
HHHH	Unnamed H	1	-2.57	57.01	na	5.31	6.4	6.33	-0.07
HIR	Llyn Hir	1	-3.78	52.29	5	6.87	5.63	6.41	0.78
HUID	Loch Bealach a Bhuirich	1	-4.95	58.19	77	4.78	6.5	6.68	0.18
IDWA	Llyn Idwal	1	-4.03	53.12	61	6.86	6.32	6.49	0.17
IOIG	Loch Iain Oig	1	-5.67	57.3	125	6.88	6.56	6.51	-0.05
IRD	Llyn Irddyn	1	-4.03	52.78	2.03	5.27	6.14	6.56	0.42
KEMP	Loch Kemp	1	-4.31	57.36	48	6.15	6.33	6.75	0.42
LACH	Lochan Lairig Cheile	1	-4.34	56.42	32	5.92	5.77	6.12	0.35
LAG	Llyn Llagi	1	-4.01	53.01	3	4.85	5.3	6.16	0.86
LAMH	Loch a Mhadaidh	1	-5.03	57.71	26.6	6.22	5.7	5.9	0.2
LNEI	Loch nan Eion	1	-5.47	57.5	41	5.99	5.78	6	0.22
LUBN	Loch Lubnaig	1	-4.29	56.29	na	6.9	6.69	6.63	-0.06
MEIK	Loch Meiklie	1	-4.6	57.33	na	6.21	6.49	6.77	0.28
MUIG	Loch Muighbhlaraidh	1	-4.3	57.82	74.5	6.61	6.48	6.77	0.29
NAHU	Loch Bealach na h-Uidhe	1	-4.95	58.19	17	4.87	6.56	6.63	0.07

NIGH	Lochan Nigheadh	1	-5.09	58.08	48	5.1	6.16	6.19	0.03
SAID	Loch Coire na Saidhe Duibhe	1	-4.64	58.28	12	6.54	6.03	6.22	0.19
SGAM	Loch Sgamhain	1	-5.18	57.53	44.5	5.27	6.29	6.24	-0.05
SKE	Loch Skerrow	1	-4.18	54.99	0	6.83	6.07	6.13	0.06
TARF	Loch Tarff	1	-4.61	57.15	87	6.83	6.79	6.85	0.06
TEAN	Loch Teanga	1	-7.29	57.32	12.04	5.72	6.07	6.33	0.26
TINK	Loch Tinker	1	-4.51	56.23	24.17	5.72	5.76	6.38	0.62
TUN	Tunnel End Reservoir	1	-1.95	53.6	na	5.83	6.22	5.88	-0.34
UIS	Loch Uisge	1	-5.58	56.63	53.44	7	6.02	6.18	0.16
UN02	Un-Named	1	-5.14	58.38	na	4.69	6.81	6.94	0.13
VEAG	Lough Veagh	1	-7.97	55.04	na	5.59	6	6.16	0.16
YBI	Llyn y Bi	1	-3.97	52.82	0.29	4.92	4.77	5.85	1.08
BALA	Lake Bala	2	-3.63	52.9	68	6.36	7.03	6.9	-0.13
BUTM	Buttermere	2	-3.27	54.53	51	6.54	6.65	6.82	0.17
CRAI	Loch of Craiglush	2	-3.56	56.58	na	6.13	7.11	6.9	-0.21
CRUM	Crummock Water	2	-3.31	54.56	52	5.27	6.87	6.91	0.04
CW021	Llyn y Fan Fawr	2	-3.7	51.88	na	6.28	6.97	6.91	-0.06
CW030	Llyn Cau	2	-3.9	52.69	na	5.86	6.29	6.53	0.24
CWEL	Llyn Cwellyn	2	-4.15	53.07	29	5.84	5.93	6.46	0.53
DOON	Loch Doon	2	-4.37	55.26	29.97	5.77	6.33	6.23	-0.1
EINI	Loch Einich	2	-3.79	57.07	29	6.55	6.23	6.46	0.23
GADA	Llyn y Gadair	2	-3.91	52.7	na	5.13	5.56	6.46	0.9
LDE	Loch Dee	2	-4.4	55.08	2.9	4.64	5.75	6.56	0.81
LOMOn	Loch Lomond (North basin)	2	-4.63	56.12	na	6.8	7.15	6.97	-0.18
LOMOs	Loch Lomond (South basin)	2	-4.63	56.12	na	6.68	7.32	7.06	-0.26
LOWS	Loweswater	2	-3.35	54.58	195	6.9	7.17	6.95	-0.22
MARE	Loch Maree	2	-5.38	57.65	49	7	6.71	6.8	0.09
MARY	St Marys Loch	2	-3.18	55.49	na	6.8	6.97	6.97	0
MUIC	Loch Muick	2	-3.17	56.93	na	6.61	5.94	6.38	0.44
RANN	Loch Rannoch	2	-4.27	56.69	69	5.33	6.35	6.41	0.06
WAST	Wast Water	2	-3.29	54.44	58	6.63	6.54	6.86	0.32
BER	Llyn Berwyn	3	-3.84	52.19	0.11	4.38	5.05	5.57	0.52
BHAI	Loch Coire a Bhaic	3	-4.99	58.22	9.5	5.59	5.55	5.81	0.26
BHAR	Loch Bharranch	3	-5.38	57.56	15	5.94	5.87	5.78	-0.09
BLU	Blue Lough	3	-5.97	54.16	-18.5	4.55	5.08	5.23	0.15
BOGA	Loch nam Badan Boga	3	-5.21	57.89	-17	4.82	5.18	5.6	0.42
CHAM	Loch a Cham Alltain	3	-4.94	58.36	6.2	4.92	5.76	5.98	0.22
CNAM	Loch Coire nan Cnamh	3	-5.34	57.08	5.5	6.15	5.51	5.56	0.05
COR	Loch Coire an Lochan	3	-3.75	57.08	13.74	4.82	5.21	5.44	0.23
CORN	Loch Bealach Cornaidh	3	-5.05	58.21	18.33	5.63	6.01	5.85	-0.16
CRAN	Cranmer Pond	3	-0.87	51.08	na	4.83	5.13	5.02	-0.11
CRIC	Loch na Cric	3	-5.1	57.99	0	5.54	5.29	5.65	0.36
GLAN	Llyn Glanmerin	3	-3.84	52.58	na	5.5	6.23	5.96	-0.27
CZSN51	Llyn Llech Owen	3	-4.08	51.82	na	6.5	5.4	5.58	0.18
DALL	Loch Dallas	3	-3.52	57.51	na	6.35	5.07	5.04	-0.03
DCAL	Loch Dubh Camas an Lochain	3	-5.6	57.91	-11	4.62	5.57	5.79	0.22

DUH	Dubh Loch	3	-3.25	56.93	2.06	5.62	5.31	5.62	0.31
ENO	Loch Enoch	3	-4.44	55.14	0	6.57	5.15	5.48	0.33
FEOI	Lochan Feoir	3	-5.01	58.18	35.75	4.96	5.91	5.95	0.04
FHIO	Lochan Fhionnlaidh	3	-5.07	58.04	-9.25	6.12	5.39	5.42	0.03
GRUA	Loch na Gruagaich	3	-4.98	58.1	-3.75	6.9	5.27	5.64	0.37
GYN	Llyn Gynon	3	-3.76	52.27	4	5.16	5.5	5.92	0.42
HAIR	Loch na h-Airbhe	3	-5.2	57.88	1.33	5.17	5.29	5.59	0.3
LAI	Loch Laidon	3	-4.64	56.65	12.81	5.79	5.44	5.79	0.35
LAR	Loch na Larach	3	-5.06	58.48	na	4.88	5.55	5.52	-0.03
LGR	Loch Grannoch	3	-4.28	54.99	na	4.8	4.98	5.53	0.55
LMCK	Lough Muck	3	-8.07	54.92	na	5.74	5.12	5.76	0.64
LOCH	Loch Toll an Lochain	3	-5.24	57.8	15.5	5.63	5.77	5.96	0.19
LOD	Lochan Dubh	3	-5.45	56.78	8.12	5.63	5.29	5.61	0.32
LON	Long Loch	3	-3.37	58.66	-10	5.53	5.89	5.73	-0.16
LOSG	Loch Bad an Losguinn	3	-5.04	57.09	3	7.06	5.85	5.77	-0.08
LYEL	Loughaunayella	3	-9.35	53.32	na	na	5.78	6.1	0.32
MAAM	Lough Maam	3	-8.11	54.99	na	6.29	5.48	5.66	0.18
MHIC	Loch Mhic Leoid	3	-3.65	57.39	44	6.2	6.23	5.62	-0.61
MWEE	Lough Maumwee	3	-9.54	53.48	na	5.37	5.86	5.93	0.07
MYN	Llyn Cwm Mynach	3	-3.96	52.8	8.5	5.22	5.69	5.95	0.26
NABE	Loch na Beiste	3	-5.39	58.06	-2.5	5.05	5.85	6.06	0.21
NAGA	Lochnagar	3	-3.23	56.96	0	6.07	5.51	5.88	0.37
NARR	Loch Narroch	3	-4.43	55.1	-14.3	5.26	4.81	5.09	0.28
NELD	Loch Neldriken	3	-4.45	55.12	-4.6	5.68	4.93	5.23	0.3
NEUN	Loch nan Eun	3	-5.01	58.22	7.75	6.48	5.65	5.78	0.13
OAKM	Oakmere	3	-2.64	53.21	na	6.6	6.44	5.59	-0.85
RLDN	Round Loch of the Dungeon	3	-4.41	55.13	na	4.73	5.15	5.9	0.75
RLGH	Round Loch of Glenhead	3	-4.43	55.09	0	6.03	5.23	5.59	0.36
UAI	Lochan Uaine	3	-3.65	57.06	14.79	6.28	5.58	5.85	0.27
VAL	Loch Valley	3	-4.44	55.1	0	4.69	5.03	5.52	0.49
VNG9402	Loch Coire Fionnaraich	3	-5.43	57.49	11.4	5.44	5.56	5.7	0.14
WOOL	Woolmer Pond	3	-0.88	51.08	na	6.22	6.02	5.92	-0.1

Table 1. Site codes, site names, cluster allocation, location (lat. and long.), equivalent alkalinity (µeq/l), measured pH (present day), diatom-inferred pH (bottom and top samples) using the EDDI training set (http://craticula.ncl.ac.uk/Eddi) and difference between inferred pH of bottom and top samples. Alkalinity data are missing for some sites (see text).

Table 2

Clu.	Code	Taxon name	pH Opt.	max %	Hab.	Note
2	CY007A	*Cyclotella glomerata* Bachmann	7.5	33	pl	
2	CY019A	*Cyclotella radiosa* (Grunow) Lemmermann	7.2	21	pl	
2	AS001A	*Asterionella formosa* Hassall	6.9	38	pl	
2	CY010A	*Cyclotella comensis* Grunow	6.8	87	pl	
2	AU020A	*Aulacoseira subarctica* (O.Müller) Haworth	6.7	52	pl	
2	SY002A	*Synedra rumpens* Kützing	6.7	21	pl/be	1
2	SY009A	*Synedra nana* Meister	6.7	24	pl/be	
2	AC035A	*Achnanthes pusilla* (Grunow) De Toni	7.0	13	be	
2	AC013A	*Achnanthes minutissima* Kützing	6.7	61	be	2
2	HN001A	*Hannea arcus* (Ehrenb.) Patrick	6.6	21	be	
2	FU002A	*Frustulia rhomboides* (Ehrenberg) De Toni	5.7	21	be	
1	FR001A	*Fragilaria pinnata* Ehrenberg	7.4	45	be	3
1	CM004A	*Cymbella microcephala* Grunow	6.8	27	be	
1	CM052A	*Cymbella descripta* (Hust.) Krammer & Lange-Bert.	6.8	19	be	
1	FR002C	*Fragilaria construens* var. *venter* (Hust.) Kramm. & Lange-Bert.	6.8	60	be	4
1	NA005A	*Navicula seminulum* Grunow	6.8	20	be	5
1	NI005A	*Nitzschia perminuta* (Grunow) M. Peragallo	6.6	22	be	
1	AC136A	*Achnanthes subatomoides* (Hust.) Lange-Bert. & Archibald	6.5	38	be	
1	AC002A	*Achnanthes linearis* (W. Smith) Grunow	6.5	24	be	6
1	BR001A	*Brachysira vitrea* (Grunow) Ross	6.4	47	be	
1	SA001B	*Stauroneis anceps var. gracilis* (Ehrenberg) Brun	6.4	16	be	7
1	CM018A	*Cymbella gracilis* (Ehrenberg) Kützing	n/a	25	be	
1	NA751A	*Navicula cryptotenella* Lange-Bertalot	6.5	31	be	
3	AC046A	*Achnanthes altaica* (Poretzky) A. Cleve	6.4	24	be	8
3	PI007A	*Pinnularia viridis* (Nitzsch) Ehrenberg	6.3	18	be	
3	FR005D	*Fragilaria virescens* var. *exigua* Grunow	6.2	86	be	
3	PI011A	*Pinnularia microstauron* (Ehrenb.) Cleve	6.2	19	be	
3	BR006A	*Brachysira brebisonii* R. Ross	6.1	28	be	
3	NA006A	*Navicula mediocris* Krasske	6.1	18	be	
3	EU051A	*Eunotia vanheurckii* Patrick	5.9	16	be	
3	AC014C	*Achnanthes austriaca* var. *helvetica* Hustedt	5.8	25	be	9
3	CM017A	*Cymbella hebridica* Grunow ex Cleve	5.7	37	be	10
3	EU002A	*Eunotia pectinalis* (O. Müll.) Rabenh.	5.7	17	be	
3	FU002B	*Frustulia rhomboides* var. *saxonica* (Rabenh.) De Toni	5.7	66	be	
3	FU002F	*Frustulia rhomboides* var. *viridula* (Breb. ex Kütz.) Cleve	5.7	35	be	
3	CM010A	*Cymbella perpusilla* A. Cleve	5.6	49	be	
3	AC022A	*Achnanthes marginulata* Grunow	5.5	44	be	11
3	EU019A	*Eunotia iatriaensis* Foged	5.5	14	be	
3	EU002B	*Eunotia pectinalis* var. *minor* (Kütz) Rabenh.	5.4	41	be	
3	PE002A	*Peronia fibula* (Brebisson ex Kützing) Ross	5.4	26	be	
3	PI023A	*Pinnularia irrorata* (Grunow in Van Heurck) Hust.	5.4	36	be	
3	EU011A	*Eunotia rhomboidea* Hustedt	5.3	49	be	
3	NA167A	*Navicula hoefleri* sensu Ross et Sims	5.3	20	be	
3	EU047A	*Eunotia incisa* W. Smith	5.2	55	be	
3	EU048A	*Eunotia naegelii* Migula	5.1	16	be	
3	BR003A	*Brachysira serians* (Bréb. ex Kütz.) Round & D. G. Mann	5	11	be	
3	TA004A	*Tabellaria quadriseptata* Knudson	4.9	42	be	

Table 2. Indicator taxa for three reference diatom assemblage clusters for UK low alkalinity waters, showing pH optima from the EDDI pH training set (http://craticula.ncl.ac.uk/Eddi), maximum percentage occurrence amongst the 121 sites (Table 1) and habitat preference. Some non-current names are used to maintain consistency with the taxonomy of the earliest data used in the database. Current names: 1. *Fragilaria capucina* var. *rumpens* (Kütz.) Lange-Bert; 2. *Achnanthidium minutissimum* (Kütz.)

Czarnecki; 3. *Staurosirella pinnata* (Ehrenb.) D.M.Williams et Round; 4. *Staurosira construens* var. *venter* (Ehrenb.) P. B. Ham.; 5. *Sellaphora seminulum* (Grunow) D.G. Mann; 6. *Rossithidium linearis* (W. Sm.) Round & Bukht; 7. *Stauroneis anceps* Ehrenberg; 8. *Psammothidium altaicum* (Poretzky) Bukht. & Round; 9. *Psammothidium helveticum* (Hust.) Bukht. & Round; 10. *Encyonema hebridicum* (W. Greg.) Grunow ex Cleve; 11. *Psammothidium marginulatum* (Grunow) Bukht. & Round.

Figure captions

Figure 1. Map of UK with 121 lakes showing location of sites in the three diatom clusters

Figure 2. Principal components analysis (PCA) of pre-acidification diatom assemblages from 121 low alkalinity lakes in the UK showing cluster boundaries and site codes.

Figure 3. Bubble plots for selected diatom taxa in Cluster 1. The size of the symbol is proportional to sample relative abundance.

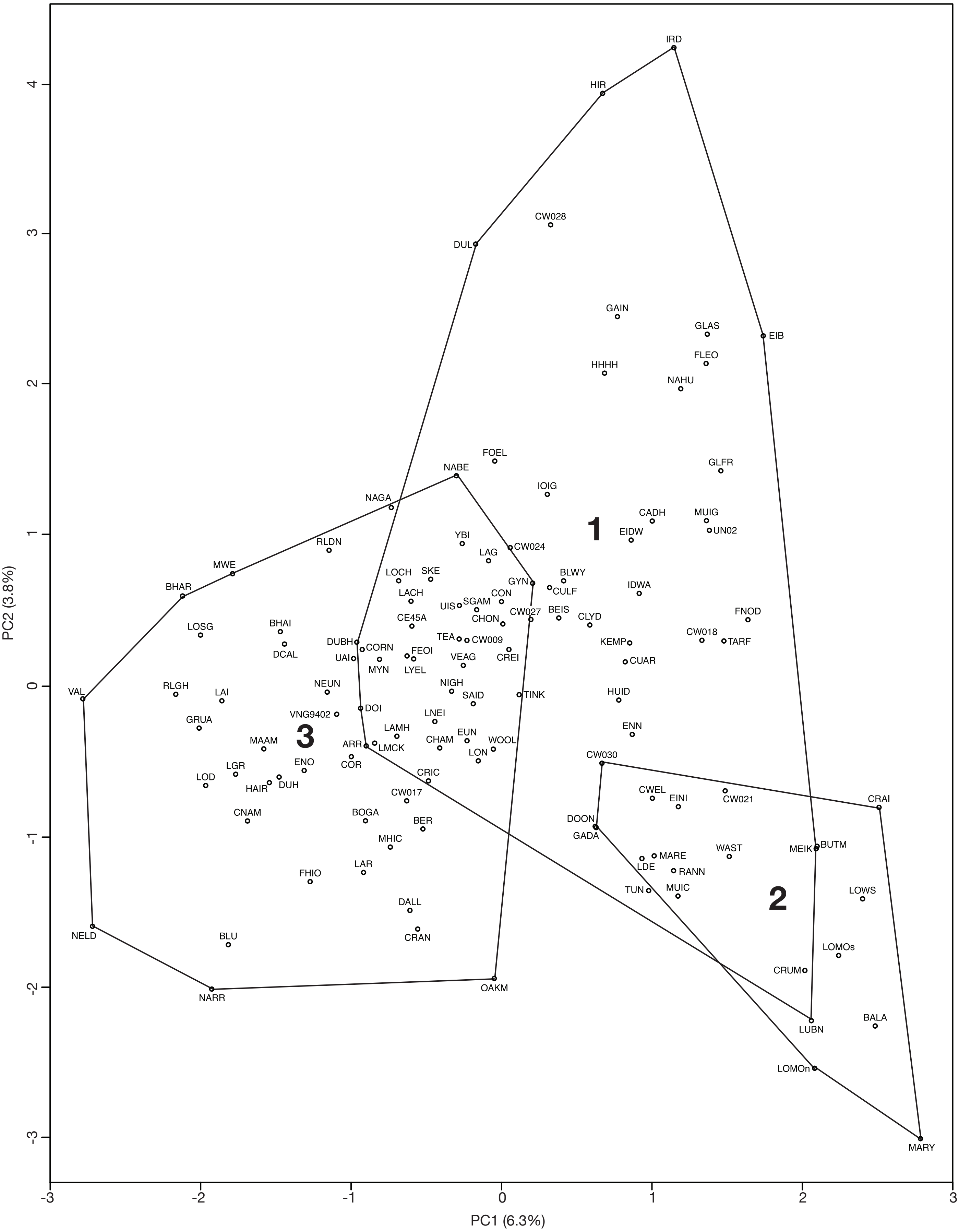
Figure 4. Bubble plots for selected diatom taxa in Cluster 2. The size of the symbol is proportional to sample relative abundance.

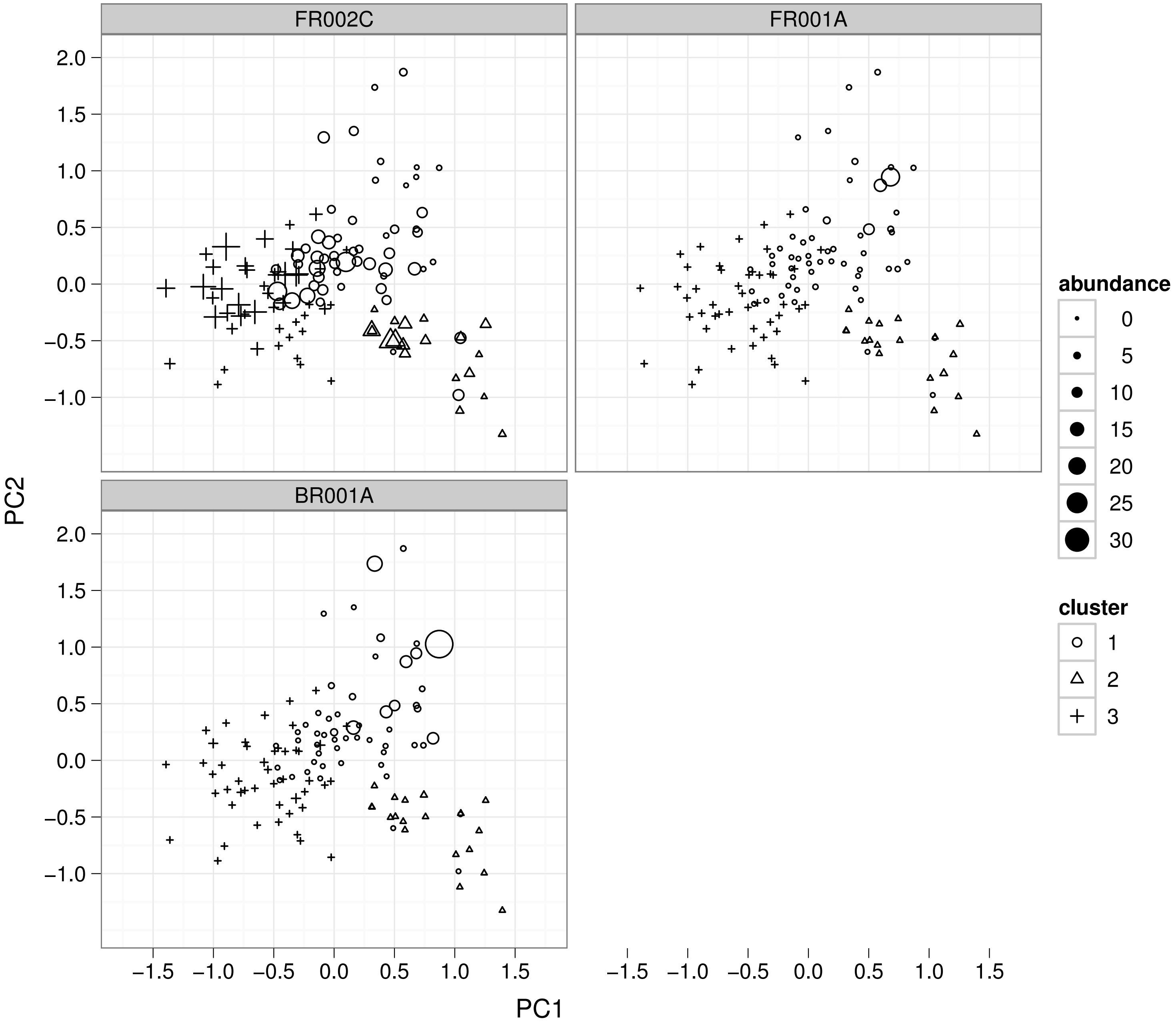
Figure 5. Bubble plots for selected diatom taxa in Cluster 3. The size of the symbol is proportional to sample relative abundance.

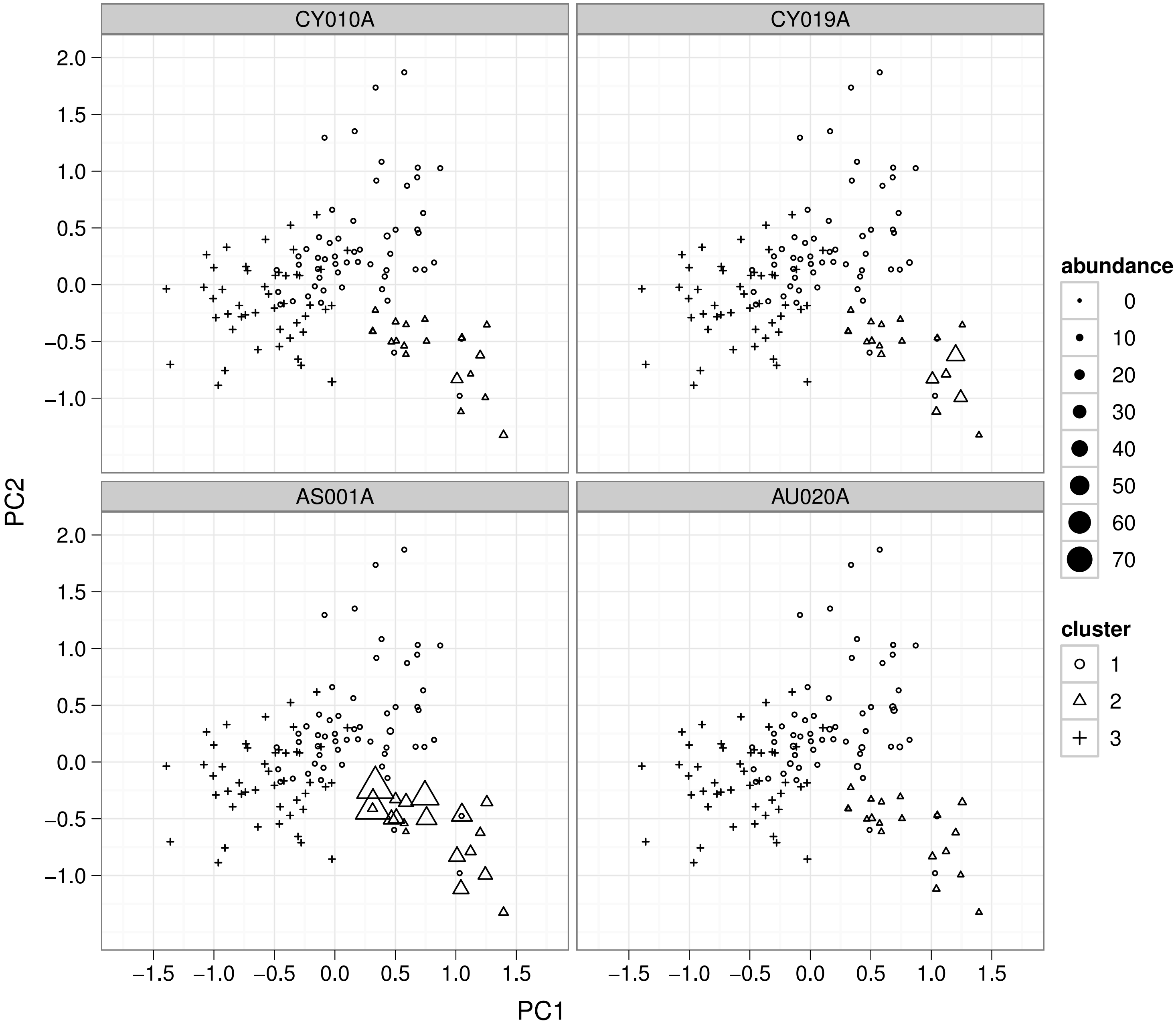
Figure 6. Boxplots of diatom-inferred pH for: (a) core bottom; (b) core top
samples; and (c) change in pH between top and bottom samples for each cluster. The horizontal dashed lines in c) are drawn at +/- RMSEP_boot for the weighted average calibration model.

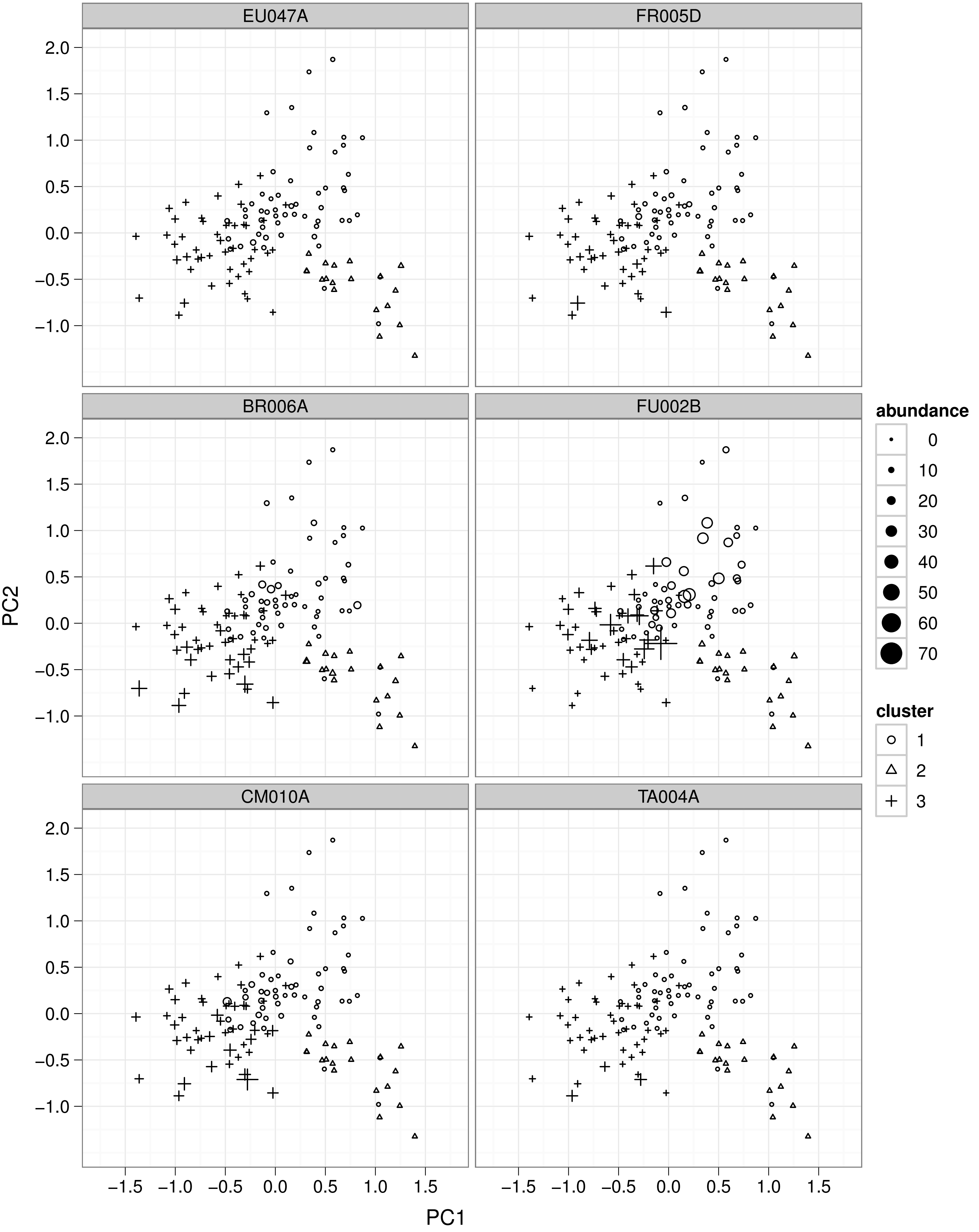
Figure 7. Boxplots for contemporary Ca^{++} (shaded?) and Ca^{++} zero (Ca_{ref}) for the three clusters.

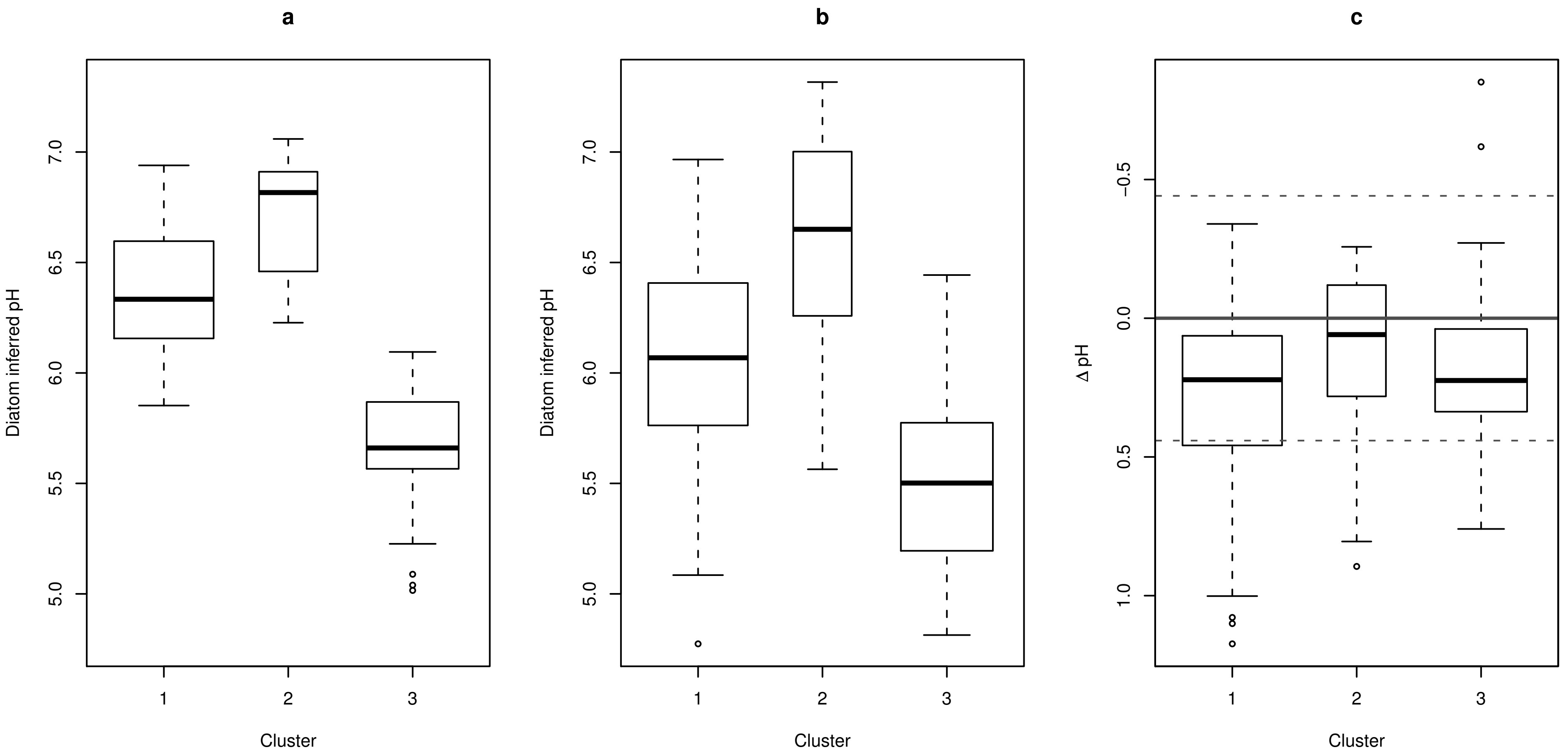

58
56
54
52
50
Latitude
-10
-8
-6
-4
-2
0
2
Longitude
Cluster 1
Cluster 2
Cluster 3

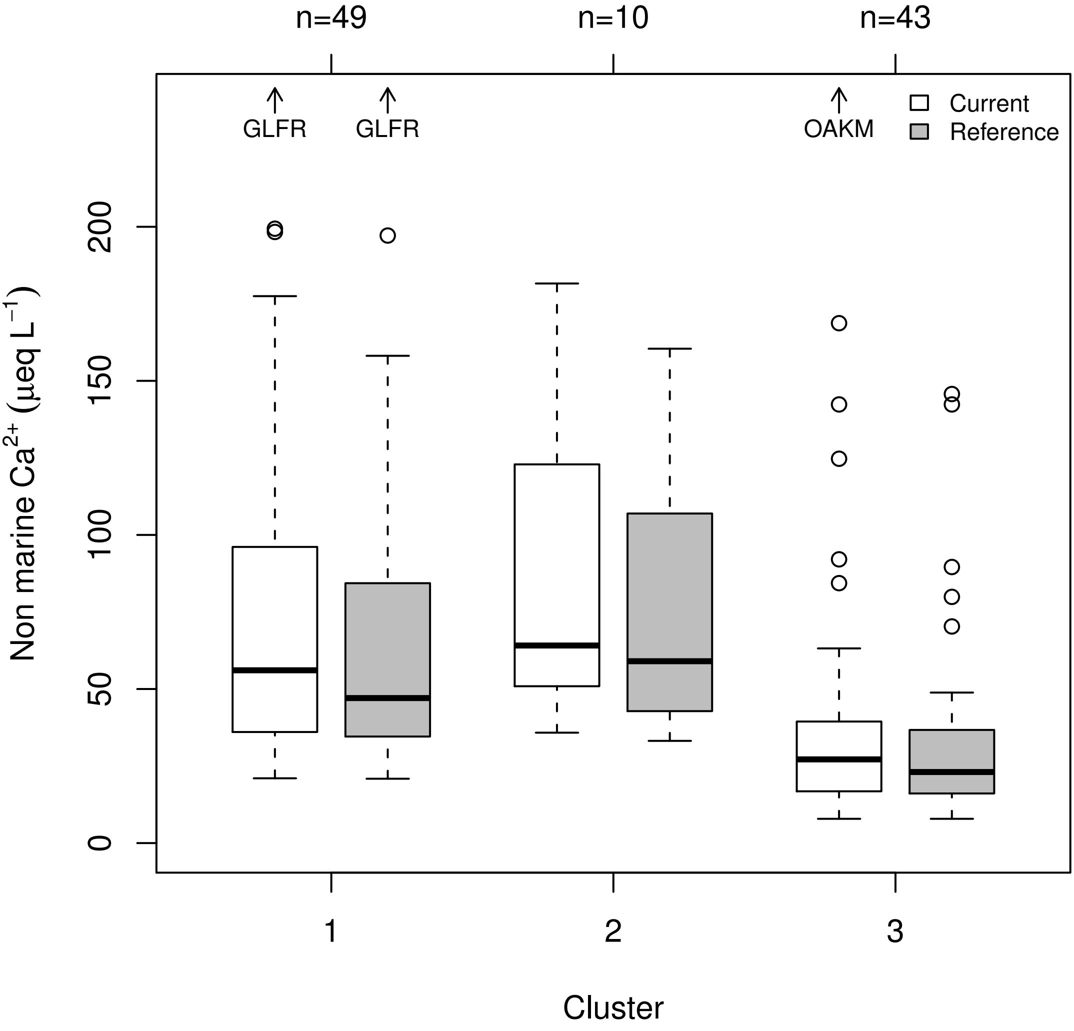

IRD
HIR
CW028
DUL
GAIN
GLAS
EIB
FLEO
HHHH
NAHU
FOEL
GLFR
NABE
IOIG
NAGA
CADH
MUIG
1
UN02
EIDW
RLDN
YBI
CW024
LAG
MWE
BLWY
SKE
LOCH
GYN
BHAR
CULF
IDWA
LACH
CON
SGAM
UIS
BEIS
CHON
CW027
CLYD
FNOD
CE45A
BHAI
LOSG
CW018
TEA
CW009
TARF
KEMP
DUBH
CORN
DCAL
CREI
FEOI
VEAG
UAI
MYN
CUAR
LYEL
NEUN
NIGH
RLGH
VAL
LAI
HUID
TINK
SAID
DOI
VNG9402
LNEI
GRUA
ENN
LAMH
3
MAAM
CHAM
EUN
WOOL
ARR
LMCK
LON
CW030
ENO
COR
LGR
CRIC
LOD
HAIR
DUH
CWEL
CW021
CRAI
EINI
CW017
CNAM
DOON
BOGA
GADA
BER
MHIC
WAST
MEIK
BUTM
MARE
LDE
LAR
RANN
FHIO
TUN
MUIC
2
LOWS
DALL
CRAN
NELD
BLU
LOMOs
CRUM
OAKM
NARR
LUBN
BALA
LOMOn
MARY
4
3
2
1
0
-1
-2
-3
PC2 (3.8%)
-3
-2
-1
0
1
2
3
PC1 (6.3%)


FR002C
FR001A
BR001A
PC2
PC1
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
abundance
0
5
10
15
20
25
30
cluster
1
2
3


CY010A
CY019A
AS001A
AU020A
PC2
PC1
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
abundance
0
10
20
30
40
50
60
70
cluster
1
2
3


EU047A
FR005D
BR006A
FU002B
CM010A
TA004A
PC2
PC1
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
abundance
0
10
20
30
40
50
60
70
cluster
1
2
3


a
b
c
Diatom inferred pH
Δ pH
Cluster
1
2
3
7.0
6.5
6.0
5.5
5.0
−0.5
0.0
0.5
1.0


n=49
n=10
n=43
GLFR
GLFR
OAKM
☐ Current
▨ Reference
Non marine Ca^{2+} (µeq L^{-1})
0
50
100
150
200
1
2
3
Cluster