

**CHEMICAL AND BIOLOGICAL
CHANGES IN CUMBRIAN LAKES DUE
TO DECREASES IN ACID DEPOSITION**

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by

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Institute of Freshwater Ecology

SUMMARY

There is chemical evidence for acidification reversal in surface waters of the Lake District, and studies of stream water invertebrates and bacteria have provided evidence for biological recovery. In this study, further investigations were performed in order to consolidate the chemical data for lakes, and to add a further biological component by examining changes in lake water diatom (brown algae) assemblages.

Chemical data were assembled for nine lakes. Overall, the data covered the period 1953-1999, although the earlier values were quite sparse. In order to maximise the information from the data, an analysis was carried out to take into account seasonal chemical variations, ie the tendency of pH and acid-neutralising capacity (ANC) to go through annual cycles (low winter values, high summer/autumn values). A model was formulated in which the seasonality was accounted for by a cosine function, parameterised with an annual level (pH or ANC at the midpoint of the cycle: pH_L , ANC_L), an amplitude (δ), and a day of maximum (d_{max}), ie a displacement of the cycle on the time axis. Values of pH_L , ANC_L , δ , and d_{max} were obtained from cases (10 for pH, seven for ANC) where there were sufficient numbers of data to define the seasonality. From these results, the dependences of δ_{pH} and δ_{ANC} on pH_L and ANC_L respectively were derived. The model equations were then used to derive values of pH_L and ANC_L for all the years in which measurements had been made. The trends in ANC_L suggest that there was a decline between the early 1950s and the 1970s, followed by an increase to the present day. The pH_L data revealed increases from the 1970s to the present. Three of the nine lakes showed highly significant ($p < 0.001$) increases in pH_L over the last 20-25 years, and four others showed significant ($0.001 < p < 0.1$) increases. Two lakes showed highly significant increases in ANC, and two showed significant increases. The significant pH increases for two of the lakes (Greendale and Scales Tarns) extend the geographical range over which acidification reversal has been observed.

The diatom assemblages of five of the seven lakes studied showed changes between 1983-85 and 1999 consistent with increases in lake water pH. Thus, there were increases in the numbers of diatoms favouring circumneutral waters and decreases in the numbers favouring acidic waters. For two of the lakes, no significant changes occurred. Diatom-inferred pH values, and changes in those pH values, agreed with the chemical data in two cases. However, such relationships were not established for the other lakes.

The results consolidate both the chemical and biological evidence for reversal of surface water acidification in the Lake District.

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1 INTRODUCTION

1.1 Background

Recent work by the Institute of Freshwater Ecology (IFE) has shown that standing surface waters in the Lake District are recovering chemically from the impacts of acid deposition (Tipping et al., 1998; 1999a,b). This work focussed on two lakes for which large long-term data sets are available, together with three smaller lakes (tarns) with less extensive data. As a result of further monitoring and consideration of additional older data, it is now possible to take into account chemical changes in four additional lakes, making a total of nine in all. The available data sets for some of the lakes now include alkalinity and acid-neutralising-capacity (ANC) values for the early 1950s. Thus there is a record of chemical change over 45 years, including the peak of acidic deposition in the United Kingdom (UK), which occurred around 1970.

We have also obtained data on the relative abundances of diatoms (brown algae) in 7 lakes, in 1983-85 and in 1999. The sensitivity of diatoms to variations in pH is well-known, and is exploited in the reconstruction of historical lake water pH (Atkinson & Haworth, 1990). Therefore it is anticipated that any changes in lakewater chemistry that have occurred during the past two decades may be reflected in changes in the diatom populations.

1.2 Objectives

The objectives of the work were to:

- (i) analyse the chemical data using a simple model that takes into account seasonal variations of pH and acid-neutralising capacity, in order to establish a single representative value of each for a given year
- (ii) analyse diatom data by assigning taxa to groups of different acid sensitivity
- (iii) compare the chemical and biological results to determine whether biological and chemical changes are related.

2 SITE DESCRIPTION

The lakes sampled in the project are all located at medium to high altitude in the English Lake District. The Lake District, situated in the north-west of England, is an area of high relief, with altitudes up to 975m above sea level, the landscape having been shaped by glaciation. Several geological formations underlie the region, including Ordovician slates of the Skiddaw Group in the north, metamorphosed igneous rocks of the Borrowdale Volcanic Group in the central part, Silurian slates in the south, and granitic rocks in the west (Moseley, 1978). The annual rainfall is in the range 1-4m, depending upon altitude and distance from the sea, and the annual temperature range (monthly averages) is *ca.* 4-15°C at an altitude of 100m (Manley, 1989). Run-off is rapid and depends strongly upon antecedent rainfall. Weathering rates of soil and rock are spatially heterogeneous and the sensitivity of surface waters to acid deposition therefore varies widely (Sutcliffe et al., 1982; Tipping, 1989, 1990). The softest and most acid waters are those underlain by rocks of the Borrowdale Volcanic Series, Skiddaw Slates and granitic intrusions. The waters considered here

have catchments on one or more of these rock types. Soils, consisting of peats and stagnopodzols (Jarvis et al., 1984), cover most of the study catchments, but in each case there are appreciable areas of bare rock. The vegetation consists mainly of grasses, bracken and *Sphagnum* moss. The land is used as rough pasture for the low-density grazing of sheep.

The properties of the studied lakes are given in Table 2.1. They are all in moorland catchments. To a first approximation they receive deposition with the same composition, although there is probably some variation with distance from the sea (for example, Devoke Water receives higher loadings of sea salts) and possibly with altitude. Tipping (1989, 1990) ascribed the differences in surface water chemistry in the upland parts of the Lake District to variations in rock weathering rates. More recent data and thinking suggest that hydrology and available surface for weathering may also play a role. It has been found that the supply of Ca^{2+} by the weathering of rocks from the Duddon catchment – and presumably at other catchments underlain by rocks of the Borrowdale Volcanic Series - depends strongly on the calcite content (Stidson, 1999). To our knowledge, there have been no major applications of lime or fertilisers to the moorland catchments, although animal slurry is applied on occasions. The waters are low ($< 5\mu\text{g l}^{-1}$) in dissolved phosphorus, and the fact that some of them are very low in Ca attests to the lack of significant liming.

Chemical deposition data for Cumbria show significant decreases in the concentrations of hydrogen ions and non-marine sulphate over the last 20-30 years, but no significant changes in the concentrations of nitrogen species or non-marine base cations (Tipping et al., 1998). Thus, in 1975-76, the volume weighted mean pH was 4.40 and the non-marine sulphate concentration $68\mu\text{eq / L}$, whereas the corresponding values in 1996 were $4.71\mu\text{eq / L}$ and $36\mu\text{eq / L}$.

	NGR	Altitude m	Mean catchment altitude m	Area km ²	Mean depth m	Land area km ²	Residence time days
1 Buttermere	NY 183 158	101	400	0.94	16.6	16.9	135
2 Codale Tarn	NY 297 088	466	610	0.015	3.3	0.40	12
3 Devoke Water	SD 158 970	233	370	0.34	4	3.1	107
4 Easedale Tarn	NY 307 088	279	510	0.11	10.5	2.7	55
5 Greendale Tarn	NY 148 075	402	550	0.021	2.8	0.85	9
6 Levers Water	SD 280 993	411	610	0.15	21	2.0	155
7 Little Langdale Tarn	NY 309 033	289	520	0.063	2.7	12.0	2
8 Scales Tarn	NY 329 282	595	720	0.020	4	0.28	30
9 Seathwaite Tarn	SD 253 987	375	590	0.27	9	4.6	55
10 Stickle Tarn	NY 287 077	469	610	0.090	8	1.8	39

Table 2.1 Lake and catchment properties (see figure 2.1 for location of lakes).

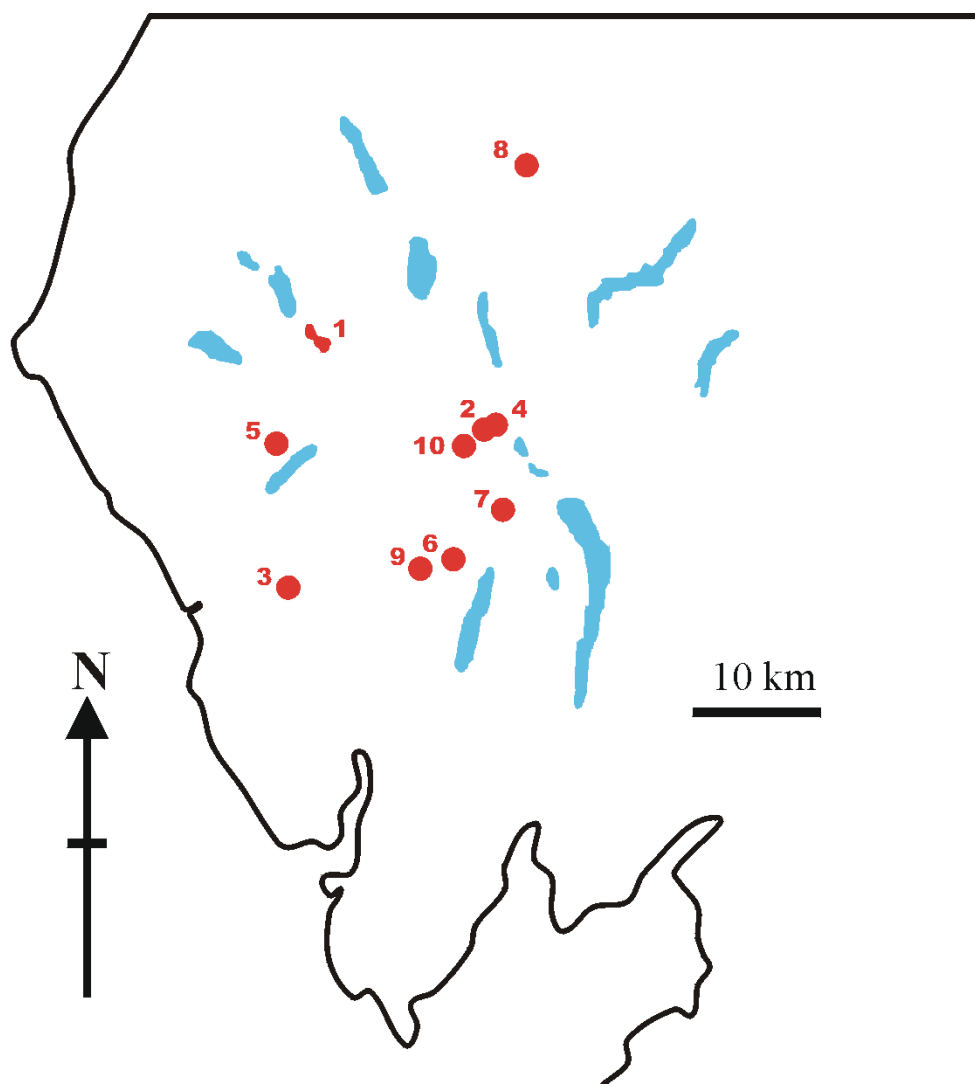


Fig. 2.1 Map of Cumbria showing lakes (numbered) studied in this work.

3 **METHODS**

3.1 **Chemistry**

The current project involves data already collected by workers at IFE, and previously, the Freshwater Biological Association (Carrick & Sutcliffe, 1982). Determinations of pH were performed with a glass electrode; older data were corrected for temperature effects as described by Tipping et al. (2000a). Alkalinity was measured by titration with standard acid and detection of the end point either with a colorimetric reagent (older data) or from Gran plots. Older data obtained by colorimetric end point detection were corrected by subtracting $20\mu\text{eq} / \text{L}$ from each value (Carrick & Sutcliffe, 1982). Base cations were determined by atomic absorption spectrometry. In early work, the equivalent sum of acid anions was determined by anion exchange, in later work, individual anion concentrations were determined by ion chromatography.

3.2 **Alkalinity and ANC**

In this report, we use the term alkalinity to mean the concentration of acid-neutralising solutes determined by titration with strong acid. The term ANC (acid neutralising capacity) means the sum of the concentrations of strong base cations (sodium (Na), magnesium (Mg), potassium (K), calcium (Ca)) minus the sum of the concentrations of strong acid anions (chloride (Cl), nitrite (NO_3), sulphate (SO_4)). In simple bicarbonate waters, the two values should be the same. However, they differ when there are significant concentrations of dissolved organic matter and/or aluminium (Al), under which circumstances the titration method is affected by the weak acid character of these solutes. Lake District waters are low in dissolved organic carbon, but the presence of dissolved aluminium in acid waters, at concentrations up to $30\mu\text{mol} / \text{L}$, means that negative alkalinity values are less negative than the corresponding values of ANC. Simulations with the chemical speciation model WHAM (Tipping, 1994) showed that the discrepancies can be explained by the hydrolysis reactions of dissolved aluminium.

Therefore, in analysing the chemical data for the lakes, we used ANC values (as well as pH) to characterise water acidity. For samples with positive ANC and alkalinity, the latter were used as a second estimate of ANC, since such samples have near-zero concentrations of Al. For samples with negative ANC and alkalinity, only the ANC value was used.

3.3 **Sampling, processing, identification and classification of diatoms**

Samples were collected using a modified plankton net, which was thrown into the lake, attached to an 8 m cord. The net was allowed to sink to the bottom of the lake, and then was dragged back over the surface of the littoral layer. The captured material was stored in a refrigerator on return to the laboratory. To avoid cross-contamination, the plankton net was thoroughly cleaned in between samplings, by soaking in warm water containing a detergent.

The samples were prepared for examination by removing excess water, and then pouring 6cm^3 into a test tube. This was reacted with 3cm^3 of hydrogen peroxide, in order to remove the organic matter from the sample material. The test tube was spun in a centrifuge, at 2000rpm, for 1 minute. The excess solution was poured off, and the

remaining contents were shaken (to re-suspend the sample material). Distilled water was added until the tube contained 10cm³ of material, and the tube was placed back into the centrifuge. This was repeated three times, in order to remove all of the hydrogen peroxide from the sample. A drop of the cleaned material was pipetted onto a cover slip, and dried under a heat lamp. The material was mounted using Naphrax (a high-resolution, commercial diatom mountant), and a medium-sized drop of this was placed onto a mount slip. A drop of xylol was pipetted onto the dried sample material, and the cover slip was then inverted and placed onto the mount slip. The slide was left to dry on a hot plate.

Diatom samples were identified and counted using a phase contrast microscope, at 100x magnification. They were viewed under cross-polarised light, using anisole oil immersion. Diatoms were identified to the species level and, where possible, to the sub-species level. Krammer & Bertalot (1986-1991) were used throughout, although Barber and Haworth (1981), Germain (1981), and Hartley et al.(1996) were often consulted. Occasional references were also made to Koppen (1975), and to Reichardt & Lange-Bertalot (1991). The first 333 (+1) diatoms from each sample were counted along the mid-transect of each slide. This number was chosen because it had been used by numerous authors (eg Haworth, 1966), and enabled the easy conversion of species abundances into percentage values. Diatom counts were used to infer lake water pH using the approach of Renberg & Hellberg (1982).

The diatoms are divided into the following classes:

- A *Acidophilous* diatoms occur at about pH 7, but mainly at pH levels below 7
- B *Circumneutral* diatoms occur at about pH 7
- C *Alkaliphilous* diatoms occur at about pH 7, but mainly at pH levels above 7
- D *Indifferent* diatoms, having no preference with respect to pH
- E *Acidobiontic* diatoms occur at pH levels below 7, but optimally at pH < 5.5
- F *Alkalibiontic* diatoms occur at pH levels above 7
- G Unkown species

4 ANALYSIS OF SEASONALITY

Inspection of lake chemistry data shows that pH and ANC display seasonal variations, the lowest values being observed in late winter / early spring and the highest in late summer / autumn. Examples are shown in Fig. 4.1. The seasonality was modelled with a simple cosine curve, parameterised with a “day of maximum” (d_{max}) and an amplitude (δ). Thus we have:

$$pH(t) = pH_L + \delta_{pH} \cos(\omega t + d_{max}) \quad (4.1)$$

$$ANC(t) = ANC_L + \delta_{ANC} \cos(\omega t + d_{max}) \quad (4.2)$$

where t is time in days, pH_L and ANC_L are the pH and ANC levels for the year in question, ie the values at the mid-points of the seasonal range, and ω is a scaling factor equal to $(2\pi / 365.25)$. Values of d_{max} and δ may depend upon the chemistry and physical properties of the water in question. They were estimated for cases where there were sufficient data points within a year to provide a good definition of the seasonality (this includes 7 for pH and 5 for ANC). Tables 4.1 and 4.2 summarise the results of the analysis.

Theoretically, the amplitude of pH should be small for acid waters, then increase for waters in the pH range around 5.5, then decrease at higher pH, reflecting the buffering characteristics of the solutions. Fig. 4.2 shows values of δ_{pH} plotted against pH_L . The results fall into the expected pattern, and the relationship between δ_{pH} and pH_L can be described by a normal curve:

$$\delta_{pH} = \frac{0.504}{0.524\sqrt{2\pi}} \exp\left(\frac{-(pH_L - 5.92)^2}{0.550}\right) \quad (4.3)$$

The value of δ_{ANC} tended to increase with ANC_L , and was described with the equation:

$$\delta_{ANC} = 0.17ANC_L + 7.3 \quad (4.4)$$

It was anticipated that the value of d_{max} might reflect (a) physical mixing processes governing the displacement of lake water by inflows, and (b) the response of the catchment to summer warming and plant uptake of nitrogen, primarily temperature controlled. For example, a high altitude lake with a large volume : catchment area ratio would be expected to have a high value of d_{max} , while a low altitude lake with a small volume:catchment area ratio would have a low value of d_{max} . The derived values of d_{max} conformed approximately to this expectation (Fig. 4.3), and the value of d_{max} could be related to catchment altitude (a_c in metres) and lake residence time (τ in years) by the equation:

$$d_{max} = 25.5(4\log_e a_c + \log_e \tau) - 489 \quad (4.5)$$

where the term in brackets is an index combining catchment altitude and lake residence time.

Equations (4.1)–(4.5) allow pH_L and ANC_L to be derived for a given lake from measured values for a particular year. Thus for each year when measurements are available a single value of either variable can be derived, and seasonal influence on the value can be factored out. This should make long-term trends easier to discern. The analysis also allows errors to be assigned to the pH_L and ANC_L values.

Lake	Years	n	δ_{pH} (SE)	d_{max} (SE)
Levers Water	1983-1989	333	0.062 (0.006)	322 (5)
	1990-1999	96	0.043 (0.017)	295 (28)
Buttermere	1983-1989	149	0.158 (0.018)	221 (7)
	1990-1999	102	0.205 (0.028)	224 (8)
Devoke Water	1983-1989	165	0.243 (0.023)	229 (6)
	1990-1999	101	0.164 (0.017)	237 (6)
Seathwaite Tarn	1983-1989	170	0.111 (0.011)	313 (6)
Codale Tarn	1996-1999	23	0.380 (0.098)	221 (16)
Easedale Tarn	1996-1999	23	0.379 (0.059)	265 (10)
Stickle Tarn	1996-1999	20	0.255 (0.040)	251 (8)

Table 4.1 Analysis of seasonality in pH: δ (seasonal range) and d_{\max} (day of maximum pH) are defined by equation (4.1). n = number of data points.

Lake	Years	n	δ_{ANC} (SE)	d_{\max} (SE)
Levers Water	1983-1989	333	2.40 (0.4)	262 (10)
Buttermere	1983-1989	149	10.8 (1.0)	241 (5)
	1990-1999	102	11.7 (1.3)	250 (7)
Devoke Water	1983-1989	165	13.4 (1.0)	247 (4)
	1990-1999	101	18.1 (1.4)	257 (5)
Easedale Tarn	1996-1999	23	17.8 (2.8)	241 (10)
Stickle Tarn	1996-1999	20	14.4 (3.3)	246 (13)

Table 4.2 Analysis of seasonality in ANC: δ (seasonal range) and d_{\max} (day of maximum ANC) are defined by equation (4.2). n denotes the number of data points.

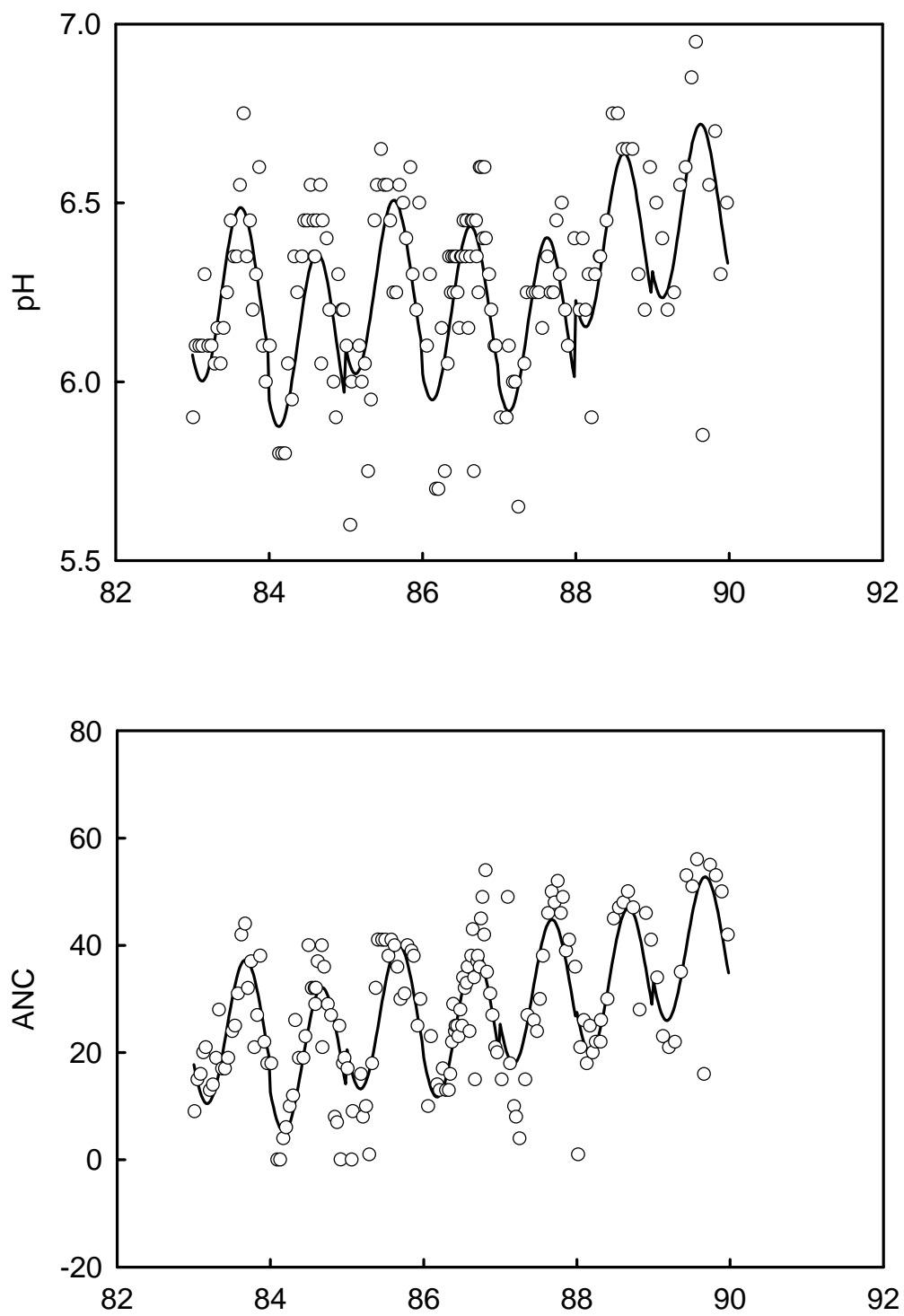


Fig. 4.1 Plots illustrating seasonality of pH and ANC in Devoke Water. The lines are model fits.

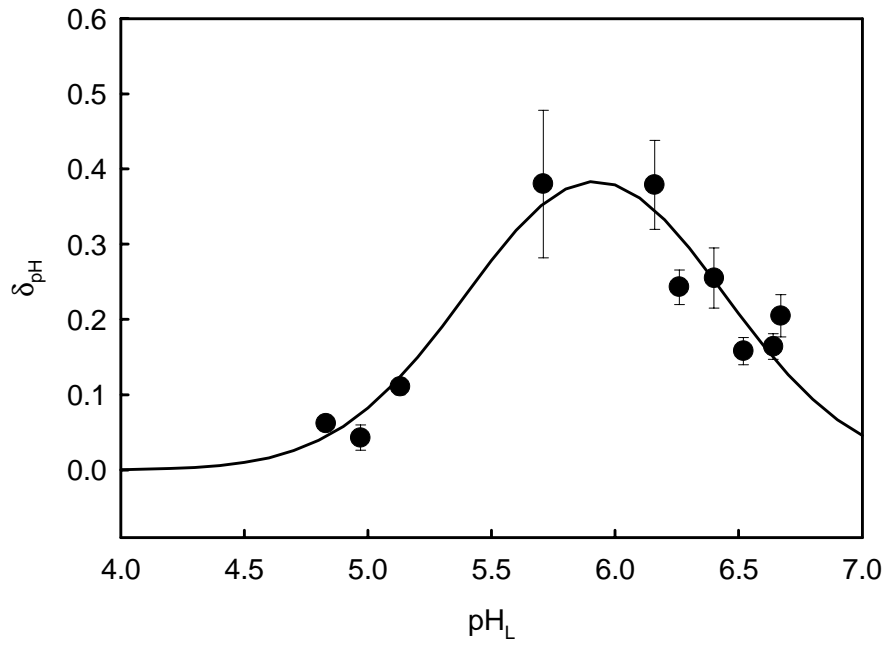


Fig. 4.2 Dependence of δ_{pH} on pH_L , fitted with equation (4.3).

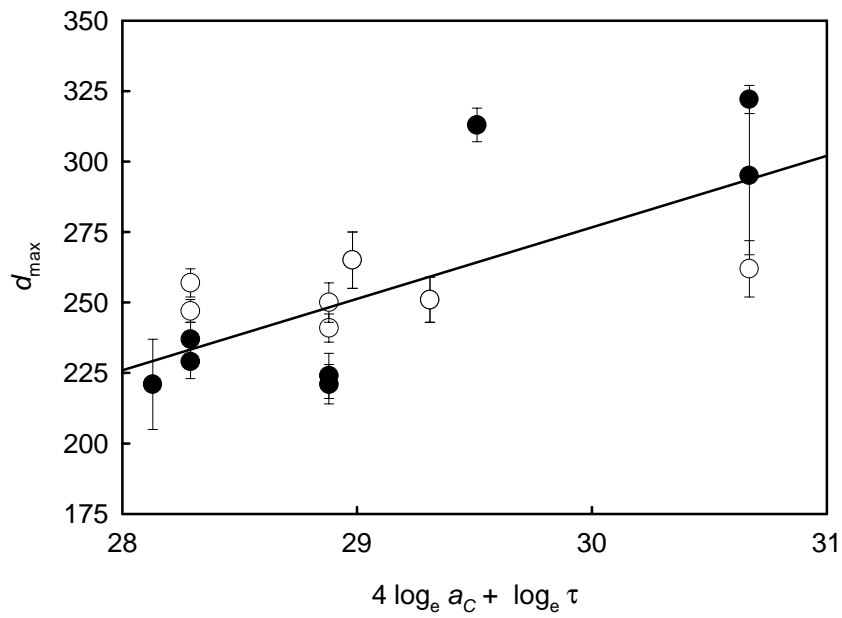


Fig. 4.3 Dependence of d_{max} on an index based on catchment altitude and lake residence time, fitted with equation (4.5).

5 CHANGES IN pH_L AND ANC_L

5.1 Qualitative trends

Figs. 5.1–5.4 show values of pH_L and ANC_L for the nine lakes. The pH increase between the mid-1970s and the present in Levers Water (Fig. 5.1) has already been reported (Tipping et al., 1998). The results for Seathwaite Tarn (Fig. 5.1) are insufficient to establish a trend, but the values parallel quite closely those for Levers Water, suggesting a general trend in the surface waters. The same parallelism is seen for ANC_L. ANC_L in Levers Water does not provide much evidence of a trend, although the 1990s values are generally greater than the 1980s values.

Fig. 5.2 compares results for Buttermere, the largest lake considered in this work, and Devoke Water. The pH_L values are quite similar in the 1980s and 1990s, both exhibiting a rising trend, and the same is true for ANC_L. The ANC_L values for the 1950s are also similar. However during the early 1970s, the pH of Buttermere was substantially greater than that of Devoke Water, and the alkalinity was also possibly greater. The difference is explained by quarrying activity in the Buttermere catchment. The extraction and processing of slate at Honister generated large amounts of fine particulate material the dissolution of which generated alkalinity and consumed protons. The quarrying ceased in the 1970s and the influence of the activity on lake chemistry is no longer detectable.

The three lakes for which data are shown in Fig. 5.3 are within 3km of one another (Fig. 2.1), and they exhibit similar temporal changes. There are increases in both pH_L and ANC_L in the 1980s and 1990s. It is noteworthy that the ANC_L values for the early 1950s are greater than the values in the mid 1970s, especially for Codale Tarn, suggesting a deterioration in water quality between these two periods. A suggestion of this development is also observed for ANC_L in Devoke Water (Fig. 5.2). Thus, it appears possible that the lakes went through minima in ANC_L, and presumably also pH_L in the period 1970-1980, ie this period saw the greatest degree of acidification. It also followed the time of the highest sulphur emissions, and, presumably, deposition.

Greendale and Scales Tarns (Fig. 5.4) are not close to one another (Fig. 2.1), and their data are placed on the same graphs only for convenience. No strong trend is established by the scanty data for Greendale Tarn, except that pH_L in 1999 was appreciably greater than found in the mid to late 1980s. The pH_L in Scales Tarn also appears to have increased between the mid-1980s and the present, as does ANC_L. ANC_L in the early 1950s was similar to that in the mid 1980s, but it is conceivable that it went through a minimum in between, as suggested for other waters in the previous paragraph.

Overall, it can be said that the results display some coherence, ie similar patterns of variability are seen in all the lakes. A trend of decreasing then increasing pH_L and ANC_L, with the lowest values between 1970 and 1980 is compatible with most of the observations. Thus, the changing chemistry of the lakes reflects changes in emissions and deposition of oxidised sulphur.

5.2 Quantitative trends

Trends in pH_L and ANC_L were assessed quantitatively by linear regression, for the eight lakes with long datasets, this excludes Seathwaite Tarn. It is acknowledged that this approach is not strictly correct because the variances of the pH_L and ANC_L values are not constant, and also because the values for different years represent different numbers of data points. However, in order to assess the long-term trend it is reasonable to attribute equal importance to each yearly value of pH_L or ANC_L . In view of the probable minima in the two variables in the period 1970-1980 (see previous section), the analyses were confined to the period 1970s – 1999. The results are shown in Tables 5.1 and 5.2.

Three of the lakes show increases in pH that are significant at the 0.1% level, and a further 4 show significant increases at the 10% level. Stickle Tarn shows an increase in pH but it is not statistically significant. The average annual increase in pH_L ranges from 0.009-0.036.

The trends in ANC_L are less certain than those in pH_L . For two lakes, Buttermere and Devoke Water the increases are significant at the 0.1% level, while for Codale Tarn and Easedale Tarn they are significant at the 10% level. The other four waters do not show significant trends. The average annual increase in ANC_L , when significant at the 10% level or better, ranges from 0.8-2.1 $\mu\text{eq} / \text{L}$.

	Period	<i>n</i>	AAC	significance
Buttermere	1982-1999	18	+0.020	$p < 0.001$
Codale Tarn	1974-1999	9	+0.025	$p < 0.1$
Devoke Water	1972-1999	21	+0.036	$p < 0.001$
Easedale Tarn	1974-1999	9	+0.022	$p < 0.1$
Greendale Tarn	1983-1999	5	+0.035	$p < 0.1$
Levers Water	1974-1999	22	+0.009	$p < 0.001$
Scales Tarn	1983-1999	6	+0.016	$p < 0.1$
Stickle Tarn	1974-1999	10	+0.018	ns

Table 5.1 Regression analysis of pH data. *n* refers to the number of years for which a value of pH_L has been derived. AAC = average annual change.

	Period	<i>n</i>	AAC	significance
Buttermere	1982-1999	18	+0.8	$p < 0.001$
Codale Tarn	1974-1999	9	+1.2	$p < 0.1$
Devoke Water	1975-1999	19	+2.1	$p < 0.001$
Easedale Tarn	1974-1999	9	+0.9	$p < 0.1$
Greendale Tarn	1983-1999	5	+0.3	ns
Levers Water	1974-1999	21	-0.2	ns
Scales Tarn	1983-1999	6	+1.3	ns
Stickle Tarn	1974-1999	10	+0.2	ns

Table 5.2 Regression analysis of ANC data. *n* refers to the number of years for which a value of ANC_L has been derived. AAC = average annual change.

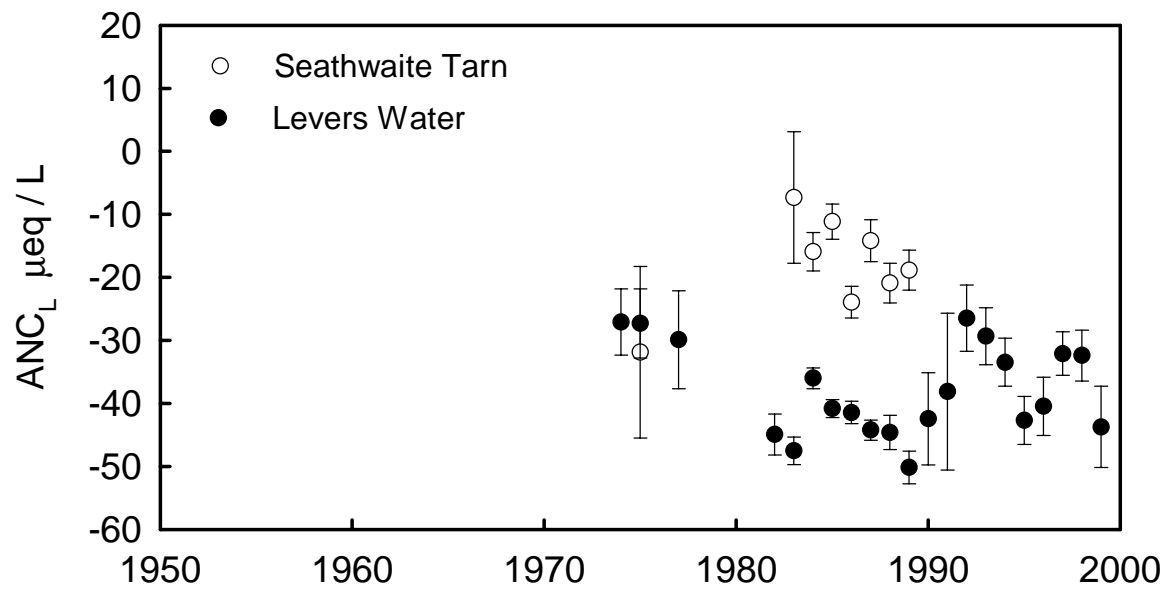
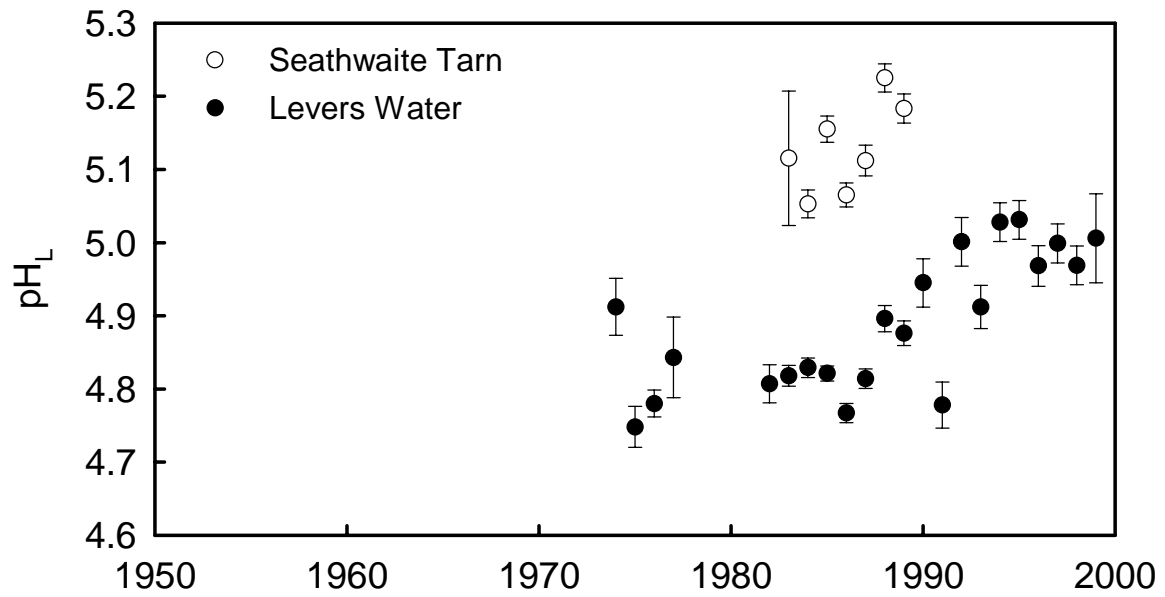


Fig. 5.1 Values of pH_L and ANC_L for Seathwaite Tarn and Levers Water.

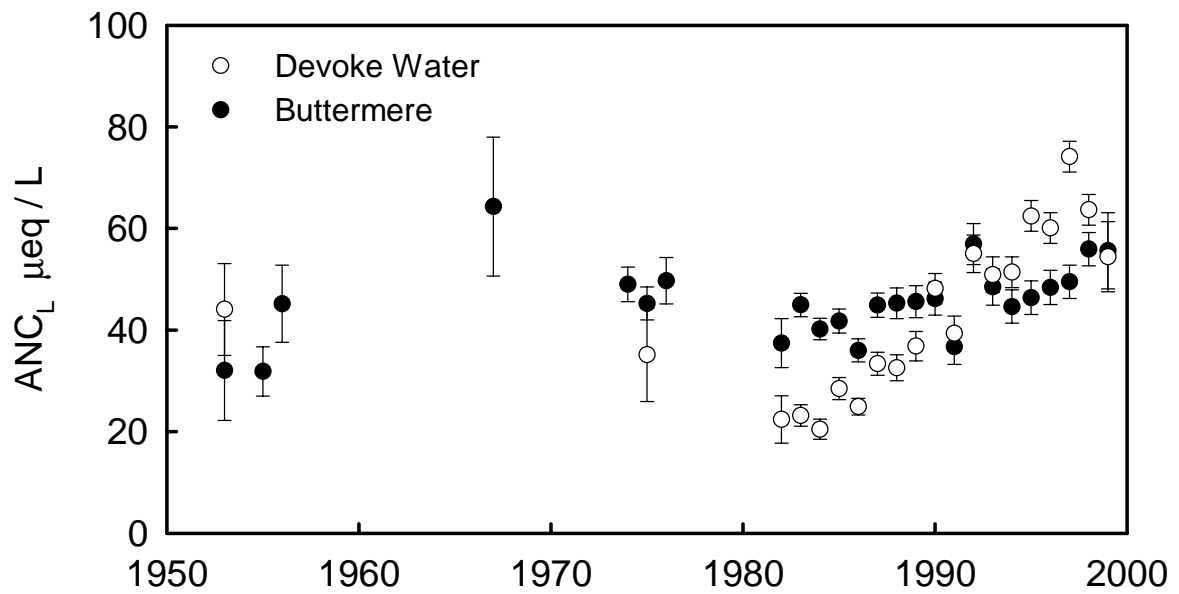
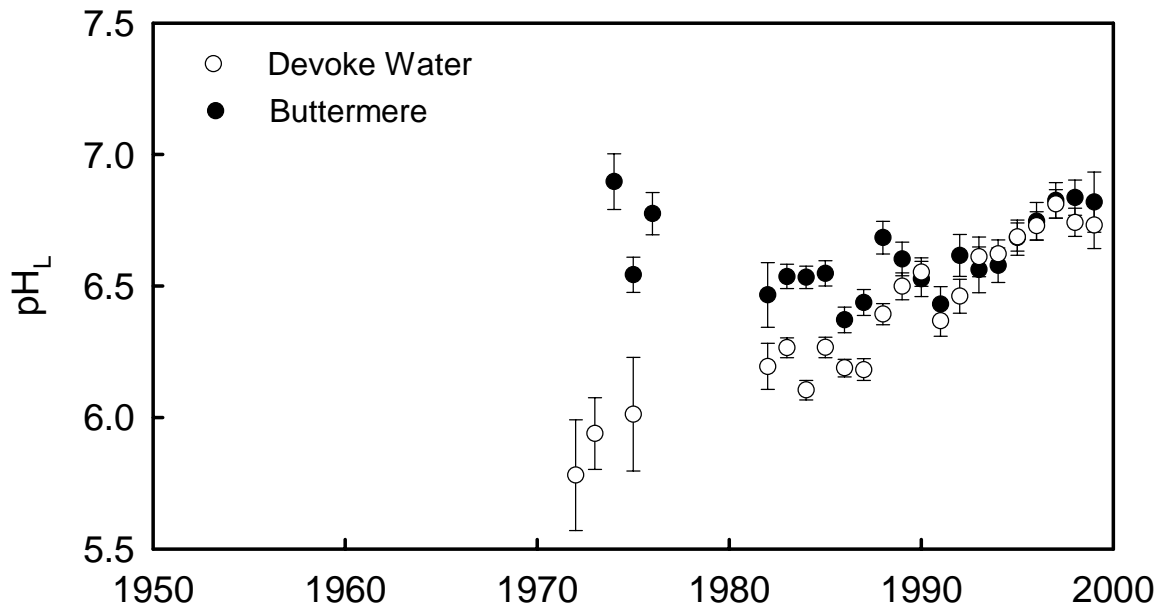


Fig. 5.2 Values of pH_L and ANC_L for Devoke Water and Buttermere

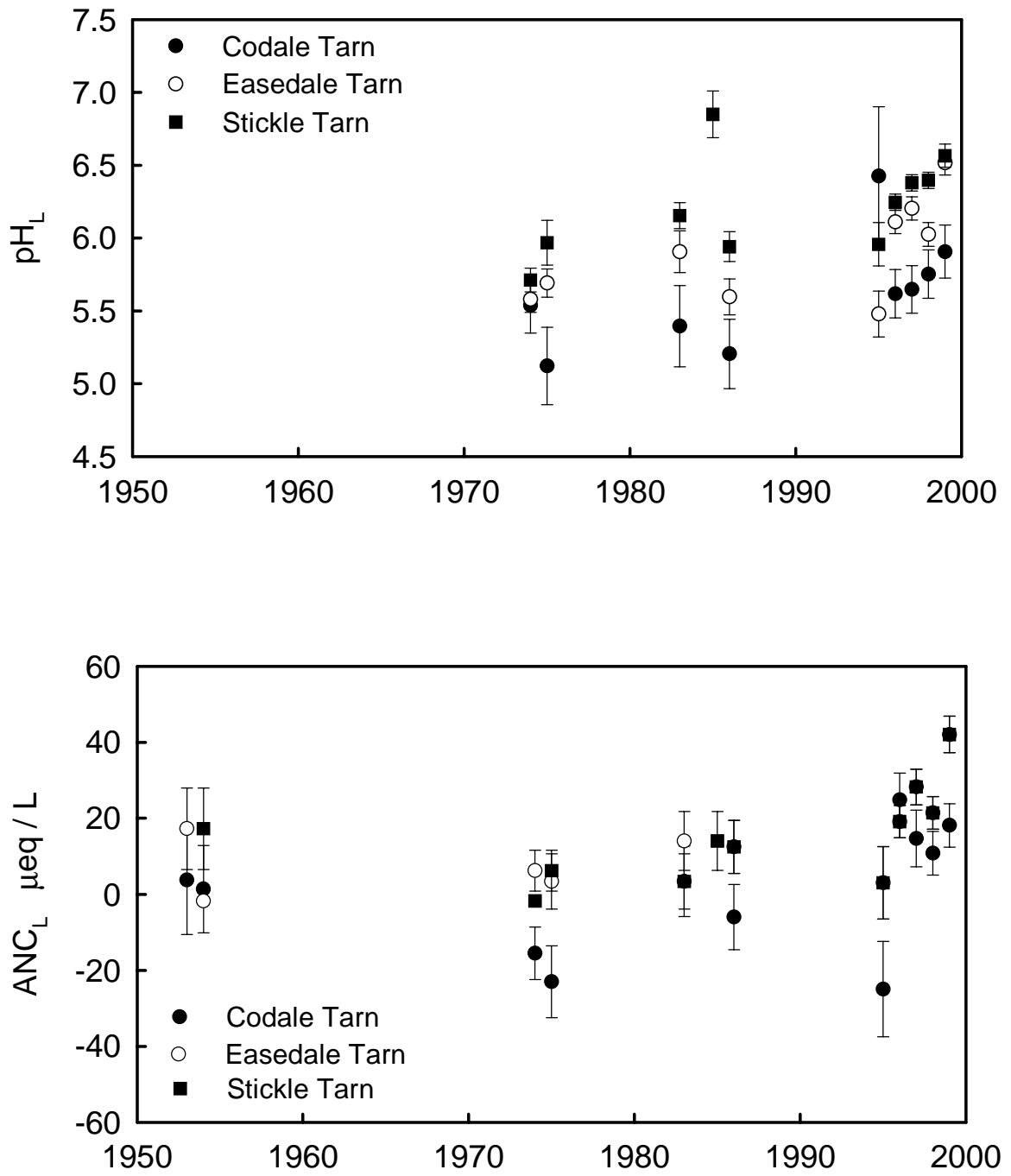


Fig. 5.3 Values of pH_L and ANC_L for Codale, Easedale and Stickle Tarns.

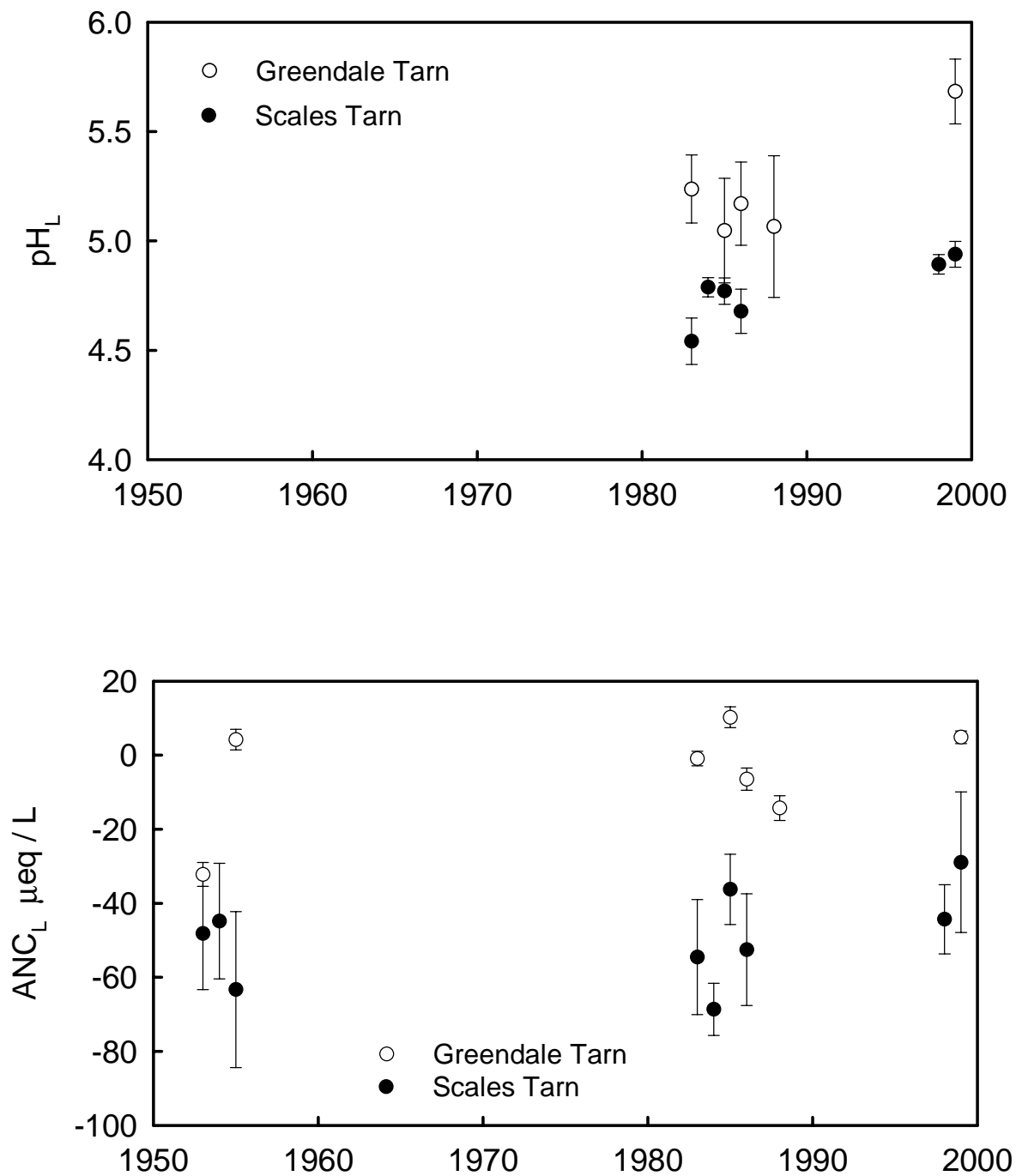


Fig. 5.4 Values of pH_L and ANC_L for Greendale and Scales Tarns.

6 CHANGES IN DIATOM SPECIES

Diatoms are sensitive to water chemistry, and this well-established fact is the basis for the use of diatom sedimentary remains to infer past pH. Here we focus on recent diatoms, comparing samples collected in 1983-1985 with samples collected in 1999. The aim was to see if the biological response had followed the chemical one.

6.1 Observations

Table 6.1 lists the numbers of individual diatoms in different classes found for the seven lakes that were studied. In four cases (Codale Tarn, Devoke Water, Little Langdale Tarn, Stickle Tarn) there were substantially fewer acidophilous species in 1999 than in the 1980s, fewer acidobiontic ones, and more circumneutral ones. These changes are consistent with increasing pH. The diatom numbers in Greendale and Scales Tarns have not changed significantly. The one exception to the trends indicating pH increase was Easedale Tarn, in which the acidophilous numbers increased and the circumneutral numbers fell, although the number of acidobiontic diatoms did fall.

The data are presented in terms of percentages of total numbers, comparing the 1980s with 1999, in Fig. 6.1. By comparing the data with the 1:1 lines it is seen that in the majority of cases the circumneutral percentage has tended to increase, while the acidophilous and acidobiontic percentages have decreased, between the early 1980s and 1999.

6.2 Diatom-inferred pH values

Values of pH inferred from the diatom assemblages are compared with observed level values in Fig. 6.2. The observed values are the means of two five-year periods (1982-1986 and 1995-1999). The first feature to note is that the diatom-inferred values are generally lower than the observed ones. This may partly be explained by the fact that the observed values are based on the yearly average, while the diatom values may be biased to the early part of the year, when pH tends to be lower than average (Fig. 4.1). Another factor is that the database on which the diatom inferences are based applies on a Europe-wide basis, and although it is expected to provide pH estimates with the correct trend, it may not, in specific local instances, give accurate values for individual waters.

If there were perfect agreement between observation and inference, the points in Fig. 6.2 would all plot on the 1:1 line, and if there had been a consistent increase in pH in all the lakes, the open circles (1980s) would be to the “southwest” of the filled circles (1999). These features are quite well approximated for two of the lakes (Codale Tarn and Devoke Water). For three of the remainder (Easedale Tarn, Greendale Tarn, Scales Tarn) the observed pH has increased but not the diatom-inferred pH, and in the case of Stickle Tarn the observed pH has not changed while the diatom-inferred value has done so.

		A	B	C	D	E	F	G
Codale Tarn	1983	256	37	11	8	18	1	6
	1999	174	125	16	8	5	0	6
Devoke Water	1985	98	194	11	3	6	0	16
	1999	39	247	16	2	0	0	5
Easedale Tarn	1983	227	70	9	1	10	0	17
	1999	261	63	6	0	6	0	4
Greendale Tarn	1984	294	16	0	8	14	0	3
	1999	292	19	1	1	13	0	9
Little Langdale Tarn	1984	150	146	10	11	13	0	5
	1999	106	211	13	4	2	0	0
Scales Tarn	1983	247	5	1	1	78	0	2
	1999	233	8	0	1	93	0	1
Stickle Tarn	1985	183	141	5	0	7	0	0
	1999	128	199	8	1	1	0	0

Table 6.1 Numbers of individual diatoms in different classes

A Acidophilous	E Acidobiontic
B Circumneutral	F Alkalibiontic
C Alkaliphilous	G Unknown
D Indifferent	

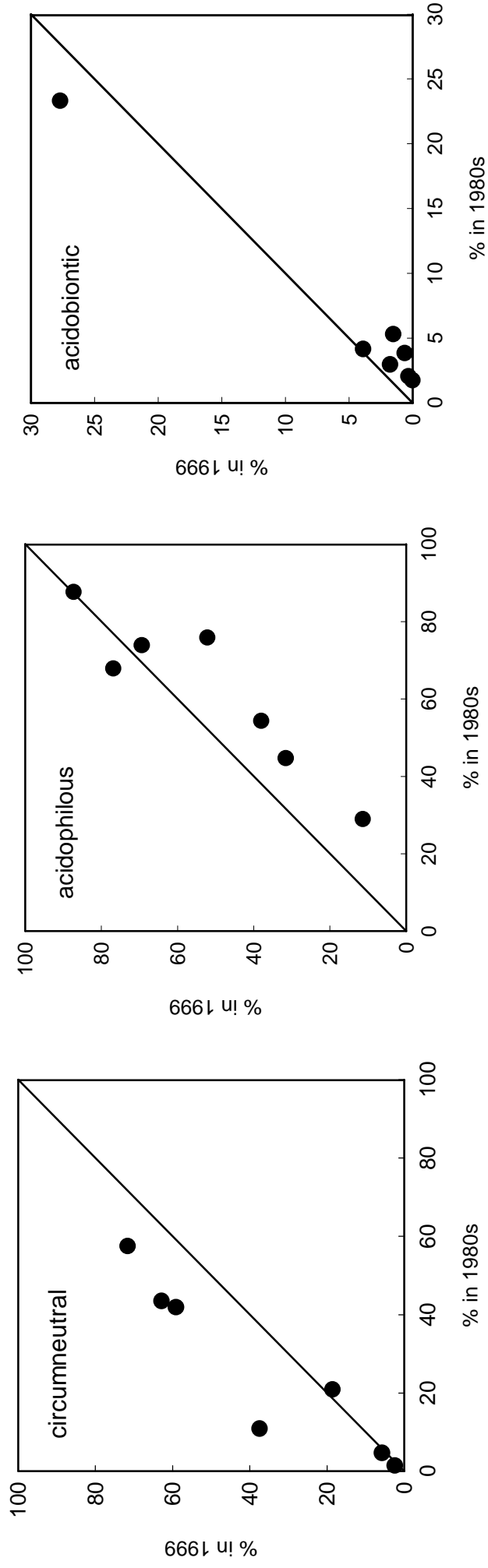


Fig. 6.1 Plots of percentages of diatom numbers in different classes, comparing 1999 with the early 1980s. The 1:1 lines are shown.

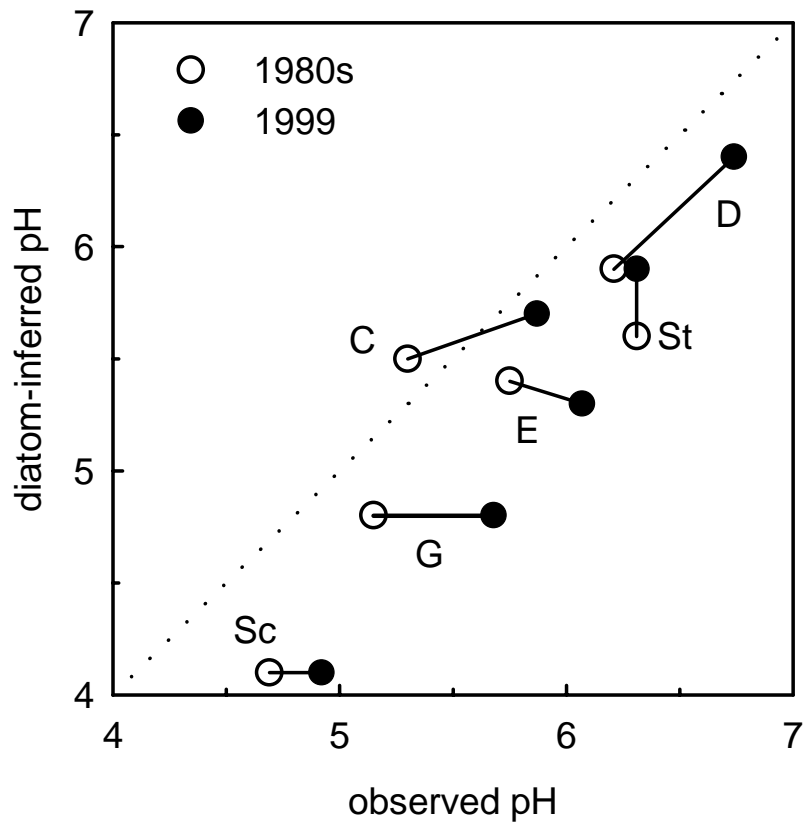


Fig. 6.2 Comparison of pH inferred from diatom assemblages with observed values. The observed values are means of pH_L for the periods 1982-1986 and 1995-1999. The lines join points for a given lake. Key to lakes: C Codale Tarn, D Devoke Water, E Easedale Tarn, G Greendale Tarn, Sc Scales Tarn, St Stickle Tarn.

7 DISCUSSION

The chemical data reinforce the conclusion that surface waters of the Lake District are showing reversal of acidification. Highly significant ($p < 0.001$) trends in pH have now been established for three lakes, and significant ($0.001 < p < 0.1$) for a further four. For ANC the corresponding numbers of lakes are two ($p < 0.001$) and two ($0.001 < p < 0.1$) respectively. The results for Greendale and Scales Tarns extend the geographical range of the findings (Fig. 2.1), and indicate that the Lake District as a whole is recovering.

The mathematical analysis to remove seasonality from the data has worked reasonably well, and enables estimates of pH_L to be made in cases where the data do not cover the whole year in question. A better, but more elaborate, approach would be also to include information on variations in inflow to the lakes, estimated by rainfall-runoff modelling. This would allow short-term variability in lake water composition to be taken into account. For example, high summer rainfall would tend to depress pH relative to the underlying level, while prolonged drought would give rise to relatively higher pH values. It would therefore be useful to apply the CHUM model (Tipping, 1996), which operates at the appropriate time scale, to all the sites. CHUM has already been applied successfully to simulate long term changes in two of the lakes, Devoke and Levers Waters (Tipping et al., 1999a), and in stream waters (Tipping et al., 1999b), and a regional application would be worthwhile.

Overall, the lake diatoms have responded as expected to the improvements in water quality, with increases in the numbers of circumneutral species and declines in the numbers of species associated with acid conditions. However, comparison of the changes with the measured changes in pH shows that the biological responses have not been exactly as would be expected from the chemistry. In Codale Tarn and Devoke Water the diatom-inferred pH values, and their changes between the 1980s and the present, are in quite good agreement. The other four tarns for which both diatom and chemical data are available show either chemical or biological improvements, but not both. One possible reason for the lack of exact agreement is wash-in of diatoms from the catchments of the waters. This might account for the discrepancies in Scales Tarn, where acid rock pools may supply “acid-biased” diatoms, and Easedale Tarn, where marshland may do so. Another confounding factor is the residence time of the diatoms in surface sediments. A reasonable average time is five years, but this may well vary from lake to lake. Therefore it is probably expecting too much for the diatom changes to track exactly the chemical changes over the relatively short timescale considered. Clearly it would highly desirable to continue the chemical monitoring and to return to the sites in five or ten years time to perform another diatom survey.

This study has added to previous results (Tipping et al., 1998; 1999a,b,c; 2000a,b) documenting the recovery of Lake District waters from the affects of acid deposition. The evidence now accumulated is as follows:

- (i) Significant increases in pH between the 1970s and the present in seven lakes.
- (ii) Significant increases in pH between the 1970s and the present in nine streams.
- (iii) Significant increases in ANC between the 1970s and the present in four lakes.

- (iv) Increases in stream invertebrate diversity between the 1960s and 70s and 1999.
- (v) Appearance of an acid-intolerant bacterium in a stream from which it was previously absent.
- (vi) Changes in lake diatom assemblages between the 1980s and 1990s, indicative of increasing lake water pH.

8 CONCLUSIONS

Two main conclusions come from this work:

- (i) The results provide additional, and geographically wider, chemical evidence for acidification reversal in the surface waters of the Lake District.
- (ii) Biological response to the chemical changes is strongly suggested by the changes in diatom assemblages.

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