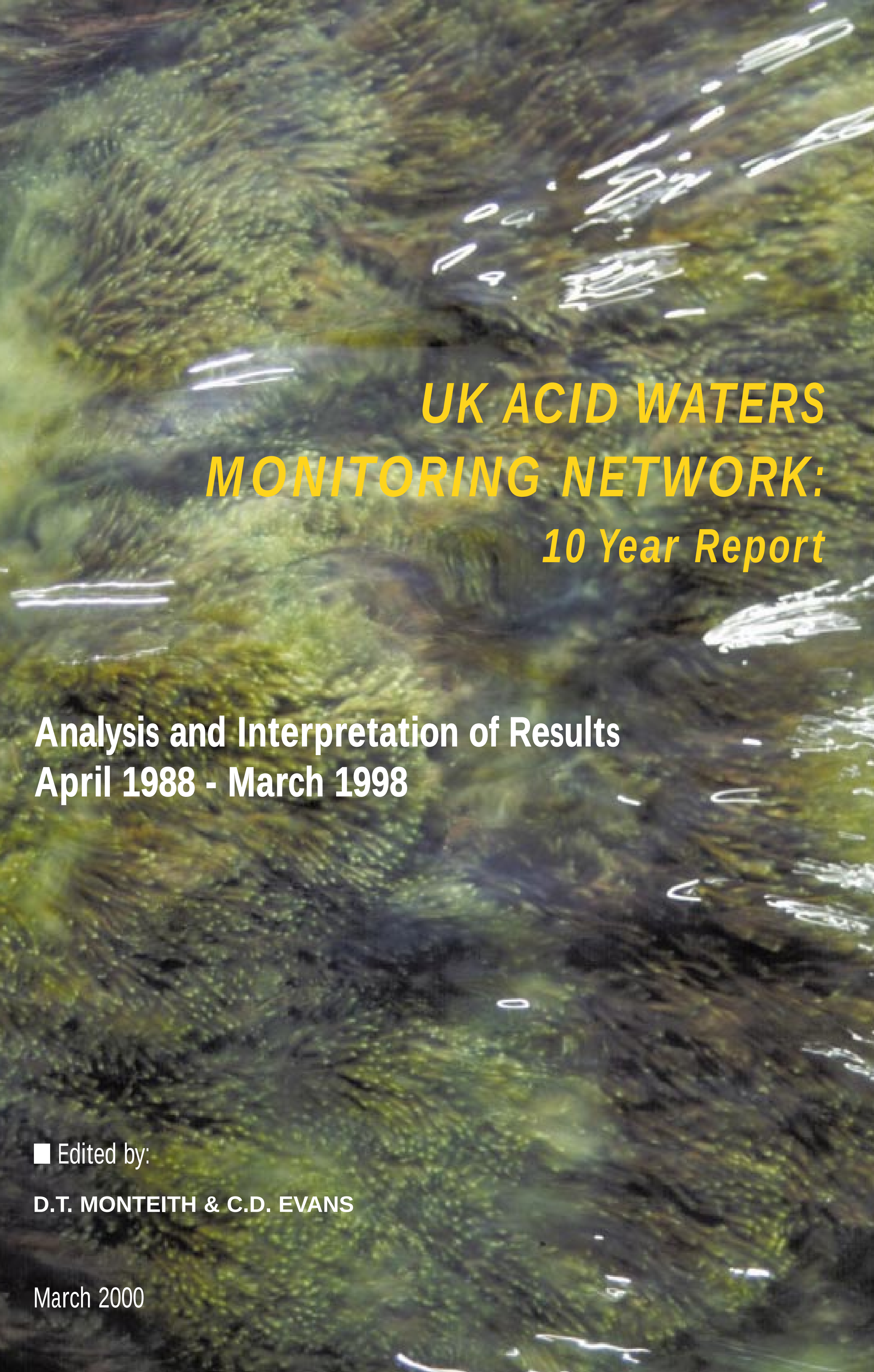

UK ACID WATERS MONITORING NETWORK:

10 Year Report

Analysis and Interpretation of Results
April 1988 - March 1998

■ Edited by:

D.T. MONTEITH & C.D. EVANS

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- Cover photograph: The acid sensitive aquatic moss *Hygrohypnum ochraceum* carpeting a fast flowing stretch of the Allt a'Mharcaidh, northeast Scotland.

Contents

Executive Summary

1) This report provides an interpretation of data collated by the United Kingdom Acid Waters Monitoring Network (UKAWMN) over the ten year period April 1988 - March 1998. It also draws on data from the UK Acid Deposition Network which has been operating since 1986.

2) Between 1986 and 1997 sulphur emissions from the UK declined by approximately 57% while those from the rest of UNECE Europe declined by 45%. UK emissions of oxides of nitrogen (NO_x) declined by approximately 14%.

3) Over the same period non-marine sulphur deposition (i.e. of anthropogenic origin) in the UK declined by approximately 52%, but the majority of the decline was dry deposition (61%). Wet deposition reduced by 42%.

4) Rates of decline in sulphur deposition are geographically skewed. In areas close to emissions sources, i.e. central and southeast England, large reductions have occurred in the flux of wet and dry sulphur deposition and in the sulphur concentration of precipitation. Smaller but significant declines have occurred at intermediate distances from sources. Although there have been reductions in sulphur deposition in the acid sensitive, high rainfall, west coast areas, these are much smaller than the reductions in sulphur emissions. Indeed at many of the high rainfall deposition monitoring sites trends in sulphur deposition are not statistically significant.

5) Small but significant increases in concentrations and deposition fluxes of nitrate (NO_3) are evident at west coast and remote monitoring stations.

6) It is the aim of this report to investigate to what extent emissions reductions have influenced the surface water chemistry and biology of acid sensitive freshwaters throughout the UK. The UKAWMN consists of eleven lakes and eleven streams which have been monitored chemically and biologically over the last decade. Historical reconstructions, based on sediment cores, have demonstrated that at least nine of the lakes have become more acid over the last 150 years as a result of acid pollutant deposition. It is likely that most streams are also in an acidified state.

7) Over the period of analysis covered by this report (1988-1998) large declines in non-marine sulphate (xSO_4) concentrations have been recorded at UKAWMN sites in the 'close-to-source' regions, i.e. at Old Lodge (southeast England) and the River Etherow (Pennines). A smaller, but still significant, decline has occured at Lochnagar (northeast Scotland). Nineteen of the twenty-two UKAWMN sites have shown no significant trend in xSO_4 concentration.

8) There is a clear spatial relationship between nitrogen deposition and NO_3 concentration in UKAWMN freshwaters. NO_3 concentrations in the most remote sites range from low to below detection limits. In these relatively low pollution environments nitrogen can limit terrestrial primary productivity, in which case virtually all nitrogen inputs are expected to be retained by catchment soils. Enhanced nitrogen inputs can result in catchment saturation and nitrogen leaching into surface waters. Since the latter is likely to be accompanied by hydrogen ions in sensitive catchments, the phenomena of nitrogen saturation presents a serious threat to acid sensitive waters. Positive linear trends have been identified at four sites which may reflect increasing saturation of their catchment soils. NO_3 concentrations at Lochnagar appear to have undergone a step-change increase which reflects a transition from a seasonal pattern to year-round leaching.

9) NO_3 concentrations have shown considerable inter-annual variability which appears to relate to climatic differences between years. Variation in NO_3 concentration can be linked to winter values for the North Atlantic Oscillation Index (NAOI), a synoptic scale variable which represents inter-annual variability in the relative dominance of westerly versus north-easterly weather conditions over the UK. At most sites NO_3 leaching has been highest after the coldest (most negative NAOI) winters.

10) Upward trends in pH, and/or alkalinity, have been identified at seven sites. This is surprising since there is no indication of downward trends in acid anion concentrations at the same sites. Due to the absence of this link, and for other reasons explored in this report, it is too early to categorically attribute these trends to long term chemical recovery from acidification. At the three sites with declining xSO_4 concentrations, NO_3 has increased, resulting in little overall change in total acidity. At Old Lodge and the River Etherow, base cation (i.e. calcium,

magnesium, potassium and sodium) concentrations have decreased. These increases in acidifying NO_3 and/or reductions in acid-neutralising base cations appear so far to have offset any positive influence of xSO_4 decreases, where observed, on surface water acidity. At Lochnagar, the decline in xSO_4 has been smaller than the increase in NO_3, and this site has continued to acidify.

11) Concentrations of chloride (derived mainly from sea-salt inputs during winter) at UKAWMN sites with westerly locations have shown cyclical variation over the monitoring period and this is highly correlated between sites. Chloride concentration variability can be linked to inter-annual variations in winter storminess, which influences levels of sea-salt deposition, and, once again, to the winter NAOI.

12) At the same west coast sites, cyclical variation is also apparent in the concentrations of non-marine base-cations and, in some cases, hydrogen ion and labile (biologically available) aluminium. Variation in these ions appears to be driven by their displacement from catchment soil ion-exchange sites by marine cations deposited in sea-salt. Inter-annual variation in pH and alkalinity may also have been influenced by variations in rainfall, which determines the proportional contributions of relatively alkaline base-flow and more acidic surface run-off. Trends in pH and alkalinity, where identified, may therefore primarily reflect a response to a decline in winter storminess, from the early 1990s to the end of the interpretative period, rather than a decline in acid deposition. The relative roles of these two effects will only become clear with further monitoring.

13) SO_4 occurs both as an acidic pollutant and, naturally, in neutral salts in sea-water and sea-spray. Analysis suggests that SO_4 storage by catchment soils may be enhanced following periods of high sea-salt inputs. Conversely, when sea-salt inputs are low and total SO_4 concentration in soil water declines, stored SO_4 may be released. Chloride on the other hand behaves conservatively, passing more rapidly into the drainage network. Since a fixed SO_4:Cl ratio (based on sea-water constitution) is used to estimate the proportion of total SO_4 which is derived from marine and non-marine sources, errors are likely to occur in the estimate, depending on the prevailing sea-salt regime. Non-marine SO_4 concentrations may therefore be underestimated during periods of high sea-salt inputs and overestimated when inputs are low. This effect may have masked the small reductions in actual non-marine SO_4 concentrations expected at some sites at intermediate distance from source areas.

14) Longer term datasets (from the early to mid-1980s to the present), available for streams in north Wales, Galloway and the Trossachs, and a loch in Galloway, demonstrate clear declines in xSO_4 and corresponding increases in pH. These underlie variations due to climate oscillations described above and provide the strongest evidence that slow chemical recovery from acidification is underway in some areas of the UK.

15) Significant increases have occurred in Dissolved Organic Carbon (DOC) concentrations at nineteen of the twenty-two sites in the Network. This is potentially of great importance to the Network, since an increase in organic acids could reduce, or even negate, reductions in acidity expected from declining mineral acid inputs. The remarkable spatial consistency suggests a general pattern of rising DOC levels in UK upland freshwaters. It is currently unclear whether these increases have been matched by an increase in water colour, and the molecular form of the DOC which has increased is not known. Mechanisms for the increase are also unclear at this stage, although the most probable hypothesis is considered to be increased microbial decomposition of soil organic matter resulting from increasing summer temperatures. UK summer temperatures over the last decade have been significantly higher than the long-term (i.e. last 30 year) mean. Under a scenario of rising global temperatures, therefore, DOC may be expected to increase further. In lakes, a rise in water colour could have the detrimental effect of reducing the depth of penetration of photosynthetically active radiation, required for plant growth. On the other hand, increasing colour would also provide aquatic

organisms with additional protection from exposure to UV-B radiation which is increasing in mid-latitudes. DOC has also been shown to reduce fish mortality under acidic conditions by both reducing the concentration of toxic labile aluminium (by complexing with it) and by reducing the toxicity of the remaining fraction.

16) The identification of climatically driven cyclicity in estimated xSO_4, NO_3, acidity and other important measures of surface water quality has major implications for detection of recovery-related trends, applicable both to the UKAWMN and to other monitoring programmes. Cyclical variations have the potential either to mask underlying anthropogenically driven trends, or to generate apparent trends as a result of natural processes. Since these variations appear to operate at approximately decadal timescales, there is clearly a need to monitor over longer time periods in order to fully characterise the impact of anthropogenic factors on surface water quality.

17) Spatial biological comparisons of multi-species datasets, i.e. epilithic diatoms (unicellular siliceous algae which grow attached to rocks), macroinvertebrates (non-microscopic aquatic invertebrates), and aquatic macrophytes (larger aquatic plants) demonstrate a generally positive relationship between the number of species found and pH. Trout densities show a roughly exponential decline with increasing labile aluminum concentration, and healthy populations are mostly restricted to sites with a positive ten-year mean Acid Neutralising Capacity (ANC, calculated as the difference between the sum of concentrations of base-cations and acid anions).

18) Multi-species biological datasets have been subject to linear time trend analysis to test for uni-directional change in species composition over the monitoring period. Where detected, changes may be indicative of biological responses to changing acidity status (i.e. ‘recovery’ or further acidification).

19) Linear trends in aquatic macrophyte assemblages were identified at five sites. These reflect reductions in overall cover rather than a turnover of species, and probably result from physical disturbance rather than chemical change.

20) Linear trends have been detected in epilithic diatom species assemblages at nine sites and five of these are indicative of an amelioration in acidity (i.e. recovery) while one is indicative of further acidification. Trends at three sites indicative of amelioration are consistent with linear trends in acidity established from analysis of water chemistry. Linear change at other sites may also be indicative of biological recovery, although as there is no evidence for sustained year-round chemical improvement at many of these, it would seem that other factors, most notably climatic, may be involved. Generally, temporal variation in acidity in lakes is reflected by variation in epilithic diatom species composition. This suggests that for lakes, chemical recovery should lead to rapid recovery of this important group of primary producers. At stream sites, inter-annual variation can be closely linked to variations in the summer rainfall regime, suggesting that flow-governed acidity at this time of year may be the primary factor in influencing the species assemblage. Trends indicative of recovery are therefore likely to take much longer to identify for streams than for lakes.

21) Linear trends have been detected in macroinvertebrate assemblages at eleven sites, but trends at only three are indicative of an amelioration in acidity, and only two of these are consistent with linear changes identified in water chemistry. Linear trends at most of the eleven sites, mainly lakes, can be linked to the declining influence of winter storm activity over the monitoring period. A particularly high proportion of variance between years in the assemblage can be explained by the January NAOI, for those sites where the January NAOI is well correlated with Cl concentration and winter rainfall. This suggests that variation in the macroinvertebrate assemblage may be primarily driven by inter-annual variation in the severity and/or duration of acid episodes resulting from the effects of sea-salt deposition and cation dilution. If this is the case, macroinvertebrate communities may be expected to show long term, but punctuated (i.e. non-linear) recovery as the intensity of the most acid events gradually declines with decreasing deposition. However, other

climate-related physical effects, such as water level oscillation, cannot be ruled out as driving factors at this stage.

22) Llyn Llagi, in north Wales, and Loch Chon, in the Scottish Trossachs, are the only sites which show trends indicative of improved conditions in both epilithic diatoms and macroinvertebrates, and concomitant reductions in acidity according to water chemistry. For Llyn Llagi, a comparison of the diatom assemblage of sediment trap samples (collected since 1991) and samples from a sediment core (taken in 1990) demonstrates that recent changes in the diatom assemblage of newly deposited lake sediment are approximately the reverse of those which occurred during the latter stages of acidification. This provides powerful evidence that biological recovery, at least at the lowest trophic level, is underway at this site. Similar changes in sediment assemblages which are indicative of recovery have occured in Loch Chon. However here it is possible that these may at least in part reflect a response to a reduction in the influence of climatically enhanced acidity over the monitoring period.

23) Few linear trends are evident in trout density or condition factor. The mobility of fish, relative to other biological groups monitored, adds to overall sample variability and for most sites it is likely that several more years of monitoring are required to allow the possible identification of trends. However, there has been a significant increase in the density of trout at Old Lodge in southwest England. This is mirrored by a decline in labile aluminium concentration and suggests that recent improvements in water chemistry may have allowed the upstream migration of fish from better buffered waters downstream. Since the decline in labile aluminium appears to be partly influenced by reductions in marine ion deposition, it is unclear to what extent this apparent ‘recovery’ will be sustained in the short-term.

24) The analysis of the 10 year dataset has highlighted several important issues and uncertainties:

a) Chemical and biological ‘recovery’ is very slight at this stage, but is predicted and needs to be identified and quantified, if, when, and where it occurs.

b) Problems have been identified in the estimation of the temporal variation in SO_4 from non-marine sources and this could account for the absence of evidence for declining xSO_4 at some sites. Further work on data from sites with co-located deposition monitoring stations may begin to address this problem.

c) Where detected, declining acid anion trends have not been accompanied by detectable amelioration in acidity to date. The period of time required for the onset of a measurable recovery response in buffering cations is as yet unclear.

d) Deposition of NO_3 may be increasing slowly in more remote areas, while continued accumulation of anthropogenically derived nitrogen may eventually lead to nitrogen breakthrough and hence further biological damage at some sites.

e) Widespread increases in DOC may be hampering chemical recovery, but the cause and effects are currently poorly understood.

f) Inter-annual variability in water chemistry and biology is considerable, relative to expected rates of recovery. A significant proportion of this variability can be explained by climatic influences. Continued monitoring should allow the quantification of climatic effects and therefore more sensitive detection of potentially underlying trends.

25) UKAWMN data are becoming increasingly valuable in the testing and calibration of acidity prediction models such as MAGIC (Cosby *et al.*, 1985) and FAB (Posch *et al.*, 1997).

26) Data from UKAWMN sites are becoming increasingly important to wider monitoring networks, including the Environmental Change Network (ECN) and the UNECE ICP (International Cooperative Programme on the Assessment and Monitoring of Acidification of Rivers and Lakes).

Contributors

R.W. Battarbee[1], W.R.C. Beaumont[2], C.D. Evans[3], D. Fowler[4], M. Gardner[5], P. Collen[6], R.J. Flower[1], R. Harriman[6], A.G. Hildrew[7], M.J. Hughes[1], A. Jenkins[3], A.M. Kreiser[1], D.T. Monteith[1], S.T. Patrick[1], B. Reynolds[8], N.L. Rose[1], R.I. Smith[4], J. Winterbottom[7].

[1]. Environmental Change Research Centre, University College London, 26 Bedford Way, London WC1H 0AP.

[2]. Centre for Ecology and Hydrology, River Laboratory, East Stoke, Wareham
BH20 6BB.

[3]. Centre for Ecology and Hydrology, Crowmarsh Gifford, Wallingford OX10 8BB.

[4]. Centre for Ecology and Hydrology, Bush Estate, Penicuik, Midlothian EH26 0QB.

[5]. Water Research Centre Ltd., Medmenham, PO Box 16, Marlow SL7 2HD.

[6]. Freshwater Fisheries Laboratory, Faskally, Pitlochry, Perthshire PH16 2LB.

[7]. School of Biological Sciences, Queen Mary and Westfield College London, Mile End Road, London E1 4NS.

[8]. Centre for Ecology and Hydrology, Bangor Research Unit, UWB, Deniol Road, Gwynwedd, LL57 2UP.

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1 Introduction

Alan Jenkins

The processes that link the emission of acidifying pollutants to the atmosphere, their transport and deposition and the subsequent acidification of soils and freshwaters are largely understood and well documented (e.g. Reuss & Johnson, 1986). The major pollutants of concern include oxides of sulphur and nitrogen derived from the burning of fossil fuels and ammonia derived largely from agricultural sources. These acidifying pollutants undergo chemical reaction in the atmosphere, are carried by the air over large distances from their sources and deposited as gases, aerosols and dissolved in rain water. Acidification of soils begins immediately as base cations are stripped from the ion-exchange complex and base saturation decreases. If the rate of supply of base cations from primary weathering in the catchment is less than the incoming flux of strong acid anions, the base cation store in the soil becomes depleted and hydrogen ions and aluminium species will accompany acid anions into the surface water, promoting acidification. The impact on biota results both from the toxicity of high hydrogen ion concentration and from the increased toxicity of aluminium at lower pH, and is manifest in decreases or loss of populations at all trophic levels.

The first legislation aimed at reducing S emissions was signed under the auspices of the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution in 1985 (the First Sulphur Protocol). The signatory countries committed themselves to a 30% reduction in S emission relative to 1980 levels by 1993. The UK did not ratify this protocol but still achieved the required emission reductions. In 1994 a Second Sulphur Protocol was signed under which the UK agreed to a c. 80% reduction in emissions, again relative to 1980, by 2010. The UK emissions are currently on track to meet this target. In addition there have been various EU Directives binding member states to similar targets. For nitrogen, the first UNECE protocol was signed in 1988 and committed to a stabilisation of the emission of oxidised nitrogen compounds at 1987 levels by 1994. In 1999, a further protocol incorporating multi-effects and multi-pollutants (sulphur, nitrogen, ozone and volatile organic compounds) was signed to introduce yet further reductions in emissions of acidifying pollutants.

The impact of the measures adopted to reduce acidic emissions should be reflected in long term trends in water chemistry and biology at acid-impacted sites. Identification of trends in long term data, however, is often complicated by changes in sampling frequency, analytical techniques and laboratories. The UK Acid Waters Monitoring Network (UKAWMN) was established in 1988 to provide a consistent water data record for chemistry and biology, across a range of acid-impacted sites, with which to assess the impact of reducing emissions of acidifying pollutants. The interpretation of trends at each site is underpinned by complimentary information from the UK Acid Deposition Monitoring Network and this allows the link between emission reductions and atmospheric deposition to be evaluated. It is unlikely that emission reductions will translate into uniform deposition reductions across the whole of the country.

This report presents the results of analysis of the first ten years of UKAWMN data. Analysis of ten year trends at UKAWMN sites in Chapters 4,5 and 7, is augmented by a brief analysis of a few longer term, high quality chemistry datasets in Chapter 6. These Chapters are preceeded by an overview of recent analysis of data from the UK Acid Deposition Monitoring Network (Chapter 2) which sets the recent acid deposition regime in spatial and temporal contexts.

Analysis has focussed on the identification and quantification of time trends in chemical and biological data which may point to improvements (i.e. recovery), stable conditions or further deterioration. The link between chemical and biological recovery is likely to be non-linear and significant time lags are expected, particularly for those organisms at the higher end of the food chain. Generally therefore, trends in chemistry and biology have been analysed in isolation and results have been integrated qualitatively. In addition, attention has been paid to the nature and causes of inter-annual variability in UKAWMN data, a significant proportion of which can be linked to variations in climate. Given the relatively large inter-annual variation observed in most datasets relative to changes with time, it is vital that these sources of ‘noise’ are better understood, so that underlying recovery trends may be more readily detected in future.

Spatial and temporal variability in the deposition of acidifying species in the UK between 1986 and 1997

2

David Fowler &
Rognvald Smith

2.1 Introduction

Prior to 1985 monitoring of precipitation chemistry in the UK was limited to a small number of locations, and a range of different protocols were used. These scattered data showed that rainfall acidity was similar in the UK to that in Scandinavia (Fowler *et al.*, 1982; RGAR, 1983). However, it was not possible with the limited data and the range of protocols for collection and analysis to map rain chemistry over the UK, and deposition budgets for the major pollutants were highly speculative.

The UK monitoring network for precipitation chemistry was set up during the mid-1980s, following a recommendation of the Acid Deposition Review Group (1985), and provided the first complete map of wet deposition of pollution for the UK in 1986 (RGAR, 1990). The monitoring from 1986 to 1997 covers a period of marked changes in emission of the primary pollutant SO_2 in the UK, which declined from 1966 kT S in 1986 to 830 kT S in 1997 (Figure 2.1). Other pollutants which contribute to soil and catchment acidification include the oxides of nitrogen NO, and NO_2, which are oxidized to NO_3^- in the atmosphere and NH_3 which when deposited may acidify soils following uptake by, and incorporation into, vegetation. During the 11 years of the deposition monitoring networks, emissions of these pollutants in the UK have also changed but by a much smaller extent than SO_2 (Figure 2.2). Pollutant emissions from other countries of Europe also influence concentrations and deposition in the UK, and in these countries sulphur (and to a lesser extent NO_x) emissions have also declined (Figure 2.1).

The period of intensive measurements of deposition of acidity in the UK is short relative to the natural variability of the weather. The observed changes in atmospheric concentrations and deposition of the pollutant gases, SO_2 and NO_x, and their oxidation products in the atmosphere, SO_4^{2-} and NO_3^-, must therefore be considered in parallel with seasonal and annual variability in the weather during the same period. However, the changes in sulphur emissions are large in both absolute and relative terms, and follow important policy decisions within the UK and elsewhere in Europe.

This short chapter is therefore centred on an analysis of the available measurements to show the degree to which the emission reductions have modified the concentrations and deposition of acidifying pollutants in the UK. The context within this report is on freshwater composition and ultimately the biological and ecological health of the freshwaters within the UK. Wet deposition of acidic pollutants in the acid sensitive uplands of western and northern Britain is therefore the central aspect of the analysis.

The UKAWMN, established in 1988, provides a slightly shorter period of measurements with which to compare deposition and surface water chemistry patterns. This chapter briefly describes the available deposition measurements, the temporal and spatial patterns in annual deposition for the UK as a whole.

The deposition data show considerable inter-site variability in both concentration and deposition as a consequence of local orographic effects and interactions with local variability in weather. As the precipitation chemistry collectors are not, in general, located close to UKAWMN sites, comparisons of temporal patterns in deposition and concentration are best between UKAWMN regional trends and wet deposition trends at the same scale. Within the last year, four new deposition stations have been sited within or nearby the catchments of UKAWMN sites, and these should facilitate more detailed catchment specific comparisons in the future.

To provide the necessary perspective in the analysis, the temporal trends in the UK patterns of wet and dry deposition are compared with trends in emissions of the major pollutants. The focus of the

Table 2.1

Monitoring sites illustrated in Figure 2.3 for the DETR wet deposition network and the UKAWMN.

Wet deposition monitoring network sites

Map Legend	*Site No*	*Name*	*East*	*North*	*SO_4^{2-} Group*
WD3	5004	Stoke Ferry	5700	2988	1
WD7	5009	High Muffles	4776	4939	1
WD10	5023	Preston Montford	3432	3143	1
WD11	5024	Flatford Mill	6077	2333	1
WD18	5117	Thorganby	4676	4428	1
WD19	5118	Jenny Hurn	4816	3986	1
WD21	5120	Wardlow Hay Cop	4177	3739	1
WD22	5121	Bottesford	4797	3376	1
WD25	5127	Woburn	4964	2361	1
WD26	5129	Compton	4512	1804	1
WD27	5136	Driby	5386	3744	1
WD5	5007	Barcombe Mills	5437	1149	2
WD9	5011	Glen Dye	3642	7864	2
WD13	5106	Whiteadder	3644	6633	2
WD15	5109	Redesdale	3833	5954	2
WD16	5111	Bannisdale	3515	5043	2
WD17	5113	Cow Green Res.	3817	5298	2
WD29	5149	Hillsborough Forest	1369	5156	2
WD1	5002	Eskdalemuir	3235	6030	3
WD2	5003	Goonhilly	1723	214	3
WD6	5008	Yarner Wood	2786	789	3
WD14	5107	Loch Dee	2468	5779	3
WD20	5119	Beddgelert	2556	3518	3
WD23	5123	Tycanol Wood	2093	2364	3
WD24	5124	Llyn Brianne	2807	2492	3
WD28	5140	Achanarras	3151	9550	3
WD30	5150	Pumlumon	2823	2854	3
WD32	5152	Balquhidder	2545	7207	3
WD4	5006	Lough Navar	192	5212	4
WD8	5010	Strathvaich Dam	2347	8750	4
WD12	5103	River Mharcaidh	2876	8052	4
WD31	5151	Polloch	1792	7689	4

UKAWMN sites

Map Legend	*Site No*	*Name*	*East*	*North*
AW1	1	Loch Coire nan Arr	1808	8422
AW2	2	Allt a'Mharcaidh	2881	8045
AW3	3	Allt na Coire nan Con	1793	7688
AW4	4	Lochnagar	3253	7859
AW5	5	Loch Chon	2421	7068
AW6	6	Loch Tinker	2445	7068
AW7	7	Loch of Glenhead	245	5804
AW8	8	Loch Grannoch	2542	570
AW9	9	Dargall Lane	2449	5786
AW10	10	Scoat Tarn	3159	5104
AW11	11	Burnmoor Tarn	3184	5043
AW12	12	River Etherow	4116	3996
AW13	13	Old Lodge	5456	1294
AW14	14	Narrator Brook	2568	692
AW15	15	Llyn Llagi	2649	3493
AW16	16	Llyn Cwm Mynach	2678	3238
AW17	17	Afon Hafren	2844	2876
AW18	18	Afon Gwy	2824	2854
AW19	19	Beagh's Burn	1353	5879
AW20	20	Bencrom River	1405	4820
AW21	21	Blue Lough	1428	4825
AW22	22	Coneyglen Burn	791	5508

Table 2.2

UK sulphur emission and deposition 1986 to 1997 and the atmospheric budget over the country (all values ktonnes)

Year	**1986**	**1987**	**1988**	**1989**	**1990**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**
UK emissions	1966	1961	1923	1860	1882	1790	1753	1584	1354	1176	1014	830
I/Ps non-UK European	120	102	75	94	80	100	86	92	78	73	90	75
Dry deposition	262	246	234	227	201	231	185	187	159	123	125	102
Wet+cloud deposition	230	226	251	229	226	223	215	186	198	155	171	132
Total deposition	492	472	485	456	427	454	400	373	357	278	296	234
Exported emissions	1594	1591	1513	1498	1535	1436	1439	1303	1075	971	808	671

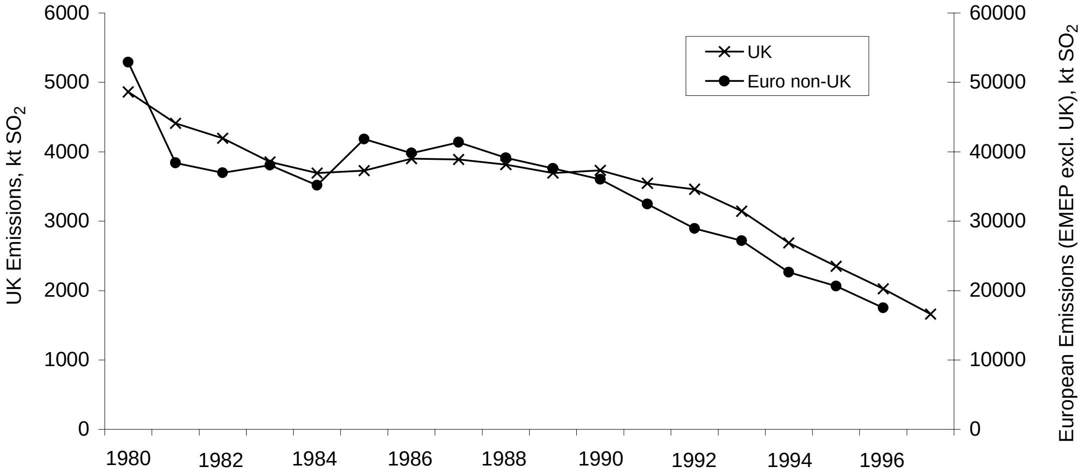


Figure 2.1

Trends in UK and non-UK European emissions of sulphur dioxide (1980-1997)

analysis presented in this chapter is an examination of all available evidence of deposition data and surface water chemistry data to show whether there is evidence of recovery. In short, have we detected a signal of reduced sulphur concentration or deposition in acid sensitive surface waters?

The Acid Deposition monitoring network is operated by NETCEN, while the wet and dry deposition maps for the UK are provided by ITE Edinburgh. This chapter has been prepared from the UK acid deposition monitoring data provided by NETCEN and the maps and process studies of ITE.

2.2 Wet and Dry Deposition

2.2.1 The wet deposition network

The composition of rain and snow is monitored at a rural network of 32 secondary sites using bulk collectors mounted 1.5 to 2.0 m above-ground sampled weekly and 5 primary sites using wet-only collectors sampled daily (RGAR, 1998). (Figure 2.3, Table 2.1).

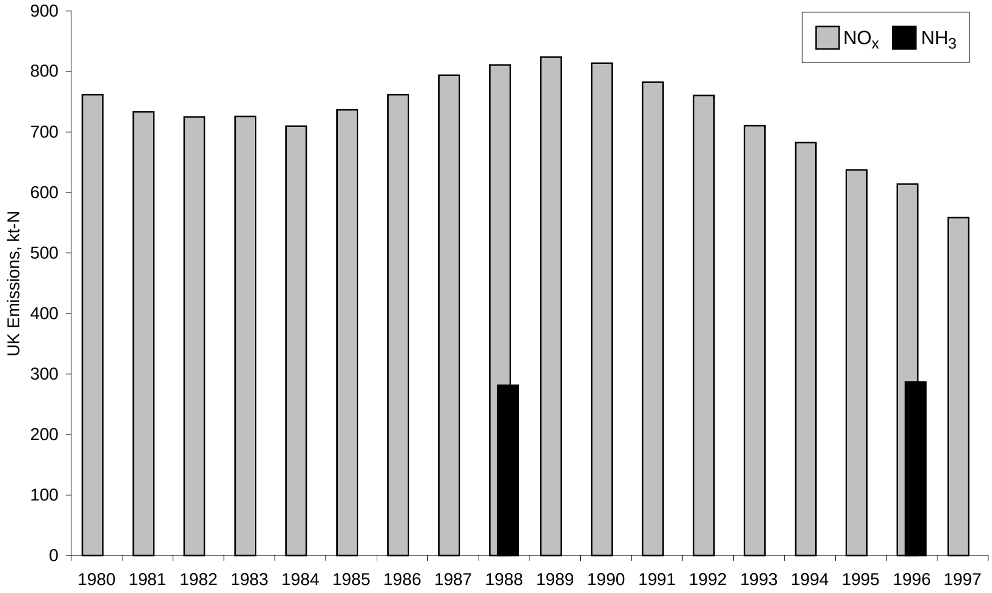
In general the monitoring sites are used to define the broad spatial patterns in rainfall composition. They do not sample the full range of the distribution of precipitation amount or composition. This is largely a practical constraint because the hill tops, where precipitation values are largest, are generally avoided as such sites are difficult to access in winter conditions, are very windy and a significant fraction of the annual deposition may occur as snow and is not collected efficiently. However, as Figure 2.3 shows, the monitoring sites cover the majority of the country and have proved suitable to define the regional distribution of precipitation chemistry (RGAR, 1998).

The weekly and daily samples are used to define the precipitation weighted annual mean concentrations of the major ions present in precipitation, SO_4^{2-}, NO_3^-, Cl^-, H^+, Na^+, NH_4^+, K^+, Ca_2^+ and Mg_2^+. These are then used to map the patterns of concentration. The mapping of precipitation weighted mean concentrations relies on Kriging methods (Webster *et al.*, 1991), assuming that the variation in space is locally random even though there is a spatial correlation.

Having mapped the precipitation weighted concentrations of each of the ions, the wet deposition is calculated as the product of the annual precipitation amount obtained from the UK Meteorological Office and provided at a scale of 5 km x 5 km. Met. Office data are used because the precipitation maps are constructed using a much larger network of gauges (in excess of 2000), which sample at ground level. The precipitation chemistry network relies on just 32 secondary sites and 5 primary sites and uses collectors mounted nearly 2 m above ground. The precipitation chemistry collectors have the advantage that they avoid some of the locally re-

Figure 2.2

Trends in UK emissions of NO_x between 1980 and 1997 and UK NH_3 emissions in 1988 and 1996



suspended contamination from soils but they under-catch precipitation amount because of the exposure of the collector to wind.

A further correction to the estimates of wet deposition is required because the Network does not adequately sample the high precipitation regions of the uplands where the wash-out of hill cloud by falling rain considerably increases wet deposition (Fowler *et al.*, 1988, 1995). The procedure used to modify the maps relies on empirical observations of the relationship between concentrations of major ions in orographic cloud and that of the upwind seeder rain (Dore *et al.*, 1992). The orographic enhancement of precipitation amount is assumed to occur entirely through seeder-feeder scavenging of orographic cloud.

The resulting maps of wet deposition were produced at a grid resolution of 20 km x 20 km from 1986 to 1994 and have recently been improved to 5 km x 5 km using a revised methodology which allows for the effects of wind-drift of falling raindrops.

2.2.1 Estimating dry deposition

The removal of the reactive pollutant gases at terrestrial surfaces by dry deposition represents the remaining major contributor to deposited acidity. Rates of dry deposition dominate the sulphur deposition inputs in regions with large ambient SO_2 concentrations (> 5 ppb) and modest rainfall (< 1000 mm). The rates of deposition are quantified using a deposition velocity ($V_{g(z)}$) at height (z):

$$V_{g(z)} = \text{flux/concentration}_{\ (z)}$$

and since concentration varies with height above ground as a consequence of deposition, the deposition velocity is also height dependent. The rate of dry deposition of SO_2 is regulated by stomatal uptake and leaf surface reaction of SO_2, especially in the presence of surface water on the vegetation, and is sensitive to the presence of other atmospheric pollutants notably NH_3 (Flechard *et al.*, 1999).

For the other acidifying pollutants, NO_2 and NH_3, rates of dry deposition are also regulated by surface processes. For NO_2 the deposition rate is primarily determined by stomatal absorption and overall rates of dry deposition are substantially smaller than those of SO_2 (Duyzer & Fowler, 1994). NH_3 by contrast is deposited rapidly on to most semi-natural vegetation (e.g. forest and moorland).

For NH_3, the surface-atmosphere exchange is

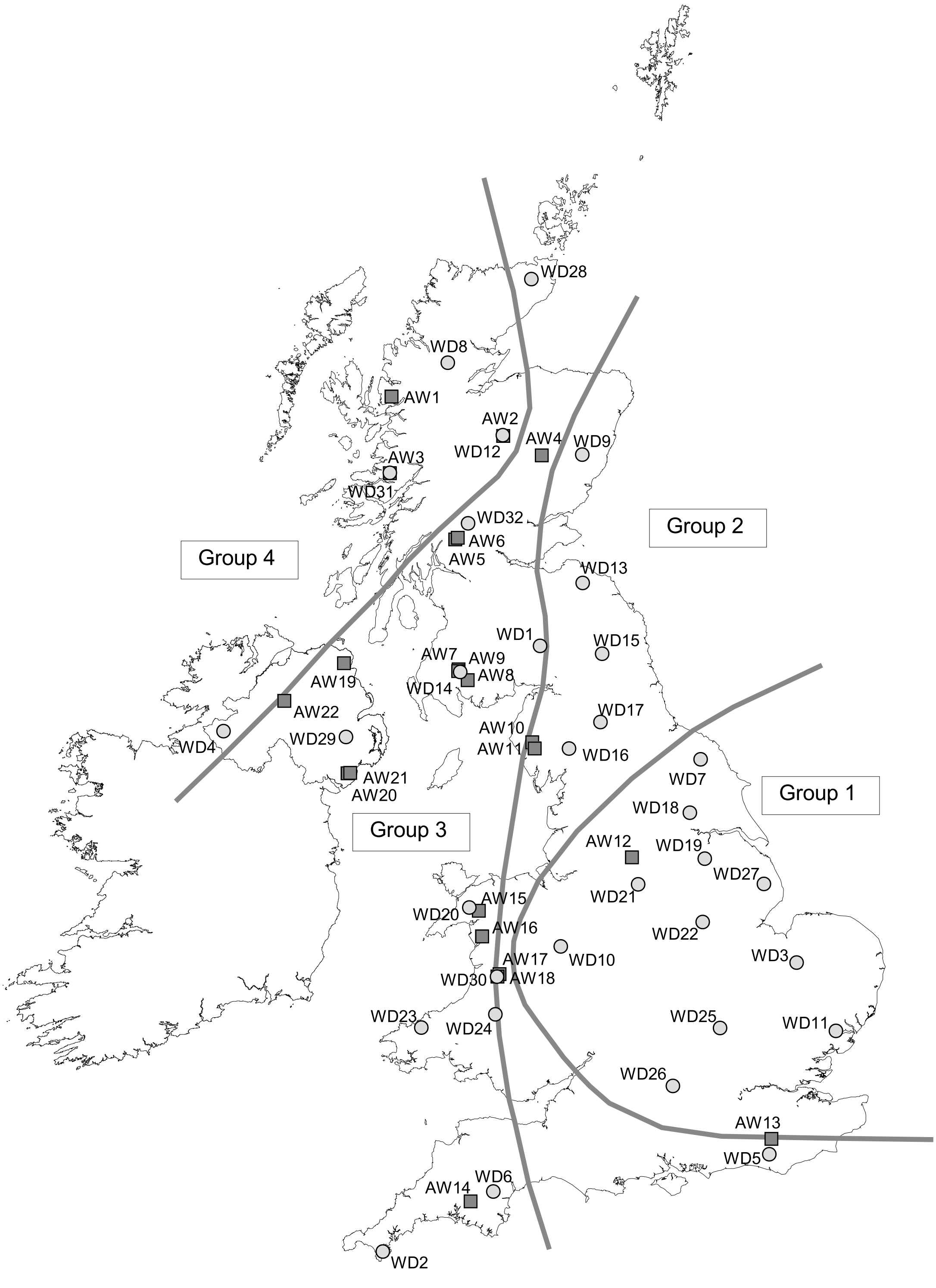


Figure 2.3

Locations of UK wet deposition monitoring stations (WD) and UKAWMN stations (AW)

The grouping of sites (1 to 4) is based on an objective hierarchical clustering method to distinguish the broad categories from the ionic composition alone (see Section 2.6)

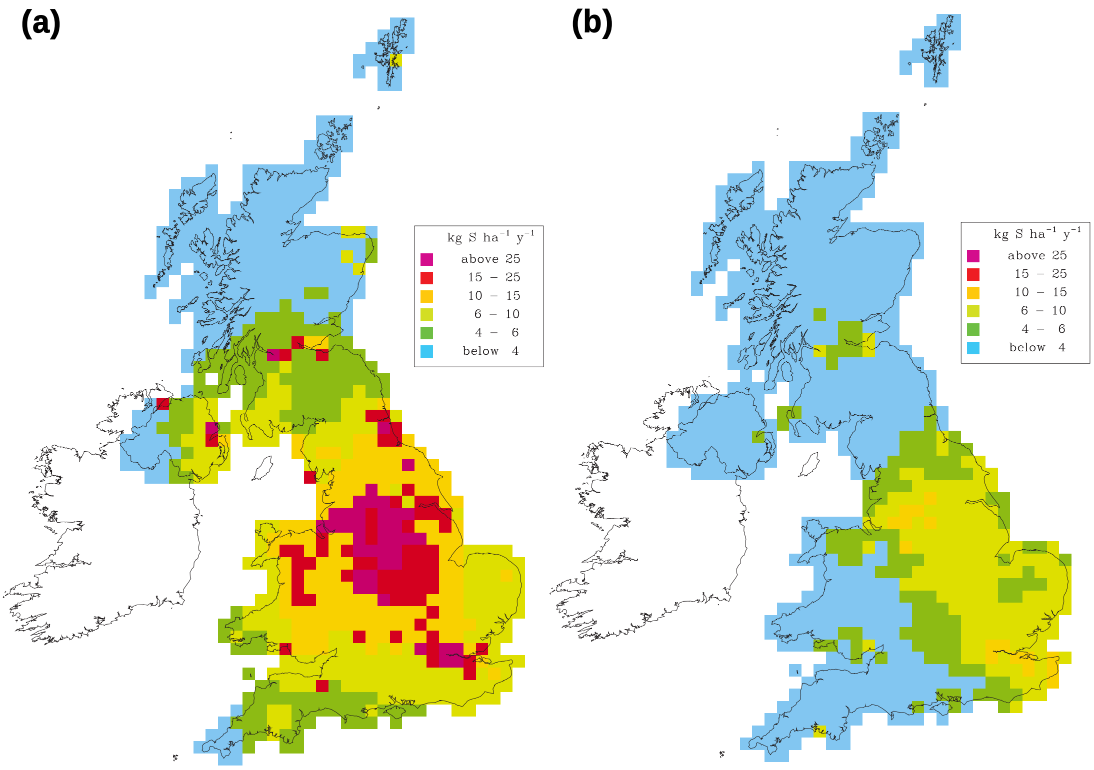


Figure 2.4

Dry deposition of sulphur 1986 (a) and 1997 (b) from measured SO_2 concentration field and the ITE dry deposition model (Smith *et al.* 1999)

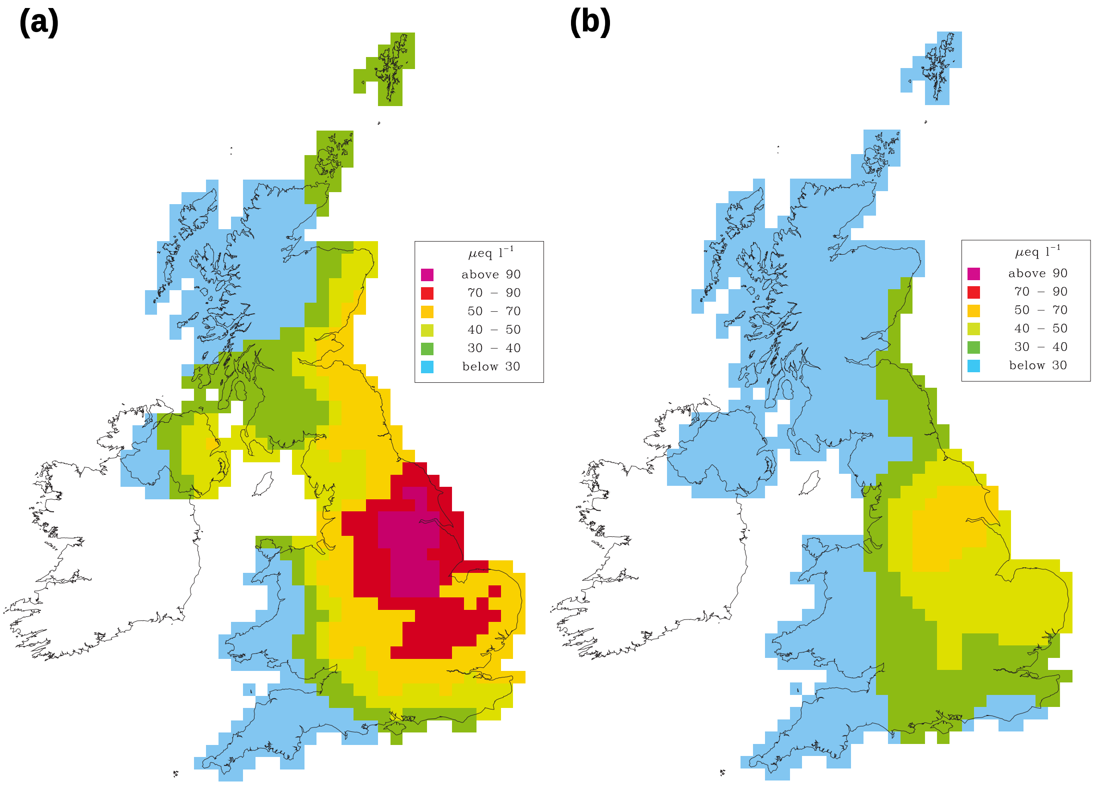


Figure 2.5

UK annual precipitation weighted mean concentrations of non-marine SO_4^{2-} in 1986 (a) and 1997 (b)

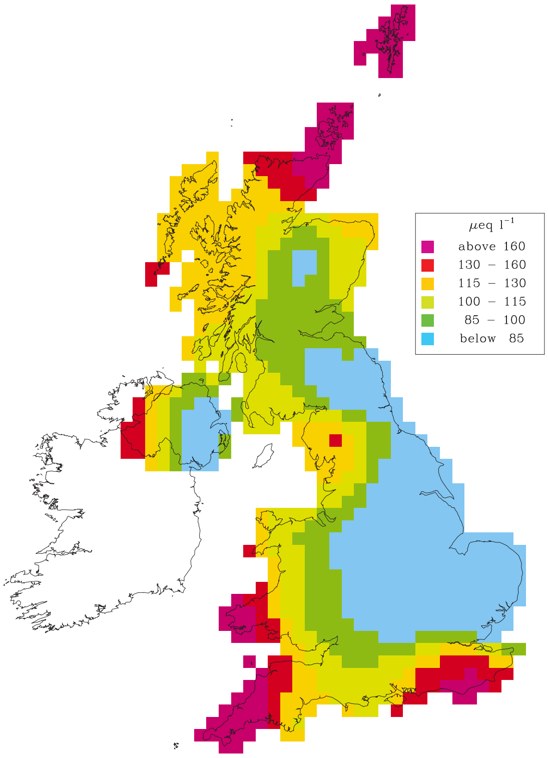


Figure 2.6

UK annual precipitation weighted mean concentration of Na$^+$ in 1997

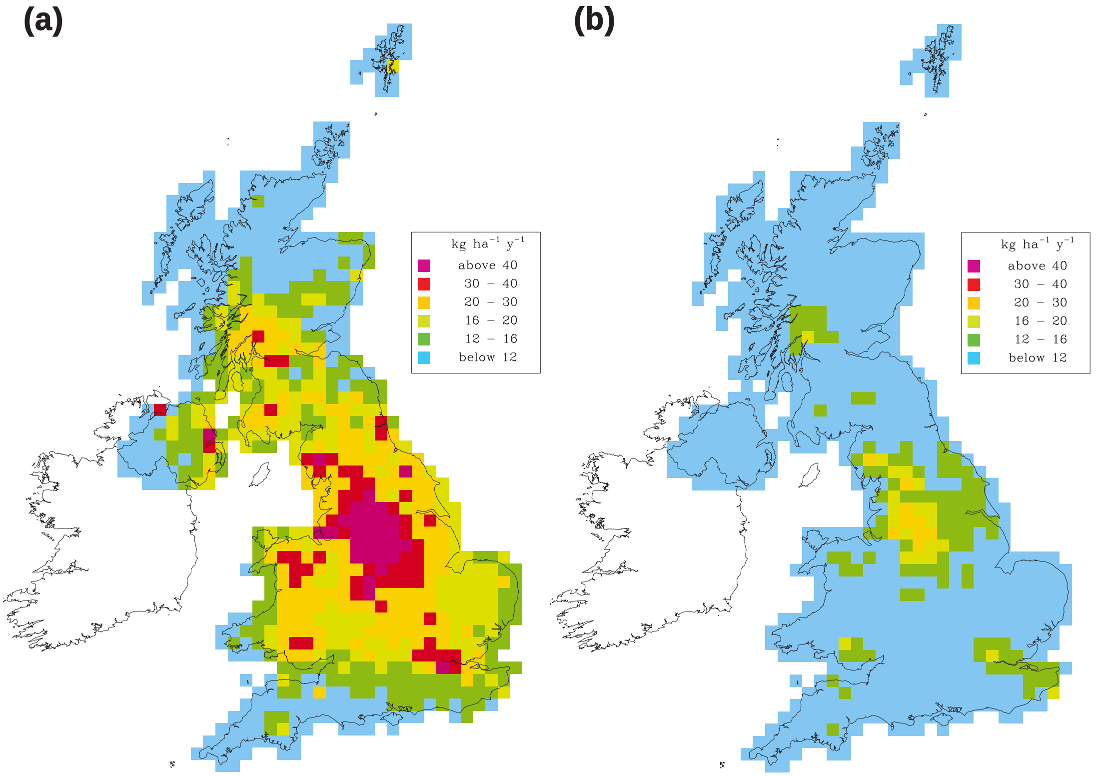


Figure 2.7

UK annual wet deposition of non-marine sulphur for 1986 (a) and 1997 (b)

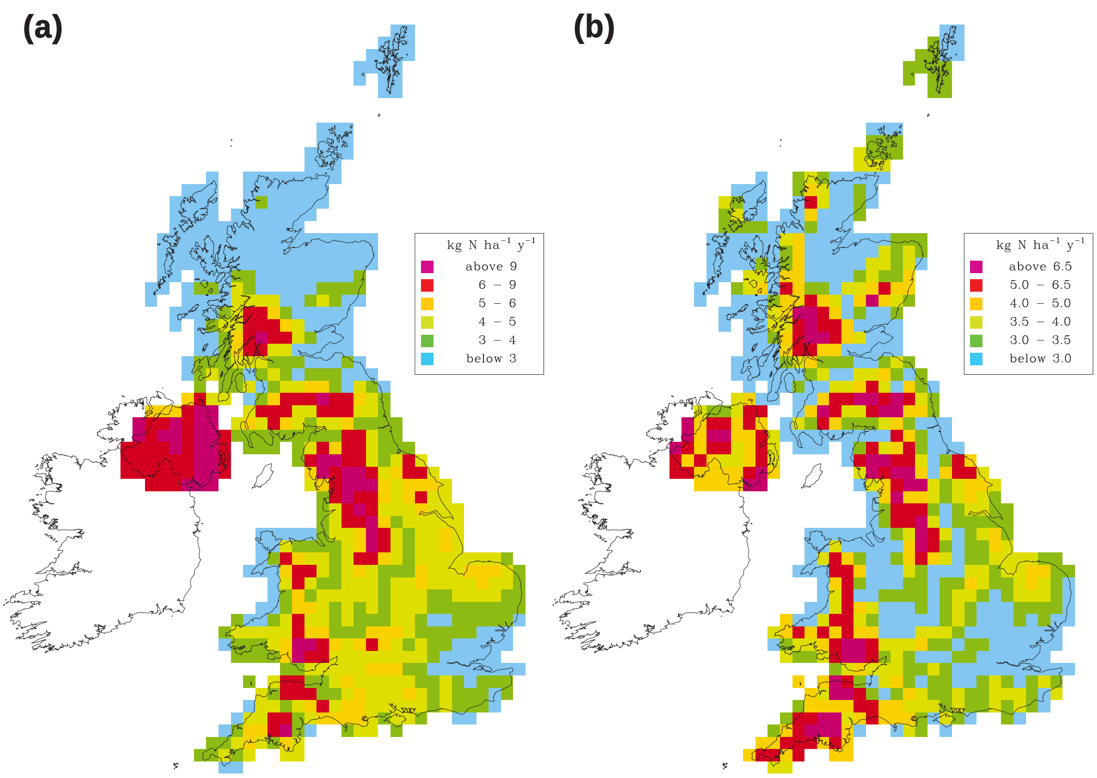


Figure 2.8

UK annual wet deposition of NH_4^+ - N (a) and NO_3^- - N (b) for 1997

complicated by the bi-directional nature of the fluxes as a consequence of NH_4^+ within the apoplast of vegetation. For heavily fertilized crops the NH_3 fluxes may represent net emission over significant periods of the growing season, whereas semi-natural vegetation and forests represent an efficient sink for NH_3, with large deposition rates (Sutton *et al.*, 1993). A detailed treatment of the processes of dry deposition is outside the remit of this chapter and descriptions of the processes may be found in RGAR (1997) and in review papers e.g. Sutton *et al.* (1993) and Fowler *et al.* (1995).

The maps of dry deposition are provided by measured concentration fields of the pollutant gases and application of a process-based model of the deposition process (Smith *et al.*, 1999). The deposition is of course land-use specific, and land-use and land-cover maps are used to identify the major land-uses within the deposition grid (forest, moorland, unfertilized grassland, fertilized grassland, arable crops and urban areas). A more detailed description of the dry deposition measurement and modelling procedure is provided within the CLAG (fluxes) report (1997). Individual parameters within the deposition model and their response to changes in environmental conditions are provided by direct field measurements. There are two continuous SO_2 dry deposition sites within the UK and approximately 40 SO_2 concentration monitoring sites to provide the interpolated concentration fields for the UK.

The dry deposition of SO_2 to the UK is illustrated in Figure 2.4a for 1986 and 2.4b for 1997. The maps show a large change in the absolute values of dry deposition especially in the source areas of the east Midlands and Yorkshire. They also reveal the relatively small contribution of dry deposition in the areas of the west and north of the UK, which are the primary focus of the UKAWMN.

2.2.3 Cloud droplet deposition

Wet and dry deposition represent the dominant pathways for pollutant deposition, but for those areas of the landscape which are in cloud for a significant part of the time, the direct deposition of cloud droplets to vegetation represents an important contribution to the deposition total (Crossley *et al.*, 1992). For sites at altitudes above 600 m in western Britain the cloud frequency lies between 3 and 10%, and at forest sites above 500 m asl in the Scottish borders, 50% of the sulphur and nitrogen input may be deposited as cloud (or occult) deposition. The total deposition maps for acidity S and N for the UK include cloud deposition, although for the country as a whole cloud deposition is not a large component.

2.3 Measured wet and dry deposition, 1986 - 1997

2.3.1 Trends in concentrations

The concentrations of all major ions show large regional variation over the UK. For the pollutant derived SO_4^{2-} in the mid-1980s the largest concentrations were in the east and south of England with mean concentrations of 80-100 µeq l^{-1} and the smallest concentrations in northwest Scotland (15-20 µeq l^{-1}) (Figure 2.5a). The value of background SO_4^{2-} is of course important and is not known precisely. However, measurements at remote sites in northwest Europe from the EMEP network indicate values of the order of 10 ueq l^{-1}, so even the remote sites in the UK receive at least half of their non sea-salt SO_4^{2-} from pollutant sources. The current (1997) concentrations of non-marine SO_4^{2-} are shown in Figure 2.5b and these also show a large northwest to southeast gradient in the UK with values in northwest Scotland remaining close to 20 µeq l^{-1}, while the peak concentrations in the east Midlands of England have declined to about 60 µeq l^{-1} SO_4^{2-}. There is also a clear west to east gradient with larger concentrations along the east coast of the UK. The change in SO_4^{2-} concentration is dramatic and represents a reduction by almost 50% and is accompanied by a reduction in acidity of the same magnitude in the source regions.

The changes in SO_4^{2-} (and acidity) with time at sites on the west coast of the UK are small and largely non-significant.

The NH_4^+, NO_3^- and H^+ concentrations show similar spatial patterns with a marked east-west gradient and peak values in East Anglia. The absolute magnitude of the east-west gradient in NO_3^- concentration is similar to that in SO_4^{2-} i.e. 40-50 µeq NO_3^- l^{-1} across the country in the most polluted areas. However, the relative gradient is larger for NO_3^- because in the remote regions of northwest Scotland concentrations of NO_3^- were very small, typically 2-5 µeq NO_3^- l^{-1} in the mid 1980s. The values in the polluted areas of 40-50 µeq l^{-1} are therefore an order of magnitude larger than those at the remote sites. Differences between SO_4^{2-} and NO_3^- concentration gradients also arise because of the presence of a background in the SO_4^{2-} concentration. Sea-salt contains appreciable quantities of SO_4^{2-}, and in calculating non-marine SO_4^{2-} a correction is made for marine SO_4 by assuming the Cl^-:SO_4^{2-} and Na^+:SO_4^{2-} ratios in bulk sea water apply in the case of precipitation. At remote locations in the west and north of Britain this is a reasonable assumption, but in the east Midlands of England Cl is present as HCl and non-marine Cl^- in aerosols from the high Cl coals produced from some east Midlands coalfields. The marine correction for these areas relies on the Na^+:SO_4^{2-} ratio to quantify the non-marine Cl deposition.

There is also SO_4^{2-} in the atmosphere from marine emissions of dimethyl sulphide (DMS) which is oxidized in the atmosphere, ultimately to SO_4^{2-}, and contributes to non-anthropogenic background SO_4^{2-} deposition. The marked east-west gradients in concentrations of the major pollutant derived ions contrast strongly with the marine derived ions especially Na^+ and Cl^-. For these ions concentrations in the west coast sites are in the range 200 - 400 µeq l^{-1}, and sea salts dominate the ionic composition of precipitation and provide the majority of the total SO_4^{2-} deposition (Figure 2.6). The inland and east coast sites, in contrast, show marine Na^+ and Cl^- concentrations in the range 50-70 µeq l^{-1} and at these sites marine SO_4^{2-} contributes only 10% -

20% of total SO_4^{2-} in precipitation. The marine and pollutant derived ions therefore change in their relative contributions to the total ionic strength of the precipitation across the UK.

2.3.2 Trends in wet deposition

Combining the concentration fields with precipitation amount and correcting for the orographic effects in the UK uplands provides the wet deposition maps. As the precipitation amounts are very large in the uplands of western and northern Britain, the wet deposition maps show a stronger influence of precipitation amount than the concentration field.

The main features of the wet deposition maps are illustrated by maps for 1986 and 1997 for non-marine SO_4^{2-} (Figures 2.7a and 2.7b). The peak in wet deposition in 1997 of 25 kg non-marine S ha^{-1} in the Pennine hills of northern England and in Cumbria is appreciably smaller than non-marine SO_4^{2-} wet deposition in 1986 (50 kg SO_4^{2-}). The rainfall amounts do vary between years but are very similar for these years, and there are no monotonic regional trends in precipitation amount over the 12 year period. There are therefore areas of the country in which substantial reductions in deposition have occurred since the mid-1980s.

Wet deposition of non-marine S at west coast sites and in the north and west of Scotland shows no clear differences between the two years. Wet deposition of NO_3^- and NH_4^+ have also remained broadly similar although small changes are evident at individual sites. The spatial distributions in wet deposition of NH_4^+ and NO_3^- are shown in Figures 2.8a and 2.8b for 1997, again illustrating the dominance of the annual maps of precipitation in controlling the pattern of wet deposition.

2.4 Trends in concentration and deposition: discussion

The main features of the regional patterns in wet deposition and the concentrations of major ions in precipitation have remained consistent throughout the monitoring period reported here, 1986-1987. However, the concentrations and deposition of sulphur have declined, with larger temporal gradients in the source regions than elsewhere. The trends in concentrations and deposition are much more important for interpretation of the UKAWMN data. For the trend analysis there are three key questions:

1. Have the reductions in UK (and other European) emissions of sulphur led to reduced S deposition in the UK and in particular in the source regions?
2. Are observed changes in concentration and deposition consistent with current understanding of the processes?
3. Is there evidence of changes other than in sulphur deposition in the UK precipitation chemistry and deposition?

The introductory section of this chapter and Figure 2.1, reveal a 57% decline in UK sulphur emissions between 1986 and 1997. Similarly, non-UK European S emissions declined by 45% between 1986 and 1997. These large changes provide an ideal signal to examine the measurement data.

Using a consistent methodology for the 12 year period, the mapped wet and dry deposition allow the mass balance of the atmosphere over the UK to be quantified. This is shown in Table 2.2. The total deposition of non-marine sulphur declines from 492 kT S in 1986 to 234 kT S in 1997, a reduction of 52%. The wet deposition declines by 42% while dry deposition declines by 61% over the 12 years, so there is a large change in the wet:dry deposition partitioning of the deposited sulphur in the UK. Clearly therefore, the answer to the first question is “yes”, there has been a marked reduction in S deposition in response to emission reductions but the area in which deposition has declined is largely restricted to the source regions. Thus the answer to question 2 is “no”, the observed change in deposition is unexpected. In particular the very large reduction in dry deposition, primarily as a consequence of a reduction in ambient SO_2 concentrations in the source region (within 100 km of the major sources), is the main cause of the much greater reduction in dry deposition. The concentrations of SO_2 declined by almost an order of magnitude at rural sites in the east Midlands.

The changes in the pattern of deposition and the partitioning into wet and dry deposition is therefore introducing non-linearity into the spatial relationship between emission and deposition of S in the UK. There are (at least) three contributions to the changes in wet-dry deposition partitioning. First, a much larger reduction in low level than high level sources of SO_2; second an observed change in the rate of SO_2 dry deposition which has gradually increased dry deposition rates in the source regions as SO_2 concentrations have fallen, and last; an oxidant limited SO_2 to SO_4^{2-} oxidation in stratiform cloud. All three processes have combined to cause the observed non-linearity in sulphur deposition but the relative contribution of each of these processes to the observed trend has yet to be quantified.

We now examine the trends in the different regions of the UK.

2.5 Regional trends in precipitation chemistry

A consequence of the smaller change in wet deposition is that the signal in declining SO_4^{2-} concentrations is smaller than it would have been given a strictly linear relationship between emissions and wet deposition, by 50%.

The observed decline in SO_4^{2-} concentration in precipitation (Appendix 1, Table 1) is clear at the sites in the east Midlands and Yorkshire - the source areas. In these areas (within 100 km of the major power stations) the non sea-salt SO_4^{2-} concentration declines at approximately 3 μeq SO_4^{2-} yr^{-1} throughout the 12 years and the (linear) trends are highly significant. At the sites close to the west coast of England, Wales and Scotland and in the west of Northern Ireland there is also a decline in non sea-salt SO_4^{2-}, but for each of these sites considered individually the decline is small and is not statistically significant. When all west coast sites are considered together, a small statistically significant linear trend of decreasing SO_4^{2-} is established.

The intermediate sites, including Eskdalemuir, Redesdale, Mharcaidh, Achanarras, Barcombe Mills and Compton show significant decreases in SO_4^{2-} averaging between 1 and 2 μeq SO_4^{2-} l^{-1} yr^{-1}. Thus the reduction in wet deposition is clearest in the same areas as the dry deposition reduction, and in fact the dry deposition on precipitation collectors contributes about 25% of the observed decline in wet SO_4^{2-} deposition in the source regions.

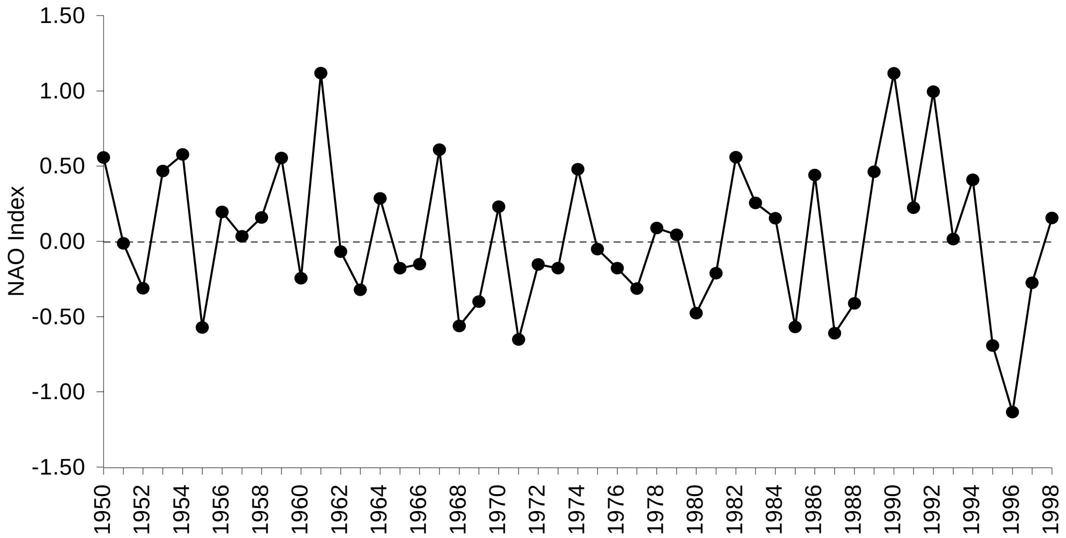
The trends are therefore weakest at the remote high rainfall sites and, in a strict sense, the observed decline in non sea-salt SO_4 at these sites is not significant. The cause of this may simply be the inter-annual noise in the meteorology obtaining a small signal. However, this raises the question of stationarity, i.e. are all other conditions remaining constant during the 12 years of monitoring? The first and most obvious indicator is precipitation amount, which shows considerable inter-year variability but no monotonic trend. The relative frequency of winds, which transport pollutants from the source areas in the UK and other countries of Europe to remote regions of the UK, has been examined in earlier analyses of UK acid deposition (RGAR 1990, 1997). More recently the North Atlantic Oscillation (NAO) has been recognised as an important influence on European climate (Hurrell, 1995) and is discussed at length in later sections of this report. The NAO provides an index of ‘westerlyness’ in the airflow over the UK. Large Index (NAOI) values (or large pressure gradients) are associated with strong southwesterly airflow and a succession of fronts and precipitation over the UK. If marked changes of the NAOI occur during the 12 years of the available wet deposition data for the UK, then it may be argued that this would introduce additional variability into the precipitation chemistry measurement and mask trends. The annual NAO values plotted in Figure 2.9 show a clear maximum in NAO in the years 1990, 1992 with smaller positive value in 1986, 1989, 1991 and 1994, while 1987, 1988, 1995, 1996 and 1997 all show negative values (reduced westerlyness). A simple correlation of Cl^- concentration against NAO, using annual data reveals relatively little structure with the exception that the largest positive value is associated with the largest mean Cl^- concentration. Thus, the precipitation chemistry data at annual scales, as used for the deposition maps, show a weak association between these two variables.

The annual Cl^- deposition however, is highly episodic, with a substantial fraction of the deposition contributed by a few rainfall events each year. The data from the UK primary precipitation chemistry sites, which provide daily collection, show that all sites in the primary network are highly episodic in Cl^- deposition (defined as sites receiving >30% of the wet deposition in < 5% of the precipitation events). Furthermore, the Cl^- deposition is largely a winter phenomenon, with 80% of the deposition in the winter months.

The implication from this rather simplistic analysis is that inter-year variability in the weather has to some extent masked the SO_4^{2-} declines at the remote sites in the north and west of the country. The changes in the ‘westerlyness’, which are evident in the NAO data, and the associated changes in sea-salt deposition clearly introduce noise into the dataset. However, if the large decline in wet deposition and dry deposition observed at the sites in the source areas of the UK (~50%) was also present at these remote sites, such a signal would have been detected. The application of NAO indices for the winter months, as applied later in this report is consistent with the winter dominated deposition of sea-salts. Since a large fraction of the ionic content of precipitation at the west coast sites is provided by sea-salts, it is unsurprising that temporal variations in sea-salt deposition are strongly correlated with surface water chemistry. However, in this chapter we are specifically examining the available data to show whether the large reductions in sulphur emissions are evident in the deposition data and how the evidence varies throughout the country. The conclusion from the analysis is that large reductions in sulphur deposition during the last decade are evident, but that in many west coast areas of the country, the decline in sulphur deposition is very small, and is much smaller than the reduction in UK or European sulphur emissions. In conclusion, the lack of detection of a significant decline in sulphur deposition at some of these remote sites has probably been influenced by variations in the weather over the monitoring period. It is probable therefore that with continued reductions in emission the declining deposition will become clear even at these remote locations.

Figure 2.9

The changes with time in the annual North Atlantic Oscillation Index (NAOI)



2.6 Deposition trends at individual sites

Statistically significant trends are found at only 13 out of the 32 sites, these being the source region sites, Jenny Hurn, Driby, Bottesford, Stoke Ferry, Woburn, Flatford Hills, Compton and High Muffles, and the intermediate sites, Barcombe Mills, Wardlow Hay Cop, Eskdalemuir, Whiteadder, and Achanarras, the east coast site in northern Scotland.

However, all sites with the exception of Yarner Wood show negative trend, and by grouping the sites using a hierarchical clustering method into the four groups shown in Table 2.1 and Figure 2.3 the trends may be broadly classified on a regional basis. The trends may be shown to be significant for all groups when the data are considered together. This is the case even at the remote and west coast sites, (groups 3 and 4) where the slope of the decrease is 0.5 μeq SO_4^{2-} l^{-1} yr^{-1} and is statistically significant. The intermediate sites (group 2) show a trend of 1 μeq SO_4^{2-} l^{-1} yr^{-1}, while the source area (group 1) sites show the clear decreasing trend of 3 μeq SO_4^{2-} l^{-1} yr^{-1} (Figure 2.10). These broad classifications seem entirely appropriate to identify the region specific trends in non-marine SO_4^{2-} deposition and show that the magnitude of the trend at these remote sites is small. If, for example, we examine the trends at the nearest acid deposition network secondary collector to the appropriate UKAWMN site, then with the exception of Barcombe Mills, all trends are non-significant. With these small changes in precipitation chemistry at the remote sites, it would hardly be surprising if site specific surface water chemistry, which is further modified by interactions within the catchment, shows no trends.

For sites at the west coast with mean non-marine SO_4^{2-} concentrations of 20 μeq l^{-1}, a reduction by 10 μeq l^{-1} would have been readily detected over the 12 years of data available. The tabulated statistics in Appendix 1, Tables 1-4 refer to the 12 years of precipitation chemistry monitoring.

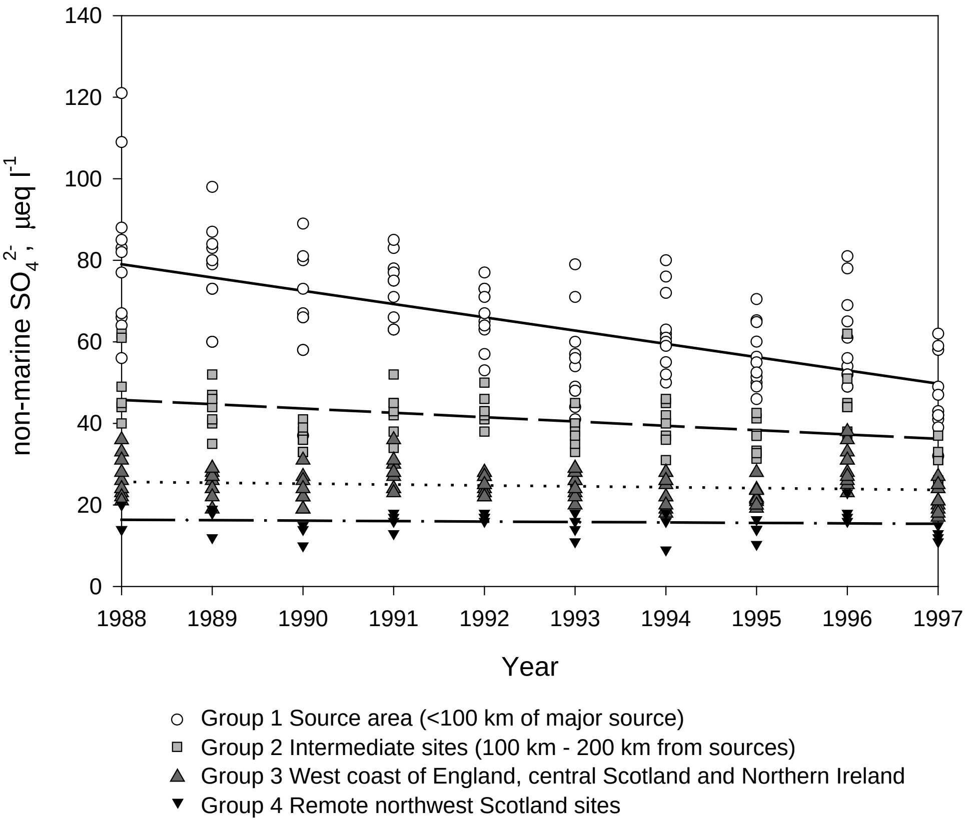


Figure 2.10

The linear trends in annual non-marine SO_4^{2-} in precipitation for four groups of sites in the UK acid deposition monitoring network. See Figure 2.3 for geographical distribution

To provide a strictly comparable set of data for comparison of the wet deposition and UKAWMN site data, the trend analysis has also been completed for the shorter (10 year) period of precipitation chemistry data of 1988 to 1997.

Considering these in turn.

Non-marine SO_4^{2-} trends (1988-1997)

(Appendix 1, Table 5)

The significant trends in SO_4^{2-} are the source area (1) and intermediate sites (2) (as with Figure 2.3) with slopes of the decline of 3 - 5 µeq SO_4^{2-} l^{-1} yr^{-1} and 1 µeq SO_4^{2-} l^{-1} yr^{-1} for the source regions and intermediate sites respectively. The remote regions consistently show a general decline but with the inter-year variability the trends are not statistically significant. The analysis of the shorter period is therefore entirely consistent with that for the 12 years.

NH_4^+ trends (1988-1997)

(Appendix 1, Table 6)

There are no consistent significant trends at the regional scale, and an even split of non-significant trends among the individual site data. While there is no evidence of a trend overall it is noticeable that in the source areas, the tendency is for a decline (Stoke Ferry, Bottesford, Jenny Hurn, Thorganby, High Muffles, Wodburn, Flatford Mills) but little can be drawn from such weak signals. Ammonia emissions are believed to have changed little over the monitoring period, but with such large changes in sulphur emissions, it is probable that changes in the aerosol chemistry have occurred, with a replacement of the ammonium sulphate by ammonium nitrate.

Cl^- trends (1988-1997)

(Appendix 1, Table 7)

The clear negative trends in Cl^- at the source area sites Bottesford, Jenny Hurn and Thorganby are entirely consistent with the decline in HCl emissions from the coal burning power-stations in the east Midlands and Yorkshire. It is surprising that the signal is not observed at High Muffles.

H^+ trends (1988-1997)

(Appendix 1, Table 8)

While H^+ has not been considered in detail in this chapter, these data merit a comment. It is notable that rainfall acidity has declined at all sites in the network over this period. The trends are significant at 16 sites and in the source areas the slope of the trend is fairly consistent at about 3 µeq H^+ l^{-1} yr^{-1} while at the intermediate and even some remote sites the trend is close to 1 µeq H^+ l^{-1} yr^{-1}. These declines are almost identical to the decline in SO_4^{2-} and in the absence of trends in NH_4^+ and NO_3^- imply that the acidity was SO_4^{2-} related. The sites not showing a significant trend are in general the west coast sites where the magnitude of the trend is < 1 µeq H^+ l^{-1} yr^{-1} and, like SO_4^{2-} at these sites, such signals are masked by the inter-year variability.

NO_3^- trends (1988-1997)

(Appendix 1, Table 9)

Unlike SO_2, the emissions of NO_x have not changed greatly during the period 1986 to 1997 (Figure 2.2). There was a gradual increase from 1986 to 1990 and since then NO_x emissions have declined steadily. These trends are somewhat smaller than those of other European countries, but overall the decline is small over the period (EMEP, 1999). The observed UK precipitation chemistry shows a small but significant increase in NO_3^- concentration at many of the remote west coast sites (Yarner Wood, Llyn Brianne, Pumluman, Bannisdale, Lough Navar and also at Eskdalemuir. The magnitude of the change seems small at about 0.5 µeq NO_3^- l^{-1} $year^{-1}$. However, the weighted mean concentration at these sites in the early years of the measurement were very small, 8 - 15 µeq NO_3^- l^{-1} and the increase represents a 20% increase in wet deposition at many of the sites. The cause of the trend is unknown, and in the absence of any measurement artefact implies an increase in aerosol NO_3^- and/or HNO_3 at these remote locations during this period. Only one site in the network (Bottesford) showed a significant decrease in NO_3^-.

The remote sites, most appropriate for the AWMN show no monotonic trends in the concentrations of any other major ion in precipitation, but considerable inter-year variability. Thus there is no evidence of other country-wide changes in major ions. A decrease in non-marine Cl^- has been observed at the east Midlands and Yorkshire sites, consistent with reduced emissions of HCl from coal combustion in these areas.

2.7 Summary

- UK and non-UK European S emissions both declined between 1986 and 1997 by approximately 55%. UK NO_x emission declined by 14% during the same period.

- Sulphur deposition in the UK declined by approximately 50% between 1986 and 1997, but the majority of the decline was dry deposition (61%), the decline in wet deposition was 42%.

- Concentrations of non-marine SO_4^{2-} and H^+ in precipitation over the period 1986-1997 and 1988 to 1997 both declined at: 3 µeq l^{-1} yr^{-1} at sites close to (<100 km) major sources (the east Midlands of England and Yorkshire) : 1 µeq l^{-1} yr^{-1} at sites 100 km to 300 km from sources. At the remote high rainfall west coast locations in Britain the decline in SO_4^{2-} concentration was barely detectable.

- There were large year to year variations but no monotonic trends in precipitation amount during the period of measurement.

- The North Atlantic Oscillation (NAO) Index showed a pronounced positive peak in the early 1990s and large sea-salt concentrations in rain during the peak and troughs in the late 1980s and mid 1990s. This cyclical change in the ‘westerlyness’ of the climate introduced variability which may have obscured the signal of SO_4^{2-} concentration and S deposition reductions at the high rainfall west coast sites.

- Very clear large reductions in both wet and dry deposition of S in the source regions of the UK and at intermediate distances from the source areas (see Figure 2.3 and Table 2.1) are evident in the measurements. There are reductions in S deposition in the high rainfall, west coast areas but the reductions are much smaller than the reductions in UK or non-UK European S emissions and at many of the high rainfall sites the trends in deposition are not statistically significant. The observed changes in precipitation chemistry measured by the UK deposition network are consistent with observed surface water chemistry measurements by the UKAWMN network.

- Small but significant increases in concentrations and deposition of NO_3^- are evident at the west coast and remote monitoring stations.

3 Methods

Chris Evans, Don Monteith, Bill Beaumont & Mike Gardner

3.1 Water Chemistry

Sampling and analytical methodologies conform to those outlined by Patrick *et al.* (1991) while the approach to Analytical Quality Control (AQC) is provided by Patrick *et al.* (1995). UKAWMN laboratories participate in an AQC programme run by the Water Research Centre, Medmenham, and results are provided to the UKAWMN in annual internal reports which are available on request. The programme has found a high standard of accuracy for all the major determinands analysed in this report. Small discrepancies have been observed in the measurement of Al which seems to result from the differing procedures used in the separation of the labile fraction. These differences were not detected until well into the monitoring period, and it is now considered more appropriate, for monitoring purposes, to maintain internal consistency rather than to improve inter-laboratory consistency.

3.1.1 Data screening

Chemical data were screened to remove erroneous values prior to analysis. Charge balance errors were calculated as:

$$CB\ (\%) = \left[\frac{\sum Base\ Cations - \sum Acid\ Anions - Alkalinity}{\sum Base\ Cations + \sum Acid\ Anions + Alkalinity} \right] *100\%$$

where all ion concentrations are in μeq l^{-1}. Charges of aluminium and organic anion species could not be quantified, and the charge balance is therefore approximate; however in general the error should

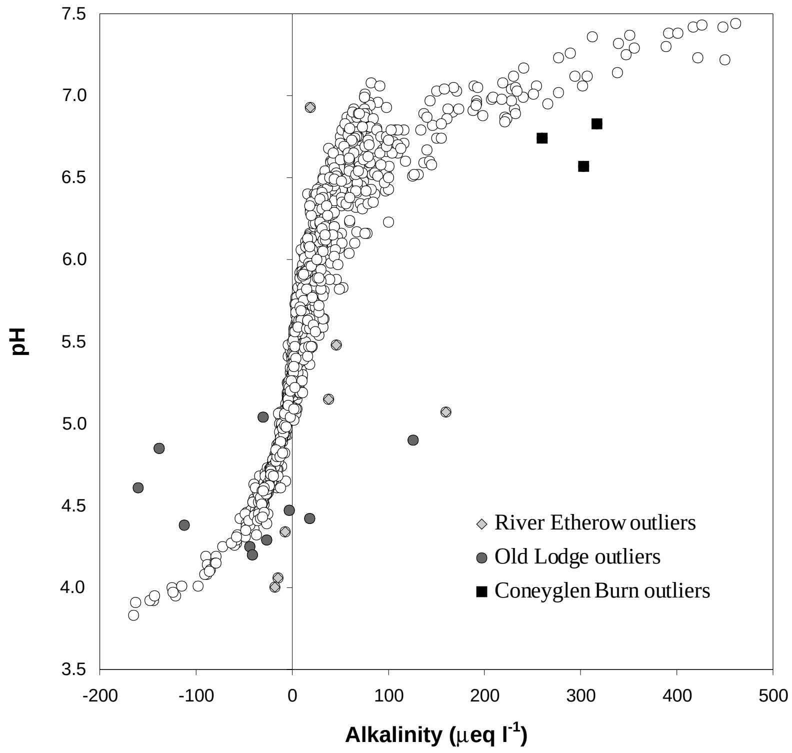


Figure 3.1

pH vs Alkalinity for the full UKAWMN dataset

be close to zero. Errors of greater than 10% were therefore taken to indicate a possible analytical error. Where this error was associated with a clear outlying value (defined as a measurement outside the range of all other measurements at that site) this value was discarded. This procedure led to the removal of one or more determinand value in a total of 14 samples. Samples with charge balance errors greater than 10% but no clear outliers were retained in the dataset.

Data were also screened on the basis of the relationship between alkalinity and pH. These determinands are closely related through carbonate equilibria, and should plot on a sigma curve (Munson & Gherini, 1991). A plot of pH vs. alkalinity for the entire UKAWMN dataset shows the expected relationship (Figure 3.1), but a small number of outliers are observed for Coneyglen Burn, the River Etherow and Old Lodge. Coneyglen Burn has very high DOC concentrations (Section 4.22) and the low pH relative to alkalinity in these samples may be explained by weak organic acidity (Munson & Gherini, 1991). However the seven outlying data points at the Etherow and ten at Old Lodge were considered to be outside the acceptable range and were removed.

Finally, wider problems were identified for unstable determinand data at the River Etherow and Old Lodge during the first three years of monitoring. At this time, unstable determinand analysis for the two sites was undertaken at local laboratories, but from April 1991 this was transferred to SOAFD, Pitlochry. Time series data for alkalinity at the Etherow, and for alkalinity, pH and NO_3 at Old Lodge show markedly higher scatter prior to the laboratory change (Figure 3.2), suggesting a poor level of analytical precision at this time. All samples at both sites failing to conform to the expected pH/alkalinity relationship were also collected during this period. The first three years of data for alkalinity at both sites, and for pH and NO_3 at Old Lodge, were therefore discarded.

3.1.2 Statistical analyses

Changes in water chemistry over the ten years were assessed using two parallel trend detection methods. The Seasonal Kendall Test (SKT) is a non-parametric procedure for detecting monotonic changes over time, developed by Hirsch *et al.* (1982). SKT has been identified by Taylor & Loftis (1989) as the most suitable non-parametric trend identification technique for water quality data containing seasonal variations, and was used in the UKAWMN five year analysis (Patrick *et al.*, 1995). Values are grouped into seasonal blocks (months for streams and quarters for lakes) and tested for trends using a ranking procedure. SKT is robust with respect to non-normality, missing or censored data and seasonality, but in its original form is sensitive to serial correlation. The method used here is therefore a modified version described by Hirsch & Slack (1984), which is robust providing auto-correlation is less than 0.6 and records extend for more than five years. Slopes associated with trends found to be significant at the 95% level were then estimated according to the method of Sen (1968), as the median of all between-year differences within each seasonal block.

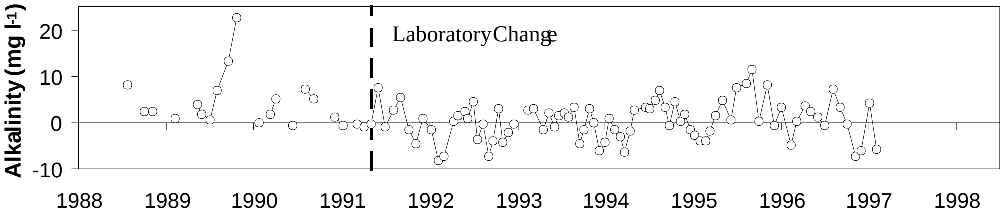
The second trend detection procedure used was simple linear regression, with a significance test adapted to take account of non-normality in the distribution of sampling times. Having first computed the r^2 value for the data arranged in chronological order, the procedure was then repeated 8000 times for data arranged in random order. Significance was determined as the position of the initial r^2 value within the distribution of all r^2 values, with a 95% significance level (i.e. the initial r^2 in the top 5% of all calculated r^2 values) taken as a threshold for trend identification. This method was used in the UKAWMN five year analysis, and is described by Patrick *et al.* (1995). It has also been used in a trend analysis of Scottish surface waters by Harriman *et al.* (1995a).

Of the two trend detection methods, SKT is particularly effective where seasonality is present, but may be more conservative in detecting trends where it is not. SKT also tends to identify changes more effectively where these occur steadily over time, whereas regression is more likely to show a significant trend resulting from a step change. Both methods are however limited to the detection of monotonic trends, whereas solute concentrations may fluctuate over

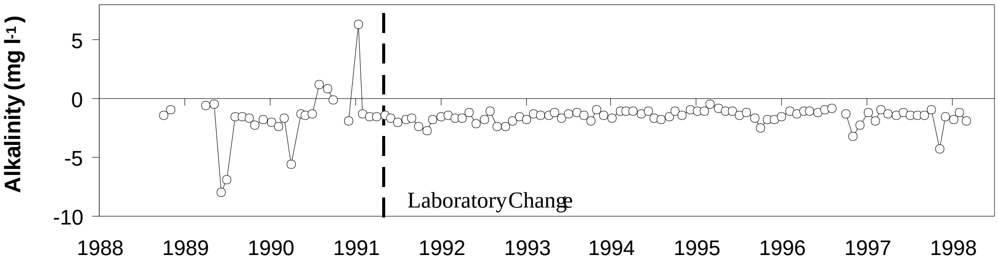
Figure 3.2

Time series data for alkalinity for the River Etherow (a) and Old Lodge (b), and pH and NO_3 for Old Lodge. Dotted line indicates time of laboratory change

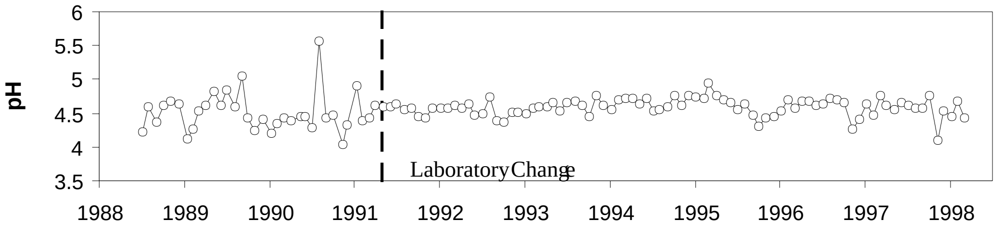
(a) Alkalinity, River Etherow



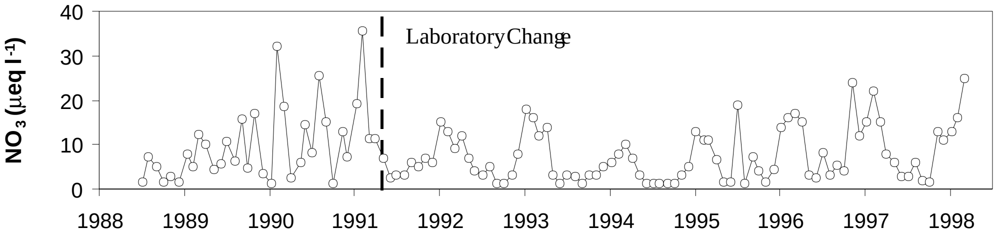
(b) Alkalinity, Old Lodge



(c) pH, Old Lodge



(d) Nitrate, Old Lodge



time in response to anthropogenic or natural changes. Robson & Neal (1996) have shown that SKT can potentially identify a significant trend in data containing only a long term cyclical signal. In order to identify more complex variations in the dataset, therefore, the Splus LOESS curve-fitting function was used (Cleveland, 1979; Becker *et al.*, 1988). The procedure provides robust smoothing using a local quadratic polynomial fit. For each date value, a weighting procedure is applied to nearby points, and a local curve fitted using a least squares optimisation. LOESS curves were added to all time series plots other than those where concentrations were consistently at or close to detection limits.

Trend analyses were undertaken for pH, alkalinity, total sulphate and non-marine sulphate, nitrate, chloride, dissolved organic carbon, the four major base cations (calcium, magnesium, sodium and potassium), total aluminium, and labile and non-labile aluminium fractions. Other measured chemical constituents were generally present at low concentrations, often below detection limits, and were therefore unsuitable for trend assessment.

■ 3.2 Biology

Sampling, analysis and quality control procedures conform to the protocols provided by Patrick *et al*. (1991) and Patrick *et al*. (1995). Following recommendations by Patrick *et al.* (1995), the aquatic macrophyte survey frequency for lakes was reduced from annual to once every two years, from 1993 onwards. Determination of fish condition factor has occasionally been prevented at a few sites by the failure of weighing apparatus in the field. Steps have now been taken to ensure this problem does not recur in the future.

3.2.1 Data screening

Data entry of multi-species records on the UKAWMN database (i.e. for epilithic diatoms, aquatic macrophytes and macroinvertebrates) involves the input of alphanumeric species codes according to recognised species coding systems. Errors could occur in the entry of a species codes or other data, such as abundance measurements. Species abundance data for the multi-variate datasets of each site were therefore plotted graphically, complete with full species names, and scrutinised visually to identify obvious outliers, or apparently missing data points. For fish data, all records of weight which were >4 times the standard deviation from the mean were omitted from the dataset. In addition, fish length was plotted against fish width for each site and outliers were identified by visual inspection. Where outliers were identified, original record-sheets were re-consulted and amendments made to the database where necessary.

3.2.2 Statistical analyses

Epilithic diatom and macroinvertebrate analyses

Epilithic diatom data consist of the frequency of all taxa occurring in a count of 300 diatom valves for each sample collected. For most sites, three replicate samples are collected in late summer to early autumn (i.e. July-September). Macroinvertebrate data consist of the frequency of all taxa collected in each one minute littoral kick sample. Sampling is conducted from April-May. From 1988-1991, three replicates were collected from each site, but since 1992 this has been increased to five. In order to reduce errors of mis-identification, some species or genera that are difficult to identify have been combined into a higher taxonomical level. The genus *Nemoura* has been spilt into two easily identifiable groups: *Nemoura* spp. 1 (long legged - including *N.cinerea*, *N. dubitans* and *N. avicularis*) and Nemoura spp. 2 (short legged - *N. cambrica* and *N. erratica*). Taxa corresponding to the Heteroptera Gerromorpha have been ignored since these are semi-aquatic and live primarily on the water surface.

The data used in all analyses consisted of all taxa identified to species level or lower. For macroinvertebrates, the acid tolerant mayfly family Leptophlebiidae, and the stonefly groups *Nemoura* sp. 1 and *Nemoura* spp. 2, were also included as a pseudo-species. Data were converted to percentages and transformed by log-ratio centring prior to Redundancy Analysis (RDA) and Principal Components Analysis (PCA). All analyses were performed using the program CANOCO 3.12a (ter Braak, 1988, 1990).

Statistical analyses followed that outlined by Patrick *et al*. (1995). Data were tested for time trends using RDA, a form of PCA in which components are constrained to be linear combinations of explanatory variables (Jongman *et al*., 1987; ter Braak & Prentice, 1988). Linear methods were deemed appropriate after detrended canonical correspondence analysis (DCCA) demonstrated that all datasets had short time constrained gradients (<3 standard deviation units).

Two forms of RDA were performed:

i) Sample year was coded as multiple ‘dummy’ variables. In this analysis the sum of constrained eigenvalues represents the proportion of the total variance in the species data which can be explained by differences between years. The remaining proportion therefore represents the variance between replicate samples from the same year.

ii) Sample year was coded as a single variable. Here, the sum of constrained eigenvalues represents the proportion of the total variance which may be explained by a linear trend (λ_1 RDA).

Statistical significance was assessed using two forms of Monte Carlo permutation test (Manly, 1991; Potvin & Roff, 1993) with 999 permutations of samples. The unrestricted permutation test assumes independence among observations and for time-series data this assumption is often invalid. The restricted permutation test restricts the range of possible permutations to preserve the autocorrelation structure of the data (ter Braak, 1990). Results for both tests are presented in the site summaries of Chapter 4 but conclusions are only based on the restricted test, which appears to be generally more conservative (i.e. fewer trends are deemed significant by this method).

PCA was also conducted for all multi-species datasets. The first axis of PCA provides the maximum variance which can be explained by a single constraining variable (λ_1PCA). The ratio of (λ_1RDA) to (λ_1PCA) therefore provides an indication of the strength of any time trend relative to random and unmodelled effects. Hill’s N_2 is a measure of the ‘effective’ number of species in a sample and allows between-site comparisons.

In Chapter 4, optimal pH values are provided for the diatom species referred to in the summary text. These values are based on statistical analysis of diatom species representation in surface sediments taken from the 167 lakes of the SWAP dataset (Stevenson *et al.*, 1991).

Fish analysis

Data considered in this report are for trout (*Salmo trutta*) and, for two sites Atlantic salmon (*S. salar*), caught by electro-fishing of stream sites and the outflow streams of lake sites. Density estimates are based upon the catch data from three individual reaches fished at each site. Reach population numbers are estimated from a series of constant-effort removal fishings using the Exact Maximum Likelihood method (Carl & Strub, 1978). A chi-square test is used to assess the validity of the assumption that a constant proportion of the fish population are caught and removed by each successive fishing.

All individuals are weighed and their lengths measured, and these data are used to calculate condition factor (CF):

$$CF = weight/length^3$$

Three parameters (density, mean condition factor, and the coefficient of variation of the condition factor) for two age classes, (0+, i.e. less than one year old; and >0+, i.e. greater than one year old) have been subject to linear regression analysis to test for time trends. All parameters are presented as time series plots in Chapter 4. However, time trends have almost invariably been insignificant and have not been included in the trend statistic data tables in the site summaries. Significant trends have been reported in the summary text when observed.

To compliment the electro-fishing surveys, a standard habitat assessment (HABSCORE III - HQS) was conducted at each reach. This method was originally developed by the Welsh Water Authority to predict fish populations and is based on empirical statistical models. The HQS gives a predicted density under ‘pristine’ conditions. By comparing observed fish density with HQS it should be possible to determine whether observed trends are due to changes in habitat or some other limiting factor such as acidity. HQS should also provide an indication of whether densities observed at UKAWMN sites are lower than would be expected were they not acidified. HQS values for most sites show considerable inter-annual variability over the monitoring period, and since few linear trends have been identified in the trout population data HQS data have not been systematically reported in Chapter 4. However, mean HQS data are considered in Section 7.1.3.

Aquatic macrophyte analysis

For lakes, relative species abundance was determined on a five point scale (i.e. comparable to the DAFOR scoring system (e.g. Palmer *et al*., 1992), following shoreline survey, shore transects and deep water grapnel trawls, as follows:

1. rare/infrequent
2. occasional but not abundant
3. widespread but not abundant
4. locally abundant
5. widespread and abundant

For streams, total macrophyte cover was estimated for each 5 metre section of a 50 m survey stretch, and each was then partitioned into proportional species abundance, to provide percentage cover for each species. Data analysed for this report are the mean species cover estimates for the 50 m stretch.

Data analysis follows that for epilithic diatoms and macroinvertebrates described above. Since replicate samples are not taken, RDA to assess the proportion of between-year and within-year variation was not performed. For lakes, raw abundance data were used (i.e. without transformation), while for streams, percentage cover data were log-transformed prior to RDA and PCA. PCA and RDA were based on a species covariance matrix.

3.2.3 Graphical and tabular presentation of data

Data presented graphically in the site summaries (Chapter 4) represent the following:

i) Epilithic diatoms. Percentage frequency of all taxa occurring at over 2% relative abundance in any one sample (for the site). Data for all replicate samples are plotted. Species are sorted from left to right in order of the year of their maximum occurrence. This provides a diagonal structure to the plot if there is any time trend.

ii) Macroinvertebrates. Percentage frequency of all taxa recorded in all replicate samples from the site. In addition, the total number of individuals recorded in each sample. These data are sorted taxonomically, so that species of common Genus, Family etc., cluster together.

iii) Trout.
a) Density of 0+ (new recruits) and >0+ (more than one year old) fish for the site;
b) Mean condition factor (CF) and its coefficient of variation for 0+ and >0+ fish; c) Length frequency histograms (Peterson graphs) to illustrate the population structure at each site for each year.

iv) Sediment traps. Sediment traps have been deployed at all UKAWMN lakes since 1991. Problems with trap retrieval were encountered at some sites during the first two years but since then samples have been collected from most sites in most years. Graphs represent the following:
a) Diatoms. Percentage frequency of all diatom taxa occurring at over 2% relative abundance in any one sample (for the site). Only one sample is collected per year.
b) Spheroidal carbonaceous particles (SCPs). SCPs are derived from high temperature fossil fuel combustion (Rose *et. al*, 1995). Palaeolimnological work has shown similar historical patterns of increase in the carbonaceous particle flux to the sediments

of all UKAWMN lakes over the last century or more (Patrick *et al*., 1995), with peak values occurring in the mid- to late 1970s. The recent introduction of emission controls have resulted in a decline in particle fluxes to sediments (Rose *et. al*, 1995). Data are provided for SCPs as numbers of particles per trap per day. Calculated fluxes show high inter-annual variability at most sites but there is no evidence for a decline in flux over the period of trap deployment at any site (Rose pers. comm.). Results have not been discussed in the site summaries (Chapter 4).

Aquatic macrophyte data are presented in tabular format:

Certain species which have been associated in ecological literature with particular levels of acidity (e.g. Farmer, 1990) have been ascribed 'indicator' status denoted by superscripts in the species tables of Chapter 4. For lakes these range from:

^{1} - extremely intolerant of acid conditions and rarely found in lakes with mean pH below 5.6;
^{2} - characteristic of mildly acid lakes but rarely found in waters with mean below pH 5.2;
^{3} - species tolerant of waters below pH 5.2 but rarely found in very acid lakes;
^{4} - acidophilic species which tend to dominate waters with mean pH below 4.5.

For streams:
^{1} - characteristic of well buffered streams prone to only occasional acid episodes;
^{2} - characteristic of well buffered to mildly acid streams;
^{3} - characteristic of permanently acid streams.

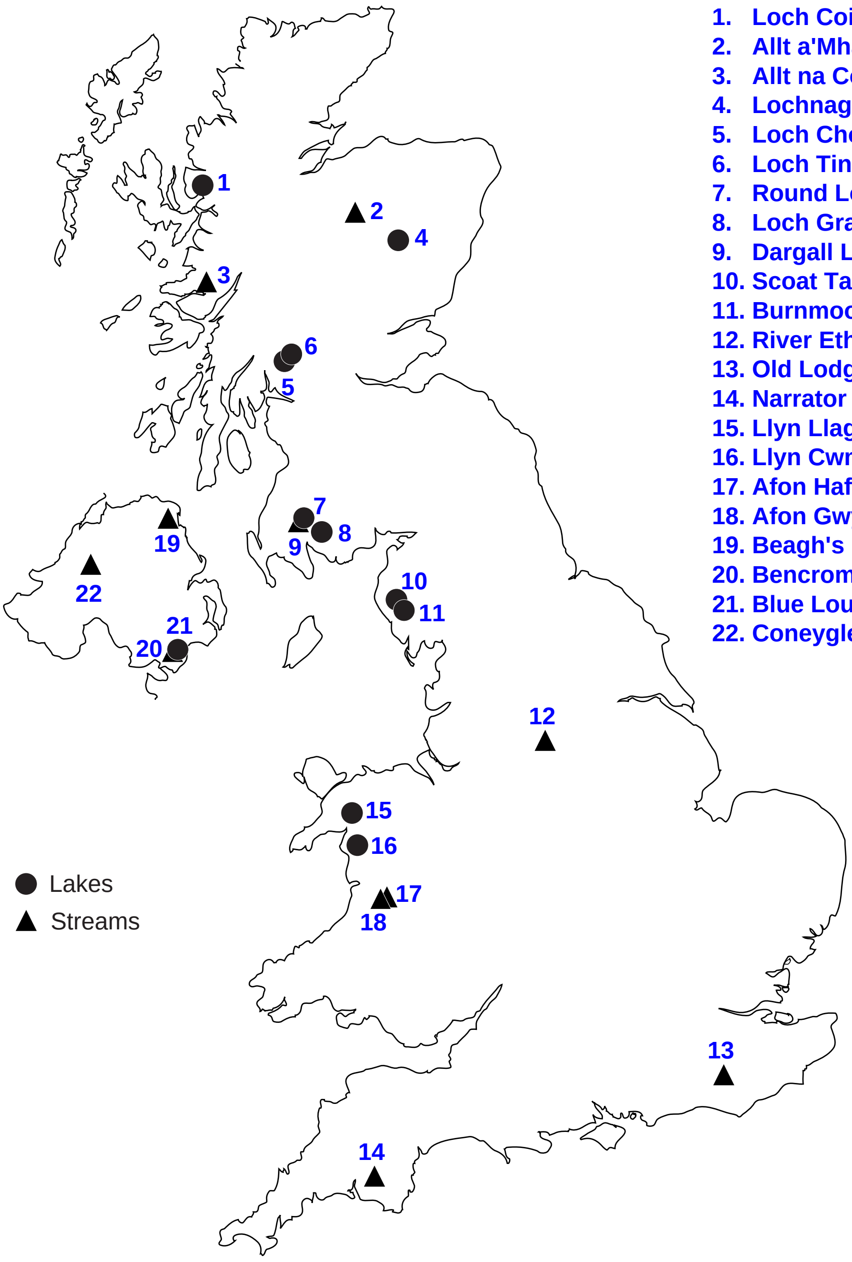
4

Site Summaries

Chris Evans, Don Monteith, Bill Beaumont, Roger Flower, & Julie Winterbottom

Figure 4.1.1

Location of UKAWMN sites



1. Loch Coire nan Arr
2. Allt a'Mharcaidh
3. Allt na Coire nan Con
4. Lochnagar
5. Loch Chon
6. Loch Tinker
7. Round Loch of Glenhead
8. Loch Grannoch
9. Dargall Lane
10. Scoat Tarn
11. Burnmoor Tarn
12. River Etherow
13. Old Lodge
14. Narrator Brook
15. Llyn Llagi
16. Llyn Cwm Mynach
17. Afon Hafren
18. Afon Gwy
19. Beagh's Burn
20. Bencrom River
21. Blue Lough
22. Coneyglen Burn

4.1 Loch Coire nan Arr

Site Review

Loch Coire nan Arr is the most northerly of all UKAWMN sites. As atmospheric pollution loads at the site were known to be low and the water chemistry relatively well buffered, the site was initially considered as a potential control for the other more impacted regions to the south. However, palaeoecological studies have since suggested that the loch has undergone very slight acidification in recent years (Patrick *et al.*, 1995). In 1991 a temporary dam was placed on the loch outflow as a means of conserving the water supply to a fish farm located beneath the site. More recently a permanent structure with sluice, has replaced this. The dam has raised mean water level at the site by at least 0.5 m loch shoreline. The water level change has clearly reduced the extent of emergent macrophyte stands at the site (see below).

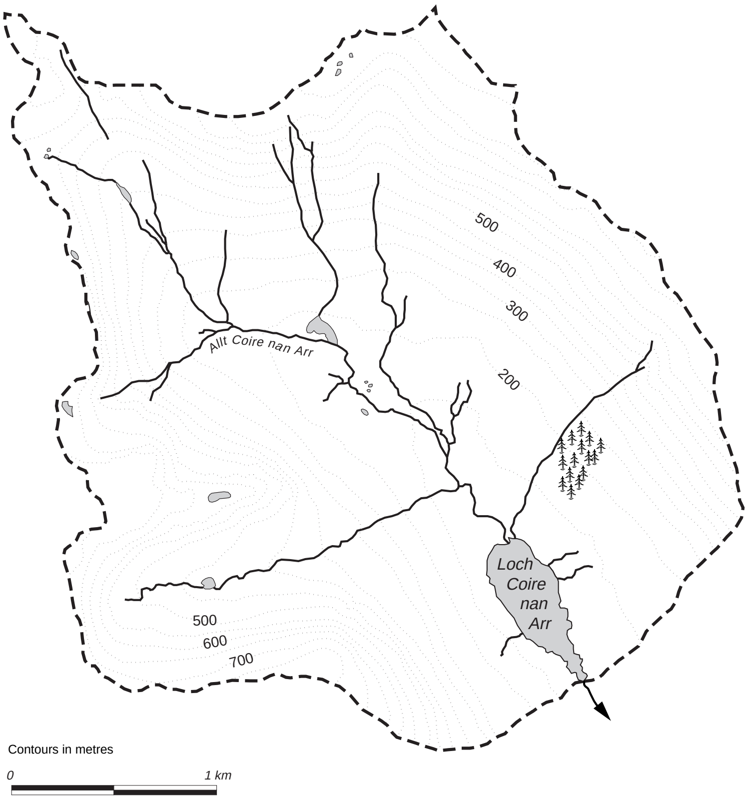


Figure 4.1.1

Loch Coire nan Arr: catchment

Table 4.1.1

Loch Coire nan Arr: site characteristics

Grid reference	*NG 808422*
Lake altitude	*125 m*
Maximum depth	*12.0 m*
Mean depth	*4.8 m*
Volume	*5.6 x 10^5 m^3*
Lake area	*11.6 ha*
Catchment area (excl. lake)	*897 ha*
Catchment: Lake area ratio	*77.3*
Catchment Geology	*Torridonian Sandstone*
Catchment Soils	*peat*
Catchment vegetation	*moorland 99%* *conifers <1%*
Net relief	*771 m*
Mean annual rainfall	*3311 mm*
1996 deposition	
Total S	*14 kg ha^{-1} yr^{-1}*
non-marine S	*8 kg ha^{-1} yr^{-1}*
Oxidised N	*3 kg ha^{-1} yr^{-1}*
Reduced N	*3 kg ha^{-1} yr^{-1}*

Table 4.1.2

Loch Coire nan Arr: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*6.39*	*6.95*	*5.75*
Alkalinity	µeq l^{-1}	*37.8*	*89.0*	*4.0*
Ca	µeq l^{-1}	*42.5*	*70.0*	*17.5*
Mg	µeq l^{-1}	*60.8*	*158.3*	*25.0*
Na	µeq l^{-1}	*232.2*	*495.7*	*130.4*
K	µeq l^{-1}	*8.5*	*15.4*	*2.6*
SO_4	µeq l^{-1}	*40.8*	*56.3*	*27.1*
xSO_4	µeq l^{-1}	*13.8*	*23.1*	*-15.6*
NO_3	µeq l^{-1}	*2.9*	*7.9*	*< 1.4*
Cl	µeq l^{-1}	*257.7*	*664.8*	*123.9*
Soluble Al	µg l^{-1}	*15.3*	*40.0*	*< 2.5*
Labile Al	µg l^{-1}	*3.1*	*7.0*	*< 2.5*
Non-labile Al	µg l^{-1}	*13.7*	*33.0*	*< 2.5*
DOC	mg l^{-1}	*2.2*	*5.2*	*< 0.1*
Conductivity	µS cm^{-1}	*39.2*	*85.0*	*21.0*

Water Chemistry

(Figure 4.1.2, Table 4.1.2-3)

Although potentially susceptible to acidification, with a ten-year mean Ca concentration of just 43 μeq l^{-1}, Loch Coire nan Arr receives low levels of anthropogenic S and N deposition and is not acidic. Mean pH is 6.39 and mean alkalinity 38 μeq l^{-1}, with labile Al concentrations at or close to detection limits. Non-marine SO_4 concentrations reflect the low deposition, with a ten year mean of 13.5 μeq l^{-1}. NO_3 concentrations have remained below 10 μeq l^{-1} throughout the monitoring period, although some seasonality is observed with concentrations above detection limits during all winter periods (Figure 4.1.2e).

The proximity of this site to the coast results in large marine ion inputs, and Na and Cl concentrations at the loch are therefore high (10 year means 203 μeq l^{-1} and 258 μeq l^{-1} respectively). Both ions show a pronounced seasonal cycle, with winter peaks resulting from large frontal storms at this time. Marine ion deposition events have been shown to cause episodic acidification through the 'sea-salt effect' (Wright *et al.*, 1988; Langan, 1989) whereby marine cations temporarily displace H^+ from soil exchange sites. This natural process is evident in pH and alkalinity minima that occur concurrently with marine ion maxima (Figure 4.1.2a,b). Some temporary retention of marine SO_4 may also occur (Evans *et al.*, in press; Section 5.3), leading to reduced or even negative xSO_4 concentrations (Figure 4.1.2d).

In accordance with the continuously low pollutant deposition at the site, no significant trends were observed for pH, alkalinity, base cations or mineral acid anions. There are also no identifiable changes in chemistry following the rise in water level in 1991. However, large and highly significant increases were observed over the last decade for both DOC and non-labile Al (Table 4.1.3). LOESS curves suggest that these increases took place fairly steadily between 1988-1996, but may have levelled off in recent years. The SKT estimated total increase over the decade of 2.5 mg l^{-1} represents a major change in water chemistry given a mean concentration in the first year of sampling of just 1.0 mg l^{-1}. Organically complexed non-labile Al shows a clear correlation with DOC, suggesting that concentrations are determined by the availability of complexing ligands (Driscoll *et al.*, 1984). Since almost all Al present is in non-labile form, total soluble Al exhibits similar behaviour (Figures 4.1.2j,k). The issue of DOC trends is discussed in detail in Section 5.2.3.

Epilithic diatoms

(Figure 4.1.3, Table 4.1.4)

The epilithic diatom flora of Loch Coire nan Arr demonstrates marked inter-annual variation over the past decade. Samples are dominated by *Tabellaria flocculosa*, (pH optima 5.4) *Brachysira vitrea* (pH optima 5.9) and *Achnanthes minutissima* (pH optima 6.4), *T. flocculosa* was most abundant between 1989-1991, gradually declined until 1997 and increased again in 1998. These changes have been largely reciprocated by *A. minutissima*. Similar patterns in species variation have

Table 4.1.3

Significant trends in chemical determinands (June 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
DOC	*mg l^{-1}*	*+0.21****	*+0.25***
Non-labile Al	*μg l^{-1}*	*+1.13***	*+1.00**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

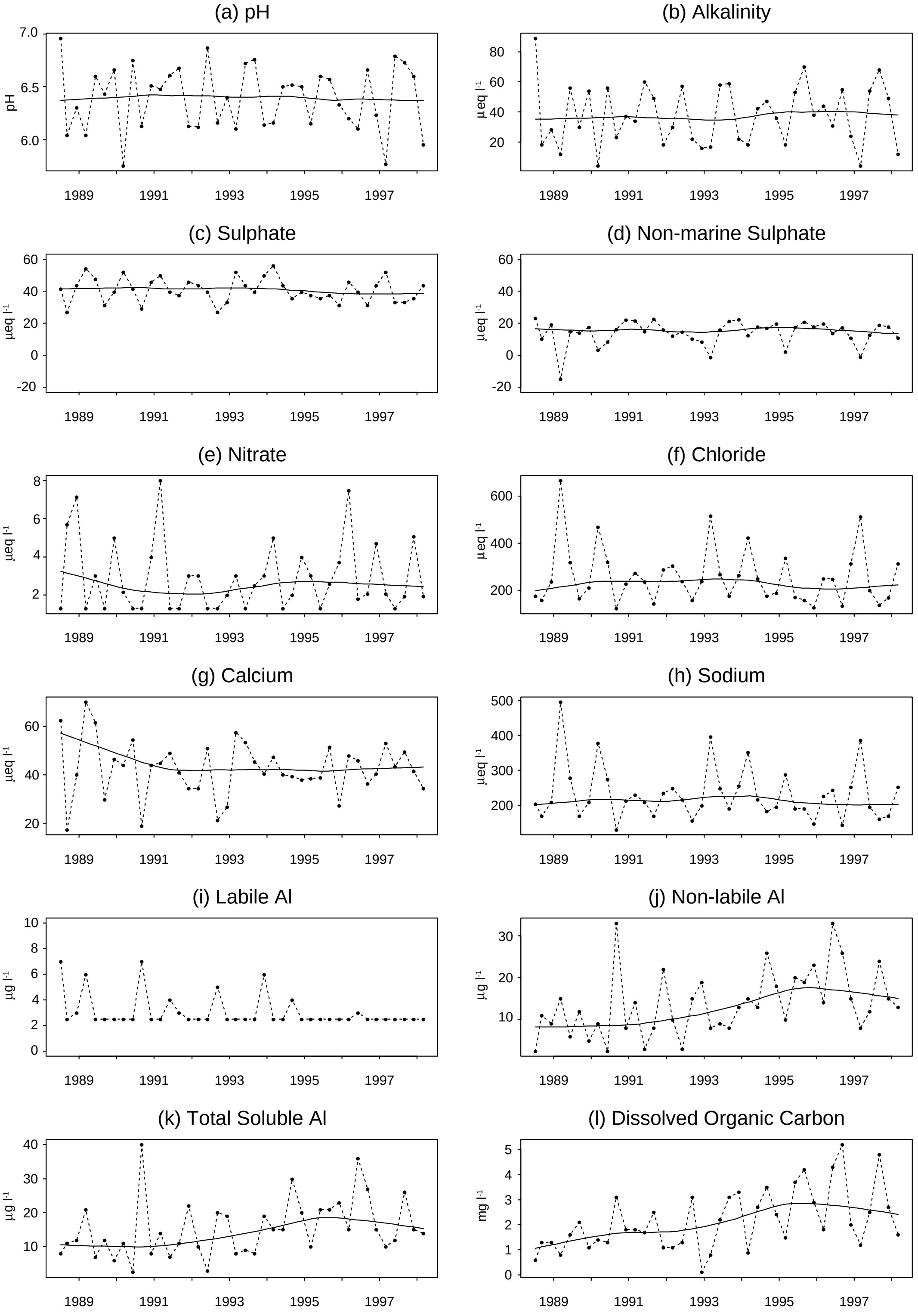


Figure 4.1.2

Loch Coire nan Arr: summary of major chemical determinands (July 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.1.4

Loch Coire nan Arr: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	294	150	6.2	0.42	0.39
Macrophytes	49	20	12.6	1.19	0.73
Invertebrates	983	48	3.0	0.78	0.52

Variance explained (%)	within year	between years	linear trend	p	
				unrestricted	restricted
Epilithic diatoms	49.9	50.1	7.0	0.01	0.24
Macrophytes	*	*	30.1	<0.01	<0.01
Invertebrates	42.4	7.6	15.8	0.00	0.01

Table 4.1.5

Loch Coire nan Arr: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	88	89	90	91	92	93	95	97
INDICATOR SPECIES								
Nitella flexilis^1	2	3	3	3	3	3	1	1
Myriophyllum alterniflorum^2	3	3	3	3	3	3	2	2
Utricularia sp.^{2}	2	3	3	2	2	0	2	2
Callitriche hamulata^3	2	3	3	3	3	3	3	3
Sphagnum auriculatum^4	0	1	1	1	1	1	1	1
Juncus bulbosus var. *fluitans*^{4}	5	5	5	5	5	4	4	4
OTHER SUBMERGED OR FLOATING LEAF SPECIES								
Batrachospermum sp.	1	1	0	0	0	0	1	0
Filamentous green algae	1	2	3	1	1	1	1	1
Fontinalis sp.	1	1	1	0	0	0	0	0
Rhytidiadelphus sp.	0	1	1	1	0	1	0	1
Lobelia dortmanna	3	3	4	4	3	3	3	3
Isoetes lacustris	4	4	4	4	4	3	3	3
Littorella uniflora	3	3	4	4	4	3	3	3
Subularia aquatica	0	0	0	0	0	0	0	1
Potamogeton natans	4	4	4	4	4	2	2	4
Potamogeton polygonifolius	0	0	1	1	0	1	1	1
Sparganium angustifolium	1	2	2	2	2	1	2	2
EMERGENT SPECIES								
Equisetum fluviatile	2	2	2	2	2	1	2	0
Ranunculus flammula	2	2	3	3	3	2	3	1
Carex nigra	1	2	2	2	2	1	2	1
Carex rostrata	0	0	1	1	0	0	0	0
Eleocharis multicaulis	2	2	1	1	1	0	0	0
Glyceria fluitans	1	1	1	1	1	0	1	0
Juncus acutifloris/articulatus	1	3	2	2	2	1	0	0
Juncus effusus	1	1	1	1	1	1	1	1
TOTAL NUMBER OF SPECIES	20	22	23	22	19	18	19	18

occured in sediment trap samples from the loch which have been collected since 1991 (Figure 4.1.6). As the sediment traps should provide an integrated annual sample, it would seem that the epilithon data are generally representative of the diatom crop for the full growing season. The varying proportion of *A. minutissima* and *T. flocculosa* appear to indicate fluctuating levels of acidity and this is also shown by the diatom inferred pH derived from pH weighted averaging applied to the whole assemblage (Figure 7.3a) which suggests a gradual increase in pH between 1990 and 1996. Although these inferences are not strongly supported by changes in water chemistry, low pH was recorded in the spring of 1990, 1997 and 1998, apparently associated with high rainfall and Cl concentrations. The floristic similarity between 1998 samples and those of 1989-1991 appear to rule out any long term trend. RDA shows time to be insignificant as a linear variable at the 0.01 level using the restricted permutation test. The extent to which species variation may be influenced by ‘natural’ oscillations in acidity will require verification by ongoing monitoring.

■ Macroinvertebrates

(Figure 4.1.4, Table 4.1.4)

The macroinvertebrate benthic fauna is moderately diverse and dominated by Chironomidae and the acid tolerant mayfly family Leptophlebiidae. Several mayfly species have been recorded throughout the study period. The acid sensitive *Baetis* spp. has appeared intermittently since 1991, *Siphlonurus lacustris* has been recorded in all years except 1990 and in most recent years *Centroptilum luteolum* replaced the acid tolerant Leptophlebiidae as the dominant mayfly. In studies of Finnish freshwaters *C. luteolum* has a pH preference of approximately 6.0 (Hämäläinen & Huttunen, 1996). The acid tolerant caddisflies *Plectrocnemia* spp. and *Polycentropus* spp. were recorded throughout most of the monitoring period, being most abundant in 1995 and 1993 respectively. However, *Plectrocnemia* spp. has been absent since 1996. RDA shows a significant linear trend at the 0.01 level. The shift in species relative abundance, and in particular the decrease in the relative adundance of acid tolerant Leptophlebid mayflies and the appearance of *C. luteolum* since 1996 is indicative of an improvement in conditions.

■ Fish

(Figure 4.1.5)

The outflow of Loch Coire nan Arr was first fished in 1989. Trout density is intermediate for UKAWMN sites. There are no significant linear trends in density, mean condition factor or coefficient of variance of condition factor for either age group over the last nine years. However, general declines in density of both groups are apparent since 1991, possibly reflecting an influence of the outflow dam on the stream population. In common with many of the other Scottish sites, very high recruitment occured in 1991. Mortality of this cohort however appears to have been high as there is no evidence of higher than average trout densities progressing through the subsequent year groups. Poorest recruitment occurred in 1992 and 1996.

■ Aquatic macrophytes

(Table 4.1.4-5)

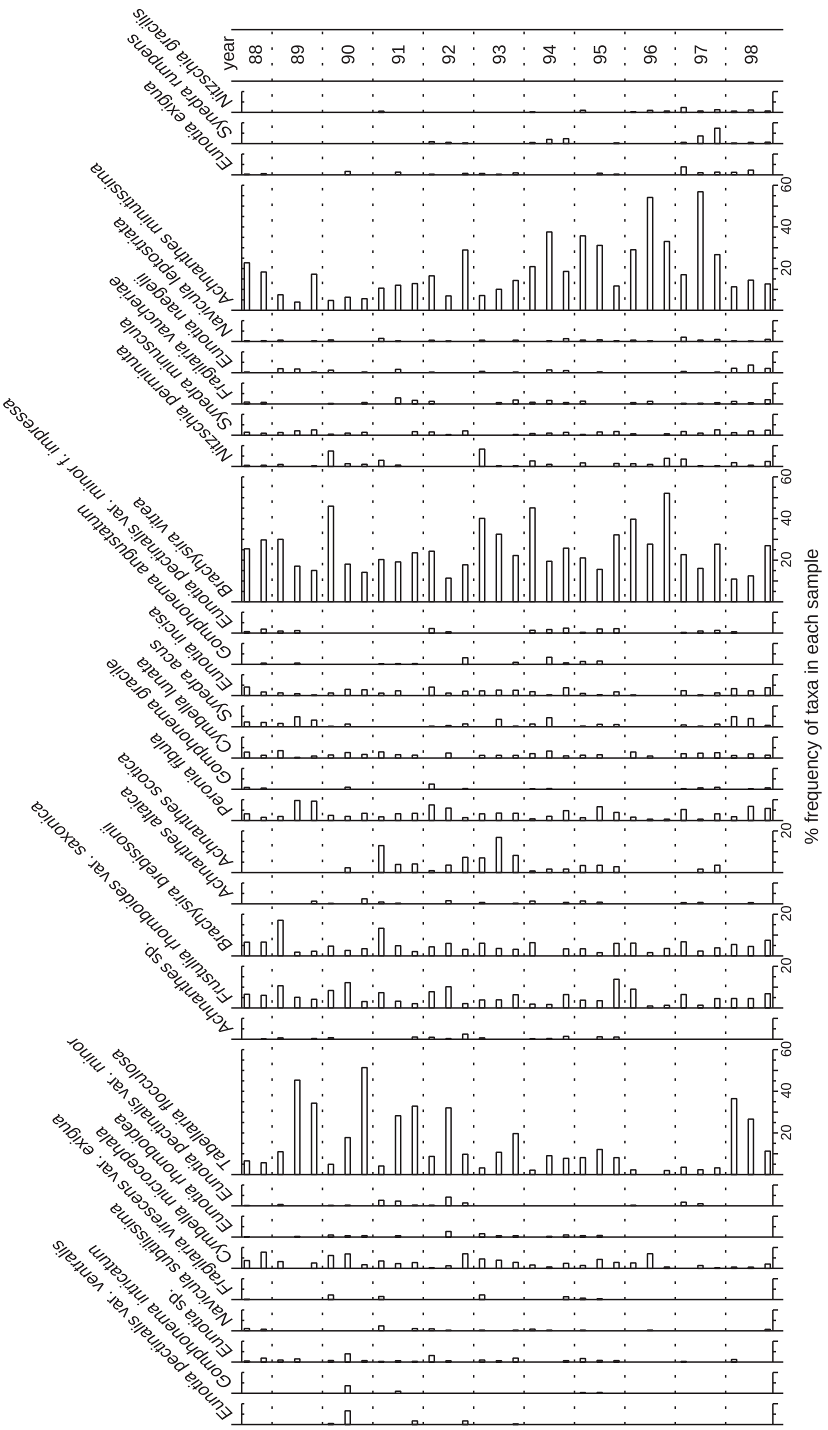
The aquatic macrophyte flora of Loch Coire nan Arr is typical of non-acid oligotrophic lakes. The submerged community is dominated by the isoetids, *Isoetes lacustris*, *Lobelia dortmanna* and *Littorella uniflora*. The acid sensitive charophyte species *Nitella flexilis*, and other species intolerant of acidity levels at the more acid UKAWMN lake sites (i.e. *Myriophyllum alterniflorum* and *Utricularia* sp.) are also present.

The installation of a dam, and the consequent increases in mean water level and level fluctuations, appear to have led to a substantial reduction in the abundance of some submerged species. In particular *N. flexilis*, which was widespread during the first few years of monitoring, is now considered rare. Conversely, *Potamogeton natans*, which forms floating leaved beds in moderately deep water, appears to have increased. Assessment of cover of

Figure 4.1.3

Loch Coire nan Arr: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



submerged species has been hampered by the problem of precise re-location of transects now that the characteristics of the lake perimeter have changed. It is highly likely that the water-level change has also been responsible for the loss of emergent stands of *Equisetum fluviatile*, *Carex rostrata* and *Eleocharis multicaulis*. It is unlikely that these species could become re-established at the site unless water level management were to cease for a considerable period. “Sample year” is significant as a linear trend according to RDA and restricted permutation tests but this almost certainly results from the effects of water level change.

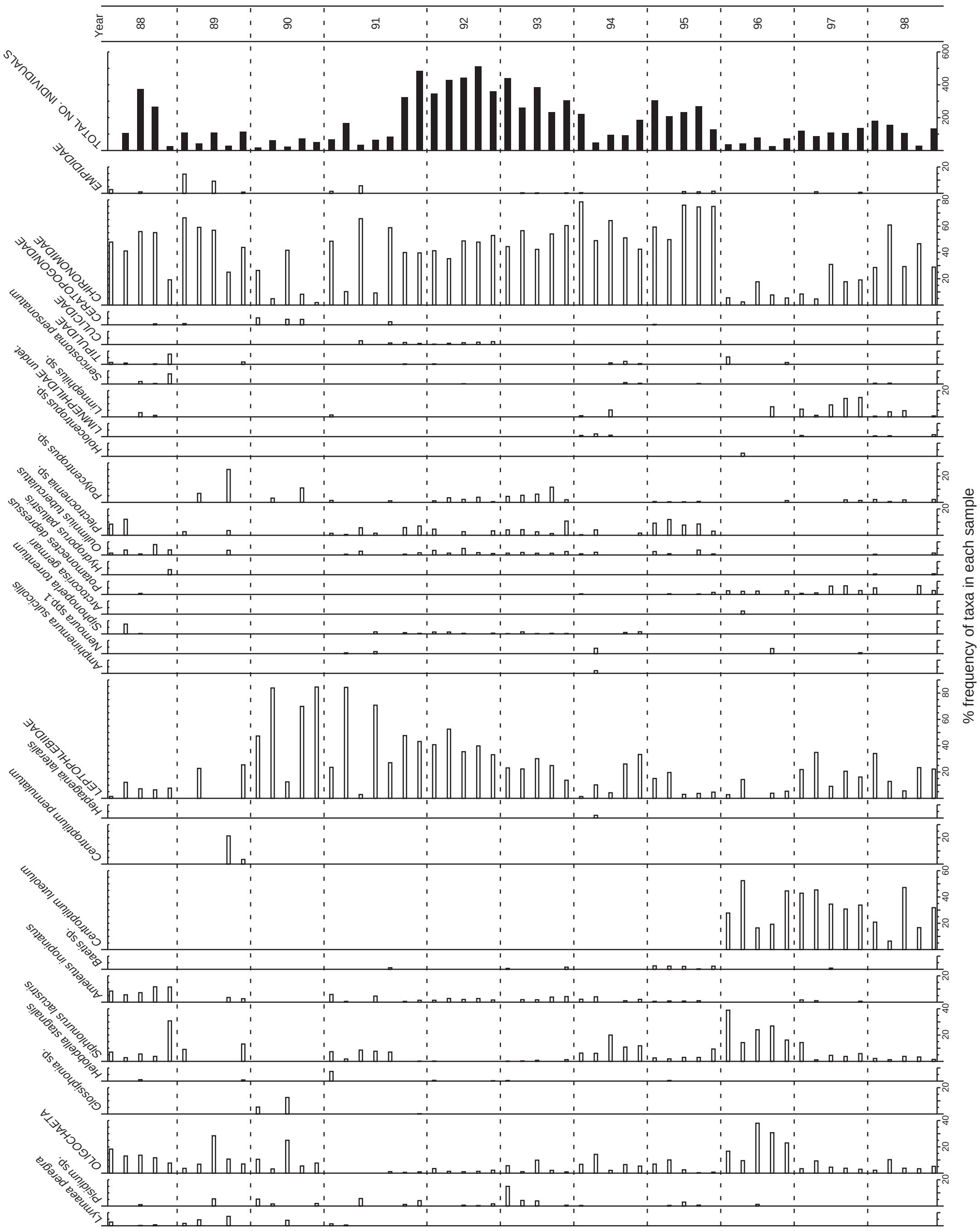
■ Summary

Despite geological sensitivity, Coire nan Arr receives very low levels of pollutant inputs, and has remained unacidic for most of the monitoring period. Episodic pH and alkalinity reductions are a feature of the site, due to large winter inputs of marine ions and high rainfall, and it is possible that these have influenced the inter-annual differences in species assemblages of diatoms and macroinvertebrates. However, negative alkalinities, have not been recorded at any time during the study period. Given the low levels of pollutant deposition, loch chemistry appears generally stable over the last ten years, but significant increases have been recorded for DOC and non-labile Al. A rise in water level following damming, and subsequent water level management since 1991, has led to considerable inundation of the loch’s former shoreline. The increased DOC at this site could therefore result from peat erosion. However, similar trends are observed at many other sites in the Network, suggesting a more general pattern of rising DOC. This issue is discussed in detail in Section 5.2.3. Changes in water level have almost certainly lead to a reduction in the representation of emergent macrophytes (through loss of habitat), while outflow regulation may have had an impact on the trout density of the outflow burn

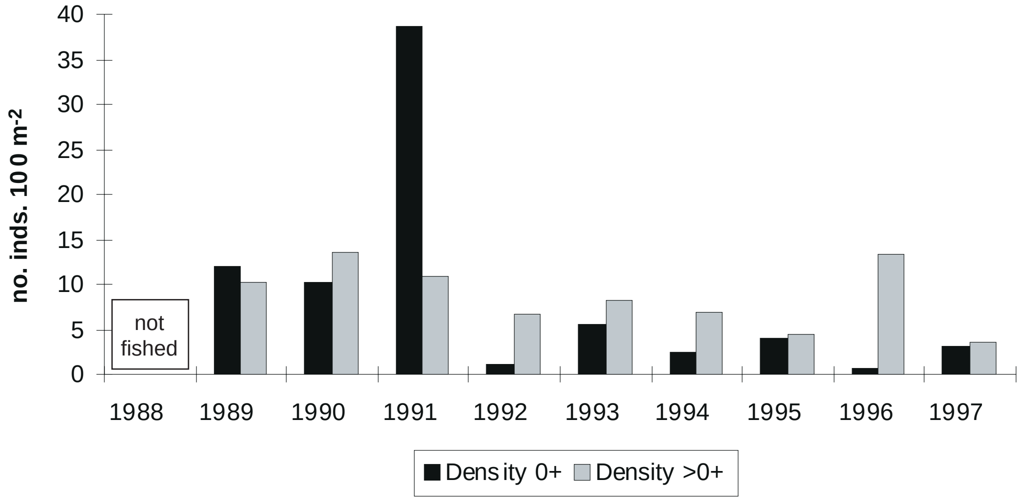
Figure 4.1.4

Loch Coire nan Arr: summary of macroinvertebrate data (1988 - 1998)

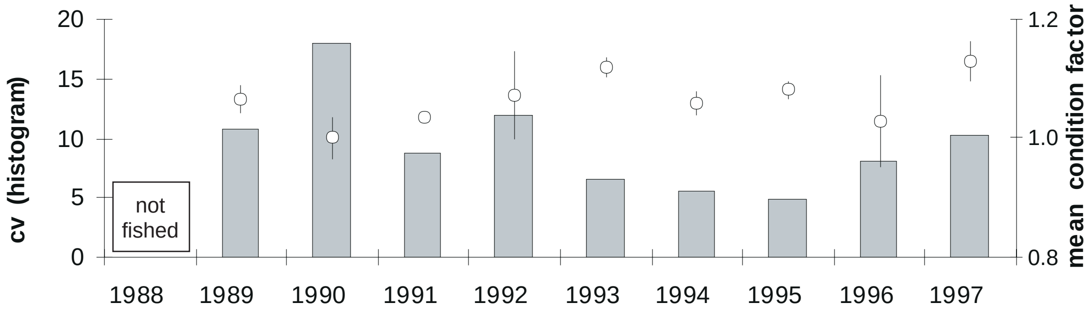
Percentage frequency of taxa in individual samples



(a) Density



(b) Condition (0+)



(c) Condition (>0+)

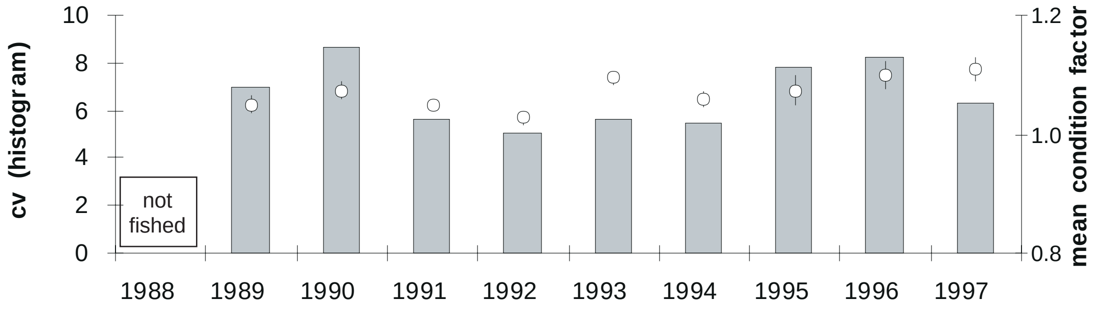


Figure 4.1.5

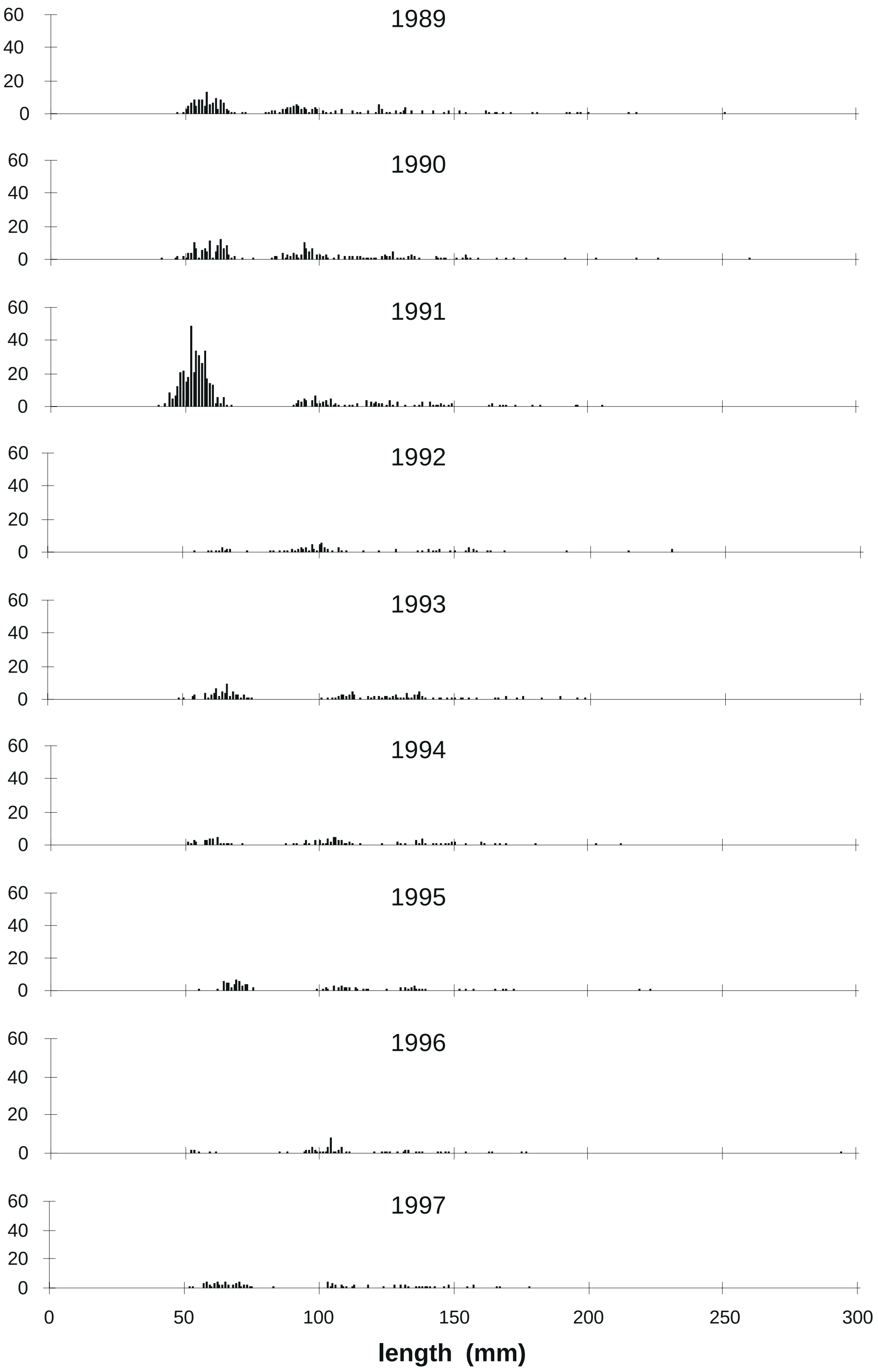
Loch Coire nan Arr: summary of fish data (1988 - 1997)

(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

Figure 4.1.5

Loch Coire nan Arr: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries (1989 - 1998)



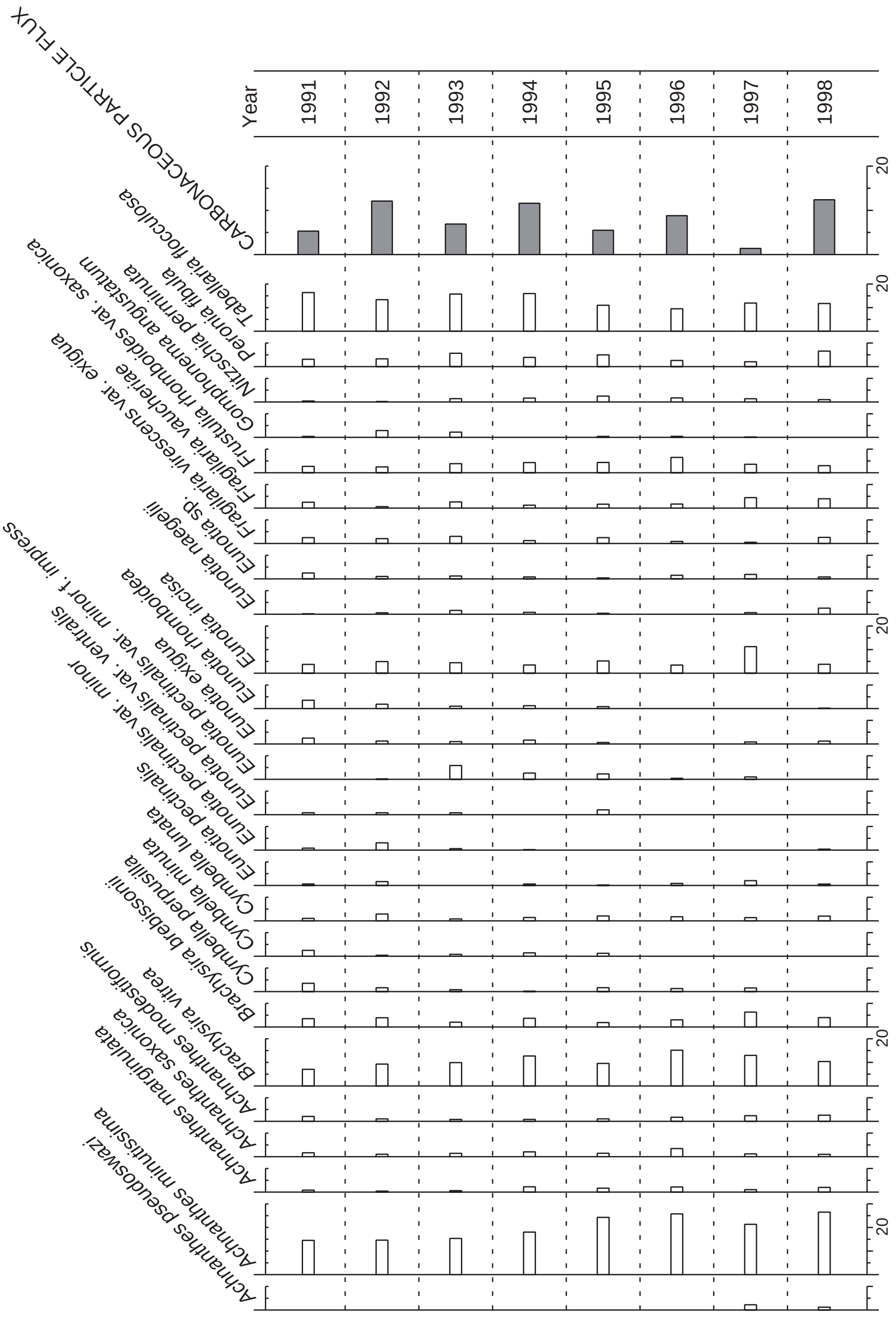


Figure 4.1.6

Loch Coire nan Arr: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year

4.2 Allt a'Mharcaidh

Site Review

The Allt a'Mharcaidh, in the western Cairngorms of northeast Scotland, is a well buffered mountain stream which is subject to occasional acid episodes. No physical changes have been observed in the study catchment since the onset of monitoring in 1988. The Allt a'Mharcaidh was studied as part of the SWAP project (e.g. Ferrier & Harriman, 1990). It is one of the two British sites represented in the UNECE Integrated Monitoring Programme (UNECE - IMP) and is also a freshwater site in the UK Environmental Change Network (ECN).

Water Chemistry

(Figure 4.2.2, Table 4.1.2-3)

The Allt a'Mharcaidh has a relatively well buffered chemistry, with a 10 year mean pH of 6.45. Although the site can be considered acid-sensitive, with a mean Ca of 42 μeq l^{-1}, S and N deposition are low. Mean xSO_4 is 33 μeq l^{-1}, whilst virtually all incoming N is retained; NO_3 concentrations in 88% of samples collected were below detection limits, and the maximum recorded was 5 μeq l^{-1}. The Allt a'Mharcaidh is however subject to acidic episodes, in which alkalinity falls to around zero and pH to <5.5. Previous work by Harriman *et al.* (1990) showed that approximately 75% of pH and alkalinity variation could be explained by flow. The main chemical change generating acidity at high flows appears to be dilution of base cations, although occasional pulses of marine ion deposition, notably in early 1993 (Figure 4.2.2) may have generated acidic episodes through the sea-salt effect. Apart from these infrequent events, sea-salt inputs are generally low, reflecting the inland location of this site.

Trend analyses show little or no chemical change at the Allt a'Mharcaidh over the last decade. The only significant trend identified is for DOC (Table 4.2.3), which is found to be increasing using

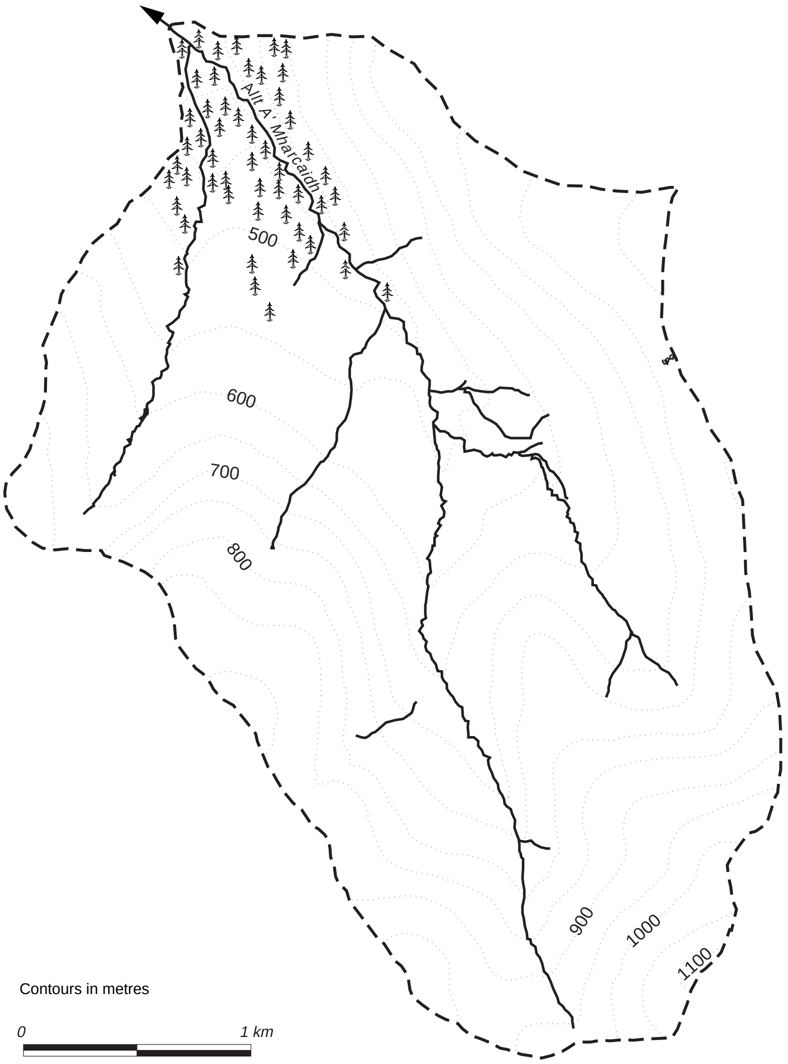


Figure 4.2.1

Allt a'Mharcaidh catchment

Table 4.2.1

Allt a'Mharcaidh: site characteristics

Grid reference	*NM 881045*
Catchment area	*998 ha*
Minimum catchment altitude	*325 m*
Maximum catchment altitude	*1111m*
Catchment Geology	*granite*
Catchment Soils	*alpine & peaty podsols, blanket peat*
Catchment vegetation	*moorland c. 98%* *native pine c. 2%*
Mean annual rainfall	*1331 mm*
1996 deposition	
Total S	*12 kg* ha^{-1} yr^{-1}
non-marine S	*8 kg* ha^{-1} yr^{-1}
Oxidised N	*3 kg* ha^{-1} yr^{-1}
Reduced N	*5 kg* ha^{-1} yr^{-1}

Table 4.2.2

Allt a'Mharcaidh: summary of chemical determinand, July 1988 - March 1998

Determinand		Mean	Max	Min
pH		6.45	7.08	5.12
Alkalinity	µeq l^{-1}	44.2	91.0	-4.0
Ca	µeq l^{-1}	42.0	60.5	4.5
Mg	µeq l^{-1}	29.2	50.0	16.7
Na	µeq l^{-1}	135.2	213.0	91.3
K	µeq l^{-1}	7.4	12.8	2.6
SO_4	µeq l^{-1}	44.4	72.9	29.2
xSO_4	µeq l^{-1}	32.9	57.9	18.3
NO_3	µeq l^{-1}	1.4	5.0	< 1.4
Cl	µeq l^{-1}	110.1	259.2	56.3
Soluble Al	µg l^{-1}	35.7	166.0	< 2.5
labile Al	µg l^{-1}	6.7	46.0	< 2.5
Non-labile Al	µg l^{-1}	29.8	150.0	< 2.5
DOC	mg l^{-1}	2.3	12.1	< 0.1
Conductivity	µS cm^{-1}	24.0	38.0	14.0

regression analysis. However the same increase is not found using SKT, and the time series plot (Figure 4.2.2) suggests that this trend may be the result of a small number of high DOC samples in recent years rather than a genuine and sustained increase.

■ Epilithic diatoms

(Figure 4.2.3, Table 4.2.4)

The epilithon of Allt a'Mharcaidh is dominated by *Synedra minuscula, Achnanthes minutissima* and *Fragilaria vaucheriae*, species typical of mildly acidic softwater streams. These taxa have shown marked variation in their relative abundance between years, *A. minutissima* showing relatively high abundances from 1991-1992 and 1994-1995. *F. vaucheriae* and rare taxa, including *Gomphonema angustatum* [agg.] and *Diatoma hyemale* var. *mesodon*, have undergone a decline in relative abundance since the onset of monitoring, while *Achnanthes modestiformis* has increased slightly. The species assemblage in 1998 samples was particularly unusual, with relatively high representation of *Brachysira vitrea, B. brebissonii, Frustulia rhomboides* var. *saxonica* and *Achnanthes marginulata*. These species have relatively low pH optima and their increase is likely to reflect a sustained period of depressed pH over the summer of 1998 resulting from unusually high flow conditions (see Section 7.4.1). RDA analysis shows time as an explanatory variable to be insignificant at the 0.01 level and no trend is apparent in diatom inferred pH for the site.

■ Macroinvertebrates

(Figure 4.2.4, Table 4.2.4)

The macroinvertebrate community of Allt a'Mharcaidh is diverse and dominated throughout the monitoring period by the acid sensitive mayfly *Baetis* spp.. Several other acid sensitive mayflies are also present in lower numbers, including *Rhithrogena semicolorata* and *Heptagenia lateralis*. The site also contains a diverse assemblage of stoneflies of which *Leuctra inermis* is most abundant, while other common taxa include *Brachyptera risi, Protonemura* spp., *Amphinemura sulcicollis* and the predatory species *Isoperla grammatica* and

Table 4.2.3

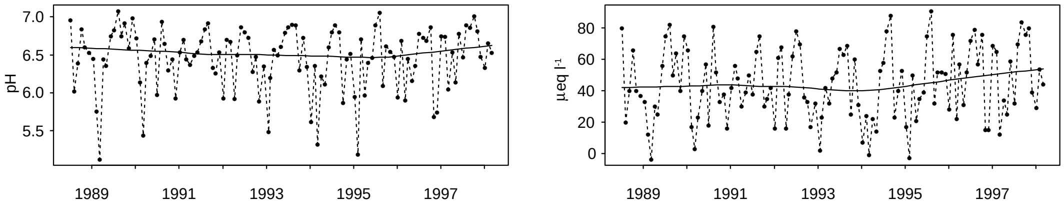
Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
DOC	mg l^{-1}	+0.11***	-

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

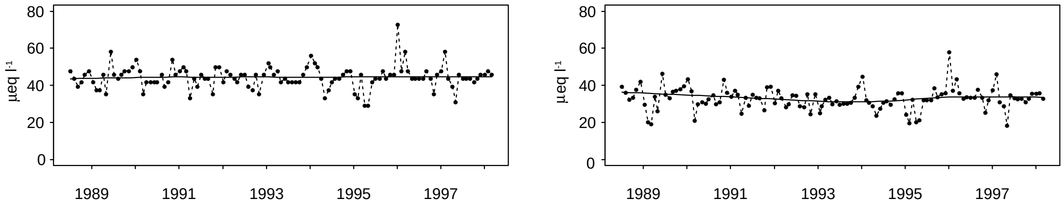
(a) pH

(b) Alkalinity



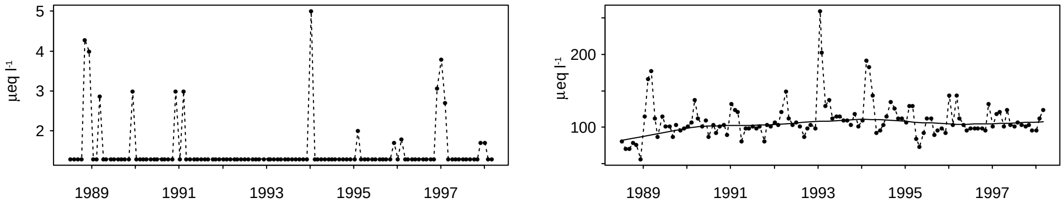
(c) Sulphate

(d) Non-marine Sulphate



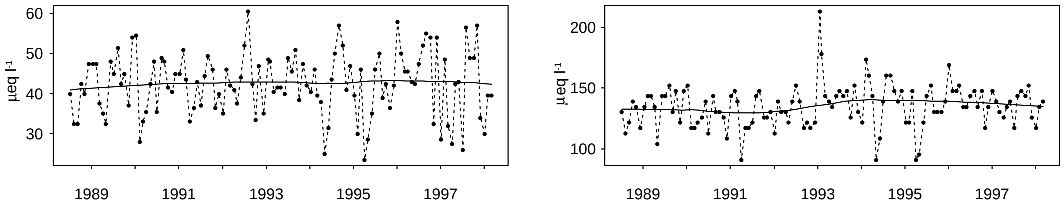
(e) Nitrate

(f) Chloride



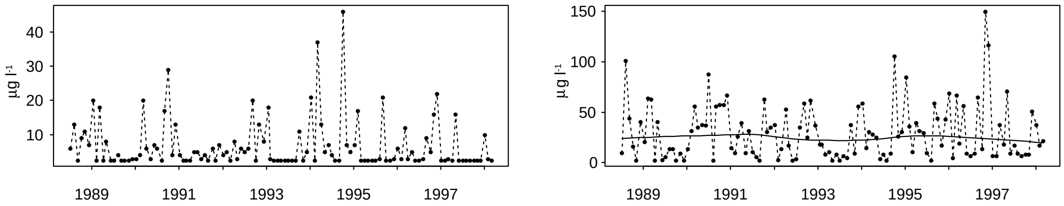
(g) Calcium

(h) Sodium



(i) Labile Al

(j) Non-labile Al



(k) Total Soluble Al

(l) Dissolved Organic Carbon

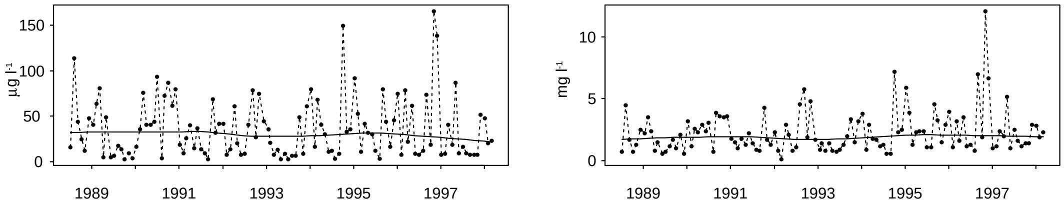


Figure 4.2.2

Allt a'Mharcaidh: summary of major chemical determinands (April 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.2.4

Allt a'Mharcaidh: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*306*	*94*	*4.2*	*0.52*	*0.49*
Macrophytes	*5*	*7*	*1.9*	*1.09*	*0.64*
Invertebrates	*173*	*33*	*4.7*	*0.30*	*0.27*

Variance				**p**	
explained (%)	**within year**	**between years**	**linear trend**	**unrestricted**	**restricted**
Epilithic diatoms	*33.9*	*66.1*	*9.8*	*<0.01*	*0.05*
Macrophytes	*	*	*30.1*	*0.01*	*<0.01*
Invertebrates	*33.5*	*66.5*	*7.5*	*<0.01*	*0.27*

Chloroperla tripunctata. The macroinvertebrate community remains relatively persistent with no marked changes in either species abundance or composition. Time as a linear trend is not significant at a 0.01 level, using RDA and associated permutation tests.

■ Fish

(Figure 4.2.5(i), (ii))

Trout densities at this site are the third highest of those found in the Network sites. Although

Table 4.2.5

Allt a'Mharcaidh: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

(% cover of 50 m survey stretch) **Year**	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**96**	**97**
INDICATOR SPECIES									
Lemanaea sp.[1]	*0.0*	*0.4*	*0.0*	*1.4*	*0.0*	*0.0*	*0.4*	*0.0*	*0.4*
Brachythecium plumosum[1]	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
Brachythecium rivulare[1]	*<0.1*	*<0.1*	*<0.1*	*0.0*	*0.0*	*0.0*	*<0.1*	*0.0*	*<0.1*
Fontinalis antipyretica[2]	*<0.1*	*<0.1*	*0.3*	*<0.1*	*0.2*	*1.3*	*2.3*	*1.3*	*0.5*
Hygrohypnum ochraceum[1]	*6.6*	*10.0*	*8.9*	*9.2*	*9.4*	*5.7*	*7.2*	*9.7*	*2.4*
OTHER SUBMERGED SPECIES									
Filamentous green algae	*0.5*	*0.7*	*2.5*	*0.3*	*1.3*	*3.2*	*27.1*	*0.9*	*<0.1*
Racomitrium aciculare	*0.1*	*0.2*	*0.7*	*1.0*	*1.3*	*0.0*	*<0.1*	*0.2*	*0.2*
Scapania undulata	*1.1*	*0.8*	*1.2*	*0.7*	*1.4*	*1.1*	*2.0*	*3.0*	*2.0*
total macrophyte cover excluding filamentous algae	*7.8*	*11.0*	*11.1*	*10.9*	*12.3*	*8.1*	*11.5*	*14.2*	*5.1*
TOTAL NUMBER OF SPECIES	*7*	*7*	*6*	*6*	*5*	*4*	*7*	*5*	*7*

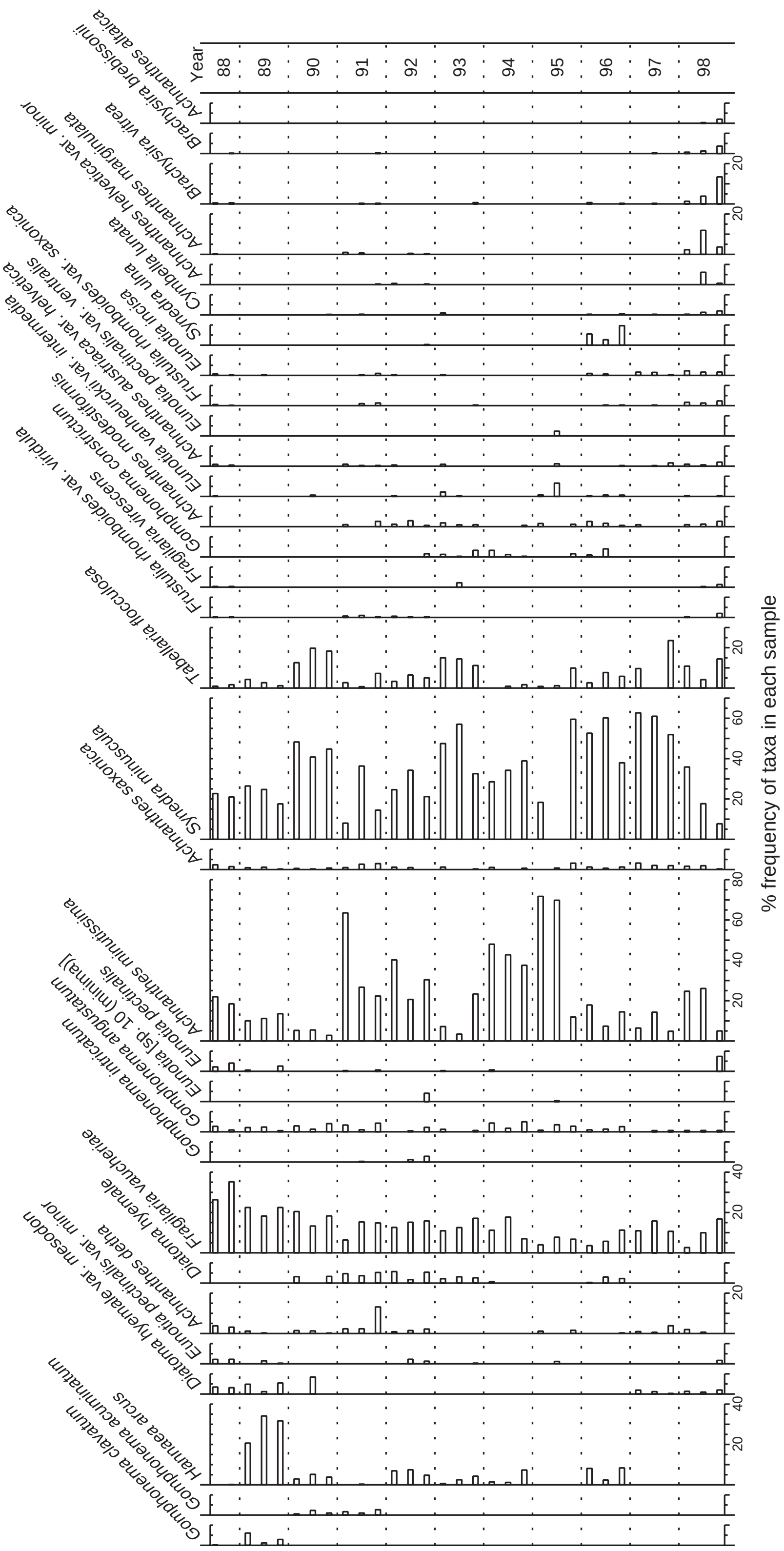


Figure 4.2.3

Allt a'Mharcaidh: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

population densities of 0+ trout show some variation over the ten years of monitoring, there is no apparent trend in this fluctuation. Most years show good recruitment with 1991, 1996 and 1997 showing the highest densities. Population densities of >0+ trout are more stable and show a significant ($p = <0.05$) positive linear trend over the ten years data. Condition factor has fluctuated over time with 1989 and 1990 showing the highest condition factors but no significant long term trends are apparent. It is interesting to note that 1991 had the highest 0+ trout population density, one of the lowest condition factors and the smallest coefficient of variation of the CF. Length frequency graphs show a balanced population structure but some evidence of recruitment failure in the year prior to 1988. Salmon data show considerable between-year variation but no trends with time in either age class (Figure 4.2.5ii). The highest densities of 0+ salmon were recorded in 1992 and 1997.

■ Aquatic macrophytes

(Tables 4.2.4-5)

The aquatic macrophyte flora of the Allt a'Mharcaidh is dominated by the acid sensitive moss *Hygrohypnum ochraceum*, which covered large areas of the survey stretch for much of the monitoring period. Cover of this species was substantially reduced in 1997, probably as a result of physical scouring following a major storm event in the early summer. Cover of the acid tolerant liverwort, *Scapania undulata* appears to have remained unaffected. The Allt a'Mharcaidh is notable for the occasional bloom of the red alga *Lemanaea* sp. which is intolerant of acid conditions. Its occurrence in 1989, 1991, 1995 and 1997 coincides with years of low summer rainfall as recorded at the nearby Meteorological Station at Aviemore, and could reflect prolonged periods of elevated alkalinity. "Sample year" is significant at the 0.01 level according to RDA and associated permutation test. The trend appears to be driven by slight increases in the cover of the moss *Fontinalis antipyretica* and the liverwort *Scapania undulata* and is unlikely to signify any chemical change at the site.

■ Summary

The Allt a'Mharcaidh is a relatively well-buffered site in a region of low acid deposition. Although large episodic pH and alkalinity depressions have been recorded, alkalinity values significantly below zero have not been observed. No definite trends have been identified for any chemical determinand or most biological groups, although data suggest a gradual increase in the density of older trout with time. The aquatic moss cover was severely reduced following extreme spate conditions in 1997 and there is also evidence that inter-annual variation in the flow regime has an important influence on other components of the macrophyte, diatom and macroinvertebrate species assemblages.

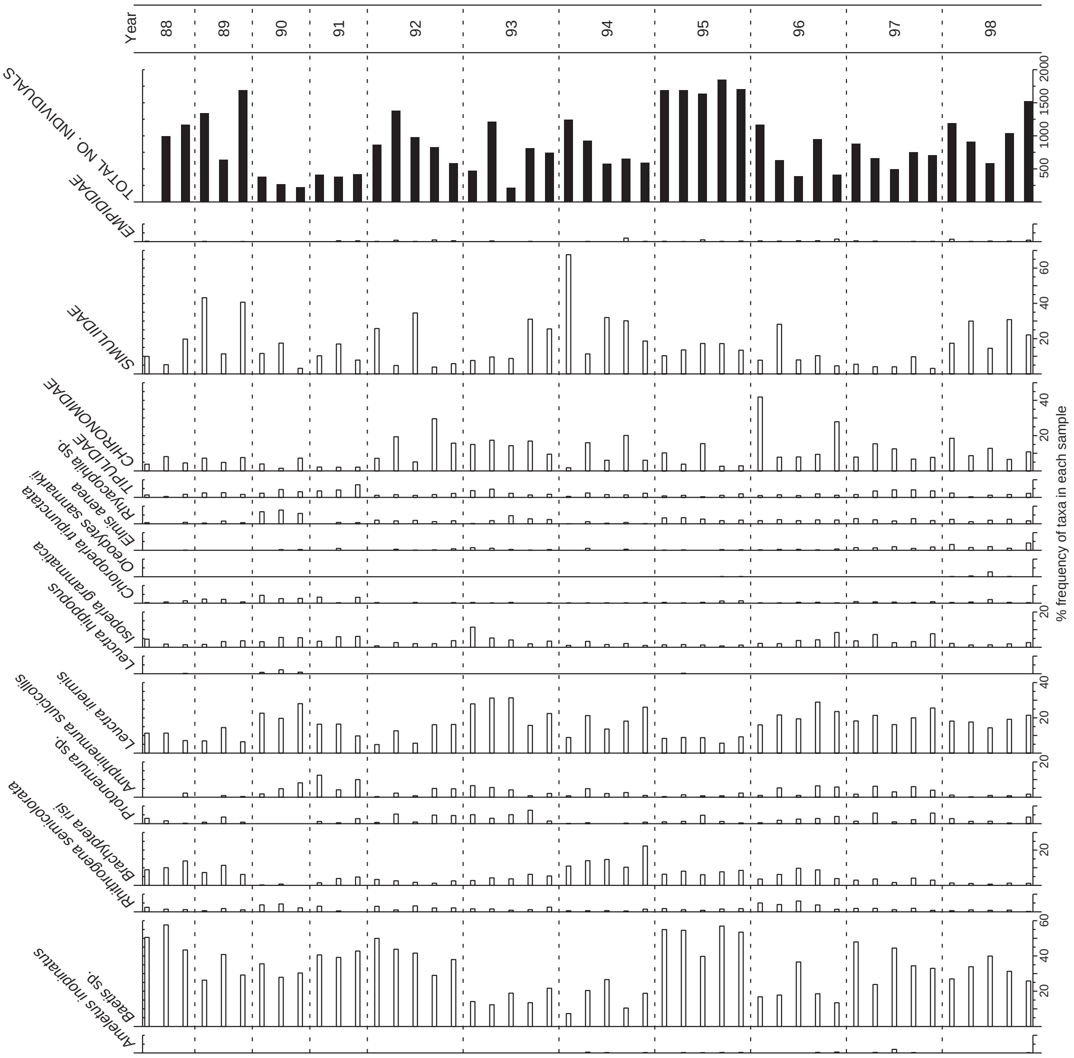


Figure 4.2.4

Allt a'Mharcaidh: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

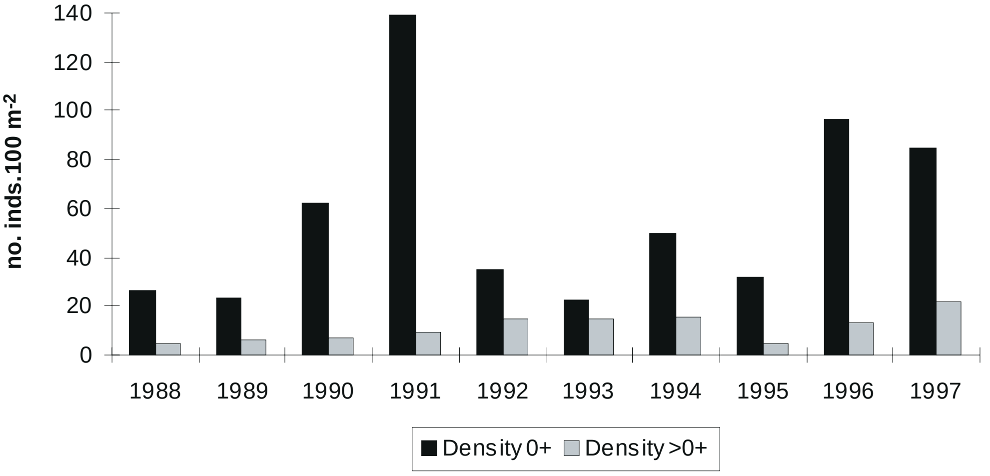
Figure 4.2.5 (i)

Allt a'Mharcaidh: summary of fish data (1988 - 1997)

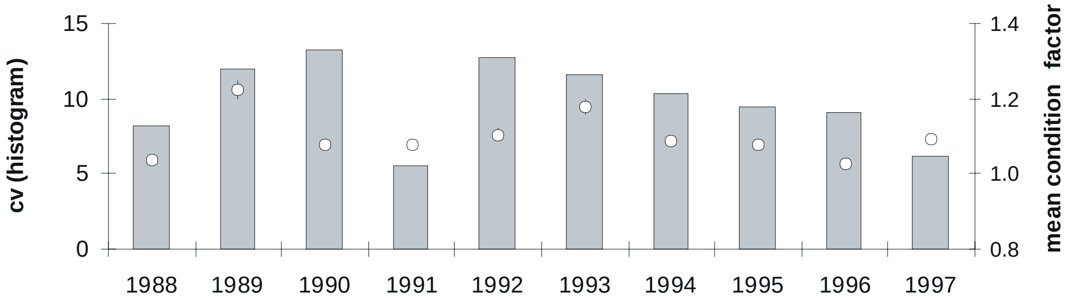
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

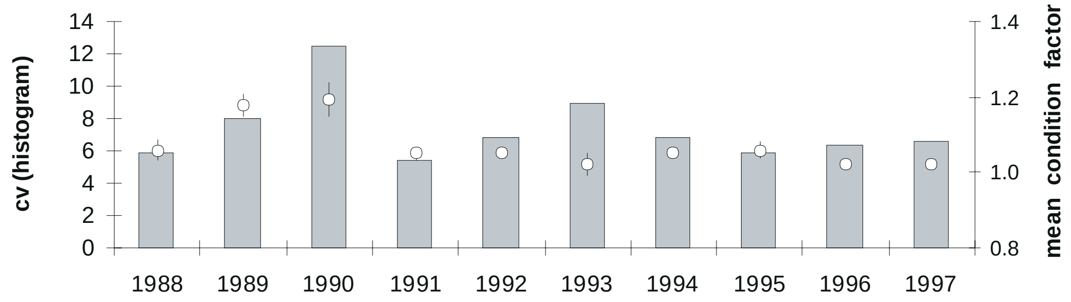
(a) Density



(b) Condition (0+)



Condition (>0+)



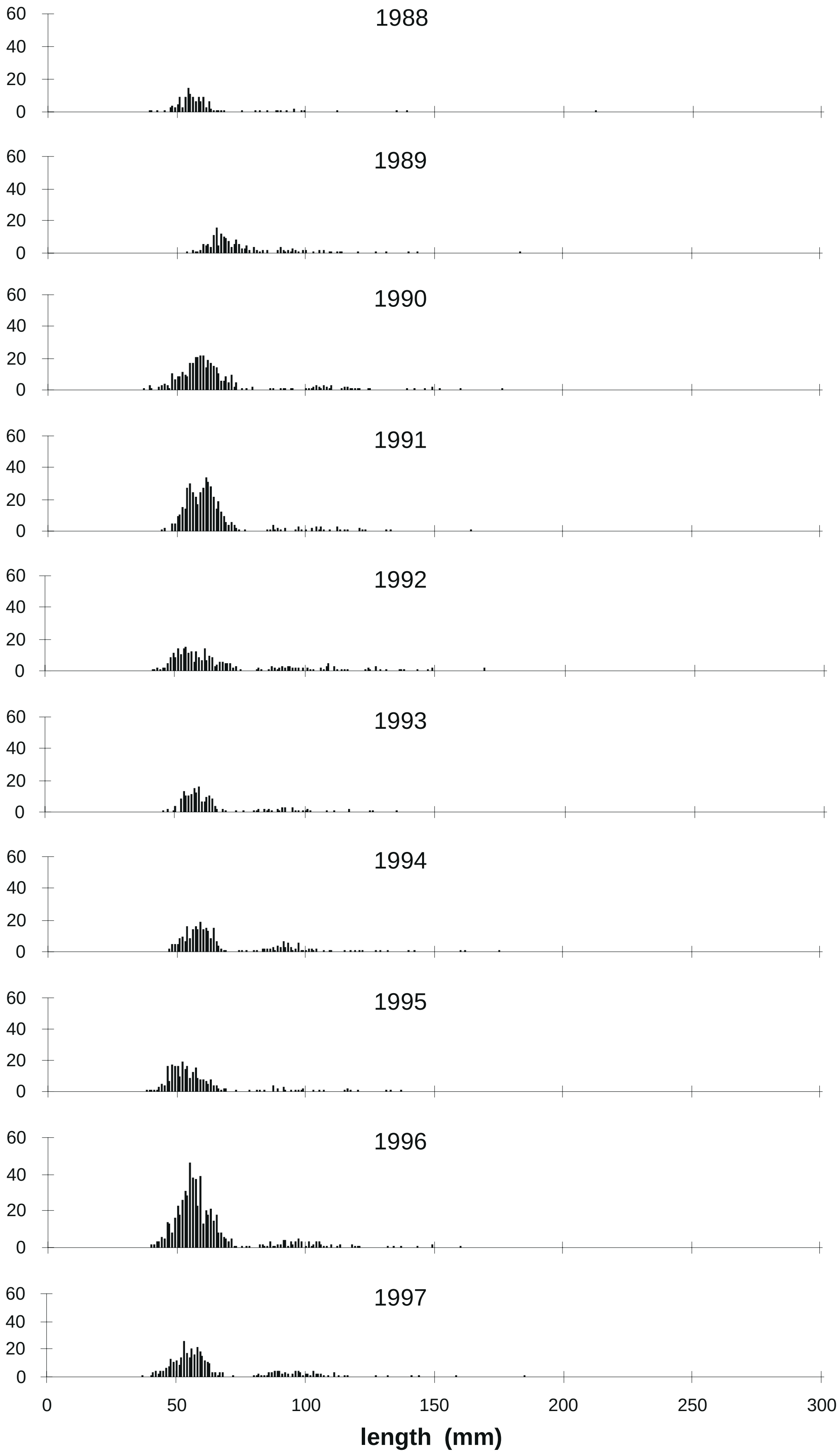


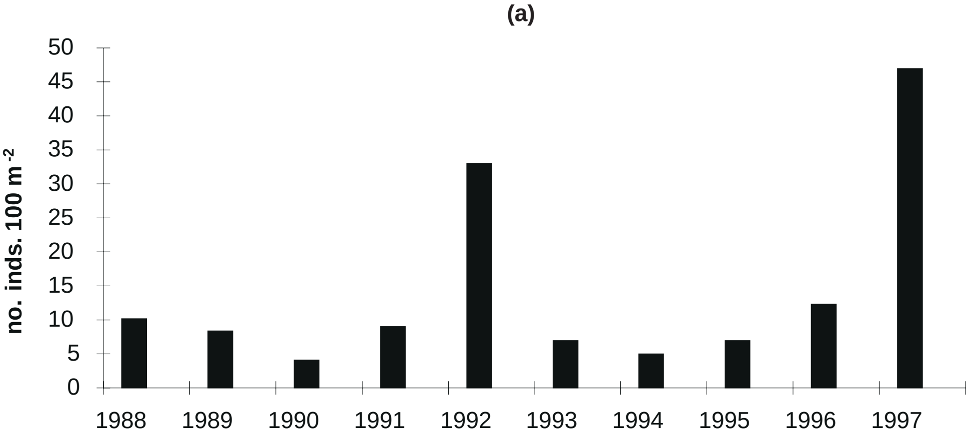
Figure 4.2.5 (i)

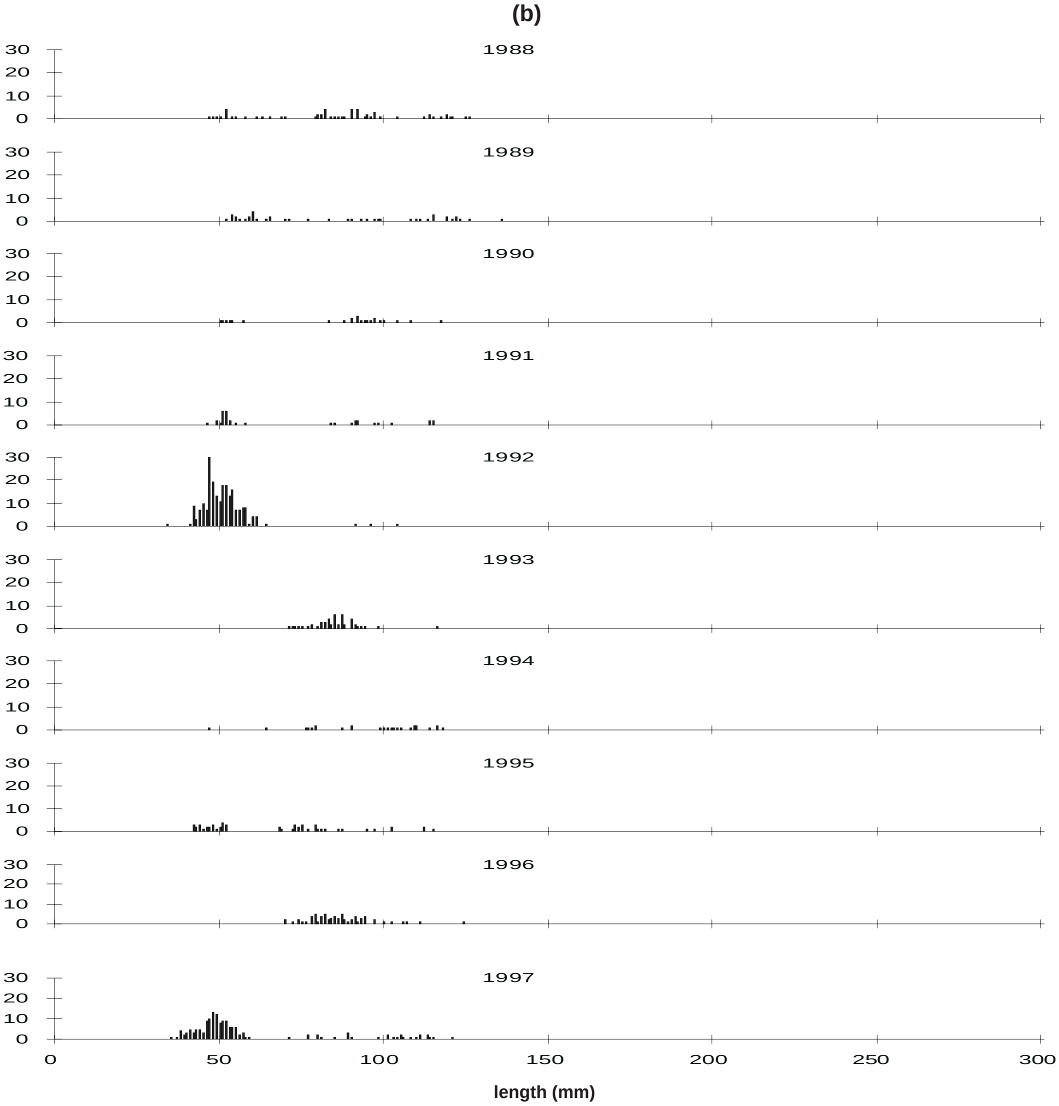
Allt a'Mharcaidh: summary of fish data (1988 - 1997)

(c) Trout length frequency summaries (1988 - 1997)

Figure 4.2.5 (ii)

Allt a'Mharcaidh: summary of fish data (1988-1997)
(a) Mean site density of salmon (all age classes)
(b) Salmon length frequency summaries (1988-1997)





4.3 Allt na Coire nan Con

Site Review

Allt na Coire nan Con, in the Strontian region of northwest Scotland, is a fast flowing stream within a partially forested catchment. The bulk of the catchment was planted (predominantly with spruce and larch) around 1970. Grazing on the upper slopes is confined to deer. Considerable felling and some re-planting has been carried out, particularly over the last 5 years (see Figure 4.3.1), including areas close to the survey and sampling stretches.

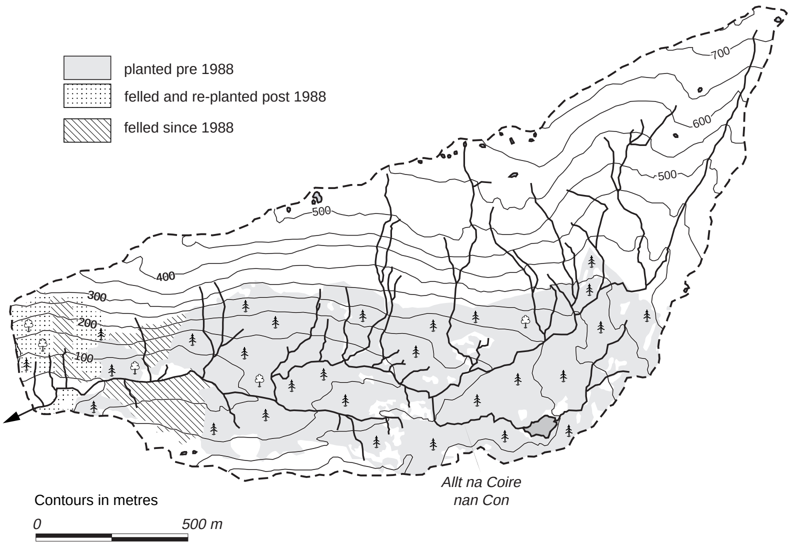


Figure 4.3.1

Allt na Coire nan Con: catchment

Water Chemistry

(Figure 4.3.2, Table 4.3.2-3)

Mean pH (5.85) and alkalinity (22 μeq l^{-1}) are somewhat lower than at Loch Coire nan Arr, the other northwest Scotland site, and mean xSO$_4$ (30 μeq l^{-1}) substantially higher. A number of acidic episodes have been recorded, with pH falling below 5.0 and alkalinity becoming negative during the most severe events. Sea-salt inputs are extremely high, since the catchment is very close to the west coast. As winter sea-salt deposition events

Table 4.3.1

Allt na Coire nan Con: site characteristics

Grid reference	*NM 793688*
Catchment area	*790 ha*
Minimum catchment altitude	*10 m*
Maximum catchment altitude	*756 m*
Catchment Geology	*schists and gneiss*
Catchment Soils	*peaty podsols, peaty gleys, peats*
Catchment vegetation	*conifers 42% recently felled 4% moorland 54%*
Mean annual rainfall	*2582 mm*
1996 deposition	
Total S	*22 kg ha^{-1} yr^{-1}*
non-marine S	*12 kg ha^{-1} yr^{-1}*
Oxidised N	*5 kg ha^{-1} yr^{-1}*
Reduced N	*6 kg ha^{-1} yr^{-1}*

Table 4.3.2

Allt na Coire nan Con: summary of chemical determinands, June 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.85*	*6.70*	*4.96*
Alkalinity	μeq l^{-1}	*21.6*	*98.0*	*-11.0*
Ca	μeq l^{-1}	*57.5*	*107.5*	*22.5*
Mg	μeq l^{-1}	*67.5*	*175.0*	*25.0*
Na	μeq l^{-1}	*262.2*	*569.6*	*152.2*
K	μeq l^{-1}	*9.0*	*18.5*	*2.6*
SO$_4$	μeq l^{-1}	*61.3*	*110.4*	*35.4*
xSO$_4$	μeq l^{-1}	*30.2*	*81.5*	*-7.7*
NO$_3$	μeq l^{-1}	*4.3*	*17.1*	*< 1.4*
Cl	μeq l^{-1}	*296.3*	*816.9*	*126.8*
Soluble Al	μg l^{-1}	*65.7*	*131.0*	*12.0*
Labile Al	μg l^{-1}	*17.4*	*98.0*	*< 2.5*
Non-labile Al	μg l^{-1}	*48.5*	*110.0*	*10.0*
DOC	mg l^{-1}	*3.9*	*10.0*	*< 0.1*
Conductivity	μS cm^{-1}	*46.3*	*108.0*	*20.0*

tend to coincide with periods of high rainfall, it is likely that the major winter acid episodes result from the net effects of marine ion displacement of H$^+$ ions and base cation dilution. NO$_3$, although still low (mean 4.3 µeq l^{-1}), is present at measurable concentrations during winter periods, suggesting the commencement of nitrogen saturation. Since estimated moorland S and N deposition are similar at the two north western sites (Tables 4.1.1 and 4.3.1), the more impacted nature of Allt na Coire nan Con may result from elevated dry deposition inputs to the large area of coniferous forest.

SKT analysis suggests a decrease in Cl over the study period, but this is not detected using regression. Since the only significant source of Cl is marine, it is likely that any apparent trend in this anion is the result of natural climatic variation. This is supported by the time series data and LOESS fit (Figure 4.3.2f) showing a period of raised Cl during the early part of the record.

Both trend detection methods indicate highly significant increases in DOC over the monitoring period, which appears to have taken place at an approximately constant rate (Table 4.3.3, Figure 4.3.2). The total estimated increase of 2.8 mg l^{-1} over the ten years is similar to that at Loch Coire nan Arr, but from a higher initial value. An associated increase is also apparent for non-labile Al. The issue of DOC trends is discussed in Section 5.2.3.

■ Epilithic diatoms

(Figure 4.3.3, Table 4.3.4)

The epilithic diatom flora of Allt na Coire nan Con shows considerable inter-annual variability. Samples from the early years of monitoring were dominated by *Achnanthes saxonica* (pH optima 5.7). This species was less abundant between 1993 - 1997, when *Synedra minuscula*, *A. minutissima* and *Brachysira vitrea* (all of which have slightly higher pH preferences) increased, but it became dominant again in 1998. The acidophilous species *Tabellaria flocculosa* was the dominant taxa in 1993. Diatom inferred pH values correlate closely with summer rainfall totals for the nearby Meteorological Station (Inverailort), suggesting that the species assemblage has been strongly influenced by natural pH variations linked to varying summer flow conditions (see section 7.4.1). “Sample year” is insignificant as a linear trend using RDA and restricted permutation test.

■ Macroinvertebrates

(Figure 4.3.4, Table 4.3.4)

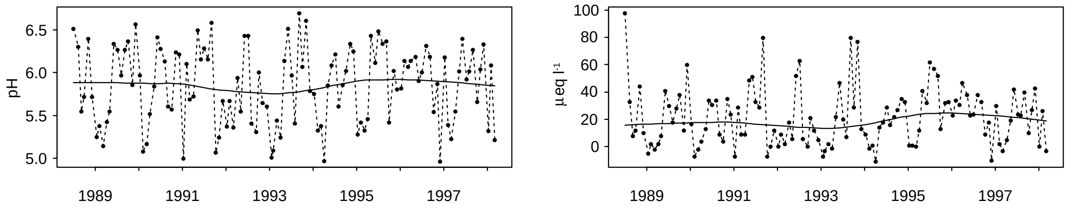
The macroinvertebrate fauna is typical of a mildly acid oligotrophic stream, and is characterised by chironomidae, Simulidae and a diverse fauna of both mayflies and stoneflies. The acid sensitive mayfly *Rhithrogena semicolorata* dominated the first seven years of

Table 4.3.3

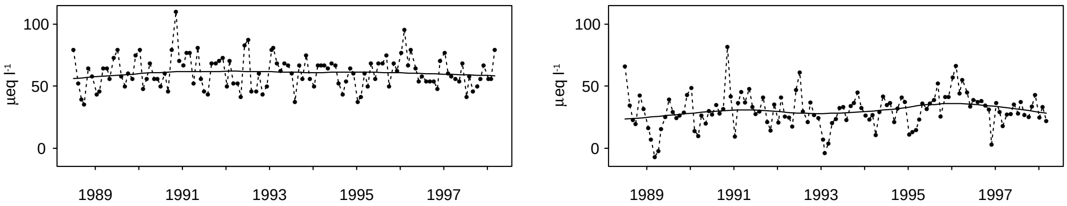
Allt na Coire nan Con: significant trends in chemical determinands (June 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
C1	µeq 1^{-1}	-	*-7.65**
DOC	mg 1^{-1}	*+0.21****	*+0.25***
Non-labile Al	µg 1^{-1}	*+1.13***	*+1.00**

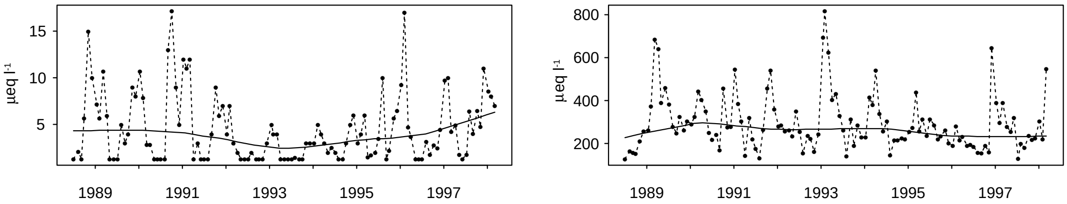
** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*


(a) pH

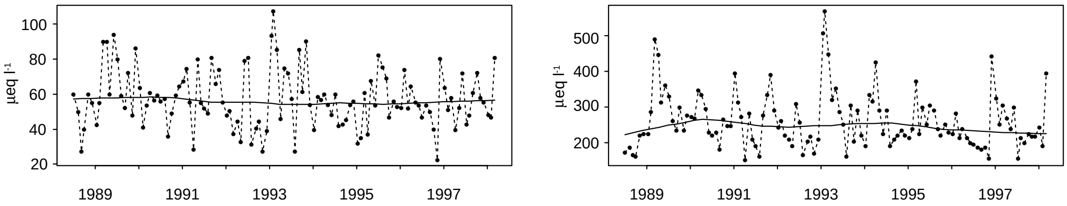
(b) Alkalinity


(c) Sulphate

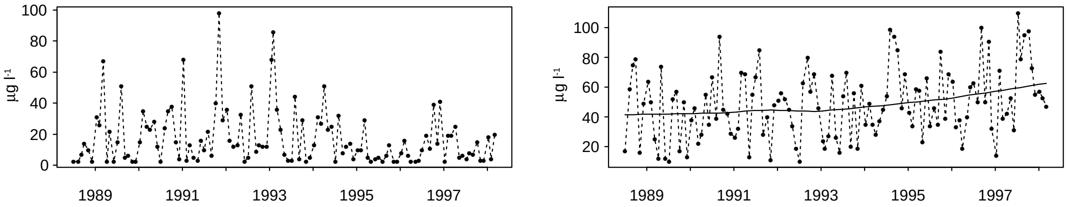
(d) Non-marine Sulphate


(e) Nitrate

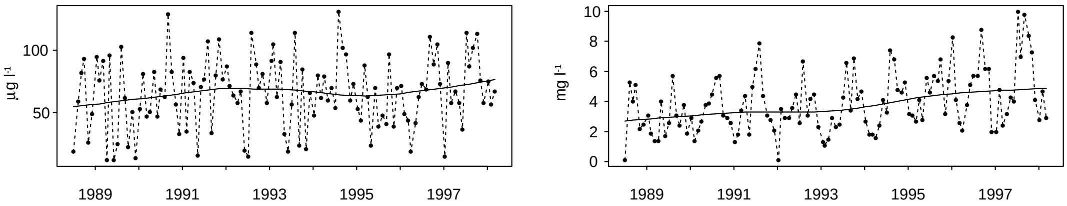
(f) Chloride


(g) Calcium

(h) Sodium


(i) Labile Al

(j) Non-labile Al


(k) Total Soluble Al

(l) Dissolved Organic Carbon

Figure 4.3.2

Allt na Coire nan Con: summary of major chemical determinands (June 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.3.4

Allt na Coire nan Con: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*325*	*65*	*3.3*	*0.36*	*0.36*
Macrophytes	*27*	*7*	*2.4*	*1.16*	*0.80*
Invertebrates	*781*	*37*	*5.1*	*0.88*	*0.67*

Variance				p	
explained (%)	**within year**	**between years**	**linear trend**	**unrestricted**	**restricted**
Epilithic diatoms	*29.0*	*71.0*	*11.8*	*<0.01*	*0.03*
Macrophytes	*	*	*45.8*	*<0.01*	*<0.01*
Invertebrates	*49.4*	*50.6*	*15.8*	*0.00*	*<0.01*

the study period, while *Baetis* spp. was present throughout and showed an increase in numbers in 1996. *Siphlonurus lacustris* appeared in 1993 and *Heptagenia lateralis*, which first appeared in 1992, has shown an increase in abundance in the latter years of the study. The stonefly community includes the detritivores *Brachyptera risi*, *Leuctra inermis* and *Amphinemura sulcicollis* as well as predators *Isoperla grammatica* and *Chloroperla tripunctata*. Several 'new' species of caddisfly were recorded after 1992, among them *Chaetopteryx villosa*, *Silo pallipes* and *Lepidostoma hirtum*, the latter intolerant of very acid conditions. Moderately acid sensitive Coleoptera *Hydraena gracilis* and *Elmis aenea* were first recorded in 1994. 1990 was a very poor

Table 4.1.5

Allt na Coire nan Con: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

(% cover of 50 m survey stretch)

Year	88	89	90	91	92	93	95	96	97
INDICATOR SPECIES									
Hygrohypnum ochraceum[1]	*16.0*	*16.2*	*16.6*	*9.4*	*3.7*	*1.5*	*0.2*	*0.4*	*0.1*
Hyocomium armoricum[1]	*<0.1*	*3.6*	*0.4*	*0.7*	*0.3*	*0.1*	*<0.1*	*0.1*	*0.2*
OTHER SUBMERGED SPECIES									
Filamentous green algae	*<0.1*	*<0.1*	*0.1*	*31.9*	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*
Marsupella emarginata	*0.2*	*<0.1*	*0.0*	*0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*<0.1*
Racomitrium aciculare	*0.5*	*3.9*	*<0.1*	*0.0*	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*
Scapania undulata	*0.8*	*0.4*	*2.5*	*2.1*	*1.1*	*0.4*	*0.3*	*0.7*	*0.0*
Juncus bulbosus var. *fluitans*	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*
total macrophyte cover excluding filamentous algae	*17.5*	*24.1*	*19.5*	*12.4*	*5.4*	*2.1*	*0.6*	*1.2*	*0.5*
TOTAL NUMBER OF SPECIES	*6*	*6*	*6*	*5*	*4*	*5*	*4*	*5*	*3*

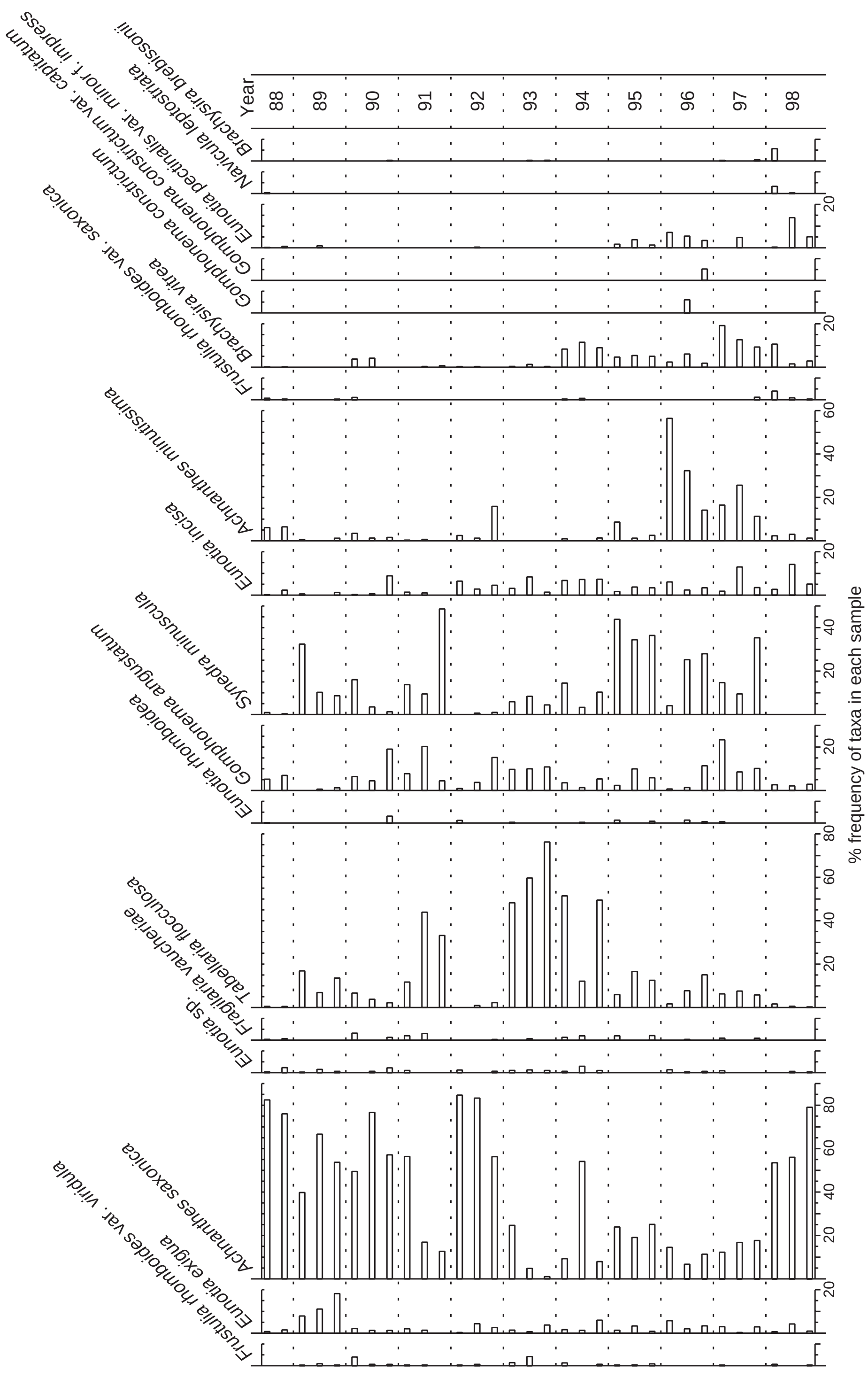


Figure 4.3.3

Allt na Coire nan Con: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

year both in number of species and abundance. Time as a linear trend accounts for 15.8% of the total variance and is significant at the 0.01 level. There is some indication of an improvement in conditions as species richness has increased in the second half of the study period, although this could be linked to a decline in spring flow conditions (Section 7.4.2).

■ Fish

(Figure 4.3.5)

Trout densities at this site are intermediate for those found on the Network. Mean population densities of both 0+ and >0+ trout show no trends over the ten years. However, in common with several other Scottish sites, densities of 0+ fish showed a peak in 1991, and higher than average recruitment also occurred in 1990 and 1995. Very low densities of >0+ fish were recorded in three consecutive years between 1992-1994 despite the high recruitment observed in 1991. Significant negative linear trends are apparent in the coefficient of variation of CF for the 0+ group ($p<0.01$ df = 8) and the condition factor of the >0+ group ($p<0.01$ df = 8). The causes of these apparently conflicting trends are unclear, with the former suggesting improved conditions for newly recruited trout and the latter possibly suggesting deterioration. Neither trend appears to relate to temporal variation in density.

■ Macrophytes

(Tables 4.3.4-5)

The aquatic macroflora of Allt na Coire nan Con was dominated by the acid sensitive moss *Hygrohypnum ochraceum* during the first few years of monitoring. However, the cover of this species reduced substantially after 1991 and by 1997 only a few isolated plants were present in the survey stretch. Given the absence of any deterioration in water chemistry, it seems most likely that the reduction in cover has resulted from physical scouring during storm events. These could have become more abrupt following clear felling within the catchment and the consequent effects on catchment hydrology. In addition, the amount of timber debris in the survey channel has increased in recent years; this is perhaps indicative of a general increase in the suspended load of the stream which would also have had a detrimental effect on plant growth. As at the Allt a’Mharcaidh, where a recent storm event is also suspected to have had an impact on the dominant moss, the ubiquitous and acid-tolerant liverwort *Scapania undulata* does not show a similar reduction in cover. The changes in cover with time are statistically significant at the 0.01 level according to RDA and associated restricted permutation tests and almost certainly result from the physical influences described above.

■ Summary

Allt na Coire nan Con is not chronically acidic, but moderate levels of anthropogenic S and N are present in runoff, thought to have been increased by the presence of forestry within the catchment. Acidic episodes have been observed, driven by sea-salt deposition and high rainfall events and the reduction in these in the latter half of the record could account for the observed changes in the macroinvertebrate community. The summer flow regime appears to have exerted a strong influence on the diatom flora, while possible changes in the hydrological pathway and increased suspended load as a result of catchment felling may have contributed to the reduction in aquatic moss cover. However at this stage there is little evidence of the effect of tree felling on water chemistry. Strong rising trends have been observed in DOC and non-labile Al. Since these are observed in several other Scottish sites they are not likely to reflect within catchment changes.

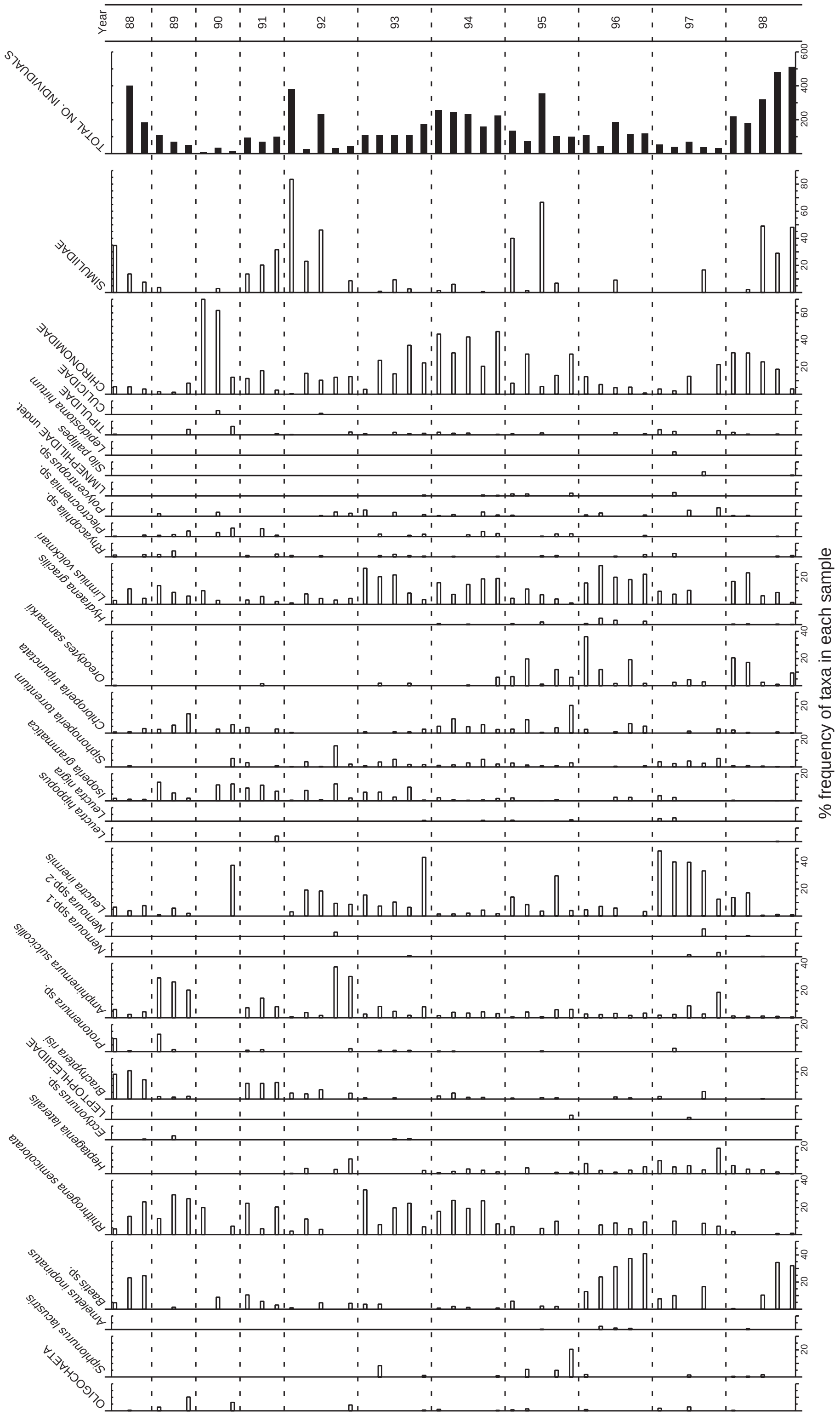


Figure 4.3.4

Allt na Coire nan Con: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

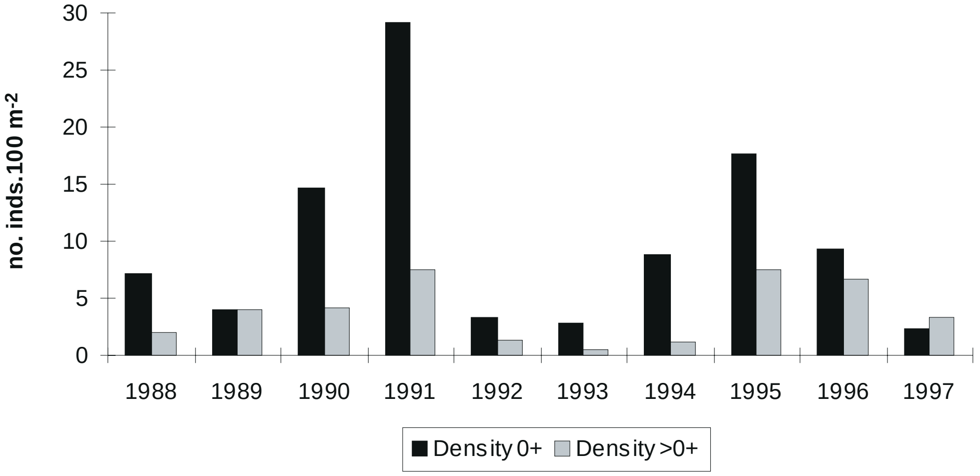
Figure 4.3.5 (i)

Allt na Coire nan Con: summary of fish data (1988 - 1997)

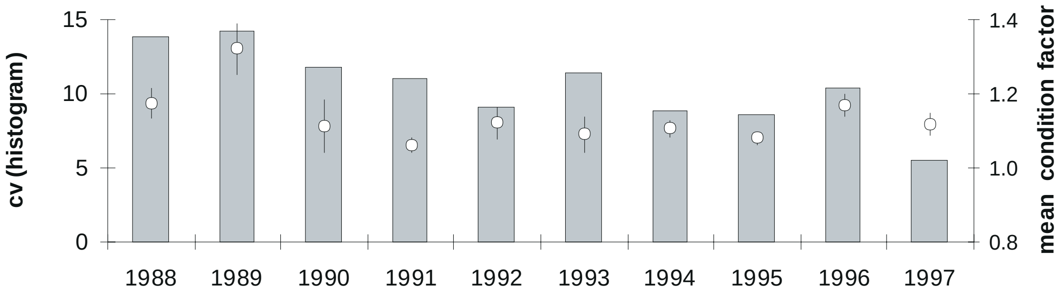
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

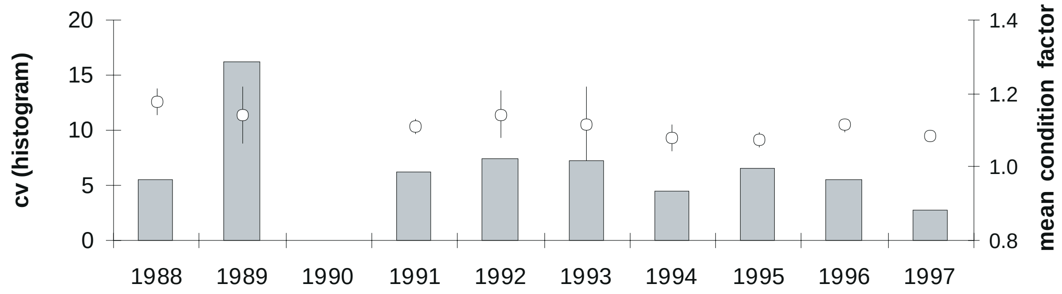
(a) Density



(b) Condition (0+)



Condition (>0+)



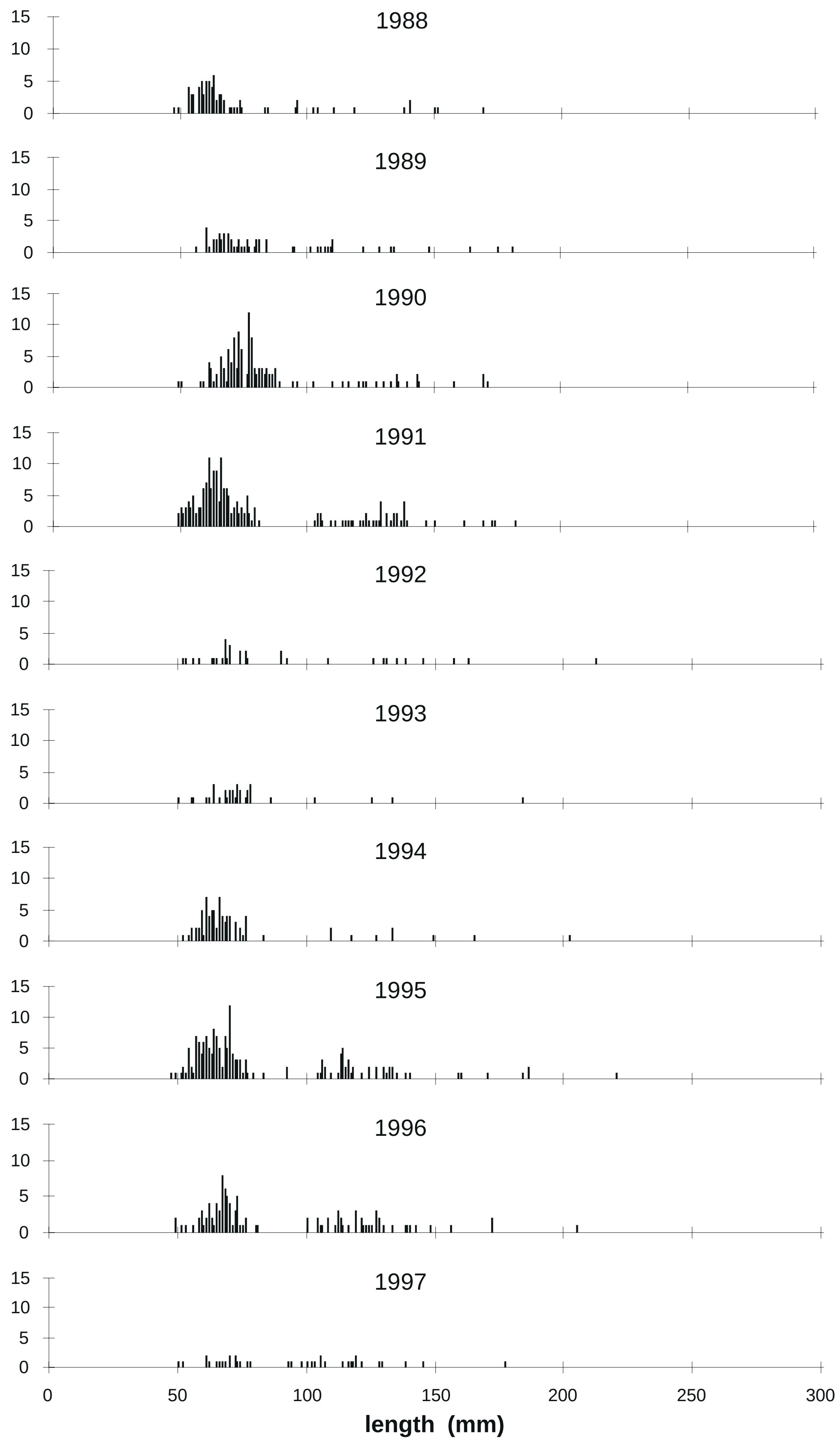


Figure 4.3.5 (i)

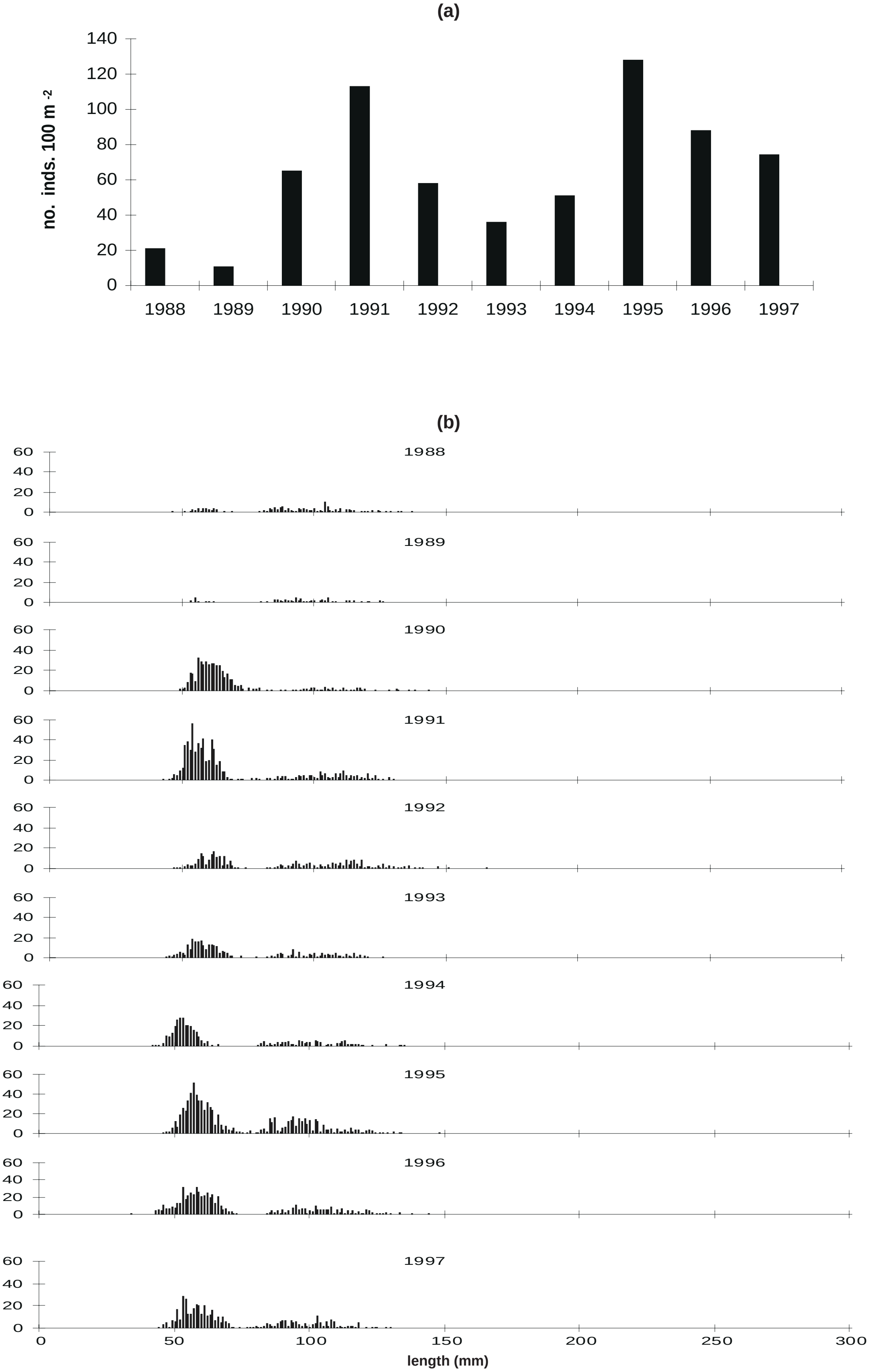
Allt na Coire nan Con: summary of fish data (1988 - 1997)
(c) Trout length frequency summaries (1988 - 1997)

Figure 4.3.5 (ii)

Allt na Coire nan Con: summary of fish data (1988-1997)

(a) Mean site density of salmon (all age classes)

(b) Salmon length frequency summaries



4.4 Lochnagar

■ Site Review

At an altitude of 785 m in the Grampian Mountains of northeast Scotland, Lochnagar is the highest of the UKAWMN lakes. Palaeoecological pH reconstruction indicates that Lochnagar acidified from around pH 5.6, in the mid-nineteenth century, to around pH 5.0 by the 1940s (Patrick *et al.* 1989, Patrick *et al.* 1995). Although prone to a considerable duration of ice cover during some winters, the extent of the freezing period has been highly variable over the past decade, with ice only present for a few days during the winter of 1997-1998. Scientific work at Lochnagar has increased since its inclusion in the EU funded mountain lakes projects AL:PE, MOLAR, CHILL and, most recently, EMERGE, in addition to a DETR study of the impact of heavy metals deposition and additional sampling carried out for the Environmental Change Network. There have been no physical disturbances in the catchment, other than occasional scree falls from the corrie back-wall, since the onset of monitoring in 1988.

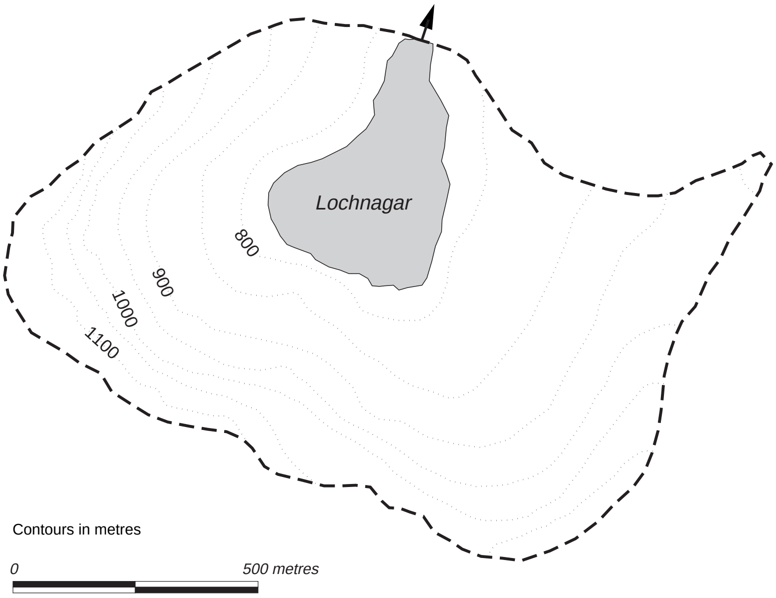


Figure 4.4.1

Lochnagar: catchment

Table 4.4.1

Lochnagar: site characteristics

Grid reference	*NO 252859*
Lake altitude	*785 m*
Maximum depth	*26 m*
Mean depth	*8.4 m*
Volume	*8.2 x 10^5 m^3*
Lake area	*9.8 ha*
Catchment area (excl. lake)	*91.9 ha*
Catchment: Lake area ratio	*9.37*
Catchment Geology	*granite*
Catchment Soils	*peats*
Catchment vegetation	*alpine - moorland 100%*
Net relief	*370 m*
Mean annual rainfall	*1536 mm*
1996 deposition	
Total S	*16 kg ha^{-1} yr^{-1}*
non-marine S	*13 kg ha^{-1} yr^{-1}*
Oxidised N	*6 kg ha^{-1} yr^{-1}*
Reduced N	*8 kg ha^{-1} yr^{-1}*

Table 4.4.2

Lochnagar: summary of chemical determinands, June 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.33*	*5.81*	*4.95*
Alkalinity	µeq l^{-1}	*0.6*	*12.0*	*-10.0*
Ca	µeq l^{-1}	*29.0*	*50.0*	*21.5*
Mg	µeq l^{-1}	*33.3*	*58.3*	*25.0*
Na	µeq l^{-1}	*93.9*	*173.9*	*69.6*
K	µeq l^{-1}	*7.4*	*12.8*	*2.6*
SO_4	µeq l^{-1}	*57.7*	*85.4*	*45.8*
xSO_4	µeq l^{-1}	*48.3*	*74.4*	*35.4*
NO_3	µeq l^{-1}	*15.7*	*30.7*	*< 1.4*
Cl	µeq l^{-1}	*89.3*	*166.2*	*50.7*
Soluble Al	µg l^{-1}	*41.8*	*147.0*	*4.0*
Labile Al	µg l^{-1}	*25.5*	*137.0*	*< 2.5*
Non-labile Al	µg l^{-1}	*16.5*	*41.0*	*< 2.5*
DOC	mg l^{-1}	*1.1*	*3.4*	*0.2*
Conductivity	µS cm^{-1}	*21.8*	*35.0*	*4.0*

Water Chemistry

(Figure 4.4.2, Table 4.4.2-3)

Lochnagar is acidic with a ten year mean pH of 5.33 and a mean alkalinity of 0.6 μeq l^{-1}. Unlike the other sites in northern Scotland, mean labile Al concentrations exceed those of non-labile Al. Much of the Lochnagar catchment comprises bare granite or thin soils, resulting in a very limited buffering capacity (mean Ca=29 μeq l^{-1}) and therefore high sensitivity to acid deposition. The mean xSO$_4$ concentration of 48 μeq l^{-1} is higher than at the other northern Scotland sites, and NO$_3$ is also moderately high with a mean of 15.7 μeq l^{-1}. It is probable that, due to the sparse soil and vegetation cover, and low ambient temperature, the catchment has little ability to immobilise incoming N deposition, and has therefore reached a more advanced stage of N saturation than lower altitude catchments in the same region. Marine ion concentrations are lower and less variable than at west coast sites, and in general it appears that the site is not subject to major episodic variations, with ranges of pH (4.95 to 5.81) and alkalinity (-10 to 12 μeq l^{-1}) among the lowest in the Network. Seasonal variations are also weak or absent, perhaps reflecting the low level of biological activity within the catchment.

Trend analyses (Table 4.4.3) indicate that the chemistry of Lochnagar has changed substantially over the last decade. Both SKT and regression suggest that xSO$_4$ has fallen slightly (5 or 8 μeq l^{-1} respectively), whilst NO$_3$ has risen over the same period (11 or 14 μeq l^{-1}). The combined effect of these trends should be a reduction in pH and alkalinity, and a declining trend is indeed observed for pH using regression, although not SKT. Examination of time series and LOESS plots confirm that a reasonably linear xSO$_4$ decline has taken place over the last ten years. However the increase in NO$_3$ and associated decrease in pH appear to have occurred during a short period, from 1992-1995, since when concentrations have remained fairly stable. The possibility that the NO$_3$ increase reflects a short term climatic fluctuation, possibly due to climatic variability, cannot therefore be ruled out at this stage; further sampling should help to clarify this issue. As at most other UKAWMN, regression analysis suggests that DOC has risen during the last ten years, in this case by approximately 0.8 mg l^{-1}.

Epilithic diatoms

(Figure 4.4.3, Table 4.4.4)

The epilithic diatom flora of Lochnagar is relatively diverse and dominated by acidophilous taxa. *Achnanthes marginulata* (pH optima 5.2) is generally the most abundant species, although *Tabellaria flocculosa* (pH optima 5.4) was more abundant in 1991 and more recently in 1997-1998. *Eunotia incisa* (pH optima 5.1) was relatively abundant from 1990-1992 but has since declined. Diatom inferred pH (derived from weighted averaging) demonstrates that the

Table 4.4.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
pH		*-0.020**	-
SO$_4$	μeq l^{-1}	*-0.94**	*-0.52**
xSO$_4$	μeq l^{-1}	*-1.00***	*-0.67***
NO$_3$	μeq l^{-1}	*+1.43****	*+1.13**
DOC	mg l^{-1}	*+0.08**	-

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

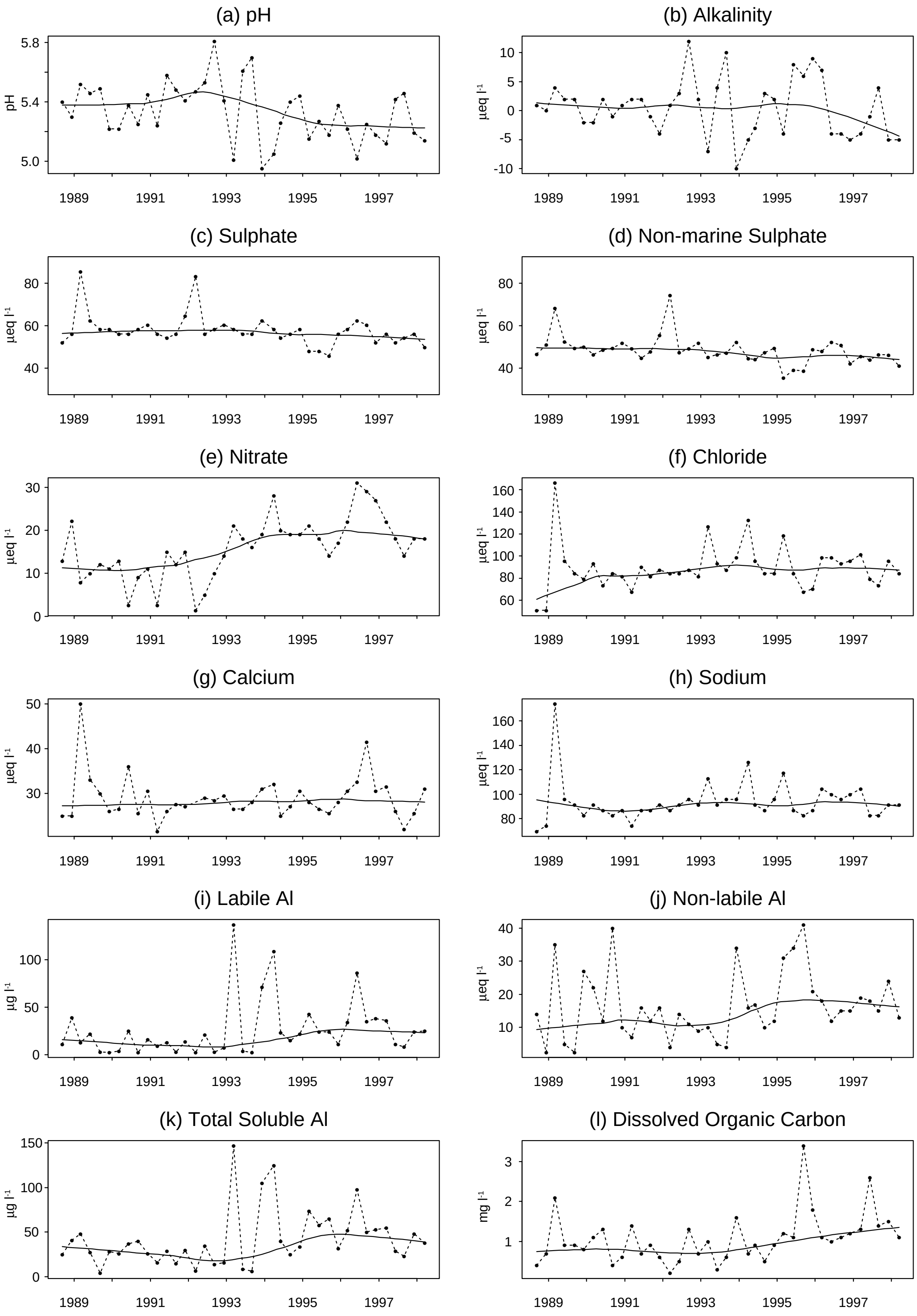


Figure 4.4.2

Lochnagar: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.4.4

Lochnagar: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*481*	*145*	*7.2*	*0.26*	*0.26*
Macrophytes	*18*	*11*	*6.5*	*0.32*	*0.30*
Invertebrates	*871*	*25*	*2.5*	*0.52*	*0.40*

Variance explained (%)	within year	between years	linear trend	p unrestricted	 restricted
Epilithic diatoms	*56.3*	*43.7*	*5.2*	*0.06*	*0.44*
Macrophytes	-	-	*15.8*	*0.34*	*0.12*
Invertebrates	*43.0*	*57.0*	*10.4*	*0.00*	*0.00*

assemblage reflects the deterioration in pH evident from water chemistry samples since 1993. Despite this, RDA and associated restricted permutation test show no significant linear time trend over the full period, at the 0.01 level. The sediment trap record for Lochnagar only began in 1991 and the sample for 1992 was lost (Figure 4.4.6). No trends are evident in this limited dataset, although there are clear similarities in species representation with the epilithon.

■ Macroinvertebrates

(Figure 4.4.4, Table 4.4.4)

The impoverished macroinvertebrate fauna is typical of a moderately acidic, high altitude lake. The fauna is dominated by chironomids and the stonefly *Capnia* spp., which is patchy in its occurrence (only one individual was recorded in

Table 4.4.5

Lochnagar: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	88	89	90	91	92	93	95	97
INDICATOR SPECIES								
Sphagnum auriculatum^4	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Juncus bulbosus var. *fluitans*^{4}	*1*	*2*	*2*	*2*	*2*	*2*	*2*	*3*
OTHER SUBMERGED SPECIES								
Filamentous green algae	*1*	*3*	*0*	*2*	*1*	*1*	*2*	*1*
Fontinalis antipyretica	*1*	*0*	*1*	*1*	*1*	*1*	*1*	*1*
Racomitrium aciculare	*0*	*0*	*1*	*0*	*0*	*0*	*1*	*1*
Cephalozia connivens	*0*	*0*	*1*	*0*	*0*	*0*	*0*	*0*
Marsupella emarginata	*0*	*0*	*0*	*0*	*1*	*0*	*0*	*0*
Nardia compressa	*1*	*1*	*3*	*2*	*3*	*2*	*2*	*2*
Plectocolea obovata	*0*	*1*	*1*	*0*	*0*	*0*	*0*	*0*
Scapania undulata	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Isoetes lacustris	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
TOTAL NUMBER OF SPECIES	*7*	*7*	*9*	*7*	*8*	*7*	*8*	*8*

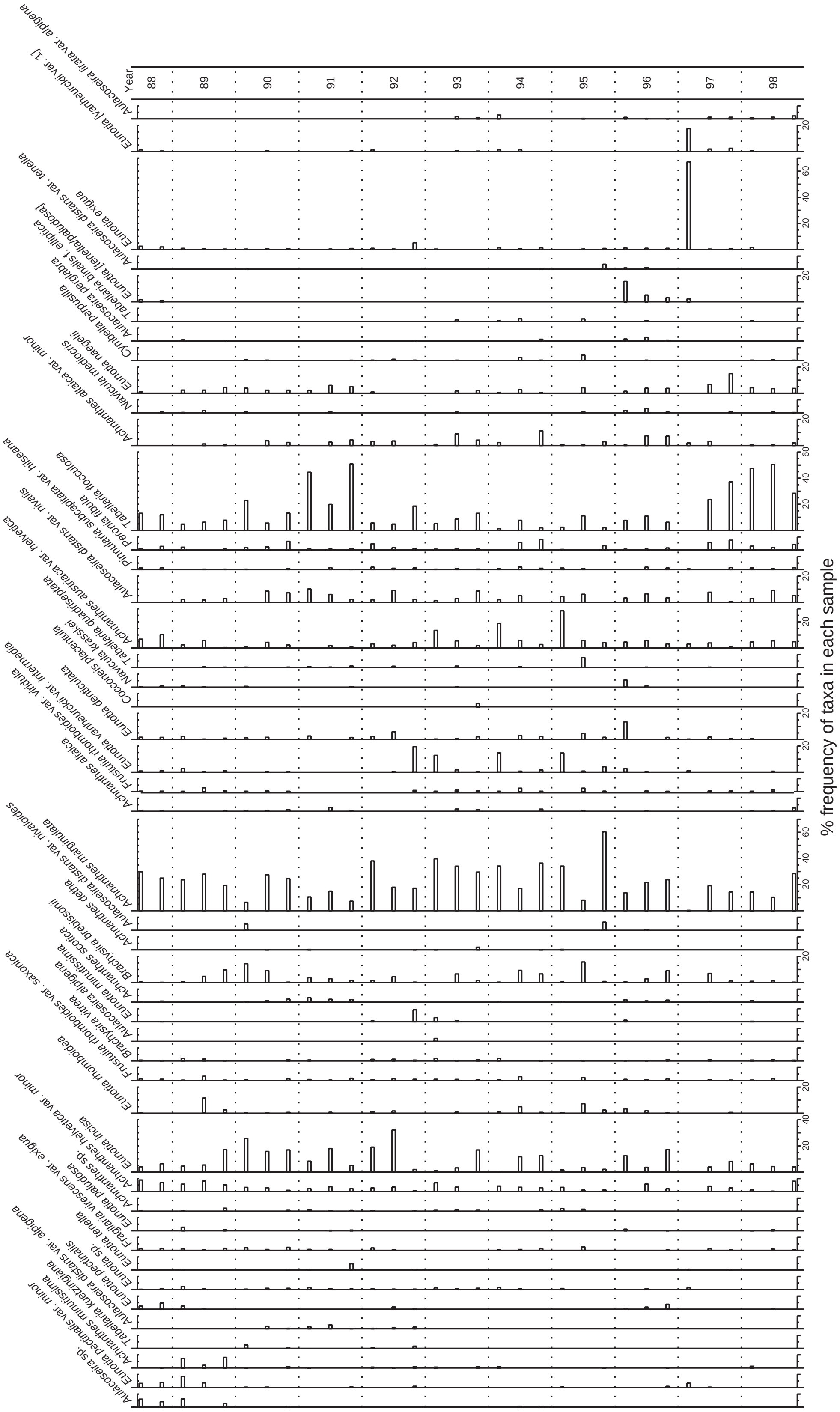


Figure 4.4.3

Lochnagar: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

1994). Several other species of stonefly are present including *Diura bicaudata* and *Siphonoperla torrentium*. Acid tolerant stoneflies *Nemurella pictetii* and *Protonemura* spp. appeared after 1991. Other common taxa include the water beetle, *Oreodytes davisii*, and members of the caddisfly family, the Limnephilidae, and the Tipulidae. Time as a linear trend is significant at the 0.01 level. The apparent shift in stonefly species, from *Nemoura* spp. to *Nemurella picteti*, the increase in the relative abundance of *Plectrocnemia* sp. and *Polycentropus* sp., and the general decline in species richness, are all indicative of increasing acidity.

■ Fish

(Figure 4.4.5)

The outflow stream of Lochnagar has been fished since 1989. The electrofishing site is significantly downstream of the water chemistry sampling point and it is likely that geological buffering results in less acid conditions than those experienced at the actual outflow. This could explain why, when the Loch trout population is believed to be impoverished, densities within the fishing stretch are high, and indeed the highest found in the Network. Densities of 0+ group fish were relatively low for the site in 1993, 1996 and 1997, but no trends are apparent over the nine years of data. Densities of >0+ group are variable, three years (1990, 1991 & 1996) being significantly above average. Condition factor and the coefficient of variation of the condition factor for both age groups also show no time trends. Length frequency graphs indicate a healthy population structure, although numbers of larger fish (>100 mm) are relatively low in certain years. This feature does not seem to be linked to the recruitment reductions mentioned above.

■ Aquatic macrophytes

(Tables 4.4.4-5)

The impoverished macroflora of Lochnagar reflects the extreme altitude and acidity of the site. *Isoetes lacustris* and *Juncus bulbosus* var. *fluitans* are the only vascular species which appear able to withstand a combination of adverse factors including low nutrient availability, the effects of ice scouring, low ambient temperature and strong wave action. The Loch is dominated by liverworts, and particularly *Nardia compressa*, while the moss *Fontinalis antipyretica* is present in a few isolated locations. The cover of *Juncus bulbosus* var. *fluitans* along two of the three fixed transects has expanded in recent years, and there is also evidence for an increase in other areas of the loch. Expansion of this species in low altitude soft-water lakes in the Netherlands is well documented and attributed to N enrichment, particularly from ammonium sources (Roelofs *et al*., 1984, Schuurkes *et al*. , 1987). It is unlikely that the NH_4 supply to the Loch has increased recently but the observed changes may be linked to rising NO_3 concentrations. Despite this observation, linear change in relative abundance with time is insignificant according to RDA and associated restricted permutation test.

■ Summary

Due to its high altitude and thin soils, Lochnagar appears to have been significantly acidified by low-moderate levels of acid deposition. Trend analyses indicate that although xSO_4 concentrations are now declining at the site, a large rise in NO_3 over the past decade has led to an overall worsening of Loch acidity. This appears to be reflected in the changing species assemblages of epilithic diatoms and macroinvertebrates, and possibly in the expansion of cover of the acidophilous aquatic macrophyte *Juncus bulbosus* var. *fluitans*. The density of newly recruited trout, downstream of the Loch outflow, has fallen over the last two years of monitoring but is still considered high for an acid system.

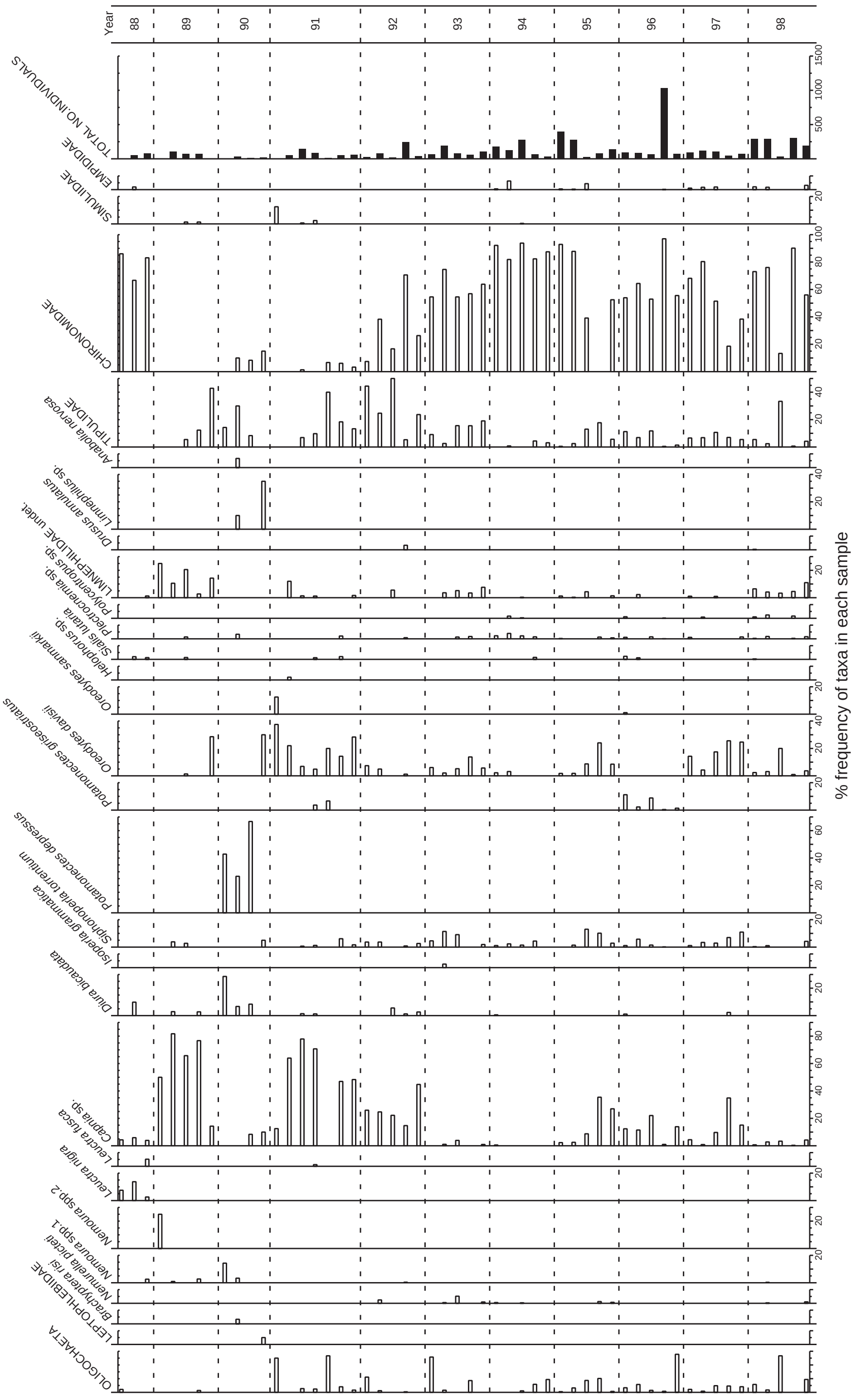


Figure 4.4.4

Lochnagar: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

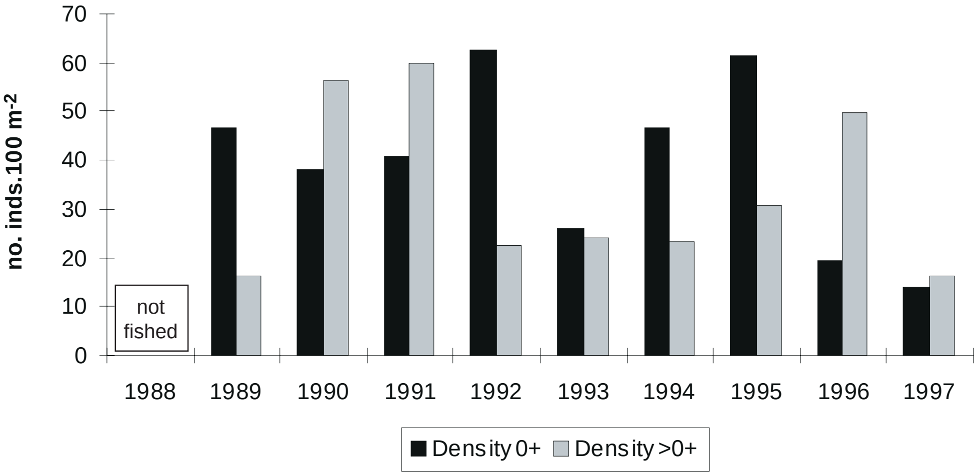
Figure 4.4.5

Lochnagar: summary of fish data (1989 - 1997)

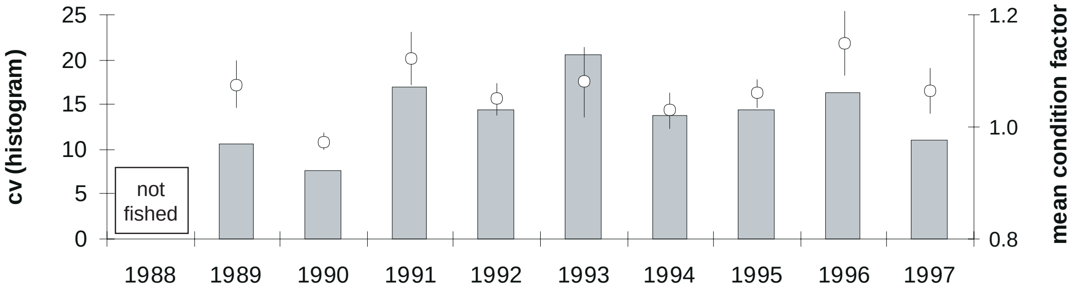
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

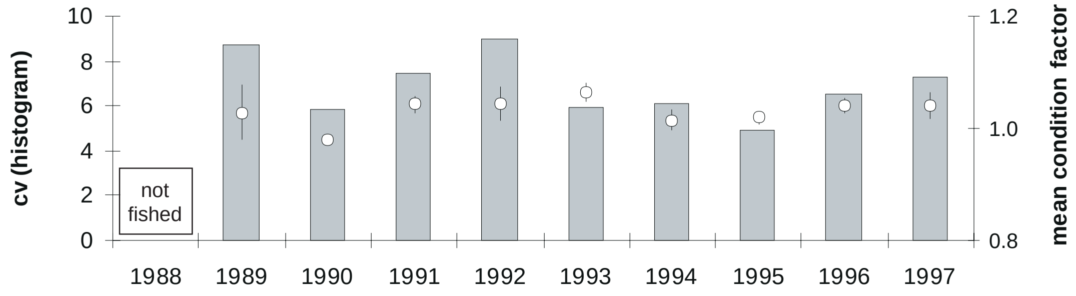
(a) Density



(b) Condition (0+)



Condition (>0+)



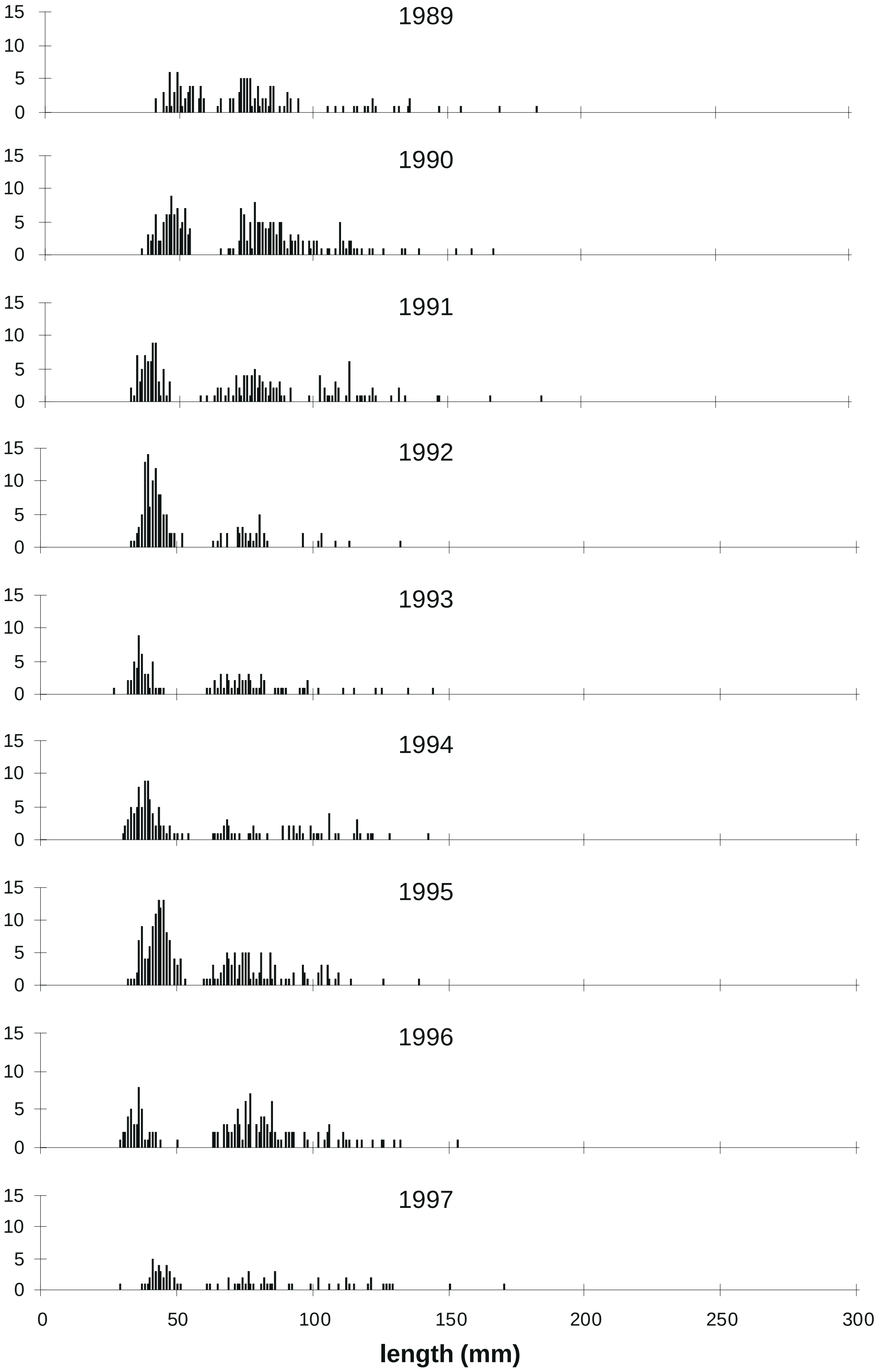


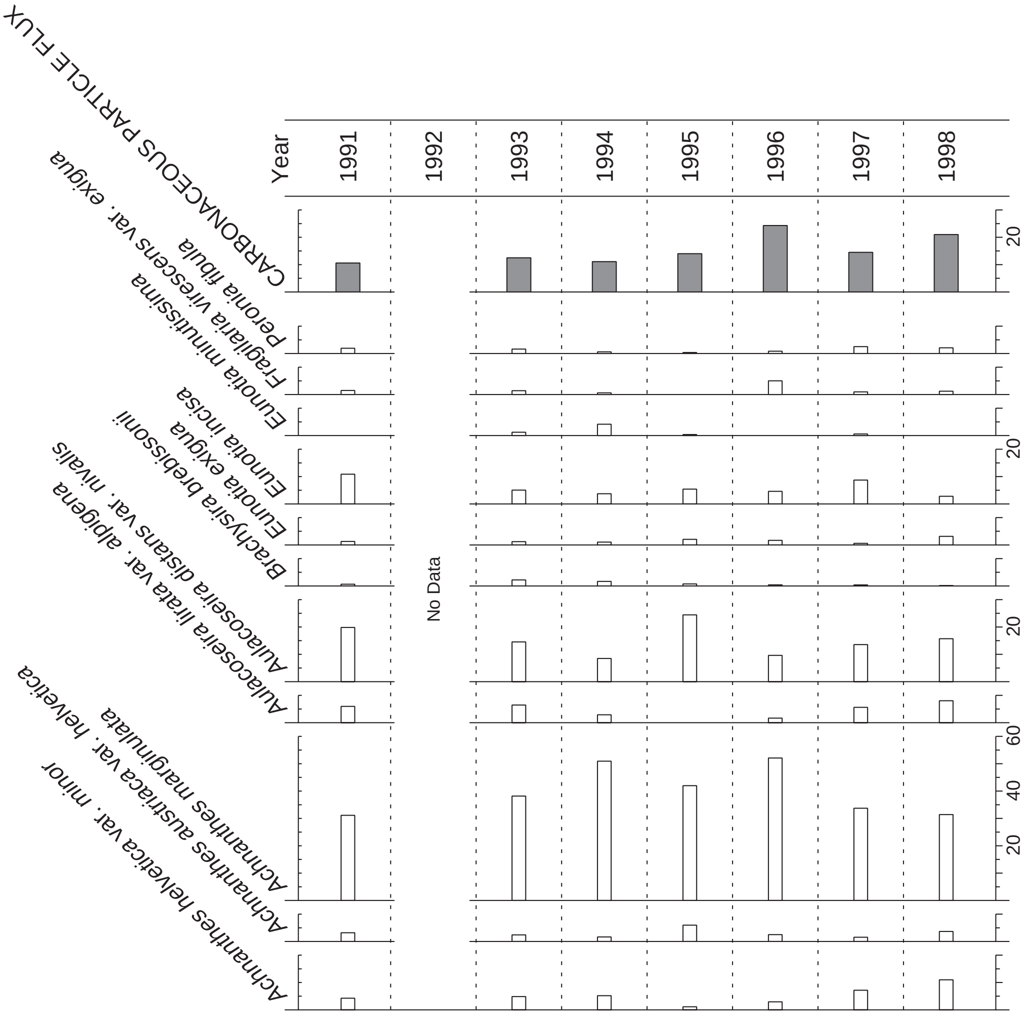
Figure 4.4.5

Lochnagar: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries

Figure 4.4.6

Lochnagar: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year



4.5 Loch Chon

■ Site Review

Loch Chon is a relatively large loch in the Trossachs region of central Scotland. Its recent palaeoecological history was studied in the SWAP programme (Battarbee & Renberg, 1990). This work suggested that the loch has undergone dramatic acidification over the last 150 years, with the pH falling from around 6.4 to around 5.0 by 1992 (Patrick *et al*., 1989; Kreiser *et al*., 1990). An accelerated rate of acidification in recent decades was attributed to afforestation of the catchment. Today large areas of the catchment are covered by mature coniferous forest. In 1995, a small forestry access road was constructed parallel to the west shore, but to date felling has been restricted to small areas to the northwest of the site (Figure 4.5.1). Local agriculture at the north end of the loch may have caused mild nutrient enrichment in the north bay, where the aquatic macroflora is more diverse, but its influence on the site as a whole appears to be negligible.

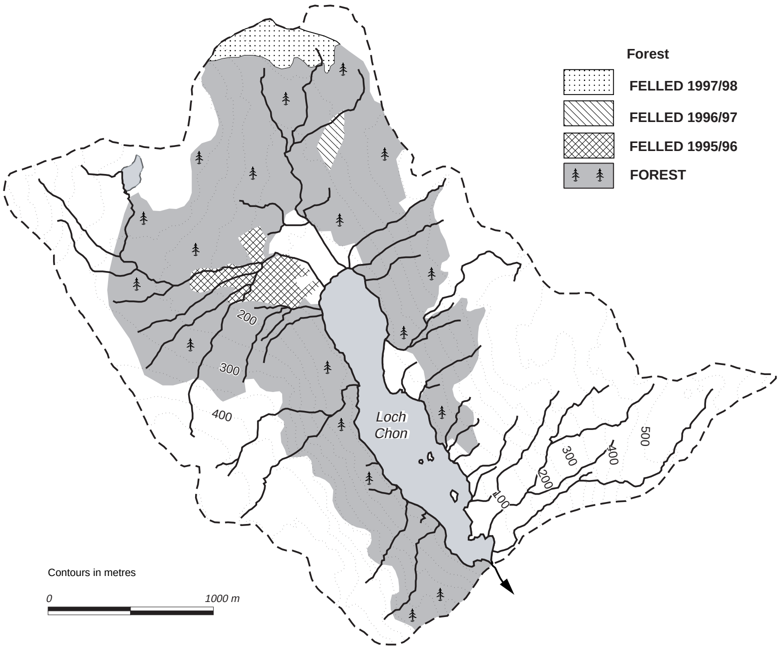


Figure 4.5.1

Loch Chon: catchment

Table 4.5.1

Loch Chon: site characteristics

Grid reference	*NN 421051*
Lake altitude	*100 m*
Maximum depth	*25 m*
Mean depth	*7.6 m*
Volume	*7.3×10^6 m^3*
Lake area	*100 ha*
Catchment area (excl. lake)	*1570 ha*
Catchment: Lake area ratio	*15.7*
Catchment Geology	*mica schists and grits*
Catchment Soils	*peaty gleys, peaty podzols*
Catchment vegetation	*conifers - 44%* *moorland - 52%* *recently felled - 4%*
Net relief	*500 m*
Mean annual rainfall	*2258 mm*
1996 deposition	
Total S	*29 kg ha^{-1} yr^{-1}*
non-marine S	*23 kg ha^{-1} yr^{-1}*
Oxidised N	*10 kg ha^{-1} yr^{-1}*
Reduced N	*13 kg ha^{-1} yr^{-1}*

Table 4.5.2

Loch Chon: summary of chemical determinands, June 1988 - March 1998

Determinand		Mean	Max	Min
pH		*5.60*	*6.47*	*4.99*
Alkalinity	μeq l^{-1}	*9.6*	*71.0*	*-8.0*
Ca	μeq l^{-1}	*78.0*	*101.0*	*64.5*
Mg	μeq l^{-1}	*50.8*	*75.0*	*41.7*
Na	μeq l^{-1}	*190.9*	*304.3*	*117.4*
K	μeq l^{-1}	*7.4*	*12.1*	*2.6*
SO_4	μeq l^{-1}	*71.9*	*91.7*	*39.6*
xSO_4	μeq l^{-1}	*48.5*	*70.4*	*24.0*
NO_3	μeq l^{-1}	*12.1*	*24.3*	*< 1.4*
Cl	μeq l^{-1}	*223.1*	*411.3*	*112.7*
Soluble Al	μg l^{-1}	*59.3*	*126.0*	*14.0*
Labile Al	μg l^{-1}	*19.9*	*69.0*	*< 2.5*
Non-labile Al	μg l^{-1}	*39.5*	*80.0*	*12.0*
DOC	mg l^{-1}	*3.2*	*6.2*	*1.7*
Conductivity	μS cm^{-1}	*39.5*	*61.0*	*23.0*

Water Chemistry

(Figure 4.5.2, Table 4.5.2-3)

Loch Chon is a moderately acidic site, with a mean pH of 5.60 and a mean alkalinity of 10 μeq l^{-1}. Mean xSO_4 is 49 μeq l^{-1} and mean NO_3 12 μeq l^{-1}. Large seasonal cycles are observed for a number of determinands including pH and Al species. Sea-salt inputs are fairly high, with large inter-annual variability evident in time series and LOESS plots for Na and Cl (Figures 4.5.2f,h). Peaks in marine ion concentrations occurred in 1989 and again 1993, each time followed by a period of steady decline. These marine ion ‘cycles’ are thought to have a significant impact on surface water chemistry and trend detection at this and other near-coast sites through a sea-salt effect operating over a prolonged, rather than only at an episodic, timescale (Evans *et al*., in press; Section 5.3).

Trend analyses suggest that both pH and alkalinity are increasing at Loch Chon: pH by approximately 0.4 units over ten years and alkalinity by 10-14 μeq l^{-1}. These increases are reasonably well supported by time series plots (Figures 4.5.2a,b), although in recent years values appear to have levelled off or perhaps begun to decline. At this stage no definite reduction in xSO_4 can be identified, and it is therefore uncertain whether genuine chemical recovery has taken place. The observed marine ion cycles may provide an alternative explanation for acidity changes (see Section 5.3.2). NO_3 appears to have risen since 1994, producing a positive trend using regression analysis but not SKT. As at Lochnagar, additional sampling is required to establish whether this represents a sustained increase or simply a short-lived climatic fluctuation. DOC has again shown a highly significant and sustained increase over the monitoring period, estimated using SKT at 2 mg l^{-1} over the ten years.

Longer term data for the Caorainn Achaidh Burn, which drains a predominantly moorland catchment 3 km west of Loch Chon, are discussed in Chapter 6.

Epilithic diatoms

(Figure 4.5.3, Table 4.5.4)

Major changes are evident in the relative abundance of epilithic diatom species in samples from Loch Chon. RDA and associated permutation tests show that “sample year” is highly significant at the 0.01 level. The time trend appears to be strongly influenced by relative declines in *Achnanthes marginulata* (pH optima 5.2) and *Eunotia incisa* (pH optima 5.1) and increases in *Brachysira brebissonii* (pH optima 5.3) and *B.vitrea* (pH optima 5.9). These changes are therefore consistent with a “recovery” response and are supported by the observed improvements in water chemistry. Caution should be taken in interpretation of these trends for the reasons given in the water chemistry section, and further years of

Table 4.5.3

Significant trends in chemical determinands (July 1988 - March 1998)

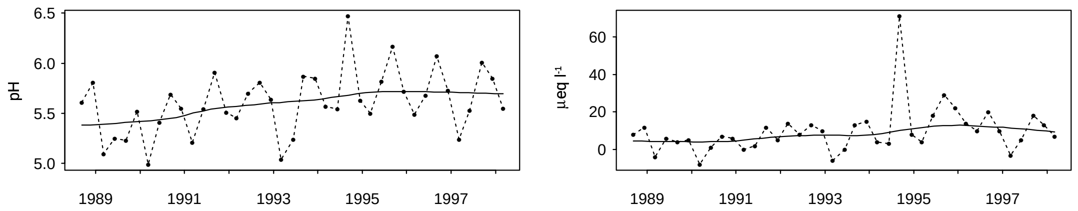
Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
pH		*+0.043**	*+0.044**
Alkalinity	μeq l^{-1}	-	*+1.00**
NO_3	μeq l^{-1}	*+0.86***	-
DOC	mg l^{-1}	*+0.16***	*+0.20***
labile Al	μg l^{-1}	*-2.72***	*-2.00***

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

Figure 4.5.2

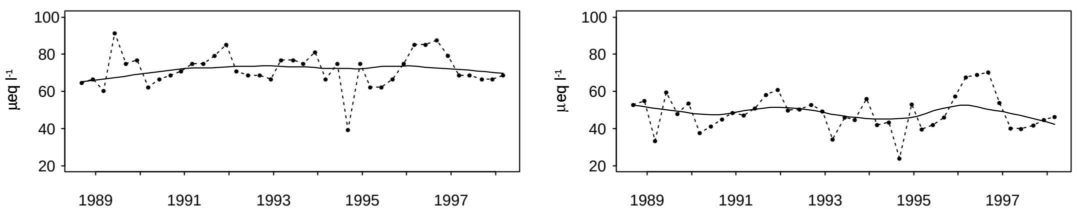
Loch Chon: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)



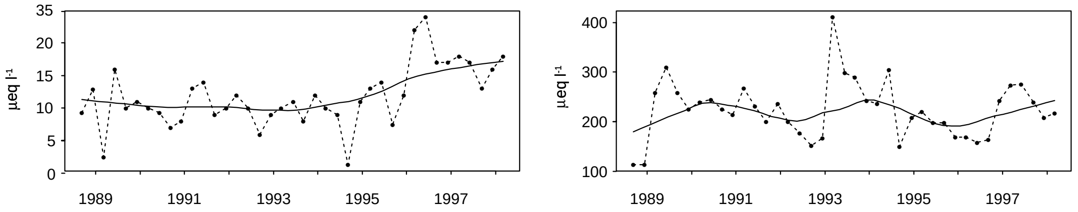
(a) pH

(b) Alkalinity



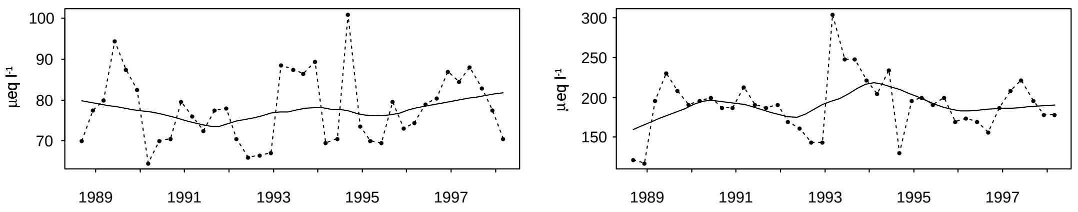
(c) Sulphate

(d) Non-marine Sulphate



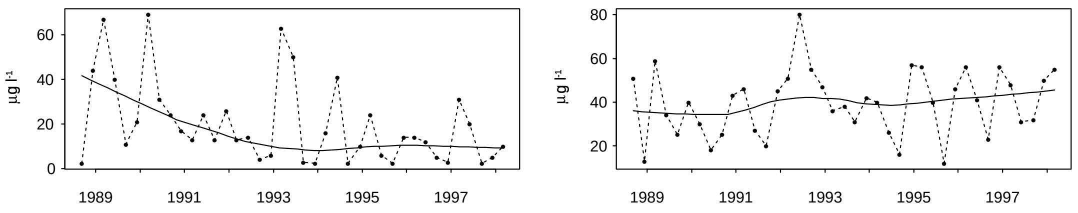
(e) Nitrate

(f) Chloride



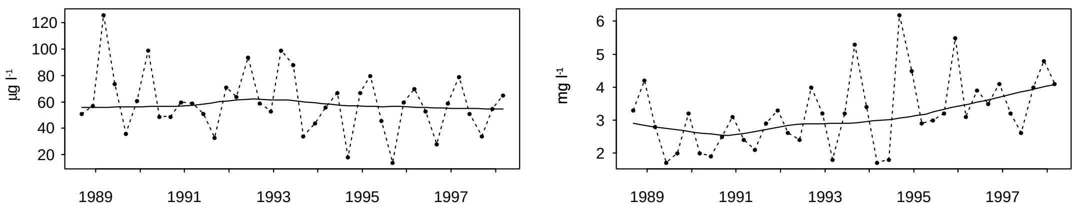
(g) Calcium

(h) Sodium



(i) Labile Al

(j) Non-labile Al



(k) Total Soluble Al

(l) Dissolved Organic Carbon

Table 4.5.4

Loch Chon: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*390*	*114*	*7.5*	*0.82*	*0.60*
Macrophytes	*35*	*27*	*16.6*	*0.94*	*0.85*
Invertebrates	*581*	*68*	*2.3*	*0.87*	*0.65*

Variance explained (%)	within year	between years	linear trend	p	
				unrestricted	restricted
Epilithic diatoms	*45.6*	*54.4*	*15.5*	*<0.01*	*<0.01*
Macrophytes	*	*	*31.5*	*0.04*	*0.19*
Invertebrates	*37.4*	*62.6*	*14.1*	*<0.01*	*<0.01*

monitoring are necessary to ascertain to what extent they represent long term uni-directional as opposed to cyclical change. Interestingly, the most abundant species, *Navicula leptostriata*, which has a relatively acid preference (pH optima 5.1), was most abundant during 1989-1990 and in 1993, periods when sea-salt deposition and January rainfall was highest and loch water was most acid. Diatom inferred pH (derived from weighted averaging) correlates highly with both measured pH and Cl concentration (see Section 7.3). This suggests that climatic effects have been major factors influencing species composition. The diatom assemblage of sediment trap samples shows some temporal similarity to that of the epilithon, in that *B. vitrea* has increased markedly with time (Figure 4.5.6). More generally however, there are marked differences. Comparison between the sediment trap time series and a sediment core profile taken at the onset of monitoring provide some evidence that real recovery in the diatom flora is underway (Figure 7.4, Section 7.2.5). The positive trend in *B.vitrea* and the negative trends in *Cymbella perpusilla* and, possibly, *Eunotia incisa*, are the reverse of those recorded in the latter stages of acidification in the sediment core. The relative contributions of emission induced improvements in water chemistry and climatic effects to this apparent reversal in the sediment diatom assemblage will only be ascertained with further monitoring.

■ Macroinvertebrates

(Figure 4.5.4, Table 4.5.4)

The macroinvertebrate fauna of Loch Chon is the most diverse and abundant of all the monitoring sites. The fauna is typical of a moderately acid lake and is dominated by the acid tolerant mayfly family, the Leptophlebiidae, which make up at least 60% of the total composition in all years. Other mayflies present included *Siphlonurus lacustris*, *Ameletus inopinatus* and *Heptagenia lateralis* which was recorded in high numbers in 1992 only. Several species of acid tolerant detritivorous stoneflies (*Nemoura* spp., *Leuctra inermis* and *Leuctra nigra*) have been recorded sporadically. Acid tolerant caddisflies such as *Polycentropus* spp., *Plectrocnemia* spp. and *Holocentropus* spp. were present throughout the study period. There is a very diverse community of corixids; *Hespercorixa sahlbergii* and *Cymatia bonsdorffi* dominated the first 4 years and *Arctocorisa germari* and *Sigara distincta* characterised the second half of the monitoring period. Time as a linear trend is significant at the 0.01 level. The trend appears to be mainly driven by changes in the species composition of

Table 4.5.5

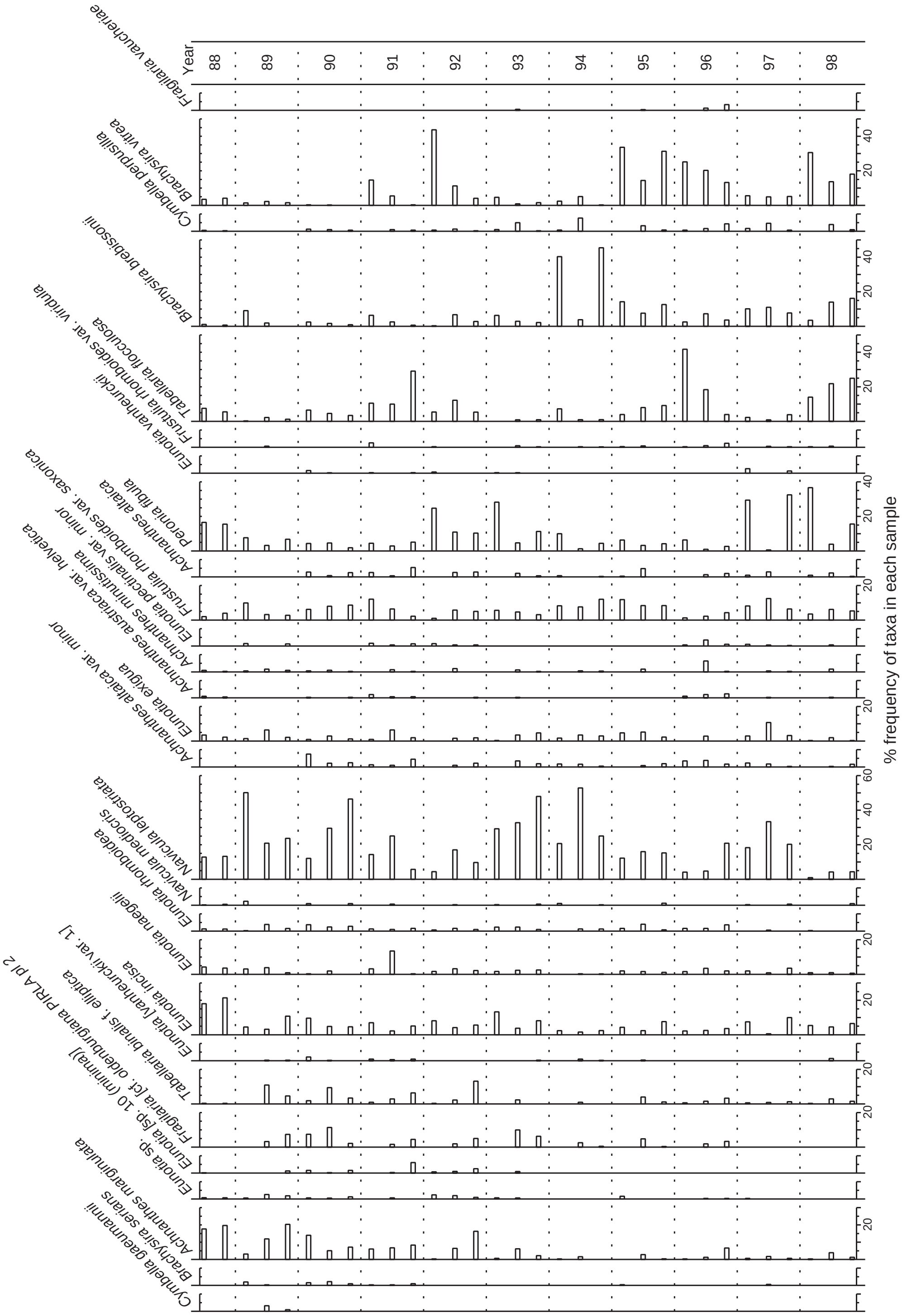
Loch Chon: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Myriophyllum alterniflorum[2]	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Utricularia sp.[2]	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Callitriche sp.[3]	*0*	*0*	*1*	*1*	*1*	*1*	*1*	*0*
Potamogeton berchtoldii[3]	*0*	*0*	*0*	*0*	*0*	*1*	*1*	*1*
Sphagnum auriculatum[4]	*3*	*3*	*2*	*2*	*3*	*3*	*3*	*3*
Juncus bulbosus var. fluitans[4]	*5*	*5*	*5*	*5*	*5*	*5*	*5*	*5*
OTHER SUBMERGED OR FLOATING SPECIES								
Batrachospermum sp.	*4*	*3*	*2*	*2*	*2*	*2*	*2*	*2*
Filamentous green algae	*4*	*4*	*4*	*4*	*4*	*3*	*4*	*2*
Calliergon cordifolium	*0*	*0*	*1*	*0*	*0*	*0*	*0*	*0*
Fontinalis squamosa	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
Marsupella emarginata	*0*	*0*	*0*	*1*	*1*	*0*	*1*	*0*
Scapania undulata	*0*	*0*	*0*	*1*	*1*	*0*	*1*	*1*
Isoetes lacustris	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Littorella uniflora	*3*	*3*	*4*	*4*	*4*	*4*	*4*	*4*
Subularia aquatica	*0*	*0*	*0*	*0*	*0*	*0*	*1*	*1*
Elatine hexandra	*0*	*0*	*0*	*0*	*0*	*0*	*1*	*1*
Lobelia dortmanna	*3*	*4*	*3*	*3*	*3*	*3*	*3*	*3*
Nuphar lutea	*1*	*1*	*2*	*2*	*2*	*2*	*2*	*2*
Nymphaea alba	*1*	*1*	*2*	*2*	*2*	*2*	*2*	*2*
Potamogeton natans	*0*	*0*	*1*	*0*	*0*	*0*	*0*	*0*
Potamogeton polygonifolius	*0*	*0*	*1*	*0*	*0*	*0*	*0*	*0*
Sparganium angustifolium	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
EMERGENT SPECIES								
Equisetum fluviatile	*1*	*1*	*2*	*2*	*1*	*1*	*1*	*1*
Hydrocotyle vulgaris	*1*	*1*	*2*	*2*	*2*	*2*	*2*	*1*
Menyanthes trifoliata	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
Ranunculus flammula	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Carex rostrata	*2*	*3*	*3*	*2*	*3*	*3*	*3*	*2*
Eleocharis palustris	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*2*
Glyceria fluitans	*1*	*1*	*2*	*2*	*2*	*3*	*2*	*1*
Juncus acutifloris/articulatus	*4*	*4*	*5*	*5*	*5*	*5*	*5*	*4*
Juncus effusus	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Phragmites australis	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
TOTAL NUMBER OF SPECIES	*23*	*23*	*27*	*26*	*26*	*25*	*29*	*27*

Figure 4.5.3

Loch Chon: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



Corixidae and Coleoptera. These species are aquatic both as nymphs and adults, but their distribution is thought to be influenced more by short term variations in weather conditions, particularly as these affect dispersal, rather than changes in water chemistry. However, species richness has shown a general increase which appears to follow the trend of rising pH, with particularly low numbers of species recorded in the high sea-salt /low pH years of 1990 and 1993. Further years of monitoring are therefore required to assess the extent to which these changes are sustained and therefore indicative of recovery.

■ Fish

(Figure 4.5.5)

The outflow stream from Loch Chon has been electrofished since 1989. Trout densities at this site are the fourth highest found in the Network sites. The mean population density of both 0+ and >0+ trout varies widely between years. As at several other Scottish sites, density patterns of 0+ fish are heavily influenced by the high recruitment year of 1991, but if this year is disregarded the data show a steady increase with time. Condition factor of 0+ fish appears to have increased gradually since 1990 although its coefficient of variation has remained stable through time. There is also evidence for a general increase in the condition factor of the >0+ group while its coefficient of variation shows marked variation between years. The length frequency graph demonstrates that despite the large recruitment in 1991 there was only a small subsequent increase in >0+ fish in 1992.

■ Aquatic macrophytes

(Tables 4.5.4-5)

The aquatic macroflora of Loch Chon is diverse and typical for moderately acid lakes with sheltered habitats. The isoetids *Lobelia dortmanna* and *Littorella uniflora* dominate much of the shallows with *Isoetes lacustris*, *Myriophyllum alterniflorum* and *Juncus bulbosus* var. *fluitans* abundant in deeper water. Sheltered areas include emergent stands of *Phragmites australis*, *Equisetum fluviatile* and *Carex rostrata*, and floating leaved beds of *Nuphar lutea*, *Nymphaea alba* and *Potamogeton natans*. The fine leaved pondweed *P. berchtoldii*, *Subularia aquatica* and *Elatine hexandra* were recorded for the first time in the bay at the north end of the Loch in 1995 and again in 1997. It is possible that the appearance of these species has resulted from the recent amelioration in acidity, although it is also feasible that the bay has been subject to slight and localised nutrient enrichment from local agriculture. Apart from these recent changes the flora for the bulk of the Loch remains unchanged throughout the decade.

■ Summary

Loch Chon has a pH intermediate among UKAWMN sites. Afforestation has clearly intensified acidification as the site is much more acidic than the nearby unafforested Loch Tinker. There is some evidence of increased pH and alkalinity over the last decade but since this has not been matched by a reduction in xSO_4 or NO_3 it is currently unclear whether this improvement is the result of reductions in acid deposition. Large natural fluctuations in marine ion concentrations and rainfall may provide alternative explanations for the observed changes in acidity. Epilithic diatoms, sediment trap diatoms, aquatic macrophytes, macro-invertebrates and the trout population, all provide indications of improved conditions. Further monitoring is essential to determine the extent to which apparent “recovery” at this site is a real response to emissions reductions as opposed to part of a climatic cycle.

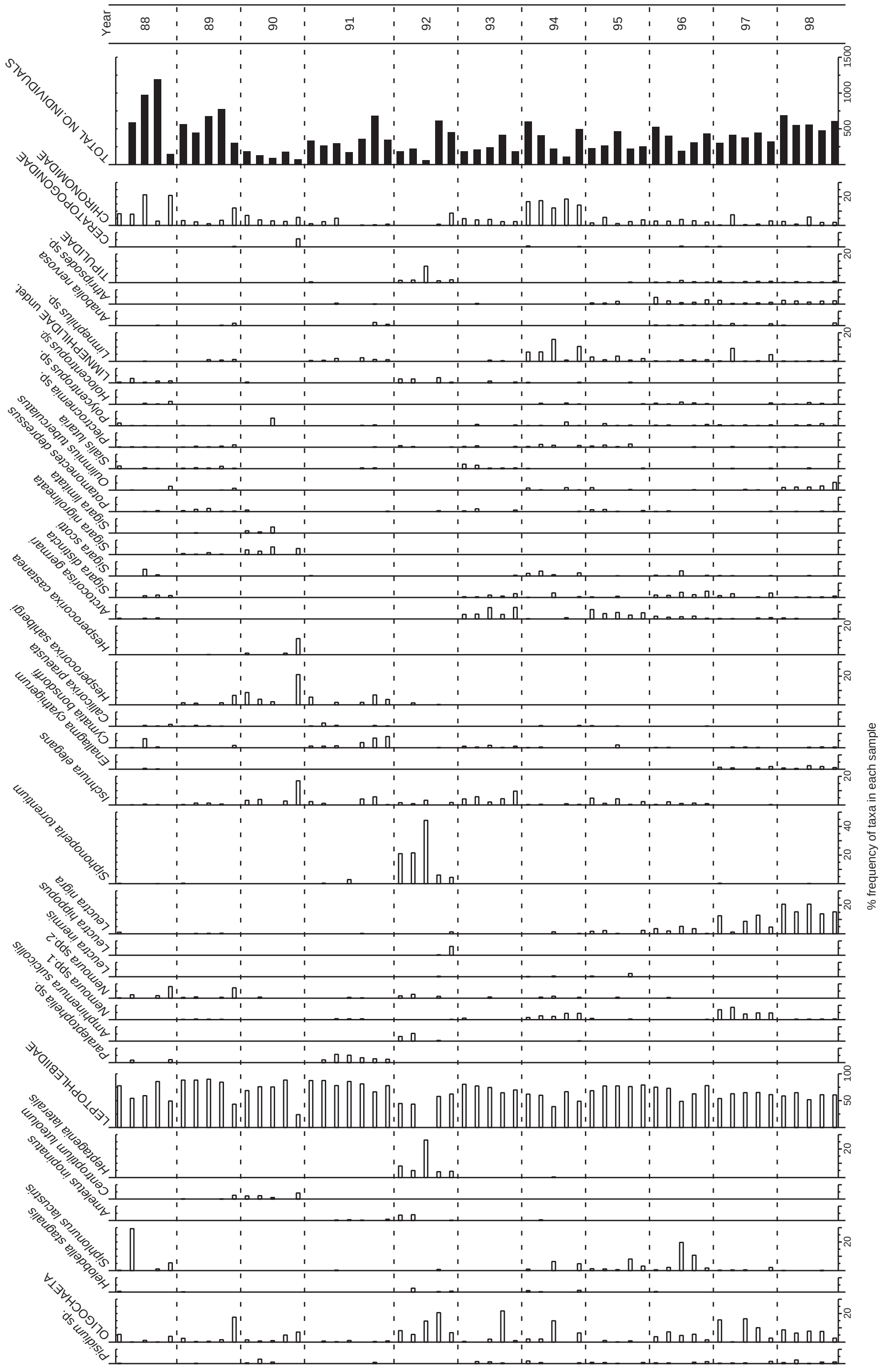
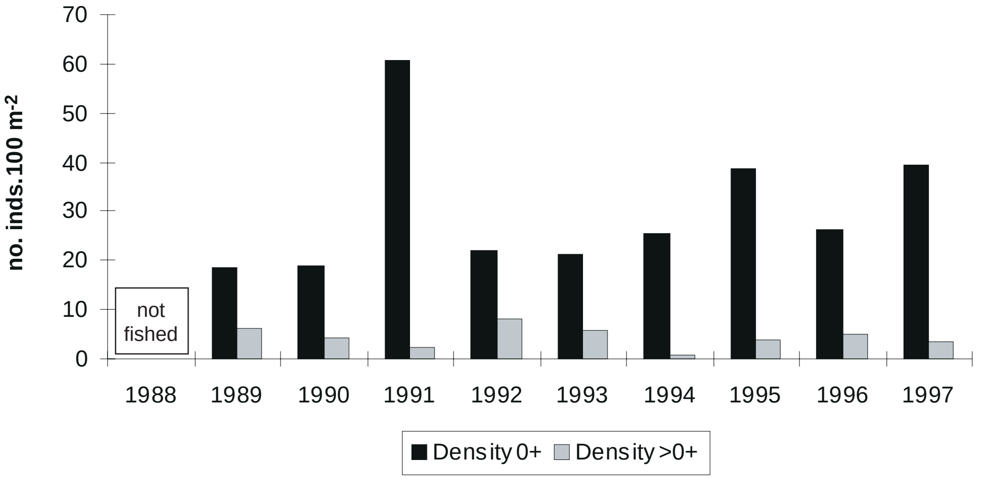


Figure 4.5.4

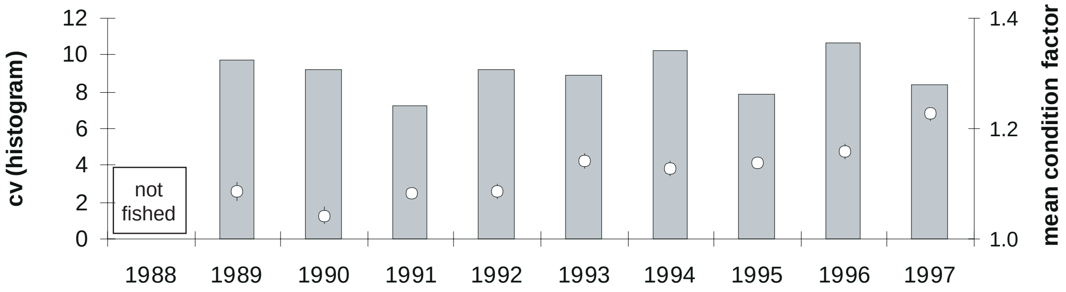
Loch Chon: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

(a) Density



(b) Condition (0+)



Condition (>0+)

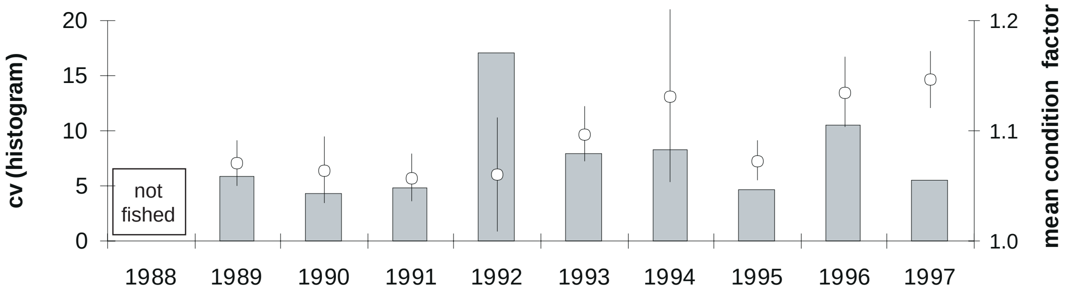


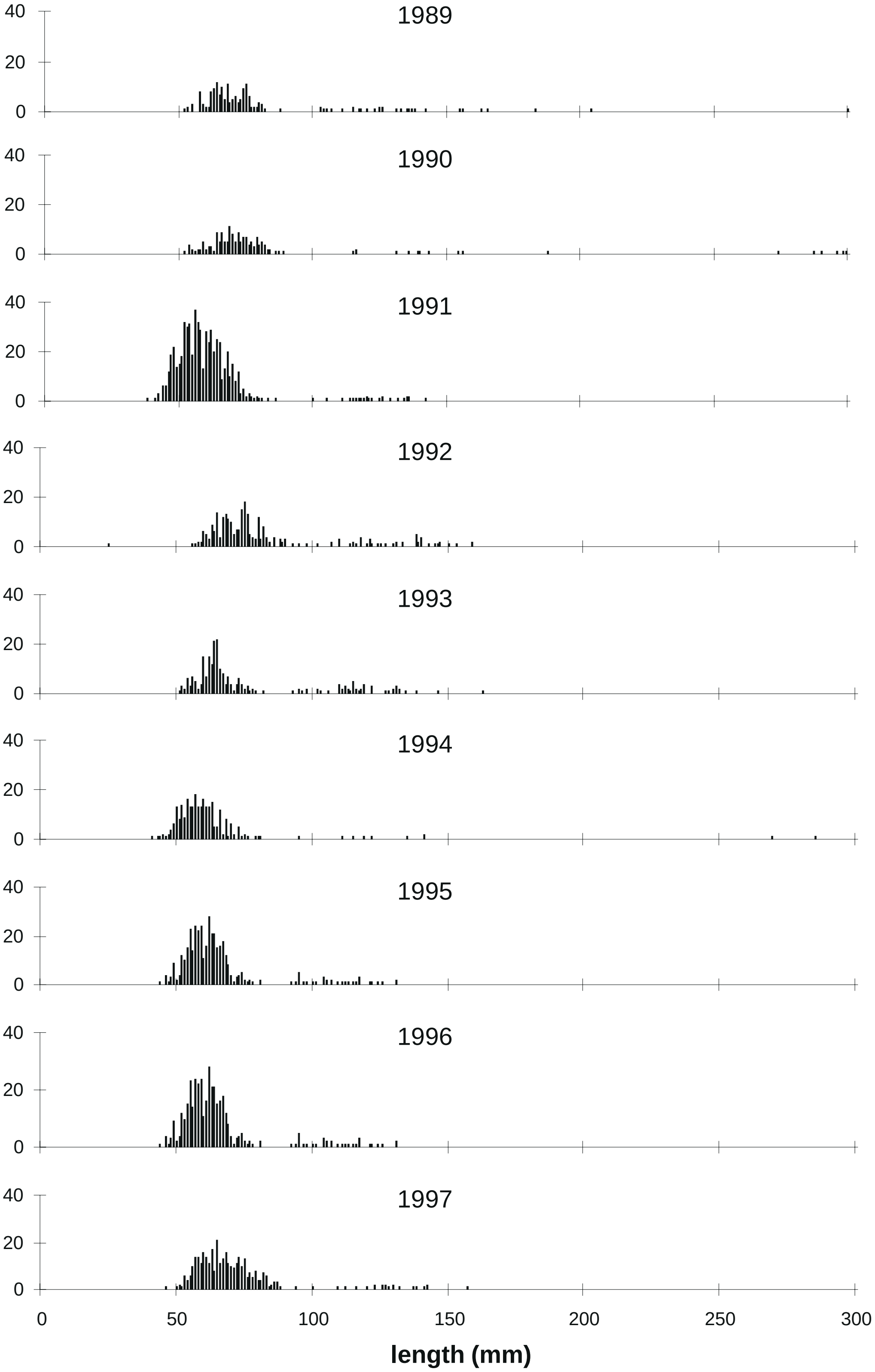
Figure 4.5.5

Loch Chon: summary of fish data (1989 - 1997)

- **(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})**
- **(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)**

Figure 4.5.5

Loch Chon: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries (1989 - 1997)



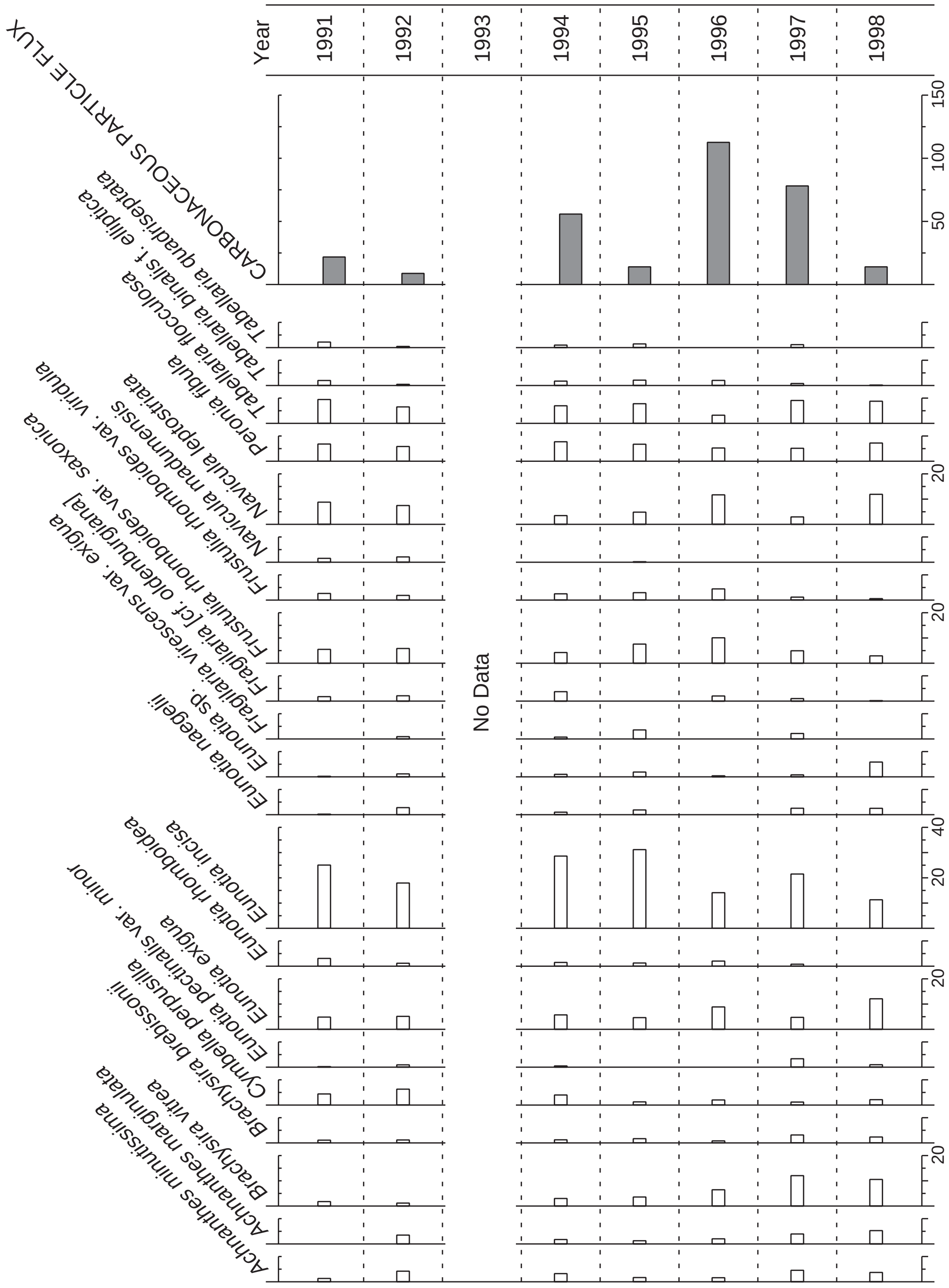


Figure 4.5.6

Loch Chon: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year

4.6 Loch Tinker

Site Review

Loch Tinker lies in a non-forested upland moorland catchment to the east of Loch Chon, and the two sites have been used as a experimental / control pair to examine the influence of forestry on acidification (Kreiser *et al.* 1990) and other aspects of water quality (Section 5.5.1). In the former study, pH reconstruction using the fossil diatom assemblage of sediment cores suggested that the loch had acidified from around pH 6.5 in the mid-19th century, to around pH 5.5 by 1991. There has been no physical disturbance within the catchment of the loch during the monitoring period. Full site descriptions of Loch Tinker are provided in Patrick *et al.* (1991) and Patrick *et al.* (1995).

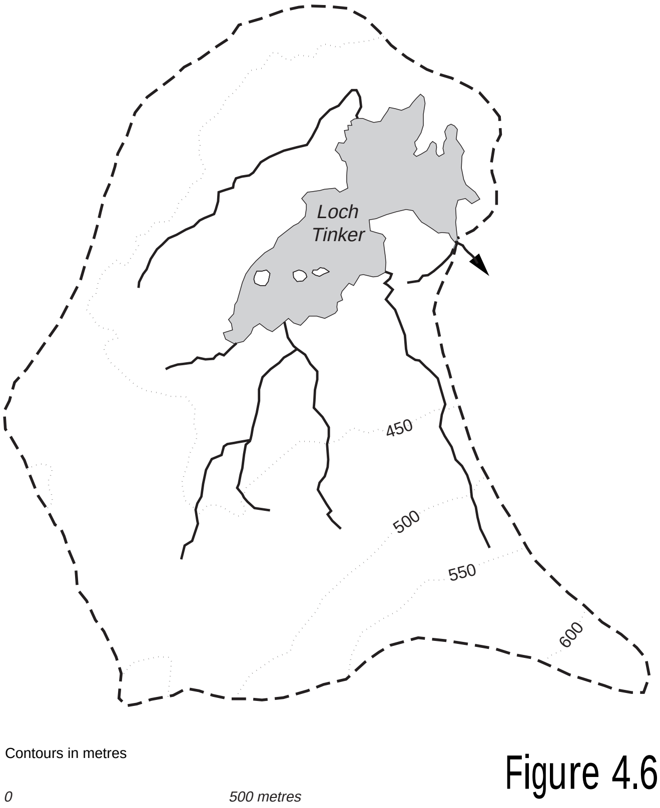


Figure 4.6.1

Loch Tinker: catchment

Table 4.6.1

Loch Tinker: site characteristics

Grid reference	*NN 445068*
Lake altitude	*420 m*
Maximum depth	*9.8 m*
Mean depth	*3.5 m*
Volume	4.0×10^5 m^3
Lake area	*11.3 ha*
Catchment area (excl. lake)	*112 ha*
Catchment: Lake area ratio	*9.9*
Catchment Geology	*mica schists and grits*
Catchment Soils	*blanket peats*
Catchment vegetation	*moorland - 100%*
Net relief	*280 m*
Mean annual rainfall	*2345 m*
1996 deposition	
Total S	29 kg ha^{-1} yr^{-1}
non-marine S	23 kg ha^{-1} yr^{-1}
Oxidised N	10 kg ha^{-1} yr^{-1}
Reduced N	13 kg ha^{-1} yr^{-1}

Table 4.6.2

Loch Tinker: summary of chemical determinands, June 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*6.13*	*6.56*	*5.42*
Alkalinity	µeq l^{-1}	*37.6*	*96.0*	*-2.0*
Ca	µeq l^{-1}	*85.0*	*127.0*	*35.0*
Mg	µeq l^{-1}	*48.3*	*91.7*	*33.3*
Na	µeq l^{-1}	*142.6*	*321.7*	*78.3*
K	µeq l^{-1}	*8.5*	*17.9*	*2.6*
SO_4	µeq l^{-1}	*55.6*	*110.4*	*37.5*
xSO_4	µeq l^{-1}	*38.5*	*99.2*	*17.7*
NO_3	µeq l^{-1}	*2.9*	*14.3*	*< 1.4*
Cl	µeq l^{-1}	*162.8*	*439.4*	*70.4*
Soluble Al	µg l^{-1}	*20.3*	*45.0*	*5.0*
Labile Al	µg l^{-1}	*3.3*	*14.0*	*< 2.5*
Non-labile Al	µg l^{-1}	*18.4*	*44.0*	*< 2.5*
DOC	mg l^{-1}	*4.7*	*8.1*	*1.9*
Conductivity	µS cm^{-1}	*31.4*	*62.0*	*21.0*

Water Chemistry

(Figure 4.6.2, Tables 4.6.2-3)

This moorland site is adjacent to the forested Loch Chon, and shows generally similar temporal variations. However it is considerably less acid, with a mean pH of 6.13, mean alkalinity of 38 µeq l^{-1} and lower Al concentrations. Mean xSO_4 is also lower, at 39 µeq l^{-1}, whilst Ca concentrations are higher (mean 85 µeq l^{-1}) (see Section 5.5.1). Palaeolimnological data indicate that Loch Tinker has acidified at a steady rate since the mid-19th century, but that unlike Loch Chon there has been no substantial pH reduction since around 1950 (Kreiser *et al.*, 1990). NO_3 concentrations at Loch Tinker were < 5 µeq l^{-1} for much of the monitoring period, but a pulse of 14 µeq l^{-1} was recorded in Spring 1996. Seasonality is high for both pH and alkalinity, and variations in marine ions are large, and similar to those at Loch Chon.

The chemistry of Loch Tinker has shown little overall change during the monitoring period. The only significant trend, identified using SKT, is a rise in DOC of around 1.8 mg l^{-1} over the decade.

Epilithic diatoms

(Figure 4.6.3,Table 4.6.4)

As for the neighbouring site (Loch Chon), RDA and associated restricted permutation tests show that “sample year” is significant at the 0.01 level in explaining changes in the relative abundance of epilithic diatoms at Loch Tinker. The trend appears to be influenced by relatively rare taxa, and more specifically, increases in *Brachysira brebissonii*, *Cymbella microcephala*, *Nitzschia gracilis* and declines in *Fragilaria vaucheriae*, *Eunotia rhomboidea* and *Synedra acus*. There is no systematic difference between the pH and DOC optima of the declining and increasing groups and these changes therefore do not indicate a shift in either variable over the last decade. Species composition is relatively stable between years, with *Brachysira vitrea* dominant in nearly all samples and persistence also seen in other relatively abundant taxa, e.g. *Tabellaria flocculosa*, *Achnanthes minutissima*, *Frustulia rhomboides* var. *saxonica* and *Cymbella lunata*. Given the absence of evidence for any trends in water chemistry (with the exception of a small rise in DOC) explanations for the subtle changes in the rarer species are unclear. The diatom species assemblage of sediment trap samples taken since 1991 exhibits even greater stability between years than the epilithon assemblage (Figure 4.6.6.), and in contrast to the epilithon there is no evidence of trends in the rare taxa described above.

Macroinvertebrates

(Figure 4.6.4, Table 4.6.4)

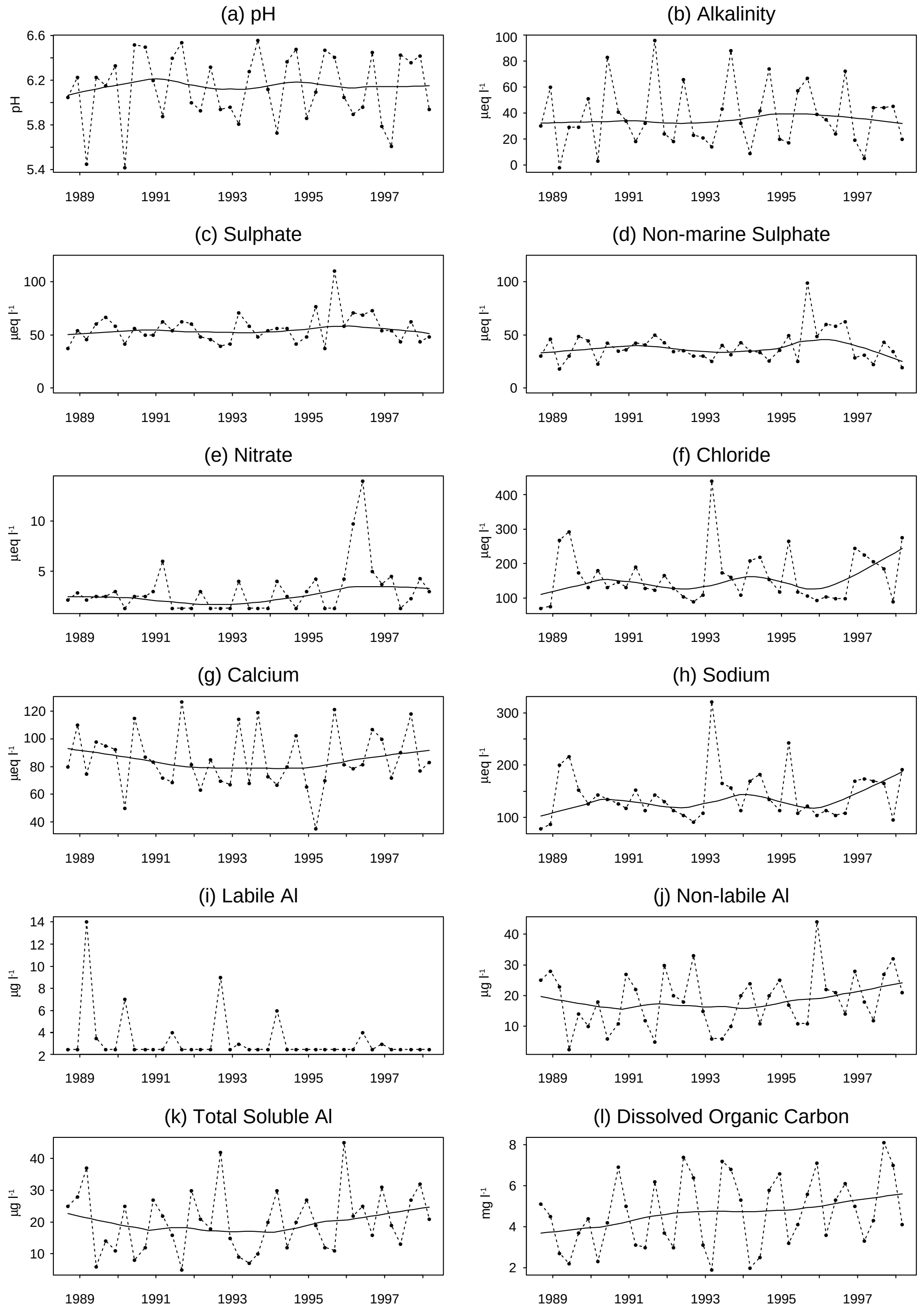
The macrobenthos is typical of a moderately acid lake, dominated by chironomids and the freshwater bivalve *Pisidium* spp. The most acid tolerant mayfly family the Leptophlebiidae and Oligochaetae characterised the first few years of the monitoring period, with numbers declining after 1991. The second half of the survey was characterised by several caddisfly species, of

Table 4.6.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
DOC	mg l^{-1}	-	*+0.183**

** Trend significant at p < 0.05; ** trend significant at p < 0.01; *** trend significant at p < 0.001*



(a) pH

(b) Alkalinity

(c) Sulphate

(d) Non-marine Sulphate

(e) Nitrate

(f) Chloride

(g) Calcium

(h) Sodium

(i) Labile Al

(j) Non-labile Al

(k) Total Soluble Al

(l) Dissolved Organic Carbon

Figure 4.6.2

Loch Tinker: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.6.4

Loch Tinker: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*318*	*145*	*6.9*	*0.64*	*0.50*
Macrophytes	*45.3*	*21*	*14.0*	*0.94*	*0.79*
Invertebrates	*1011*	*36*	*2.4*	*0.81*	*0.73*

Variance				p	
explained (%)	**within year**	**between years**	**linear trend**	**unrestricted**	**restricted**
Epilithic diatoms	*53.0*	*47.0*	*9.4*	*<0.01*	*<0.01*
Macrophytes	*	*	*34.7*	*0.05*	*0.25*
Invertebrates	*54.8*	*45.2*	*15.5*	*<0.01*	*<0.01*

which *Mystacides* spp. dominated (this species increased in abundance after 1995) and was accompanied by *Sericostoma personatum, Anabolia nervosa* and *Limnephilus* spp.. Other characteristic species include the beetle *Oulimnius tuberculatus, Sialis lutaria* and the Polycentropodids *Plectrocnemia* spp. and *Polycentropus* spp. which both occurred in intermittent years. There have been sporadic recordings of stoneflies in low numbers and Corixids were only present in 1990 and 1991. 1989 and 1990 were both poor years in terms of species richness and abundance. There is a significant linear trend through time in the macroinvertebrate data and given the relative decline in Leptophlebids could be indicative of slightly improved conditions. However, there is no upward trend in species richness with time which might be expected to accompany a “recovery” response.

Fish

(Figure 4.6.5)

The outflow stream of Loch Tinker has been fished since 1989. Mean trout densities are extremely low and statistical analysis of trends in the data are therefore inappropriate. Length frequency graphs clearly show the years of recruitment failure and the decline in older trout present.

Aquatic macrophytes

(Tables 4.6.4-5)

Although at considerably higher altitude than Loch Chon and less acid, Loch Tinker is characterised by a similar assemblage of aquatic plants. The main floristic differences between sites probably arise from the greater exposure of this site to wind and the more peaty nature of the water at this site which results in a more restricted depth range for the deeper growing species such as *Isoetes lacustris*. The acidophilous *Juncus bulbosus* var. *fluitans* is far less abundant in Loch Tinker, perhaps reflecting the more alkaline conditions. In the five year interpretative report (Patrick *et al.*), two species were identified as having been lost to the site. *Sparganium angustifolium*, which was not recorded for three years after 1989 has re-appeared since 1995. However, there has been no record of the acid sensitive charophyte *Nitella* sp. since 1988. Interestingly, and in common with Loch Chon, *Subularia aquatica* was recorded at the site for the first time in 1997. There is little information on the pH tolerance of this oligotrophic species and the environmental

Table 4.6.5

Loch Tinker: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Nitella flexilis[1]	*1*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
Myriophyllum alterniflorum[2]	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Utricularia sp.[2]	*0*	*0*	*1*	*1*	*1*	*1*	*2*	*1*
Callitriche hamulata[3]	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Sphagnum auriculatum[4]	*1*	*1*	*1*	*2*	*2*	*2*	*2*	*2*
Juncus bulbosus var. *fluitans*[4]	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
OTHER SUBMERGED OR FLOATING SPECIES								
Batrachospermum sp.	*1*	*1*	*1*	*2*	*2*	*2*	*0*	*2*
Filamentous green algae	*1*	*2*	*3*	*3*	*2*	*2*	*1*	*1*
Fontinalis antipyretica	*0*	*1*	*1*	*1*	*1*	*2*	*1*	*1*
Marsupella emarginata	*0*	*0*	*0*	*0*	*1*	*0*	*0*	*0*
Equisetum fluviatile	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*4*
Isoetes lacustris	*0*	*1*	*2*	*2*	*2*	*2*	*2*	*2*
Littorella uniflora	*2*	*2*	*3*	*4*	*4*	*4*	*4*	*4*
Lobelia dortmanna	*3*	*4*	*4*	*4*	*4*	*4*	*4*	*4*
Subularia aquatica	*0*	*0*	*0*	*0*	*0*	*0*	*2*	*2*
Glyceria fluitans	*1*	*1*	*2*	*2*	*2*	*2*	*2*	*1*
Potamogeton natans	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Potamogeton polygonifolius	*0*	*0*	*1*	*1*	*1*	*1*	*2*	*1*
Sparganium angustifolium	*2*	*1*	*0*	*0*	*0*	*1*	*2*	*1*
EMERGENT SPECIES								
Menyanthes trifoliata	*1*	*1*	*1*	*1*	*1*	*2*	*1*	*1*
Ranunculus flammula	*0*	*1*	*2*	*2*	*2*	*2*	*2*	*2*
Carex rostrata	*4*	*4*	*4*	*4*	*4*	*4*	*3*	*4*
Eleocharis palustris	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Juncus acutifloris/articulatus	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Juncus effusus	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
TOTAL NUMBER OF SPECIES	*18*	*20*	*21*	*21*	*22*	*22*	*22*	*23*

significance of its apparently recent establishment is unclear. There is no other evidence for floristic change at Loch Tinker over the last decade.

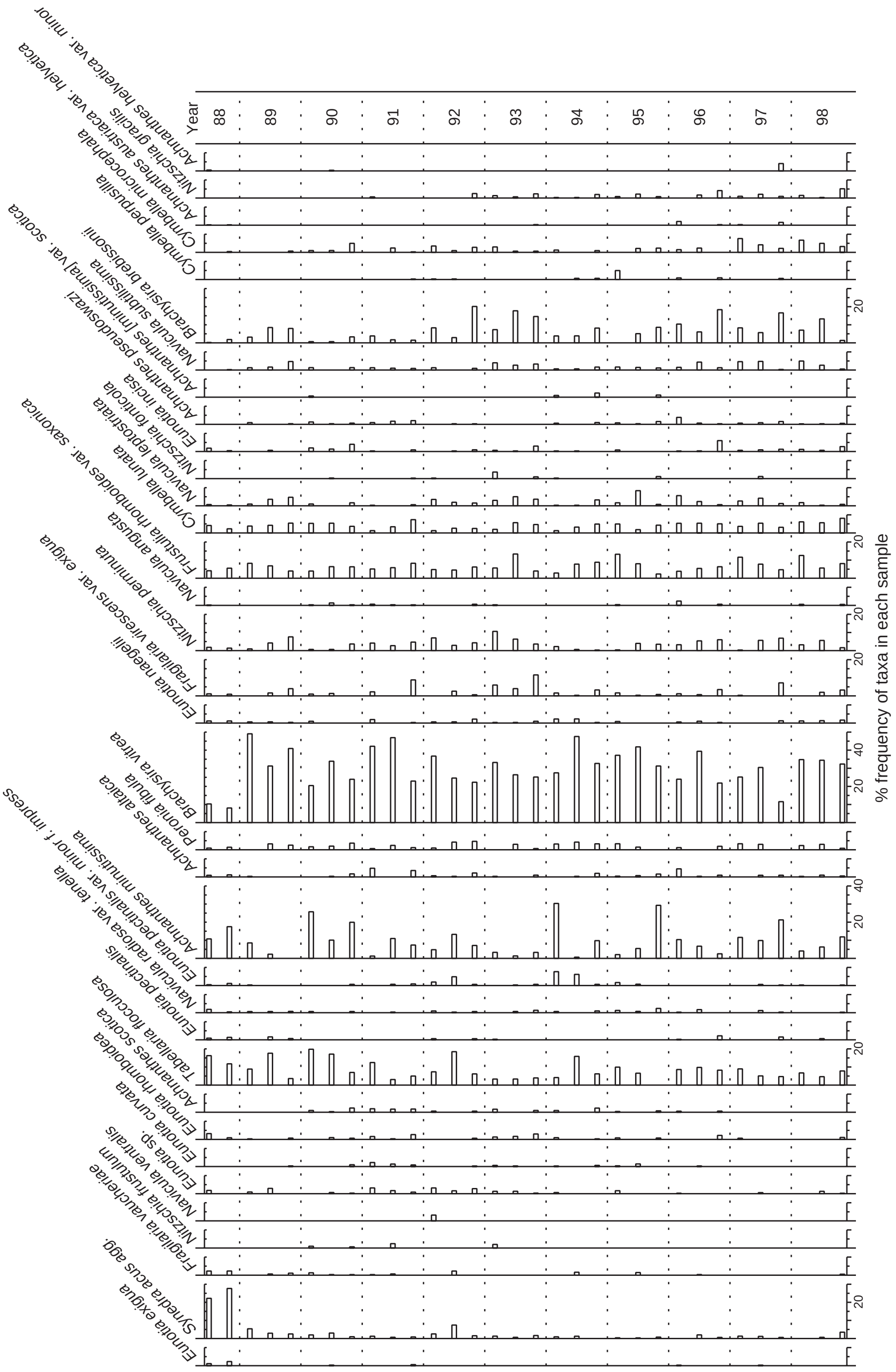
■ Summary

Loch Tinker is a relatively well buffered site, and is significantly less acidic than the neighbouring forested catchment, Loch Chon. Apart from natural variations related to seasonality and marine ion deposition, the chemistry of the Loch has remained largely constant over the last ten years. Linear trends have been observed in epilithic diatoms and macroinvertebrates, but these are not indicative of any amelioration in acidity, while the trout population of the outflow has remained at a very low density.

Figure 4.6.3

Loch Tinker: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



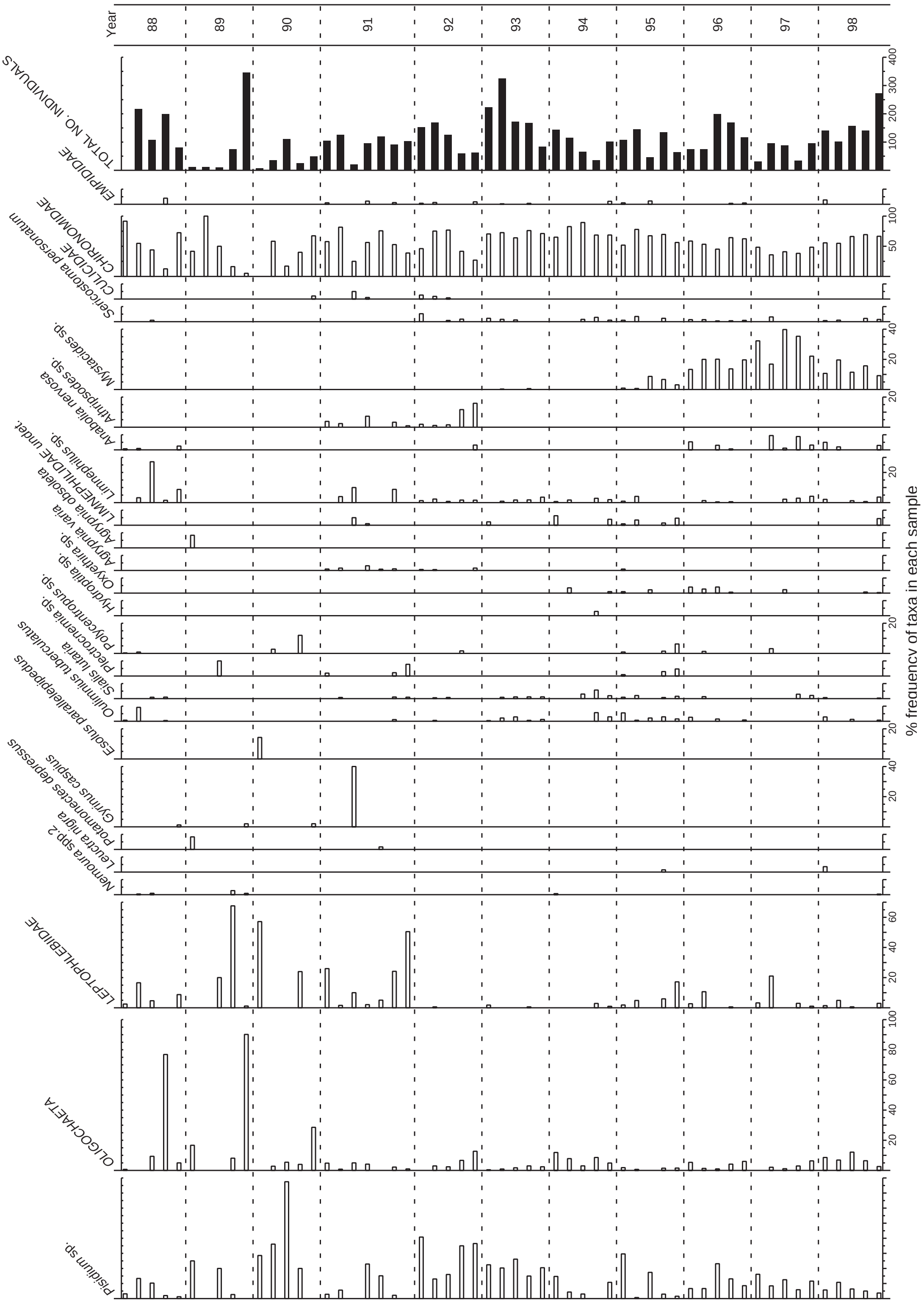


Figure 4.6.4

Loch Tinker: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

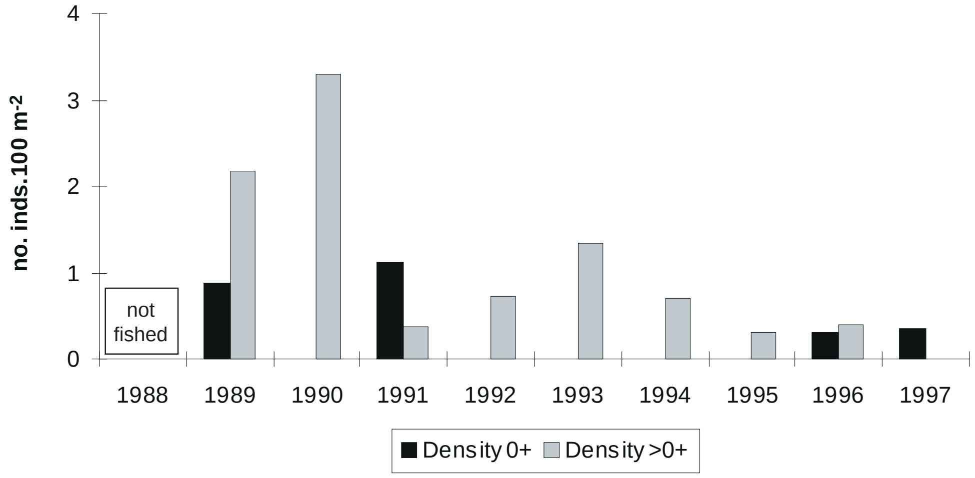
Figure 4.6.5

Loch Tinker outflow: summary of fish data (1989 - 1997)

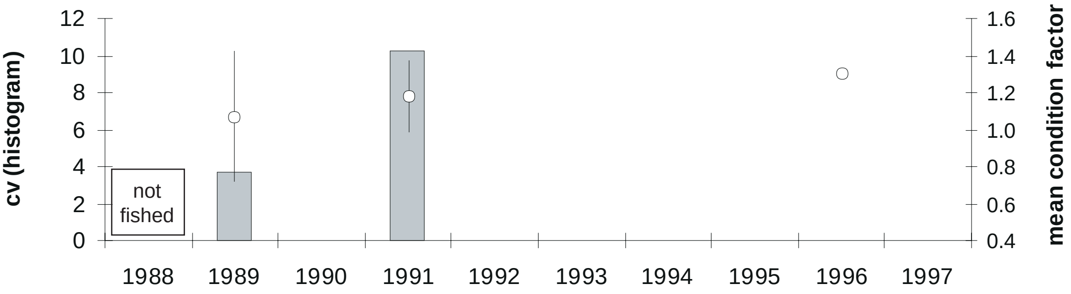
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

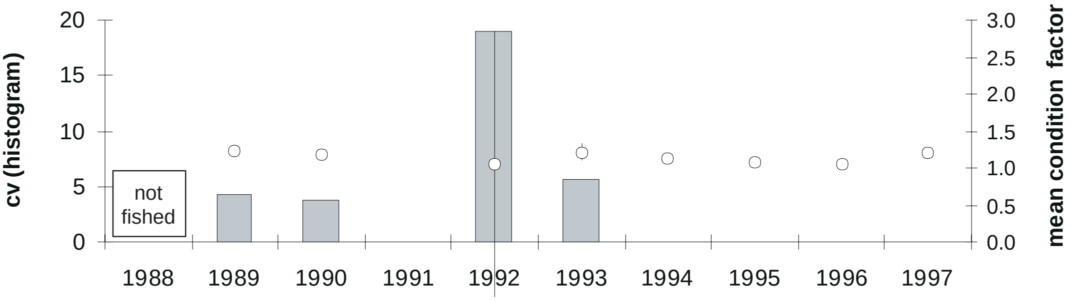
(a) Density



(b) Condition (0+)



Condition (>0+)



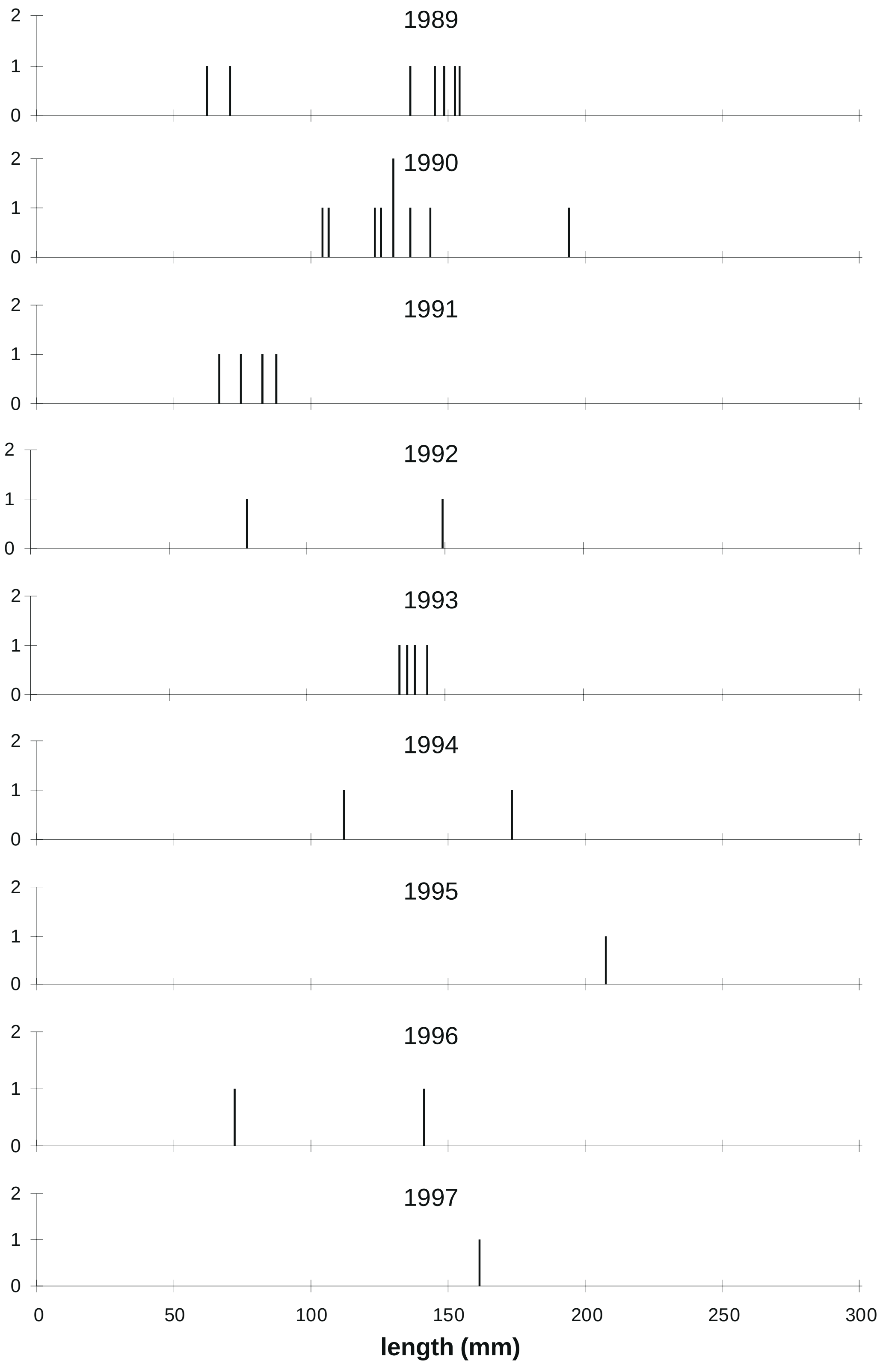


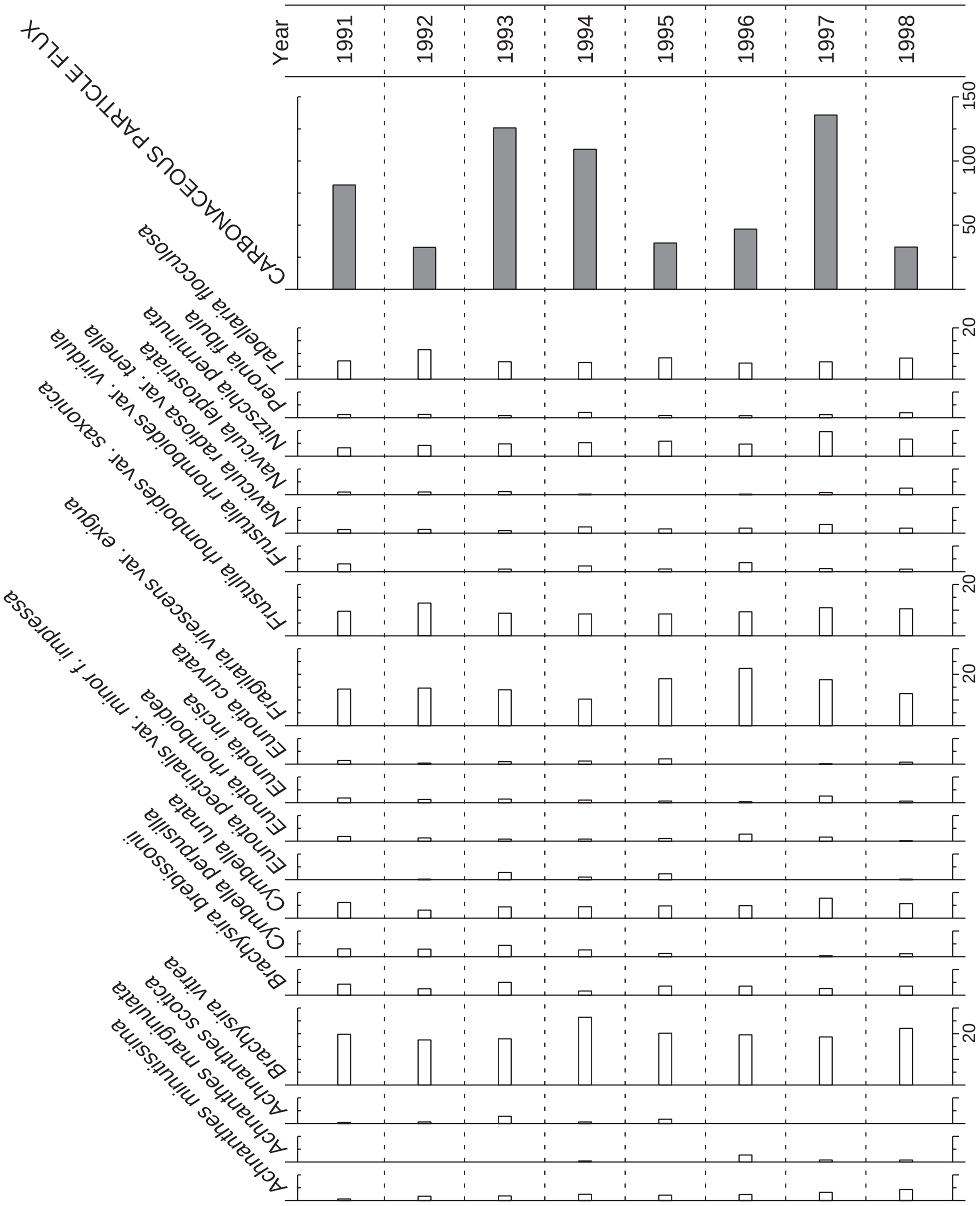
Figure 4.6.5

Loch Tinker: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries

Figure 4.6.6

Loch Tinker: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year



4.7 Round Loch of Glenhead

Site Review

Round Loch of Glenhead, in the Galloway region of southwest Scotland, has been central to studies on acidification since the problem was first investigated in the UK (e.g. Flower *et al.*, 1987; Harriman *et al.*, 1987; Battarbee *et al.*, 1988). Although severely acidified, palaeoecological work on a sediment core taken in 1989 indicated that the site had undergone a slight and very recent improvement in pH (Allott *et al.* 1992). There has been no physical disturbance in the Loch catchment since the onset of monitoring.

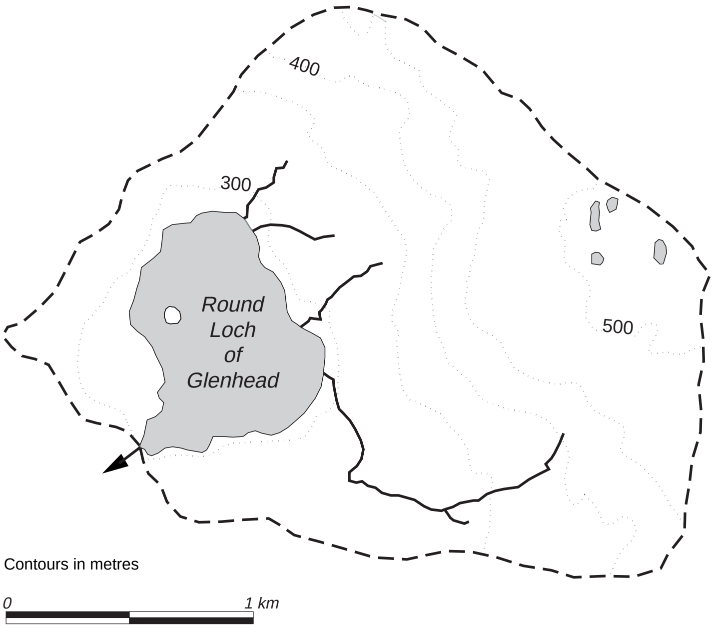


Figure 4.7.1

Round Loch of Glenhead: catchment

Table 4.7.1

Round Loch of Glenhead: site characteristics

Grid reference	*NX 450804*
Lake altitude	*295 m*
Maximum depth	*13.5 m*
Mean depth	*4.28 m*
Volume	*5.3×10^5 m^3*
Lake area	*12.5 ha*
Catchment area (excl. lake)	*95.1 ha*
Catchment: Lake area ratio	*7.5*
Catchment Geology	*tonalite, tonalite/granite*
Catchment Soils	*peat, peaty podsols*
Catchment vegetation	*moorland - 100%*
Net relief	*236 m*
Mean annual rainfall	*2342 mm*
1996 deposition	
Total S	*35 kg ha^{-1} yr^{-1}*
non-marine S	*28 kg ha^{-1} yr^{-1}*
Oxidised N	*13 kg ha^{-1} yr^{-1}*
Reduced N	*21 kg ha^{-1} yr^{-1}*

Table 4.7.2

Round Loch of Glenhead: summary of chemical determinands, June 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*4.90*	*5.21*	*4.72*
Alkalinity	µeq l^{-1}	*-12.2*	*6.0*	*-22.0*
Ca	µeq l^{-1}	*33.0*	*42.0*	*25.0*
Mg	µeq l^{-1}	*45.8*	*66.7*	*33.3*
Na	µeq l^{-1}	*174.3*	*247.8*	*130.4*
K	µeq l^{-1}	*8.2*	*12.8*	*2.6*
SO_4	µeq l^{-1}	*67.5*	*114.6*	*45.8*
xSO_4	µeq l^{-1}	*47.1*	*89.8*	*31.9*
NO_3	µeq l^{-1}	*7.1*	*24.3*	*< 1.4*
Cl	µeq l^{-1}	*195.2*	*298.6*	*121.1*
Soluble Al	µg l^{-1}	*95.1*	*146.0*	*55.0*
Labile Al	µg l^{-1}	*60.2*	*111.0*	*9.0*
Non-labile Al	µg l^{-1}	*34.9*	*70.0*	*16.0*
DOC	mg l^{-1}	*3.0*	*5.0*	*1.6*
Conductivity	µS cm^{-1}	*36.7*	*49.0*	*28.0*

Water Chemistry

(Figure 4.7.2, Tables 4.7.2-3)

Round Loch of Glenhead is chronically acidic, with a mean pH of 4.9 (range 4.7 to 5.2), a negative mean alkalinity, and high concentrations of labile Al. The catchment has a low buffering capacity, with a mean lake-water Ca of only 33 µeq l^{-1}, and a mean xSO_4 of 47 µeq l^{-1}. NO_3 concentrations are low, with a mean of 7 µeq l^{-1}, although concentrations generally remain above detection limits throughout the year.

Trend analyses suggest that Cl, Na and Mg have all declined significantly over the last decade (Table 4.7.3). However, it is considered likely, that these apparent trends are the result of natural variations in marine ion deposition. This is supported by time series (Figure 4.7.2) showing a period of elevated Na and Cl during 1989-1992. As at Lochs Chon and Tinker, increased marine base cations may cause a displacement of non-marine cations from soil exchange sites through the sea-salt effect (Section 5.3). This is evident at Round Loch for both Ca (Figure 4.7.2g), which is higher during the earlier part of the record, and for labile Al (Figure 4.7.2i), which clearly tracks Na and Cl concentrations throughout the monitoring period. Observed declining trends for both determinands may therefore also be linked to marine ion variations.

Both regression and SKT identify a rising trend in NO_3. Although this may be partly influenced by high concentrations during 1996, a more general increase is evident from Figure 4.7.2e in both winter maxima and summer minima over the ten years. DOC and non-labile Al have also risen fairly steadily over this time, as at other sites. Significant rising trends identified after five years for SO_4 and xSO_4 (Patrick *et al.*, 1995) are no longer observed, and time series (Figures 4.7.2c,d) suggest that concentrations peaked around 1992-1994. More recent data suggest that sulphate concentrations have now begun to decline.

Some sampling was undertaken at Round Loch of Glenhead prior to the initiation of the UKAWMN, and this is discussed in Section 6.

Epilithic diatoms

(Figure 4.7.3, Table 4.7.4)

The epilithon of the Round Loch of Glenhead is dominated by the acidobiontic species, *Tabellaria quadriseptata*, *Eunotia incisa*, *Brachysira brebissonii* and *Frustulia rhomboides* var. *saxonica*. Of these, the former is most abundant in the majority of samples and, given its pH optima of 4.9, provides an indication of the severely acid conditions of this site. An increase in the proportion of *Navicula*

Table 4.7.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
Cl	µeq l^{-1}	*-8.99***	*-9.43**
Na	µeq l^{-1}	*-6.78****	*-6.52**
Mg	µeq l^{-1}	*-1.33***	*-1.19**
Ca	µeq l^{-1}	*-0.75***	*-0.73**
NO_3	µeq l^{-1}	*+0.86****	*+0.61**
DOC	mg l^{-1}	*+0.09**	*+0.13***
Non-labile Al	µg l^{-1}	*+1.94***	*+2.31**
Labile Al	µg l^{-1}	-	*-2.63**

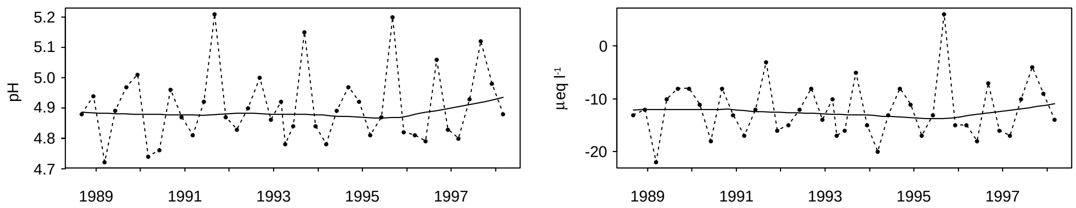
** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

Figure 4.7.2

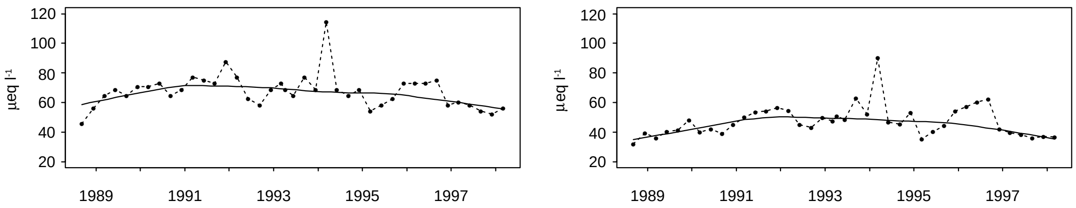
Round Loch of Glenhead: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

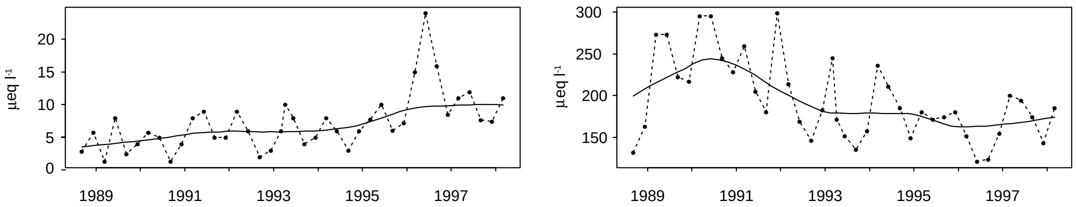
(a) pH (b) Alkalinity



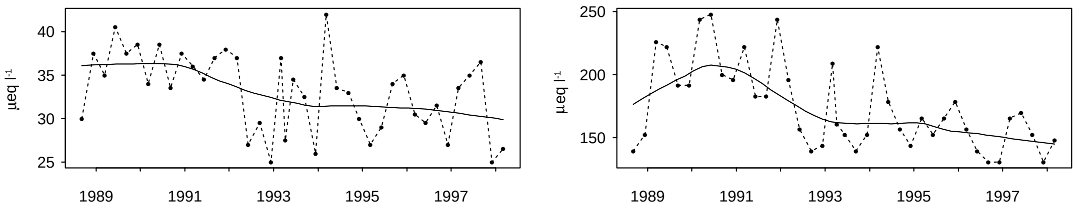
(c) Sulphate (d) Non-marine Sulphate



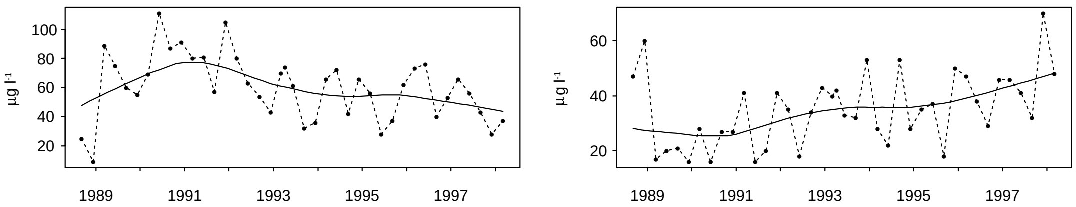
(e) Nitrate (f) Chloride



(g) Calcium (h) Sodium



(i) Labile Al (j) Non-labile Al



(k) Total Soluble Al (l) Dissolved Organic Carbon

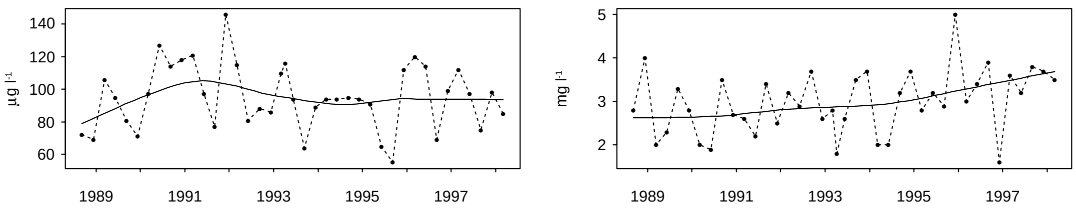


Table 4.7.4

Round Loch of Glenhead: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*289*	*87*	*6.8*	*0.29*	*0.27*
Macrophytes	*39*	*17*	*8.9*	*0.55*	*0.53*
Invertebrates	*486*	*26*	*1.8*	*0.14*	*0.14*

Variance				p	
explained (%)	**within year**	**between years**	**linear trend**	**unrestricted**	**restricted**
Epilithic diatoms	*53.2*	*46.8*	*6.8*	*0.02*	*0.13*
Macrophytes	*	*	*22.9*	*0.16*	*0.24*
Invertebrates	*72.5*	*27.5*	*2.9*	*0.09*	*0.50*

leptostriata during 1995-1997 is indicative of a mild amelioration of pH over this period. However, RDA and associated permutation test shows that “sample year” is not significant at the 0.01 level and there is no temporal pattern in the diatom inferred pH derived from weighted averaging. The epilithon assemblage is floristically very similar to the assemblage of sediment trap samples which have been collected since 1991 (Figure 4.7.6). These also show no evidence of any time trend.

Macroinvertebrates

(Figure 4.7.4, Table 4.7.4)

Round Loch of Glenhead has a relatively species poor fauna characterised by the most acid tolerant mayfly family, the Leptophlebiidae, chironomids and the caddisflies *Plectrocnemia* spp. and *Polycentropus* spp.. Detritivorous stoneflies of the genus *Nemoura spp.* were recorded intermittently. Other common taxa include the water beetles *Potamonectes depressus* and *Potamonectes griseostriatus* and several other species of caddisfly. Fluctuations in faunal abundance have occurred, with 1992 and 1996 being particularly poor years. The species composition has remained relatively persistent and RDA shows that a linear trend with time is insignificant.

Fish

(Figure 4.7.5)

The outflow stream of Round Loch of Glenhead has been electrofished since 1989. Mean population numbers are low. Densities of 0+ trout rose during the first three years but have since declined, with a total recruitment failure in 1993 followed by consistently low numbers. Densities of >0+ fish show two years of higher population density (1994 and 1995); however neither follow on from a high recruitment year and most years show low densities. The length frequency histograms also indicate the poor population structure present at the site. The mean condition factor of both age classes has remained stable and their coefficients of variance show no trends. HABSCORE HQS values have remained relatively constant and observed densities are well below those predicted.

Aquatic macrophytes

(Tables 4.7.4-5)

The relatively impoverished aquatic flora of this loch reflects the acidity of the system. The submerged vascular flora is restricted to the acid tolerant isoetid species, *Isoetes lacustris, Lobelia dortmanna* and *Littorella uniflora*, and the

Table 4.7.5

Round Loch of Glenhead: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Sphagnum auriculatum[4]	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
Juncus bulbosus var. *fluitans*[4]	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*4*
OTHER SUBMERGED OR FLOATING SPECIES								
Batrachospermum sp.	*1*	*2*	*2*	*1*	*1*	*0*	*1*	*1*
Filamentous green algae	*3*	*3*	*4*	*3*	*5*	*1*	*4*	*2*
Mnium hornum	*0*	*1*	*0*	*0*	*0*	*1*	*0*	*0*
Racomitrium aquaticum	*0*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Diplophyllum albicans	*0*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Marsupella emarginata	*0*	*0*	*1*	*1*	*1*	*0*	*1*	*1*
Nardia compressa	*0*	*1*	*3*	*3*	*3*	*3*	*3*	*3*
Scapania undulata	*1*	*1*	*1*	*1*	*0*	*1*	*1*	*1*
Isoetes lacustris	*3*	*3*	*4*	*4*	*4*	*3*	*4*	*3*
Littorella uniflora	*2*	*2*	*2*	*2*	*1*	*2*	*2*	*2*
Lobelia dortmanna	*4*	*4*	*5*	*5*	*5*	*5*	*5*	*5*
Glyceria fluitans	*1*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Potamogeton polygonifolius	*1*		*1*	*0*	*0*	*0*	*0*	*1*
Sparganium angustifolium	*1*	*1*	*1*	*1*	*2*	*1*	*2*	*2*
EMERGENT SPECIES								
Ranunculus flammula	*0*	*1*	*2*	*2*	*2*	*2*	*2*	*2*
Carex rostrata	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
Eleocharis palustris	*2*	*2*	*0*	*0*	*0*	*0*	*0*	*1*
Juncus acutifloris/articulatus	*0*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
TOTAL NUMBER OF SPECIES	*13*	*18*	*15*	*14*	*13*	*13*	*14*	*16*

acidophilous rush *Juncus bulbosus* var. *fluitans* which is particularly abundant in some sandy, shallow water locations. Rocks within the littoral are covered with liverworts, and chiefly by *Nardia compressa*. The acidophilous moss *Sphagnum auriculatum* is only present in a few locations. Apart from reductions in the emergent species *Carex rostrata* and *Eleocharis palustris*, which appear to have been affected by grazing by deer, there is no evidence of change in floristic composition over the decade and no significant time trend according to RDA and associated permutation test.

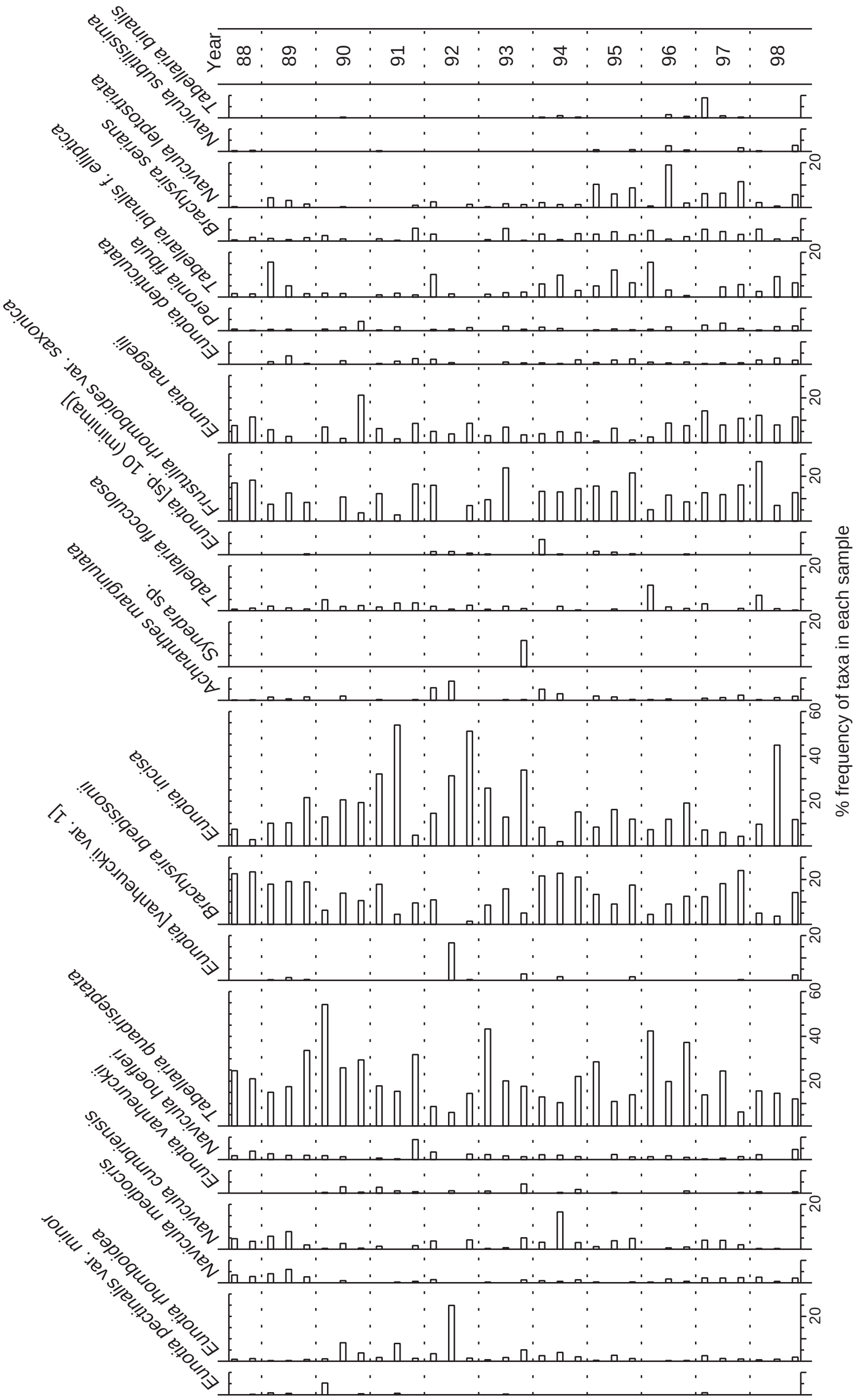
■ Summary

Round Loch of Glenhead is a severely impacted site with little ability to neutralise incoming acid deposition. A pronounced cyclical change in marine ions has taken place during the last ten years, which can be linked to climatically-driven fluctuations in deposition inputs, and which may have had a significant impact on variations in acidity related variables such as labile Al. NO$_3$ concentrations, although low, appear to have risen over the decade, whilst SO$_4$ and xSO$_4$ concentrations rose to a peak in the middle part of the record and have since declined. No overall trend has been observed in either pH or alkalinity or in any biological group. However, by including chemical measurements made prior to UKAWMN monitoring, it is clear that large reductions in xSO$_4$ have occured over a longer time scale and there is also evidence for a slight improvement in pH. This is consistent with the palaeoecological evidence which suggested small improvements, according to the fossil diatom assemblage, in the mid- to late 1980s.

Figure 4.7.3

Round Loch of Glenhead: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



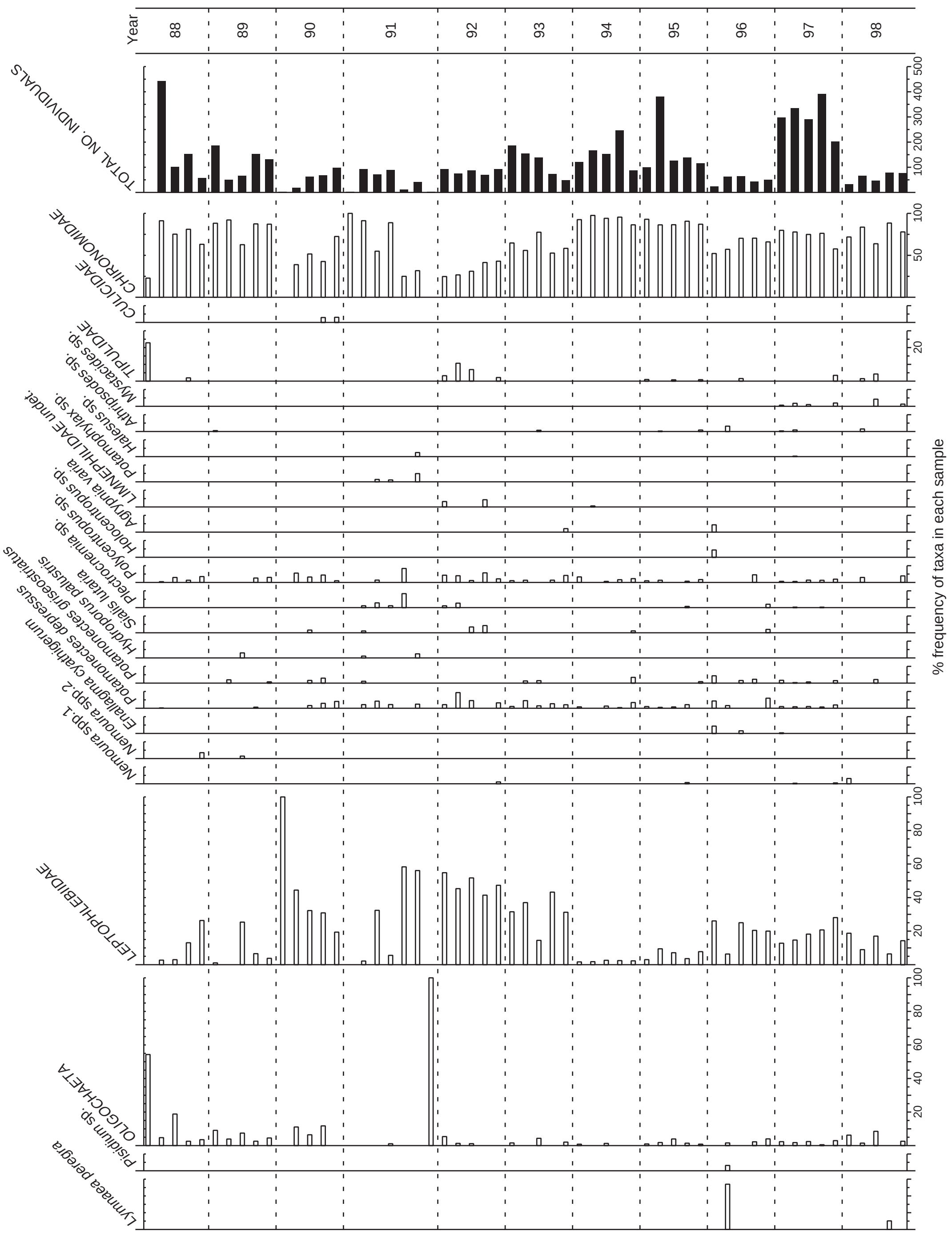


Figure 4.7.4

Round Loch of Glenhead: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

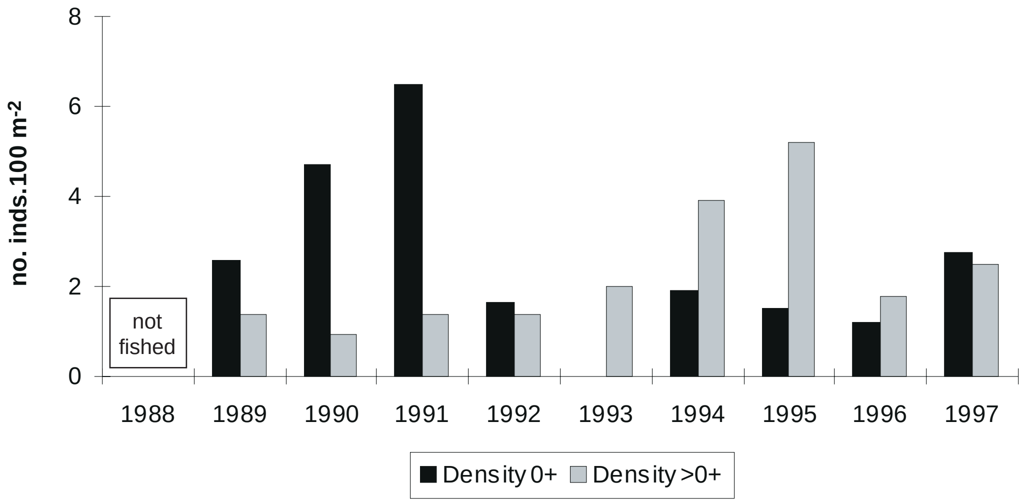
Figure 4.7.5

Round Loch of Glenhead: summary of fish data (1989 - 1997)

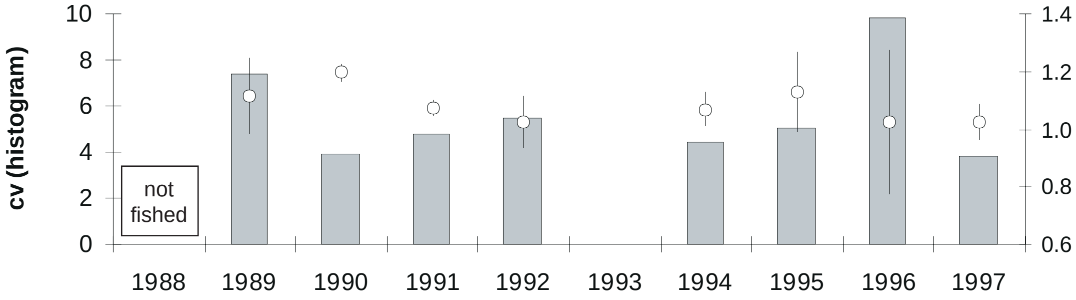
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

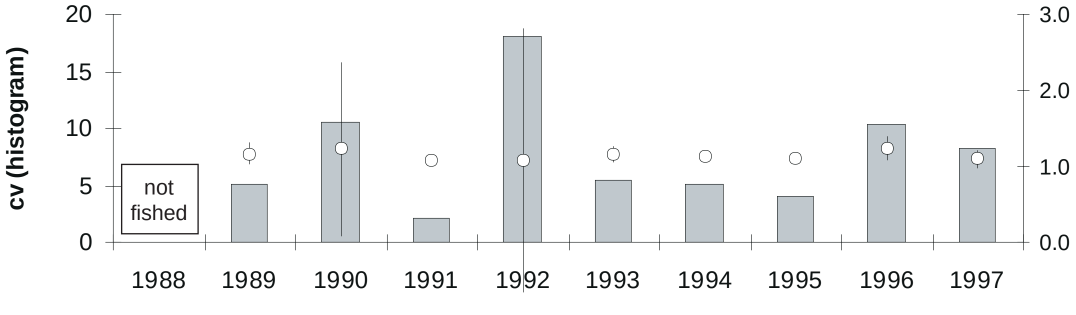
(a) Density



(b) Condition (0+)



Condition (>0+)



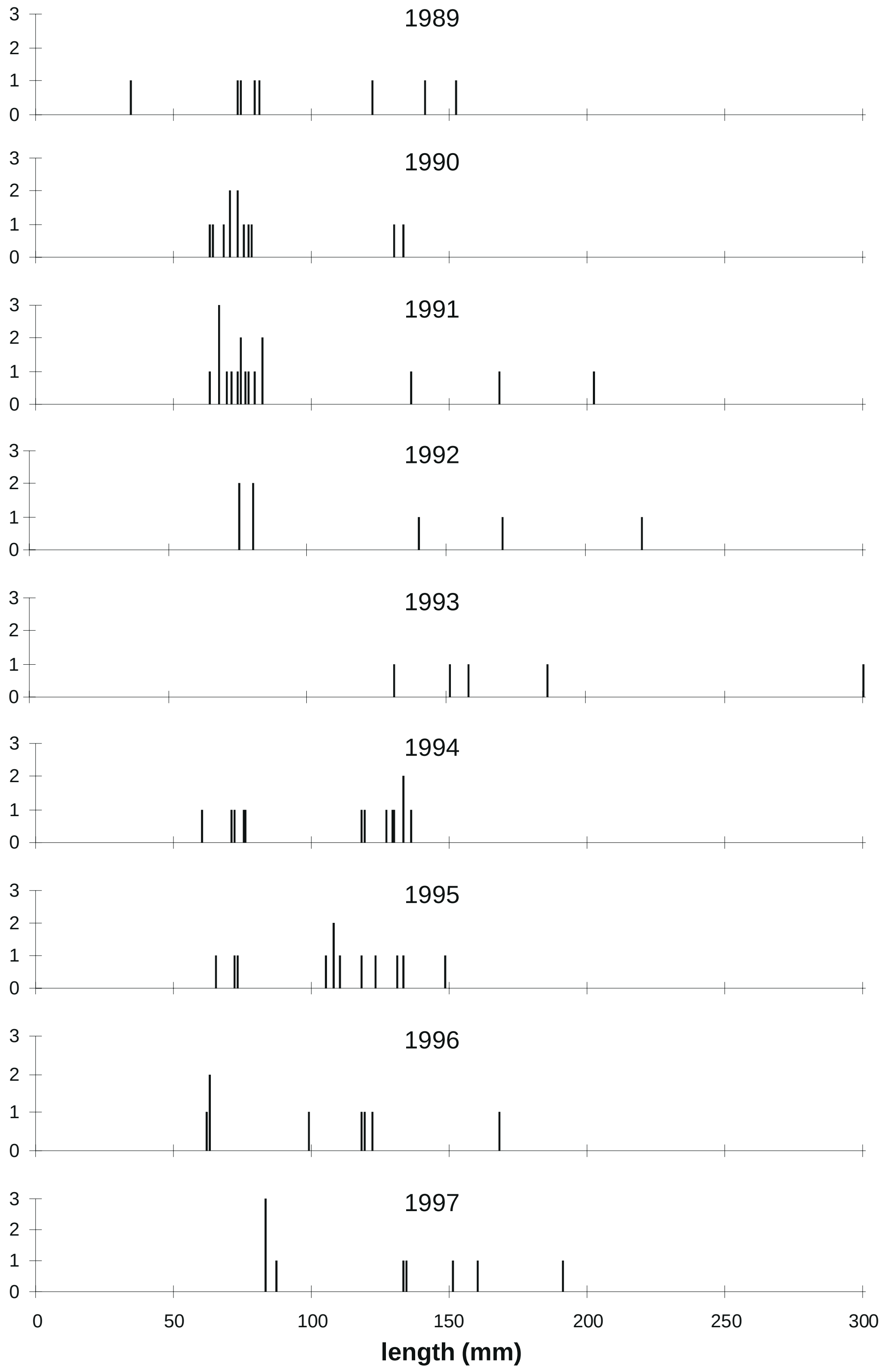


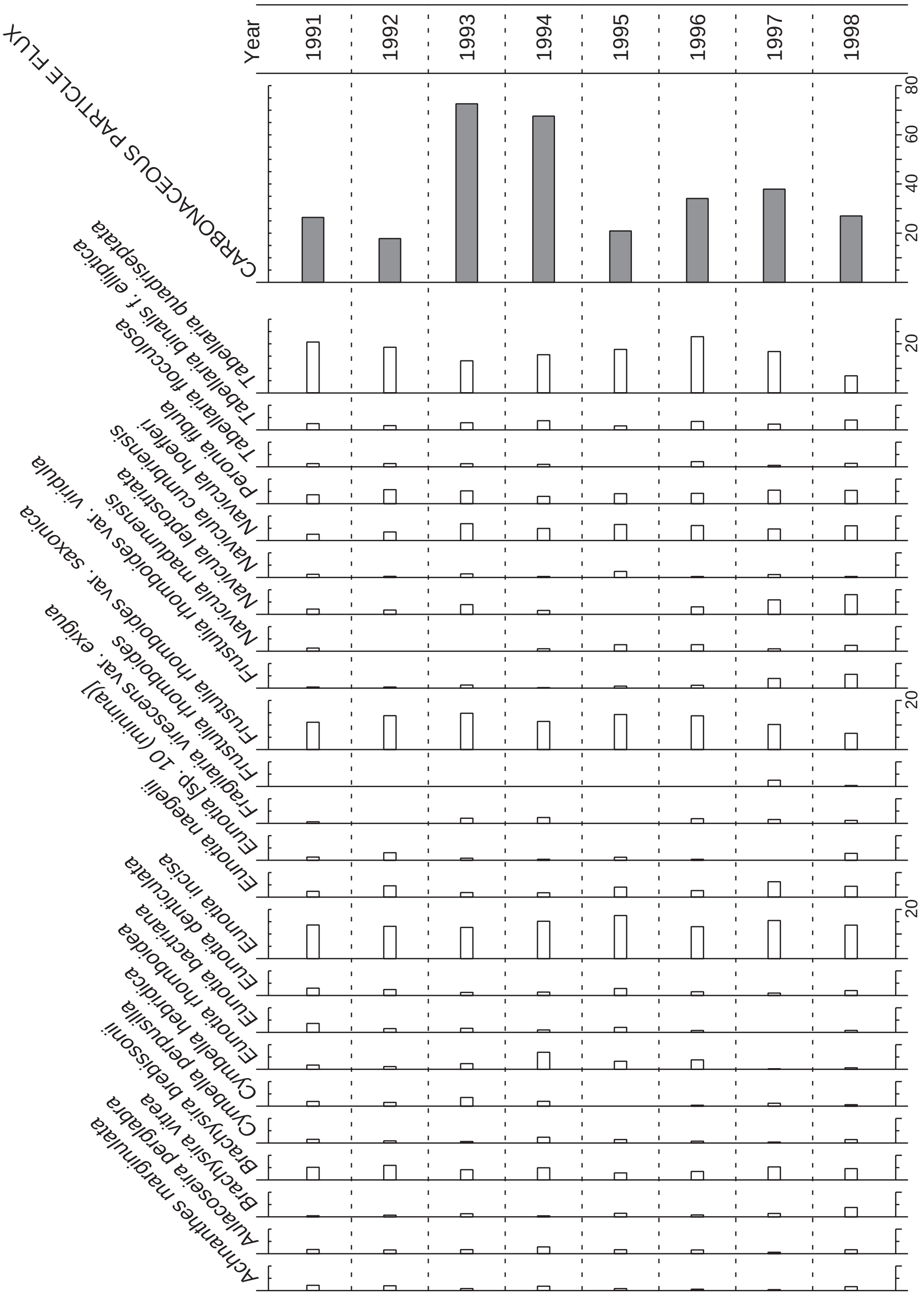
Figure 4.7.5

Round Loch of Glenhead: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries

Figure 4.7.6

Round Loch of Glenhead: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year



4.8 Loch Grannoch

Site Review

Loch Grannoch is a large loch in the Galloway region of southwest Scotland. In contrast to the neighbouring site, Round Loch of Glenhead, a large proportion of the catchment is under managed coniferous forest, part of which is approaching maturity. Despite this, no felling had been carried out over the period analysed in this report. Flower *et al.* (1990) observed a floristic difference between the diatom assemblage of a surface sediment sample, taken in 1988, and that of the upper layers of a sediment core taken two years previously. This was attributed to phosphorus and potassium fertiliser application in the catchment, peaking in 1985, which is likely to have raised nutrient levels in the Loch. There was little indication at the time that this had affected Loch pH. Paleoecological pH reconstruction, using the

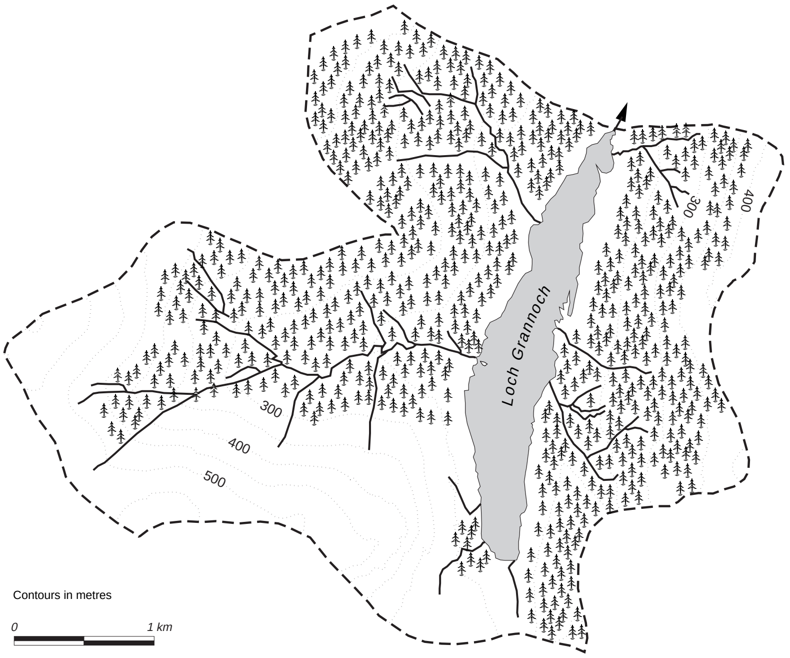


Figure 4.8.1

Loch Grannoch: catchment

Table 4.8.1

Loch Grannoch: site characteristics

Grid reference	*NX 542700*
Lake altitude	*210 m*
Maximum depth	*20.5 m*
Mean depth	*6.4 m*
Volume	*7.4 x 10^6 m^3*
Lake area	*114.3 ha*
Catchment area (excl. lake)	*1287 ha*
Catchment: Lake area ratio	*11.3*
Catchment Geology	*granite*
Catchment Soils	*peats, peaty podsols, peaty gleys, skeletal soils*
Catchment vegetation	*conifers - 70% moorland 30%*
Net relief	*391 m*
Mean annual rainfall	*2286 mm*
1996 deposition	
Total S	*32 kg ha^{-1} yr^{-1}*
non-marine S	*26 kg ha^{-1} yr^{-1}*
Oxidised N	*12 kg ha^{-1} yr^{-1}*
Reduced N	*21 kg ha^{-1} yr^{-1}*

Table 4.8.2

Loch Grannoch: summary of chemical determinands, September 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*4.61*	*5.04*	*4.27*
Alkalinity	µeq l^{-1}	*-27.8*	*2.0*	*-58.0*
Ca	µeq l^{-1}	*48.0*	*62.5*	*31.0*
Mg	µeq l^{-1}	*54.2*	*75.0*	*25.0*
Na	µeq l^{-1}	*223.0*	*313.0*	*147.8*
K	µeq l^{-1}	*6.4*	*10.3*	*2.6*
SO_4	µeq l^{-1}	*98.5*	*143.8*	*66.7*
xSO_4	µeq l^{-1}	*71.7*	*114.2*	*48.3*
NO_3	µeq l^{-1}	*17.1*	*39.3*	*2.9*
Cl	µeq l^{-1}	*257.2*	*425.4*	*157.7*
Soluble Al	µg l^{-1}	*313.3*	*715.0*	*106.0*
Labile Al	µg l^{-1}	*225.2*	*552.0*	*38.0*
Non-labile Al	µg l^{-1}	*80.9*	*283.0*	*22.0*
DOC	mg l^{-1}	*4.3*	*12.8*	*2.7*
Conductivity	µS cm^{-1}	*52.5*	*78.0*	*31.0*

fossil diatom assemblage from a more recent sediment core, suggest that the loch has progressively acidified, from at least the mid-nineteenth century (pH 5.2) to pH 4.5 by 1989 (Patrick *et al*., 1995).

Water Chemistry

(Figure 4.8.2, Table 4.8.2-3)

Mean lake-water pH and alkalinity at Loch Grannoch are the second lowest in the Network; pH has only exceeded 5.0, and alkalinity exceeded zero, in one sample (summer of 1996). Al concentrations are extremely high, and are dominated by the labile fraction. Mean xSO_4, at 72 µeq l^{-1}, is significantly above that at the nearby Round Loch of Glenhead, appearing to confirm that afforestation has enhanced pollutant inputs (see Section 5.5.2). Significant NO_3 leaching is occurring, with mean concentrations of 17 ueq l^{-1} and a strong seasonal cycle with concentrations ranging over an order of magnitude from 3 to 39 µeq l^{-1}.

Variations in surface water chemistry over the monitoring period have been very similar to those at Round Loch of Glenhead. Marine ions showed a pronounced peak in 1989-1991 (e.g. Figures 4.8.2f,h) producing apparent declining trends in Cl, Na, Mg and Ca. SO_4, and xSO_4 concentrations rose until the mid-1990s but have since shown a marked decline (Figures 4.8.2c,d). No significant trends were obtained for pH or alkalinity, but LOESS curves (Figures 4.8.2a,b) suggest that both may have declined slightly since monitoring began. This would be consistent with MAGIC modelling work by Jenkins *et al*. (1997a), predicting worsening acidification of the Loch despite reduced deposition under a scenario of continued forestry. Alternatively, pH may have been temporarily raised around the onset of monitoring, by the effect of fertiliser run-off enhancing within-lake productivity (see epilithic diatom Section). Time series also suggest that NO_3 may have risen (Figure 4.8.2e), although any change is difficult to identify with confidence given the degree of seasonality. A significant increase was observed in DOC using SKT, of around 1.3 mg l^{-1} over the decade.

Epilithic diatoms

(Figure 4.8.3,Table 4.8.4)

Marked changes in the epilithic flora of Loch Grannoch support the water chemistry evidence that Loch Grannoch has acidified over the past decade. *Tabellaria quadriseptata*, indicative of severely acid conditions, has increased substantially in relative abundance, and particularly since 1994. Prior to 1993, representation of *T. quadriseptata* had never exceeded 5% in any sample but by 1998 it comprised over 50% of valves counted in all samples. This increase has been reciprocally matched by reductions in *Asterionella ralfsii*,

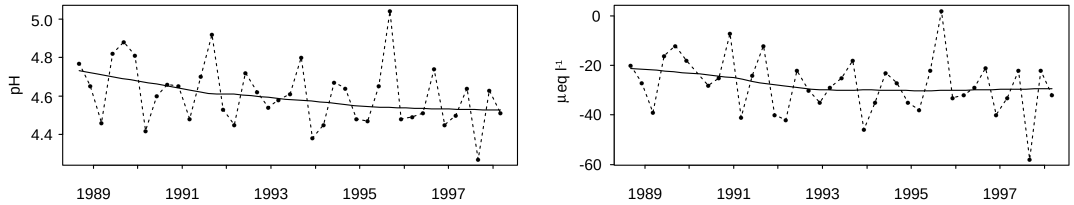
Table 4.8.3

Significant trends in chemical determinands (July 1988 - March 1998)

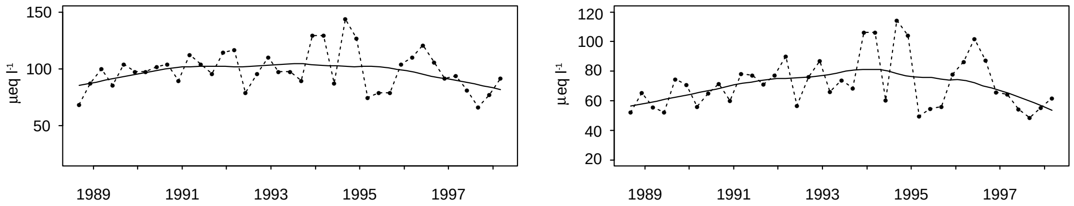
Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
Cl	µeq 1^{-1}	*-8.90**	*-8.45**
Na	µeq 1^{-1}	*-5.48***	*-6.52**
Mg	µeq 1^{-1}	-	*-1.67**
Ca	µeq 1^{-1}	*-1.45****	*-1.65**
DOC	mg l^{-1}	*+0.21**	*+0.13***

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

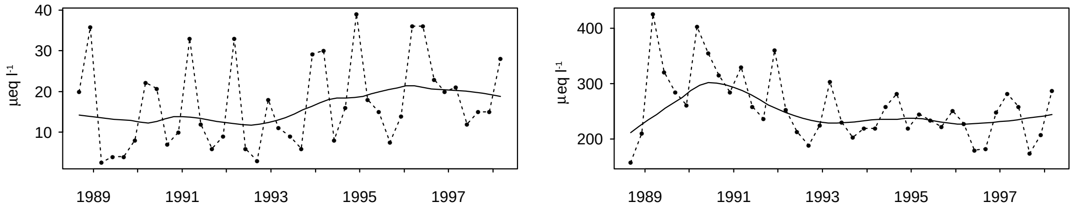
(a) pH (b) Alkalinity



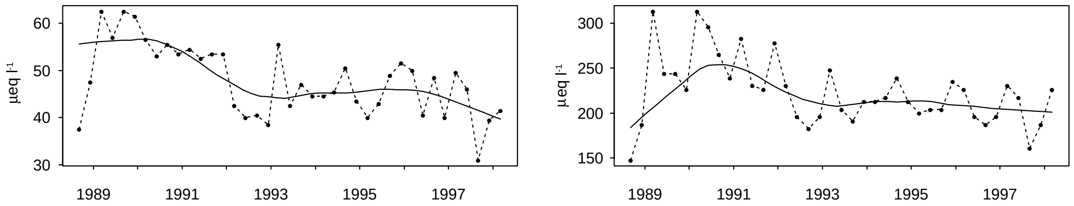
(c) Sulphate (d) Non-marine Sulphate



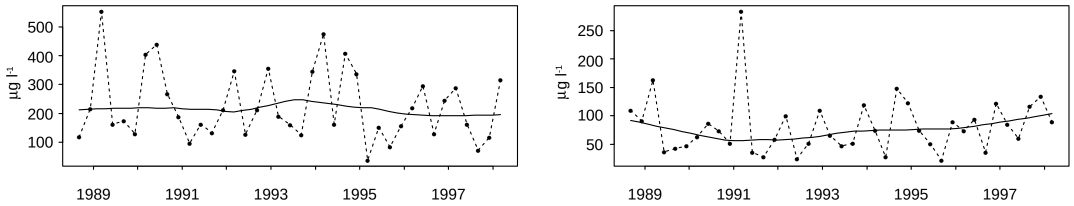
(e) Nitrate (f) Chloride



(g) Calcium (h) Sodium



(i) Labile Al (j) Non-labile Al



(k) Total Soluble Al (l) Dissolved Organic Carbon

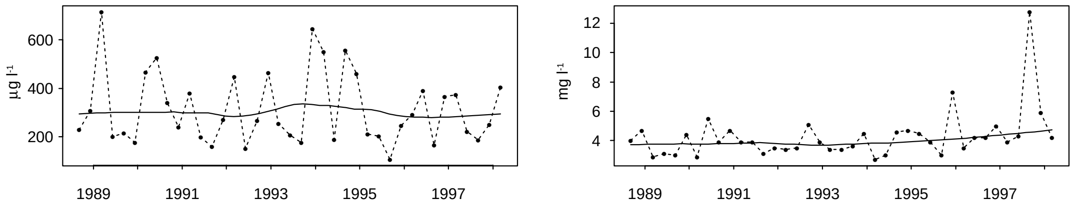


Figure 4.8.2

Loch Grannoch: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.8.4

Loch Grannoch: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_2PCA
Epilithic diatoms	*601*	*102*	*4.3*	*1.57*	*0.82*
Macrophytes	*31*	*22*	*12.8*	*0.83*	*0.59*
Invertebrates	*820*	*44*	*2.8*	*1.02*	*0.64*

Variance explained (%)	within year	between years	linear trend	p	
				unrestricted	restricted
Epilithic diatoms	*40.1*	*59.9*	*26.0*	*< 0.01*	*< 0.01*
Macrophytes	*	*	*25.5*	*0.05*	*0.07*
Invertebrates	*46.6*	*53.4*	*13.1*	*< 0.01*	*< 0.01*

Pinnularia subcapitata var. *hilseana* and *Tabellaria flocculosa*, the latter two having slightly higher pH optima and the former the same as *T. quadriseptata* (pH optima 4.9). *A. ralfsii* was only observed in the Loch in abundance for the first time in 1988, and being characteristic of peatland disturbance and nutrient enrichment (Liehu *et al.*, 1986), its occurence was attributed to phosphorus and potassium fertiliser application which peaked around 1985. Sediment cores demonstrate that, prior to the expansion of this species, *T. quadriseptata* was the dominant diatom, and sediment trap samples (Figure 4.8.6) suggest that the last ten years has seen a gradual return to the pre-1988 flora, with *T. quadriseptata* at similar abundances now to then. These data therefore provide an alternative explanation for the recently observed pH decline, as this would be expected following a decline in within-lake productivity, following a decline in lake nutrients. For the epilithic diatom assemblage, time as a linear variable is highly significant at the 0.01 level according to RDA and associated permutation tests, and can account for 26% of between-sample variance. This is close to the maximum variance which can be explained by the 1st axis in Principal Components Analysis (i.e. 32%) and therefore emphasises the strength of the unidirectional change in the species assemblage with time.

■ Macroinvertebrates

(Figure 4.8.4, Table 4.8.4)

The macroinvertebrate fauna is dominated by the acid tolerant mayfly family, the Leptophlebiidae, and by the Chironomidae. Other mayflies present include *Siphlonurus lacustris* and *Ameletus inopinatus* which have both shown an increase in abundance in the last few years. Only two individuals of the acid sensitive *Baetis* spp. were recorded, in 1993 and 1994. The stonefly community was most abundant in the first four years of monitoring and included acid tolerant *Nemoura* spp. and *Nemurella pictetii*. More recently the stoneflies have been impoverished and were absent in 1998. The first few years were also characterised by a diverse community of corixids and water beetles. These have declined in recent years with only *Potamonectes depressus* being present throughout the survey. Of the caddisflies, *Plectrocnemia* spp. and *Polycentropus* spp. were both present in most years up to 1995, while *Cyrnus* spp. appeared in 1994. Several species of case-bearing caddis have been recorded intermittently (e.g. *Agrypnia varia*, *Anabolia nervosa* and *Oecetis ochracea*). Time as a linear trend is significant at the 0.01 level according to RDA and associated permutation tests. There appears to have been a

Table 4.8.5

Loch Grannoch: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Drepanocladus fluitans[4]	*1*	*1*	*1*	*1*	*2*	*1*	*2*	*1*
Sphagnum auriculatum[4]	*3*	*3*	*3*	*3*	*4*	*4*	*4*	*4*
Juncus bulbosus var. *fluitans*[4]	*2*	*2*	*2*	*2*	*3*	*2*	*3*	*2*
OTHER SUBMERGED OR FLOATING LEAF SPECIES								
Filamentous green algae	*2*	*3*	*3*	*1*	*1*	*1*	*1*	*2*
Amblystegium sp.	*0*	*1*	*1*	*0*	*1*	*0*	*1*	*0*
Atrichum sp.	*1*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
Brachythecium sp.	*1*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Calliergon sp.	*1*	*1*	*0*	*0*	*1*	*0*	*1*	*0*
Hygrohypnum sp.	*1*	*1*	*2*	*1*	*0*	*1*	*0*	*1*
Mnium hornum	*1*	*1*	*1*	*1*	*1*	*0*	*1*	*0*
Plagiomnium sp.	*0*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Cephalozia connivens	*0*	*0*	*1*	*0*	*0*	*0*	*0*	*0*
Marsupella emarginata	*0*	*1*	*1*	*1*	*1*	*1*	*1*	*0*
Nardia compressa	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*4*
Isoetes lacustris	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*4*
Littorella uniflora	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Lobelia dortmanna	*2*	*2*	*2*	*2*	*2*	*3*	*3*	*3*
Nymphaea alba	*0*	*1*	*1*	*1*	*1*	*2*	*2*	*1*
Glyceria fluitans	*0*	*1*	*1*	*0*	*0*	*0*	*0*	*0*
EMERGENT SPECIES								
Equisetum fluviatile	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Ranunculus flammula	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
Carex rostrata	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Eleocharis palustris	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Juncus acutifloris/articulatus	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Phragmites australis	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
TOTAL NUMBER OF SPECIES	*19*	*23*	*21*	*18*	*19*	*17*	*19*	*16*

shift in species representation to a fauna indicative of less acid conditions, although the concomitant decline observed in species richness would normally be associated with worsening conditions. It is interesting to note that, although water chemistry LOESS plots suggest an overall deterioration in pH over the decade, there is an upward trend in March pH which appears to relate to a decline in climatically driven episodic effects.

■ Fish

(Figure 4.8.5)

The outflow of Loch Grannoch has been electrofished since 1989, although very few fish have been captured. The length frequency histogram shows that all these fish were old specimens and no recruitment has taken place at the site since at least 1989.

Aquatic macrophytes

(Tables 4.8.4-5)

As for the neighbouring Round Loch of Glenhead, the submerged aquatic macrophyte flora of Loch Grannoch is also limited to the relatively few species tolerant of high levels of acidity, i.e., *Isoetes lacustris*, *Lobelia dortmanna*, *Littorella uniflora* and *Juncus bulbosus* var. *fluitans*. Several emergent species, including *Phragmites australis* and *Equisetum fluviatile*, in addition to floating-leaved stands of *Nymphaea alba*, are also present in restricted locations, probably benefiting from the shelter offered by a more complex shoreline. The acidophilous moss *Sphagnum auriculatum* forms a substantial carpet over large areas of the Loch bottom at the north end, while another moss associated with particularly acid conditions, *Drepanocladus fluitans* has also been recorded at low abundance, in most years. There is no significant time trend in the DAFOR adundance data using RDA and associated restricted permutation test.

Summary

Loch Grannoch is severely acidified, with conditions seemingly worsened by the presence of forestry. Non-marine sulphate concentrations are high, and significant nitrogen leaching is occurring. Time series suggest that, if anything, pH and alkalinity are continuing to decline at the site, but trends are partly obscured by both pronounced seasonal cycles for a number of determinands, and the impact of large interannual fluctuations in marine ions. It is also possible that recent changes represent a gradual return to conditions prior to fertilizer application to the catchment in the mid-1980s. The trout population of the outflow burn has remained particularly low, while the aquatic macrophyte assemblage has been stable. Species changes in the other two biological groups provide conflicting indications of direction of change in acidity. The macroinvertebrates may have benefited from a general improvement in spring acidity resulting from a reduction in sea-salt deposition and spring rainfall generated episodes, while the epilithic diatoms seem to indicate a more general deterioration in conditions experienced during the growing season.

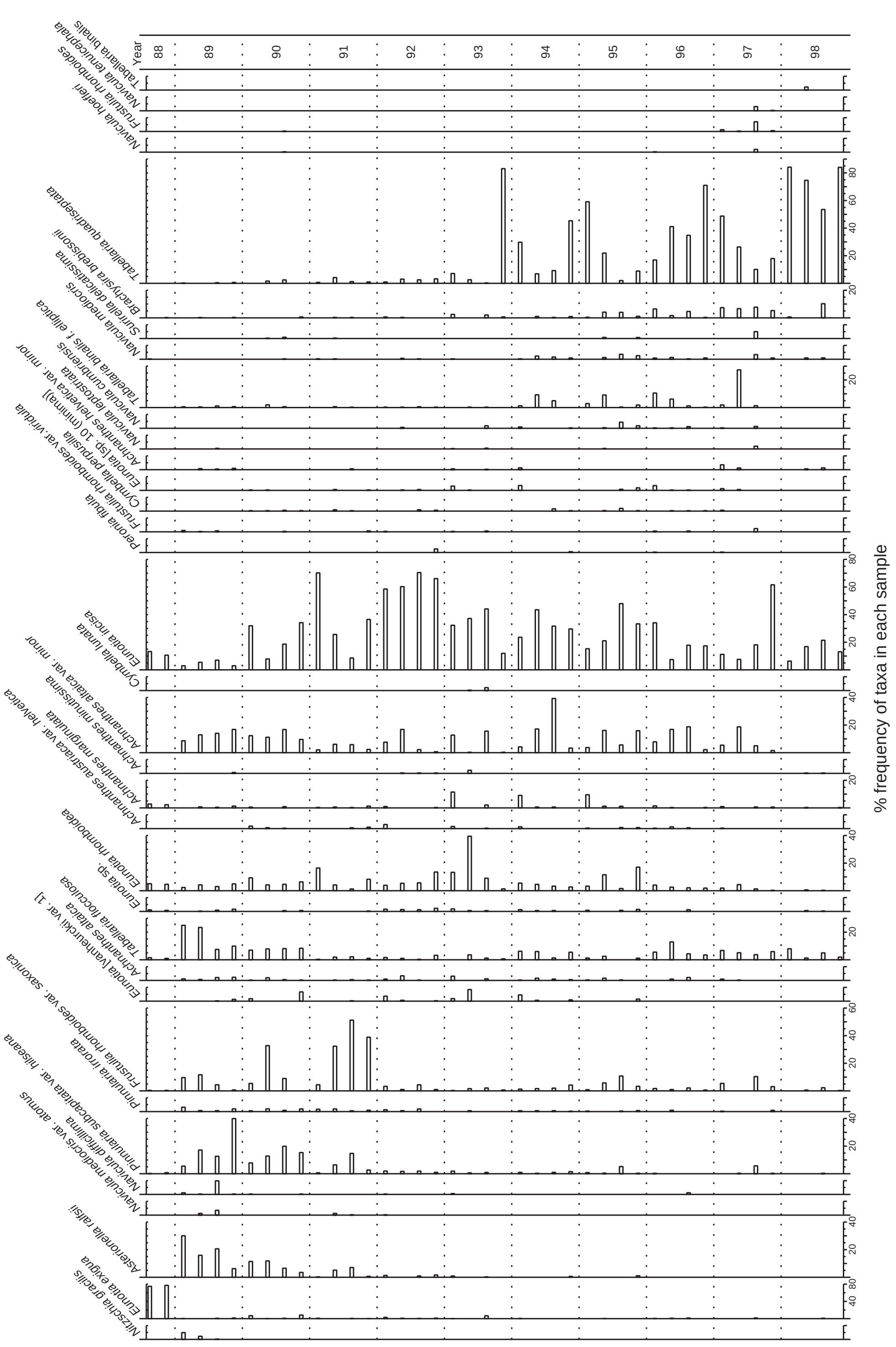


Figure 4.8.3

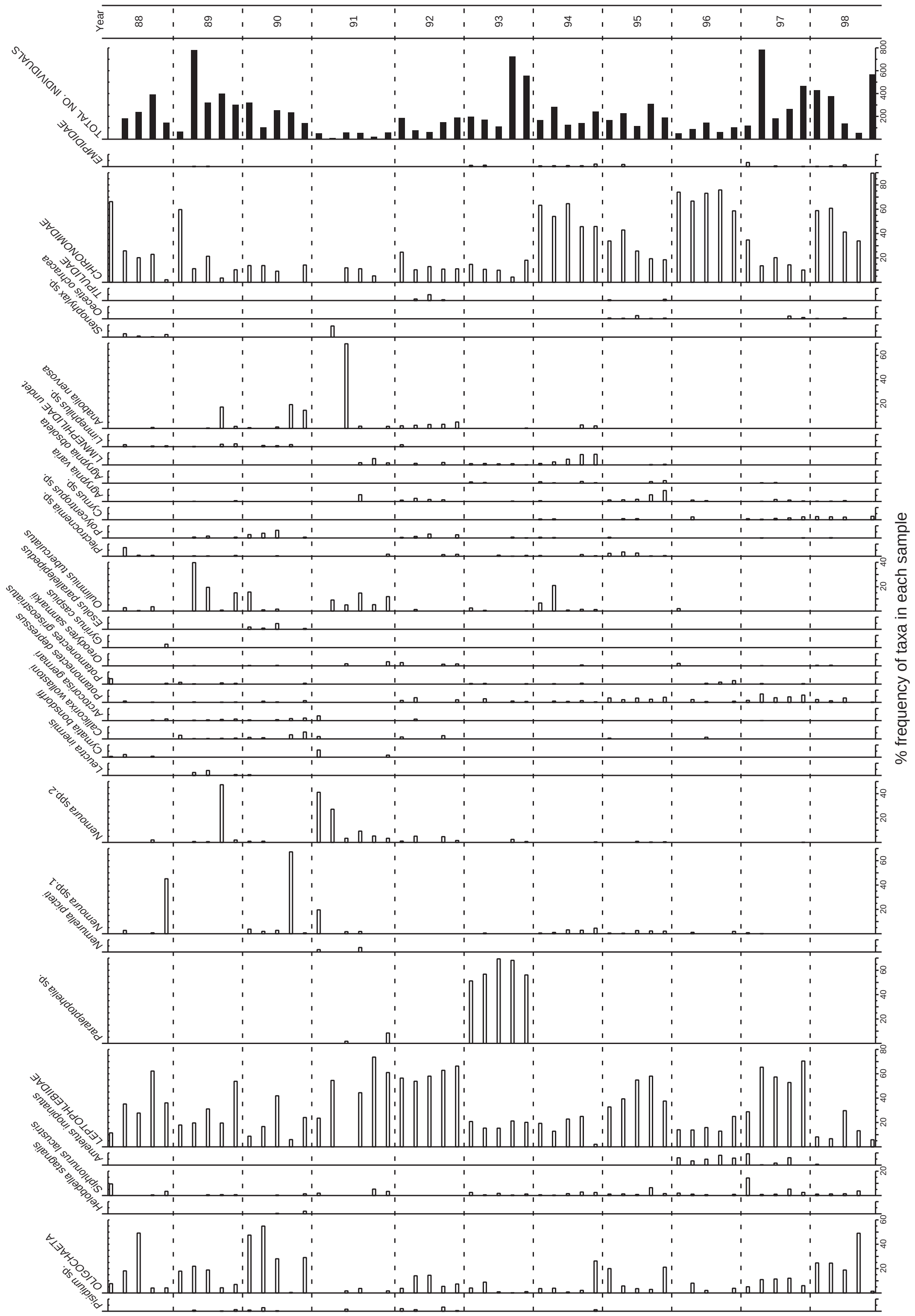
Loch Grannoch: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

Figure 4.8.4

Loch Grannoch: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples



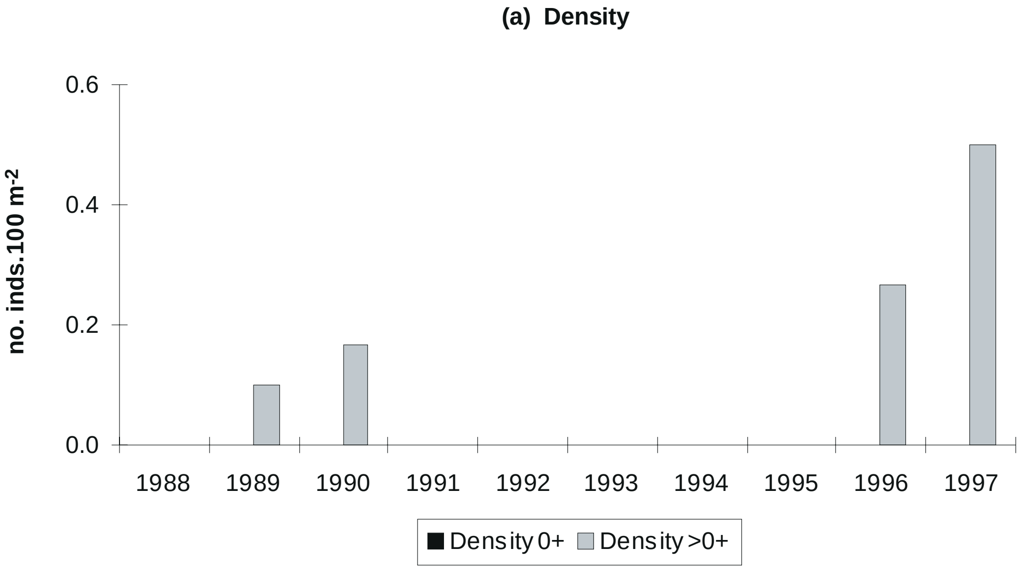


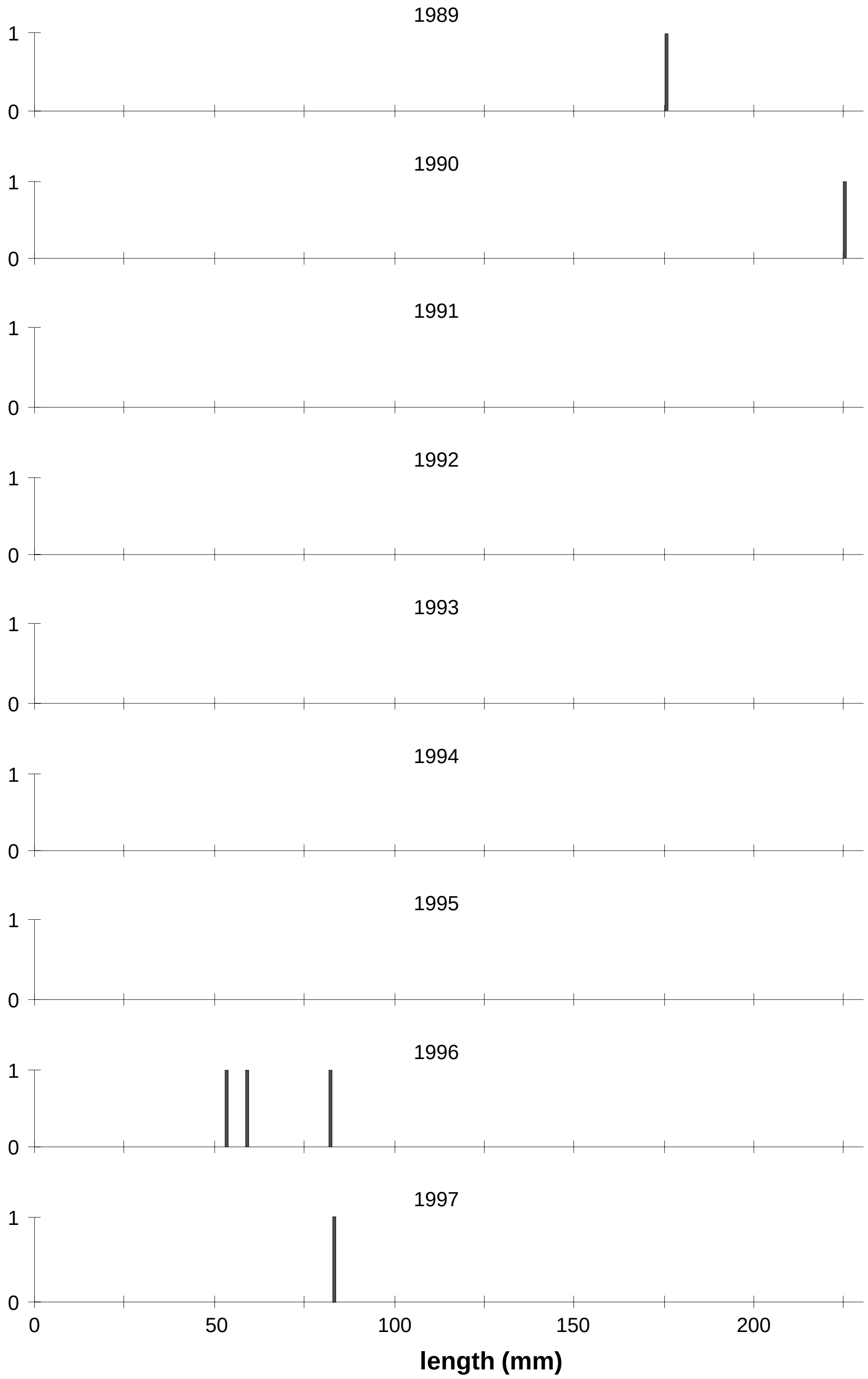
Figure 4.8.5

Loch Grannoch: summary of fish data (1989 - 1997)

(a) Trout population density for 0+ and >0+ age classes (individual 100 m^{-2})

Figure 4.8.5

Loch Grannoch: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries



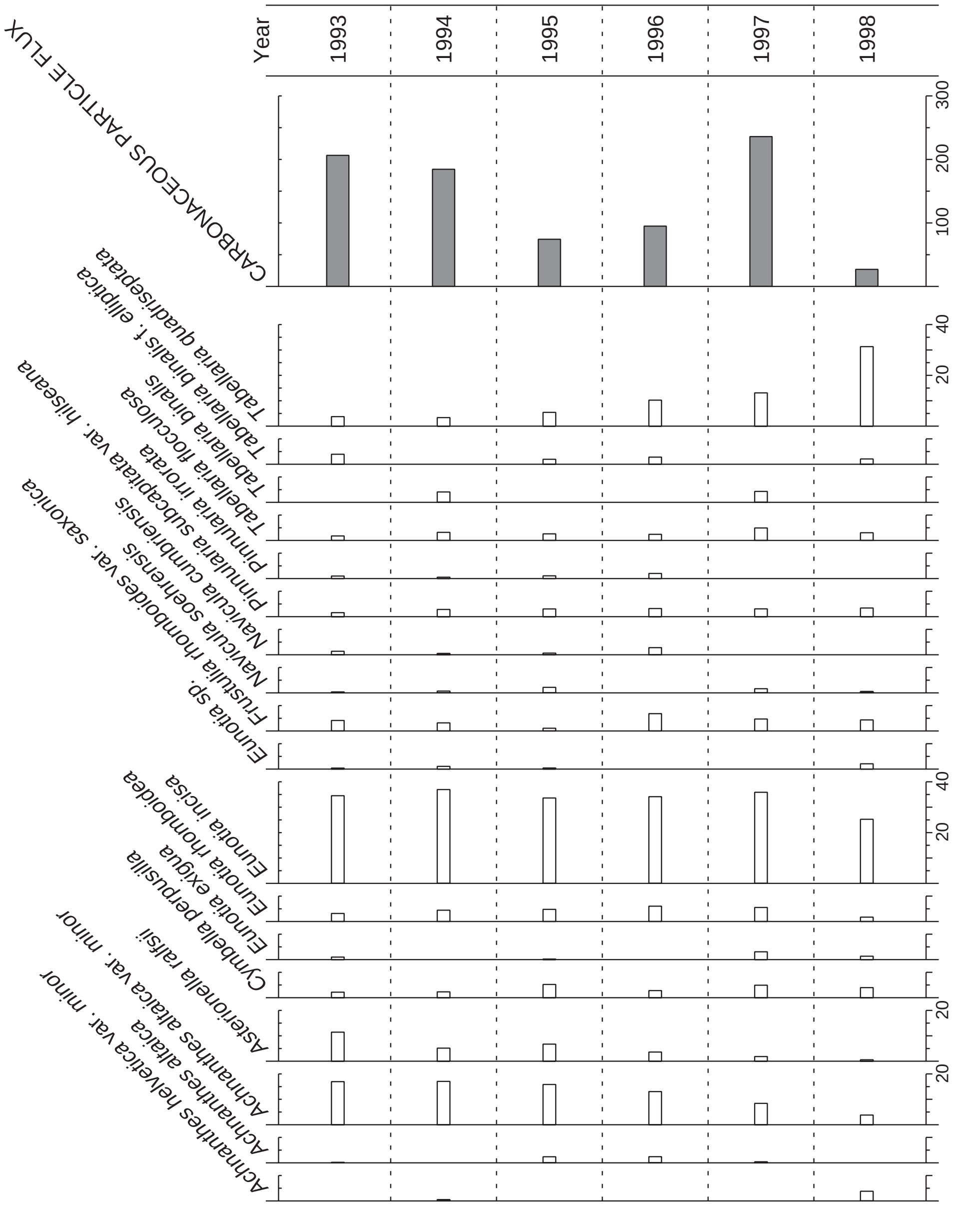


Figure 4.8.6

Loch Grannoch: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year

4.9 Dargall Lane

Site Review

The Dargall Lane burn, a tributary of Loch Dee, runs approximately 2 km to the south of Round Loch of Glenhead in the Galloway region of southwest Scotland. The site has been subject to considerable hydrochemical and biological investigation since 1980 (e.g. Burns *et al.*, 1984; Cosby *et al.*, 1986; Harriman *et al.*, 1997; Langan, 1987; Giusti & Neal, 1993). No catchment disturbances have been observed since the onset of monitoring by the UKAWMN in 1988.

Water Chemistry

(Figure 4.9.2, Tables 4.9.2-3)

Dargall Lane is less acidic than the two Galloway lochs, although mean alkalinity is only 4 µeq l^{-1} and frequently becomes negative. Mean xSO_4 is higher than at Round Loch of Glenhead, the other moorland site in the region, and Giusti (1999) has argued that weathering of shales at Dargall Lane may constitute a significant internal SO_4 source.

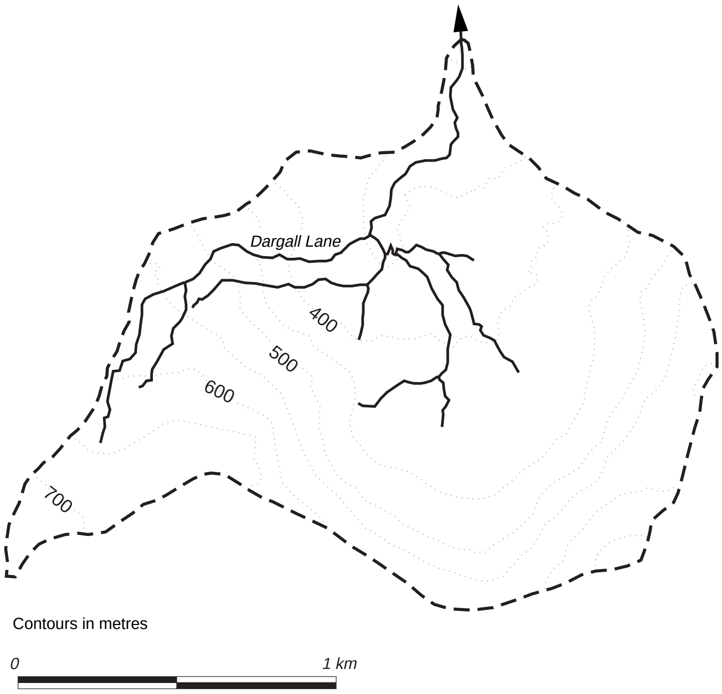


Figure 4.9.1

Dargall Lane: catchment

Table 4.9.1

Dargall Lane: site characteristics

Grid reference	*NX 449786*
Catchment area	*210 ha*
Minimum Catchment altitude	*225 m*
Maximum Catchment altitude	*716 m*
Catchment Geology	*greywackes, shales, mudstones, black shale*
Catchment Soils	*podsols, peaty gleys, blanket peat*
Catchment vegetation	*moorland - 100%*
Mean annual rainfall	*2426 mm*
1996 deposition	
Total S	*30 kg ha^{-1} yr^{-1}*
non-marine S	*25 kg ha^{-1} yr^{-1}*
Oxidised N	*11 kg ha^{-1} yr^{-1}*
Reduced N	*19 kg ha^{-1} yr^{-1}*

Table 4.9.2

Dargall Lane: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.52*	*6.45*	*4.91*
Alkalinity	µeq l^{-1}	*4.0*	*44.0*	*-12.0*
Ca	µeq l^{-1}	*49.5*	*80.5*	*23.0*
Mg	µeq l^{-1}	*53.3*	*83.3*	*25.0*
Na	µeq l^{-1}	*168.7*	*282.6*	*91.3*
K	µeq l^{-1}	*9.2*	*17.9*	*2.6*
SO_4	µeq l^{-1}	*79.8*	*110.4*	*41.7*
xSO_4	µeq l^{-1}	*60.2*	*90.6*	*31.7*
NO_3	µeq l^{-1}	*10.7*	*45.7*	*< 1.4*
Cl	µeq l^{-1}	*186.2*	*366.2*	*95.8*
Soluble Al	µg l^{-1}	*49.3*	*143.0*	*3.0*
Labile Al	µg l^{-1}	*32.6*	*133.0*	*<2.5*
Non-labile Al	µg l^{-1}	*17.0*	*65.0*	*<2.5*
DOC	mg l^{-1}	*1.7*	*5.9*	*0.3*
Conductivity	µS cm^{-1}	*35.3*	*59.0*	*21.0*

Higher Ca concentrations (mean 50 μeq l^{-1}) compared to Round Loch suggest that base cation weathering may also be higher. NO_3 concentrations show a strong seasonal cycle, exceeding 40 μeq l^{-1} during some winters but falling below detection limits for at least three months during every summer of the record (Figure 4.9.2e).

Although this stream exhibits a wider range of chemical variation than the two loch sites, changes in marine ions over time have been similar, with a peak in 1990. Again, this has led to the detection of declining trends for Cl, Na, Mg, and Ca (Table 4.9.3). There is some evidence for reduced acidity at the site, with increasing alkalinity and declining labile Al identified by both SKT and regression, and declining SO_4 by regression. However no accompanying trend is obtained for xSO_4, and time series plots (Figures 4.9.2,c,d) suggest concentrations peaked in the mid-1990s followed by a decrease, as at the other Galloway sites. The more acidic conditions in the early part of the record may be thus in part due to the 'sea-salt' displacement of soil acid cations by elevated marine base cations (Section 5.3) and by a changing flow regime (flow recorded at the time of sampling was generally highest around 1990). DOC and non-labile Al both show significant rising trends, DOC having increased by 1 mg l^{-1} during the last ten years. Dargall Lane has been monitored at high resolution since 1983. These data therefore present a longer term perspective of water chemistry trends and are presented in Chapter 6.

■ Epilithic diatoms

(Figure 4.9.3, Table 4.9.4)

Dargall Lane has undergone considerable variation in epilithic diatom species relative abundances during the past decade. *Peronia fibula* (pH optima 5.3) has been consistently abundant, but there has been an apparent shift from *Eunotia* species with relatively low pH optima (e.g. *E. naegelii* (5.0); *E. incisa* (5.1))in the early 1990s to an abundance of *Tabellaria flocculosa* (pH optima 5.4) between 1992-1997. These changes are consistent with LOESS plots for pH and alkalinity at this site which indicate apparent amelioration in water chemistry over the same period. *Eunotia* species increased in abundance again in 1998, indicating that the observed changes are perhaps more cyclical and climatically driven, rather than linear "recovery" responses. "Sample year" is not significant at the 0.01 level according to RDA analysis and associated permutation test.

Table 4.9.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
Alkalinity	μeq l^{-1}	*+0.92**	*+0.85**
SO_4	μeq l^{-1}	*-0.75**	-
Cl	μeq l^{-1}	*-6.59****	*-5.63**
Na	μeq l^{-1}	*-4.43****	*-4.35**
Mg	μeq l^{-1}	*-1.33****	*-1.39**
Ca	μeq l^{-1}	*-0.95***	*-1.17**
DOC	mg l^{-1}	*+0.11****	*+0.10***
Non-labile Al	μg l^{-1}	-	*+0.86**
Labile Al	μg l^{-1}	*-2.15**	*-1.33**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

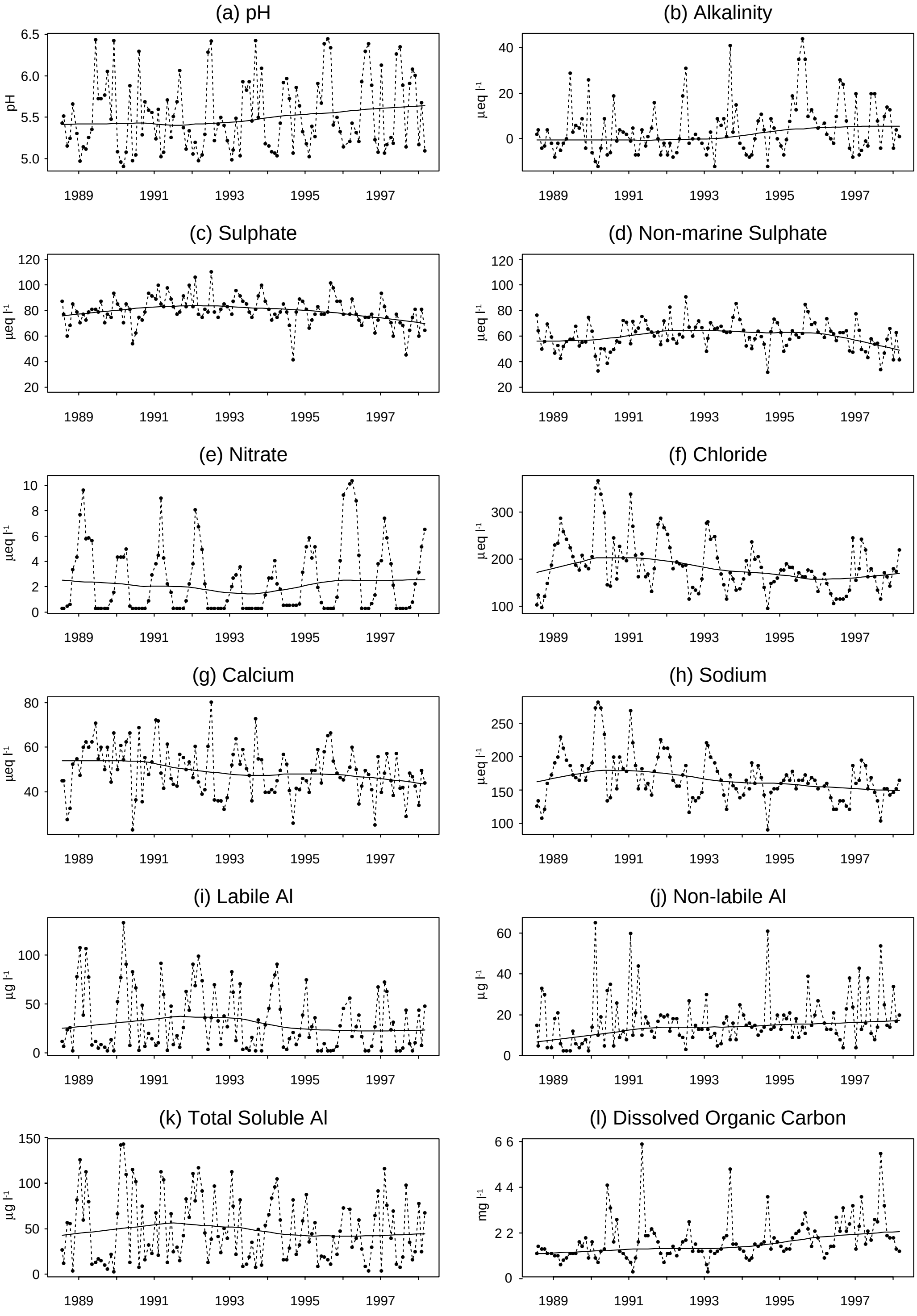


Figure 4.9.2

Dargall Lane: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.9.4

Dargall Lane: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*155*	*79*	*4.4*	*0.24*	*0.21*
Macrophytes	*25.5*	*6*	*1.9*	*0.12*	*0.12*
Invertebrates	*395*	*24*	*4.8*	*0.19*	*0.18*

Variance				p	
explained (%)	**within year**	**between years**	**linear trend**	**unrestricted**	**restricted**
Epilithic diatoms	*41.8*	*58.2*	*6.6*	*0.04*	*0.22*
Macrophytes	*	*	*8.0*	*0.55*	*0.78*
Invertebrates	*45.6*	*54.4*	*6.0*	*0.02*	*0.43*

■ Macroinvertebrates

(Figure 4.9.4, Table 4.9.4)

The fauna of Dargall Lane is characterised by acid tolerant species. Detritivorous stoneflies dominate with *Amphinemura sulcicollis* occurring in the highest densities. Other stoneflies include *Leuctra inermis*, *Leuctra hippopus* and the predatory *Isoperla grammatica* and *Siphonoperla torrentium.* The acid tolerant *Plectrocnemia* spp. was recorded throughout the study. Over the monitoring period there has been an increase in species richness with a few species not tolerant of acid conditions such as *Oxyethira* spp. and *Hydropsyche siltalai* appearing in the last 5 years. This shift in species composition may therefore indicate a decrease in acidity (however see Section 7.4.2). RDA shows no significant linear trend between years.

■ Fish

(Figure 4.9.5)

Although this site has been electrofished since 1988, weighing of fish only commenced in the following year. Total trout density is intermediate for UKAWMN sites. Mean population density of both 0+ and >0+ fish has varied widely between years and no temporal trends are apparent. The condition factor of the 0+ fish underwent a steady decline between 1989 and 1995, but the past two years have seen an increase back to 1989 levels. There are no significant linear trends in the mean condition factor or coefficient of variation of the condition factor for either age group.

■ Aquatic macrophytes

(Tables 4.9.4-5)

The aquatic macroflora of the Dargall Lane consists almost exclusively of bryophytes, and in particular the acid tolerant liverwort species, *Scapania undulata* and *Nardia compressa*. A third species, *Marsupella emarginata* is also recorded consistently. Estimates of the cover of individual species appear to have been affected by the sporadic occurence of filamentous green algae which has a strong influence on the overall cover estimates of each survey section. There is no evidence of a linear time trend in species cover according to RDA and associated permutation test.

Table 4.9.5

Dargall Lane: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**96**	**97**
INDICATOR SPECIES									
Nardia compressa[4]	*0.3*	*9.0*	*31.4*	*34.6*	*25.9*	*23.3*	*26.8*	*24.0*	*5.9*
OTHER SUBMERGED OR FLOATING SPECIES									
Filamentous green algae	*10.9*	*25.4*	*9.8*	*5.5*	*0.6*	*0.6*	*9.3*	*0.8*	*46.5*
Marsupella emarginata	*0.0*	*<0.1*	*0.0*	*0.3*	*2.3*	*0.1*	*1.1*	*0.6*	*0.0*
Pellia sp.	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
Scapania undulata	*15.4*	*15.6*	*7.9*	*6.7*	*5.9*	*4.1*	*14.8*	*8.3*	*2.1*
Juncus bulbosus var. *fluitans*	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
total macrophyte cover excluding filamentous algae	*15.7*	*24.6*	*39.3*	*41.6*	*34.1*	*27.5*	*42.7*	*32.9*	*8.0*
TOTAL NUMBER OF SPECIES	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*3*

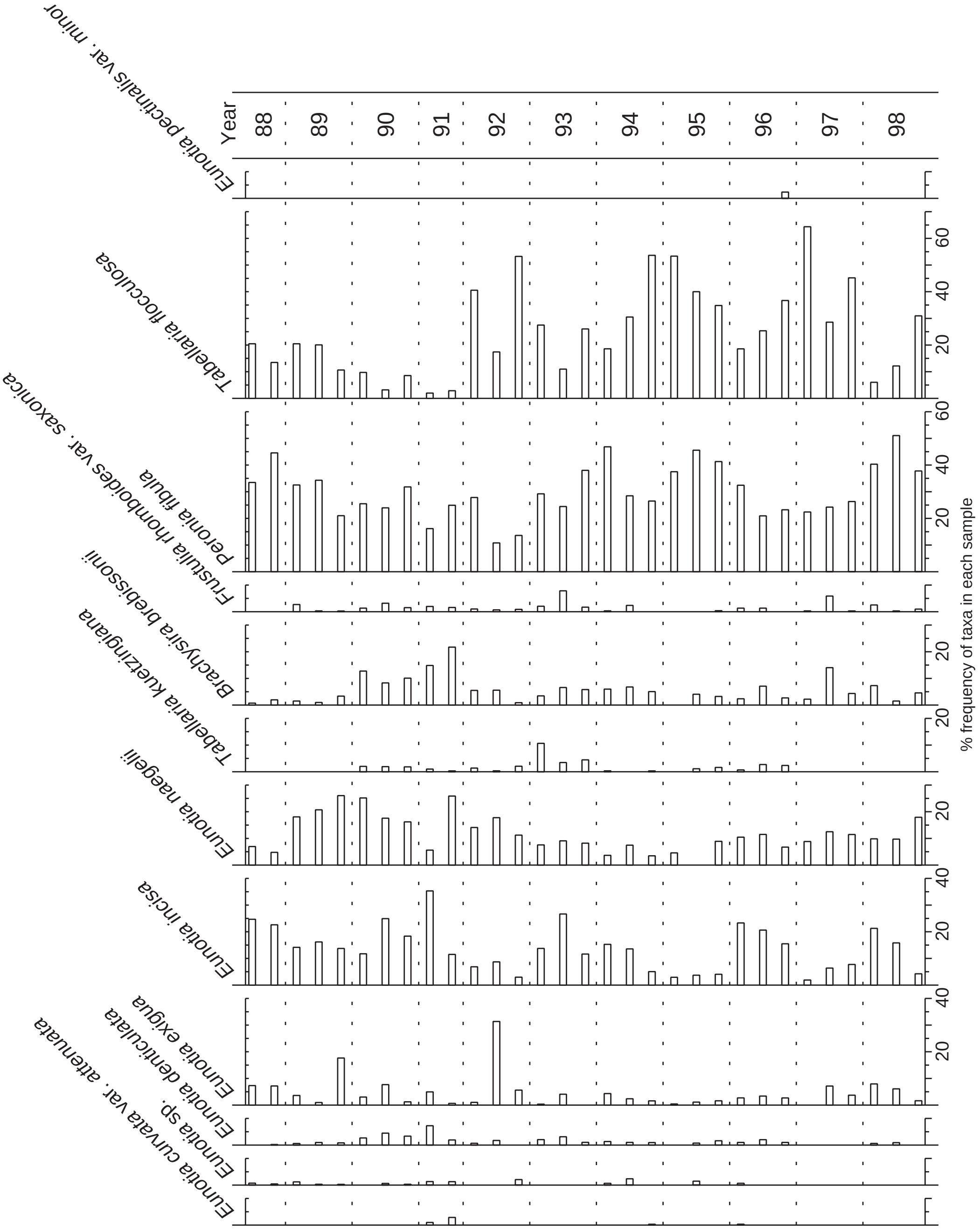
Summary

Dargall Lane is less acidic than the nearby loch sites, due to a higher supply of base cations within the catchment, but it frequently becomes acidic during higher flows. An apparent increase in alkalinity over the monitoring period is not accompanied by clear changes in xSO_4 or NO_3. This may therefore, as at other sites, represent a response to a decline in marine ion inputs and rainfall which were high during the early part of the record. Changes in the epilithic diatom and macroinvertebrate communities are consistent with a general reduction in acidity in recent years although neither are significant as linear trends. DOC and non-labile Al concentrations have both risen significantly since 1988.

Figure 4.9.3

Dargall Lane: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



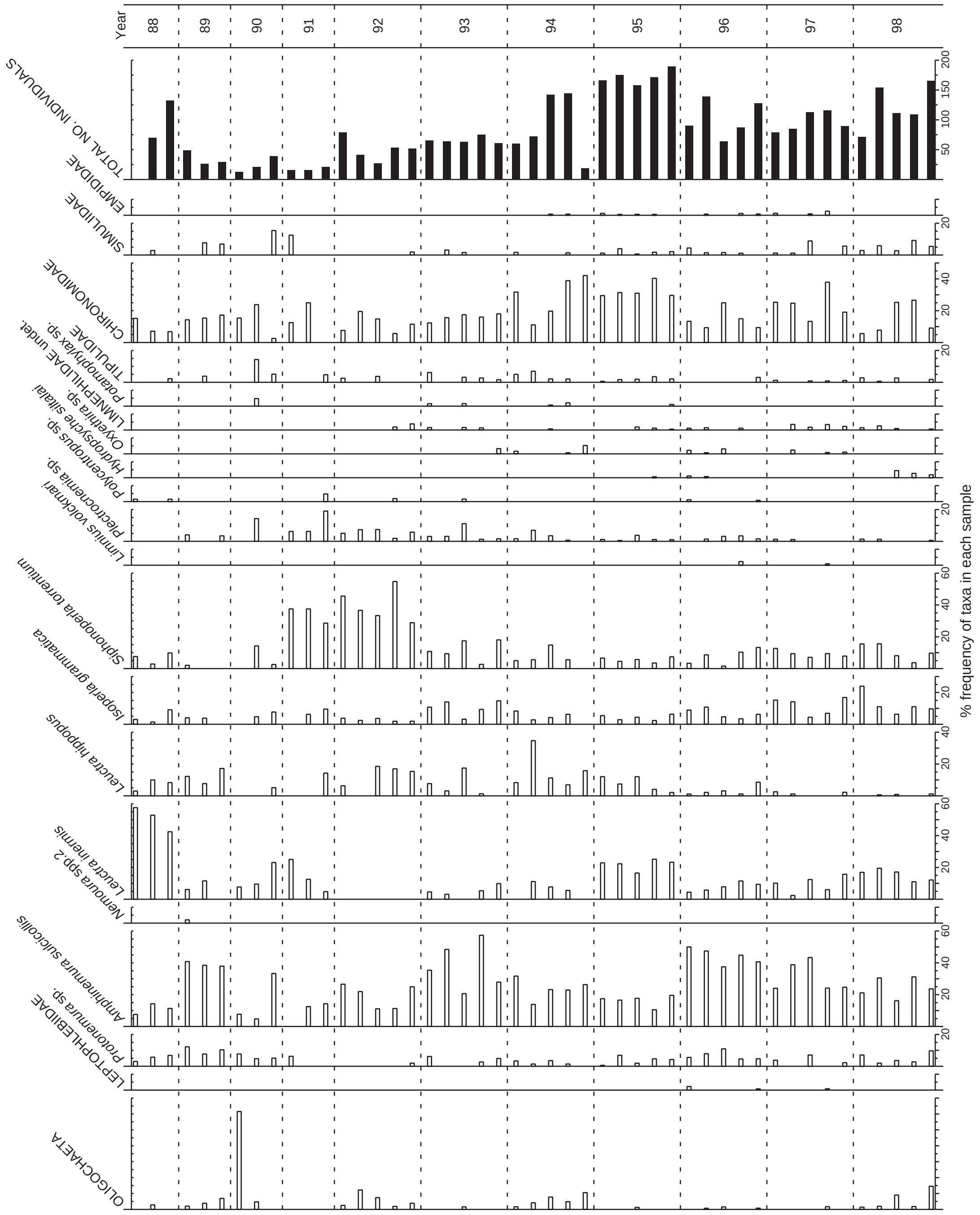


Figure 4.9.4

Dargall Lane: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

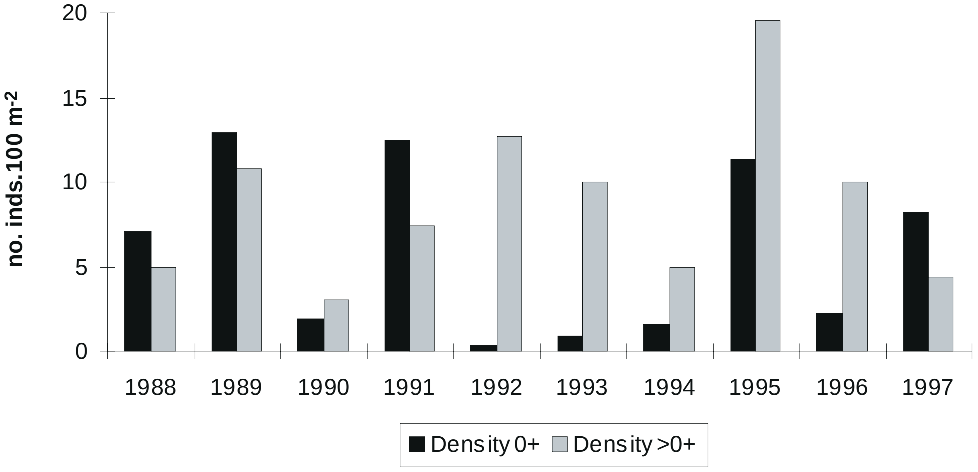
Figure 4.9.5

Dargall Lane: summary of fish data (1988 - 1997)

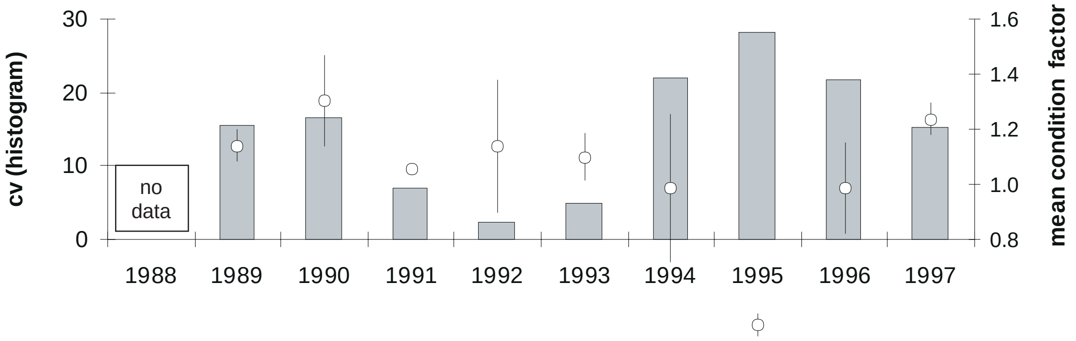
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

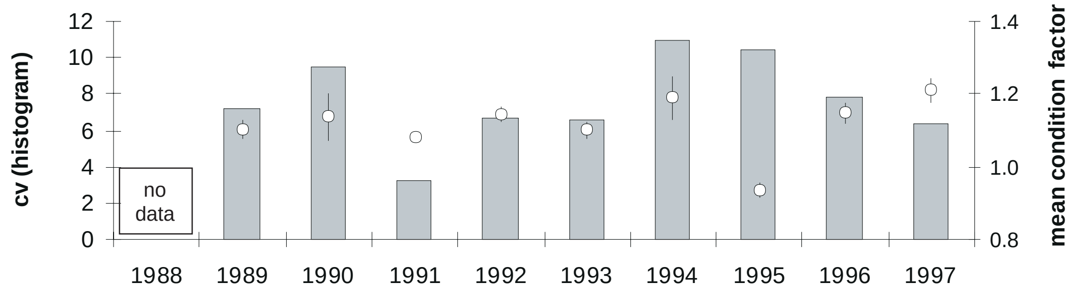
(a) Density



(b) Condition (0+)



Condition (>0+)



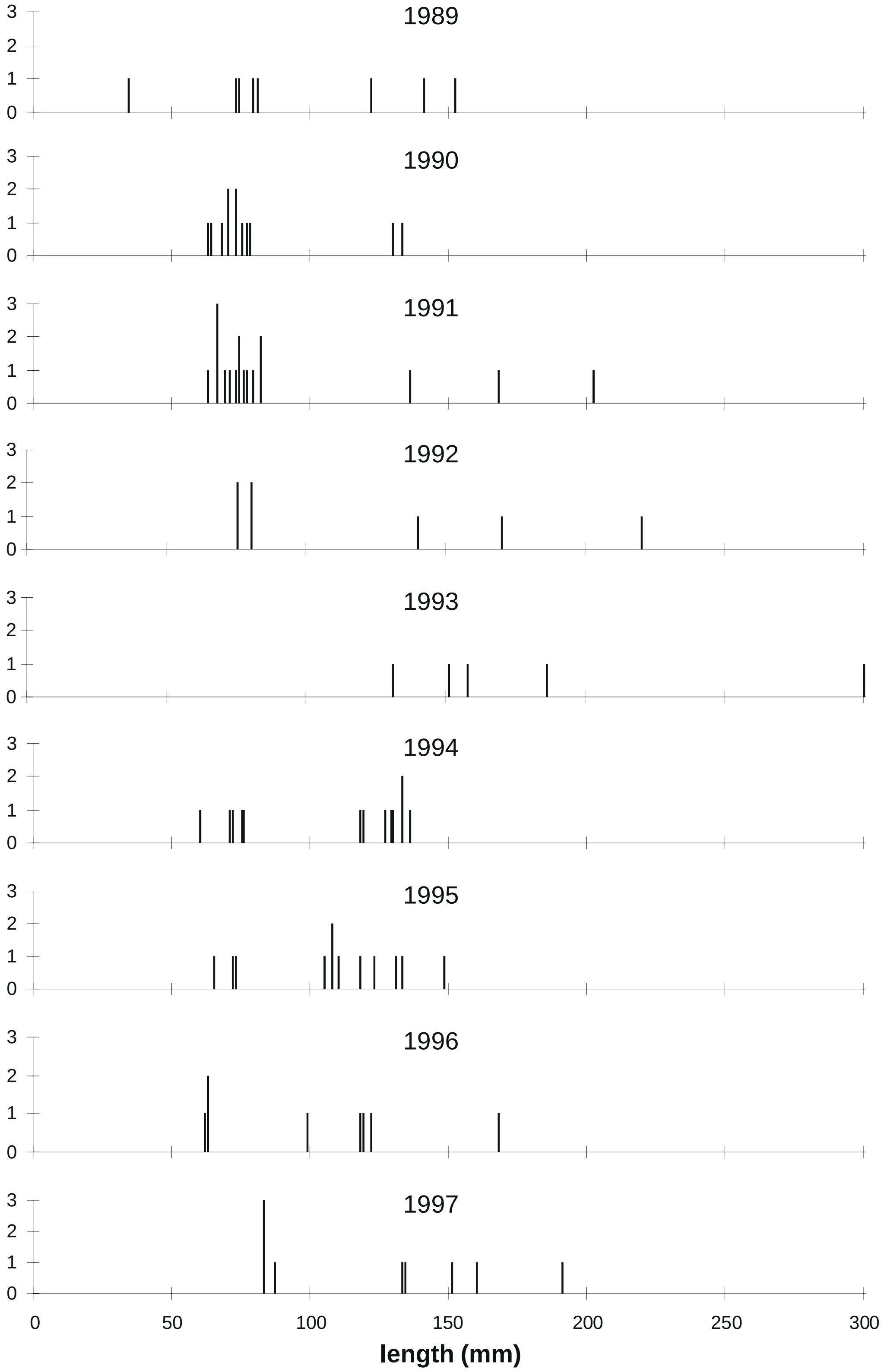


Figure 4.9.5

Dargall Lane: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries

4.10 Scoat Tarn

Site Review

Scoat Tarn is one of the highest of the Tarns in the English Lake District. Diatom-based pH reconstruction, using a sediment core taken in 1989, suggests that the site has acidified from around pH 5.9 in the early nineteenth century, to pH 4.7 in the 1980s (Patrick *et al.* 1995). There is no evidence of any physical disturbance or changes in grazing regime in the catchment over the past decade. Since the recent addition of an atmospheric deposition collector within the catchment, samples are also being analysed by the UK Acid Deposition Network. This should enhance understanding of the relationship between deposition and surface water chemistry at the site over the coming years.

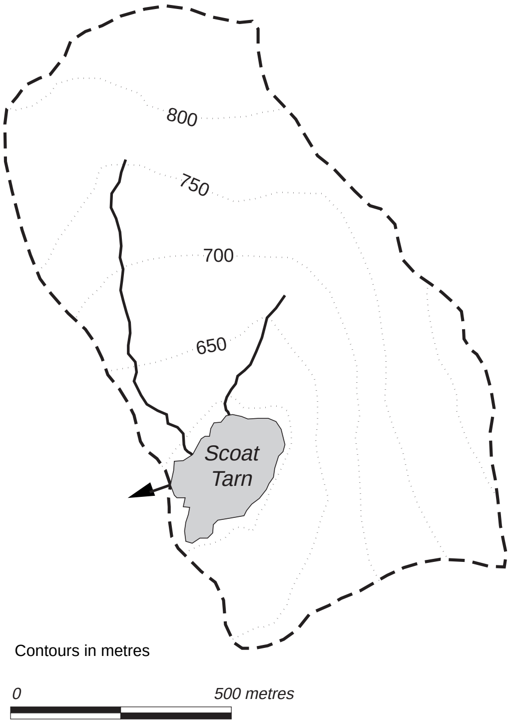


Figure 4.10.1

Scoat Tarn: catchment

Water Chemistry

(Figure 4.10.2, Tables 4.10.2-3)

With a mean pH of 4.99 and a mean alkalinity of 8 μeq l^{-1}, Scoat Tarn is the fifth most acidic site in

Table 4.10.1

Scoat Tarn: site characteristics

Grid reference	*NY 159104*
Lake altitude	*602 m*
Maximum Depth	*20 m*
Mean Depth	*10 m*
Volume	*4.2 x 10^5 m^3*
Lake Area	*5.2 ha*
Catchment area (excl. lake)	*95 ha*
Catchment: Lake area ratio	*18.2*
Catchment Geology	*Borrowdale volcanics*
Catchment Soils	*shallow peaty rankers*
Catchment vegetation	*moorland - 100%*
Net Relief	*239 m*
Mean annual rainfall	
1996 deposition	*3482 mm*
Total S	*31 kg ha^{-1} yr^{-1}*
non-marine S	*26 kg ha^{-1} yr^{-1}*
Oxidised N	*12 kg ha^{-1} yr^{-1}*
Reduced N	*23 kg ha^{-1} yr^{-1}*

Table 4.10.2

Scoat Tarn: summary of chemical determinands, June 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*4.99*	*5.23*	*4.57*
Alkalinity	μeq l^{-1}	*-8.4*	*6.0*	*-26.0*
Ca	μeq l^{-1}	*32.5*	*48.0*	*23.0*
Mg	μeq l^{-1}	*48.3*	*75.0*	*33.3*
Na	μeq l^{-1}	*163.9*	*265.2*	*126.1*
K	μeq l^{-1}	*7.9*	*15.4*	*2.6*
SO_4	μeq l^{-1}	*60.8*	*72.9*	*35.4*
xSO_4	μeq l^{-1}	*41.5*	*54.2*	*16.5*
NO_3	μeq l^{-1}	*21.4*	*47.9*	*5.7*
Cl	μeq l^{-1}	*185.6*	*326.8*	*118.3*
Soluble Al	μg l^{-1}	*121.4*	*300.0*	*12.2*
Labile Al	μg l^{-1}	*108.9*	*293.8*	*2.5*
Non-labile Al	μg l^{-1}	*12.6*	*76.0*	*3.0*
DOC	mg l^{-1}	*0.9*	*2.7*	*<0.1*
Conductivity	μS cm^{-1}	*35.1*	*49.0*	*24.0*

the UKAWMN. Alkalinity has only been positive during one period in 1995, and Al concentrations are high and dominated by the labile fraction. Although xSO_4 concentrations are slightly lower than at the Galloway sites (mean 41.5 μeq l^{-1}), NO_3 concentrations are higher, with a mean of 21.4 μeq l^{-1}. The mean $NO_3/(NO_3 + xSO_4)$ ratio of 0.34 demonstrates that NO_3 is a major contributor to acidity at this site. In five of the ten years of data, NO_3 concentrations exceeded those of xSO_4 on an equivalent basis in spring, implying that NO_3 is the main acidifying anion at a time when pH and alkalinity tend to be lowest. Ca concentrations are low (mean 32.5 μeq l^{-1}), indicating that the thin soils of this high elevation catchment have little capacity to buffer acid inputs.

Time series for Scoat Tarn (Figure 4.10.2) show striking similarities to those observed in Galloway; concentrations of Cl and Na rise to a pronounced peak in 1990-1991 before falling to much lower levels in the later part of the record. This suggests strongly that the two regions, both of which border the Irish Sea, have experienced the same variability in marine ion deposition over the last decade. Again this appears to have influenced non-marine ions, with Ca showing the same cyclical variation over the monitoring period. As a result of these changes, declining trends are observed for both Na and Ca using regression analysis. An increase in pH and decrease in labile Al are observed using both trend detection methods, which would seem to indicate recovery at the site. However since high marine cation inputs are likely to have caused displacement of H^+ and Al from the soil during the early part of the record, while higher winter/spring rainfall probably reduced the proportion of the flow contribution from groundwater, it is possible that these trends are the result of climatic variation. This hypothesis is supported by the lack of clear trends for xSO_4, which appears to show the same mid-1990s peak as at the Galloway sites, or for NO_3, which shows no clear pattern other than a strong seasonal cycle. DOC, as at other sites, exhibits a highly significant rising trend, with an estimated increase of 1 mg l^{-1} from a 1988-1989 mean concentration of only 0.5 mg l^{-1}. Although the rate of increase is similar to many other sites, the proportional increase is relatively large and might be expected to have an observable effect on water transparency. However, secchi disc measurements taken each summer provide no evidence of any decrease in light attenuation in the visible spectrum at this time of year.

■ Epilithic diatoms

(Figure 4.10.3, Table 4.10.4)

Scoat Tarn is dominated by *Eunotia* taxa which tend to have low pH optima, and particularly *E.incisa* (pH optima 5.1). As at several other sites, *E. incisa* was particularly abundant in 1989 (only 1 sample collected), 1990, and in 1998. Uni-directional trends in species abundance have only occurred with a few relatively rare taxa. For

Table 4.10.3

Significant trends in chemical determinands (July 1988 - March 1998)

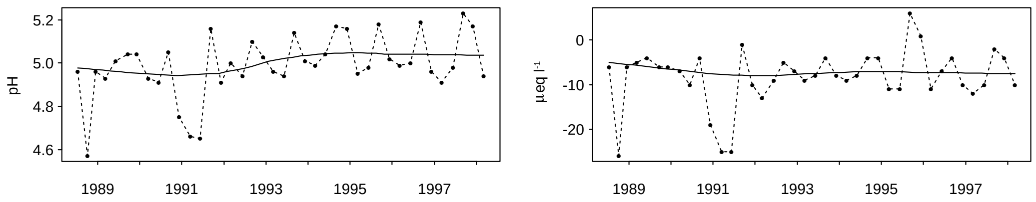
Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
pH		*+0.021***	*+0.013**
Na	μeq l^{-1}	*-3.83**	-
Ca	μeq l^{-1}	*-0.85**	-
DOC	mg l^{-1}	*+0.12****	*+0.10****
Labile Al	μg l^{-1}	*-6.89**	*-7.67**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

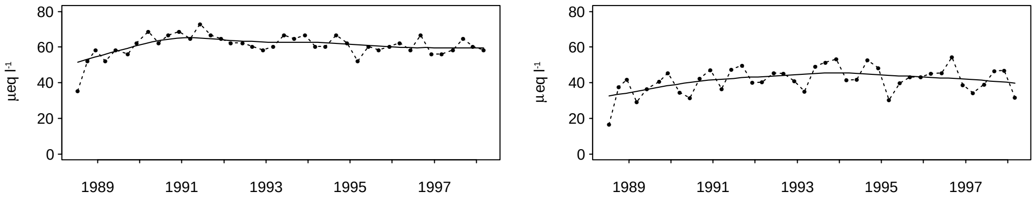
Figure 4.10.2

Scoat Tarn: summary of major chemical determinands (July 1989 - March 1997)

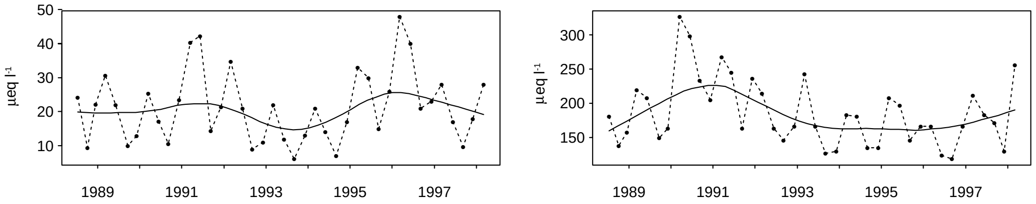
Smoothed line represents LOESS curve (Section 3.1.2)


(a) pH

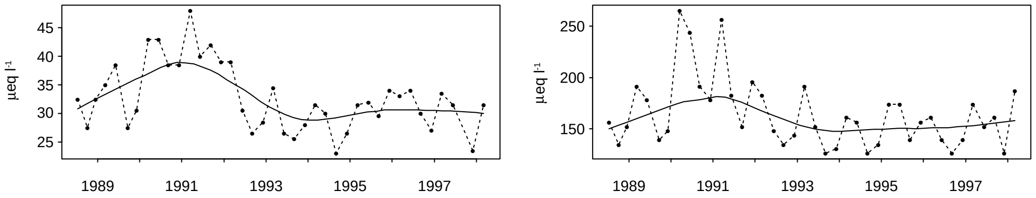
(b) Alkalinity


(c) Sulphate

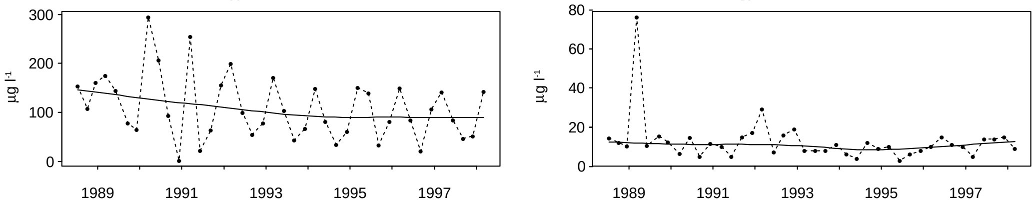
(d) Non-marine Sulphate


(e) Nitrate

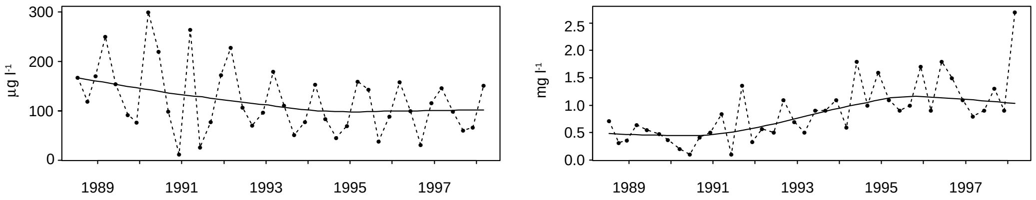
(f) Chloride


(g) Calcium

(h) Sodium


(i) Labile Al

(j) Non-labile Al


(k) Total Soluble Al

(l) Dissolved Organic Carbon

Table 4.10.4

Scoat Tarn: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*360*	*149*	*7.0*	*0.51*	*0.47*
Macrophytes	*38*	*24*	*13.6*	*0.66*	*0.51*
Invertebrates	*1185*	*31*	*1.2*	*0.69*	*0.61*

Variance explained (%)	within year	between years	linear trend	p unrestricted	 restricted
Epilithic diatoms	*50.1*	*49.9*	*9.2*	*<0.01*	*0.02*
Macrophytes	*	*	*19.9*	*0.17*	*0.33*
Invertebrates	*65.5*	*34.5*	*12.0*	*<0.01*	*<0.01*

example *E. monodon* and *E. bigibba* were only recorded until 1991, while *E. vanheurckii* and *Aulacoseira distans* var. *nivalis* have increased slightly in more recent years. These apparently temporal changes are slight compared to the overall variability between samples and "sample year" is not significant according to RDA and associated restricted permutation test. The diatom species assemblage of sediment trap samples collected since 1991 also show no obvious time trend (Figure 4.10.6). The species balance in these samples differs from the epilithon, with *Tabellaria binalis* the dominant taxon and *E.incisa* relatively rare.

■ Macroinvertebrates

(Figure 4.10.4, Table 4.10.4)

The fauna, typical of an acid lake, is species poor and dominated by chironomids. The first four years were characterised by a diversity of dytiscid beetles such as *Agabus arcticus*, *A. bipustulatus* and *Hydroporus lacustris*. However, in more recent years these species have been absent. Other common taxa include the acid tolerant caddisfly group, the polycentropodids. *Plectrocnemia* spp. was the dominant caddisfly in the first eight years of the survey. *Polycentropus* spp. was first observed in 1995, and *Cyrnus* spp. in 1996. Detritivorous acid tolerant stoneflies (*Nemoura* spp., *Leuctra hippopus* and *Leuctra nigra*) were recorded in low numbers in intermittent years. One mayfly individual, *Ephemerella ignita* was recorded in 1997. There is a significant linear time trend, but changes are largely within the acid tolerant polycentropodid group and are not indicative of a change in acidity.

■ Fish

(Figure 4.10.5)

The outflow stream from Scoat Tarn has been electrofished since 1989. Population densities are very low and no 0+ trout have been caught. Densities of >0+ fish, whilst fluctuating, increased slightly between 1989-1994. Since then there have been three successive years of decline and densities in 1997 were the lowest recorded. Neither the mean condition factor nor the coefficient of variation of the condition factor shows any pattern over the years. The length frequency histograms illustrate the atypical nature of the population present at this site.

The trout population of the sampling stretch does not therefore demonstrate any response to the significant decline in the concentration of soluble labile Al over the nine years. However, given the low concentration of DOC, Al levels are still in excess of those considered to be physiologically detrimental.

Table 4.10.5

Scoat Tarn: relative abundance of aquatic macrophyte flora (1988 - 1997)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Sphagnum auriculatum[4]	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Juncus bulbosus var. *fluitans*[4]	*3*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
OTHER SUBMERGED OR FLOATING SPECIES								
Filamentous green algae	*2*	*2*	*2*	*2*	*2*	*2*	*1*	*1*
Amblystegium sp.	*1*	*1*	*0*	*2*	*0*	*1*	*0*	*1*
Brachythecium sp.	*0*	*1*	*0*	*0*	*0*	*1*	*0*	*0*
Campylopus sp.	*0*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Dicranella sp.	*1*	*1*	*1*	*0*	*0*	*1*	*0*	*1*
Hygrohypnum eugyrium	*0*	*0*	*0*	*1*	*0*	*0*	*0*	*0*
Hyocomium armoricum	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
Pohlia sp.	*0*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Polytrichum sp.	*1*	*1*	*1*	*1*	*0*	*1*	*0*	*1*
Racomitrium aquaticum	*2*	*2*	*1*	*1*	*1*	*1*	*1*	*1*
Rhytidiadelphus squarrosus	*1*	*1*	*1*	*0*	*0*	*1*	*0*	*1*
Sphagnum auriculatum	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Cephalozia bicuspidata	*1*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Diplophyllum albicans	*0*	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Marsupella emarginata	*1*	*2*	*2*	*1*	*2*	*0*	*2*	*1*
Nardia compressa	*2*	*2*	*4*	*4*	*4*	*4*	*4*	*3*
Plectocolea obovata	*2*	*2*	*2*	*2*	*1*	*2*	*1*	*1*
Scapania undulata	*0*	*1*	*1*	*1*	*1*	*0*	*1*	*0*
Isoetes echinospora	*1*	*1*	*1*	*1*	*1*	*0*	*0*	*1*
Isoetes lacustris	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*4*
Littorella uniflora	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Lobelia dortmanna	*2*	*2*	*2*	*1*	*1*	*1*	*1*	*1*
Sparganium angustifolium	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
TOTAL NUMBER OF SPECIES	*18*	*23*	*18*	*18*	*15*	*17*	*14*	*18*

■ Aquatic macrophytes

(Tables 4.10.4-5)

The aquatic macrophyte flora of Scoat Tarn is very similar to that of the other more acid lakes in the UKAWMN. The isoetids, *Isoetes lacustris*, *Lobelia dortmanna* and *Littorella uniflora* and the acidophilous rush *Juncus bulbosus* var. *fluitans* are the only submerged vascular species. In comparison to the more peat-stained waters of sites, such as Loch Tinker, these plants are able to survive at greater depths, and the deepest growing species, *I. lacustris,* is found to a depth of 4.2 m. Perhaps surprisingly, despite a doubling in DOC over the decade, which might have led to a reduction in transparency, there is no evidence of any reduction in the depth limit of *I. lacustris* with time. The acid tolerant *Sparganium angustifolium* which has floating leaves, is present in the bay of one inflow stream. Scoat

Tarn also supports a diverse aquatic bryophyte flora, amongst which the acidophilous species *Sphagnum auriculatum* is dominant. Again, due to the high transparency, bryophytes are able to grow at considerable depths (i.e. >10 m). "Sample year" is insignificant as a linear trend according to RDA and associated permutation test.

■ Summary

Scoat Tarn is chronically acidic, with alkalinity below zero in 95% of samples. NO_3 is a more important contributor to acidity here than at any other UKAWMN site, with concentrations frequently exceeding those of xSO_4 during spring. Marine ions exhibit major inter-annual variations, which appear to have a significant impact on lake acidity, whilst DOC and non-labile Al have both increased. Apparent chemical improvements are likely to be climatically driven and do not appear to have had a significant influence on the biology of the Tarn.

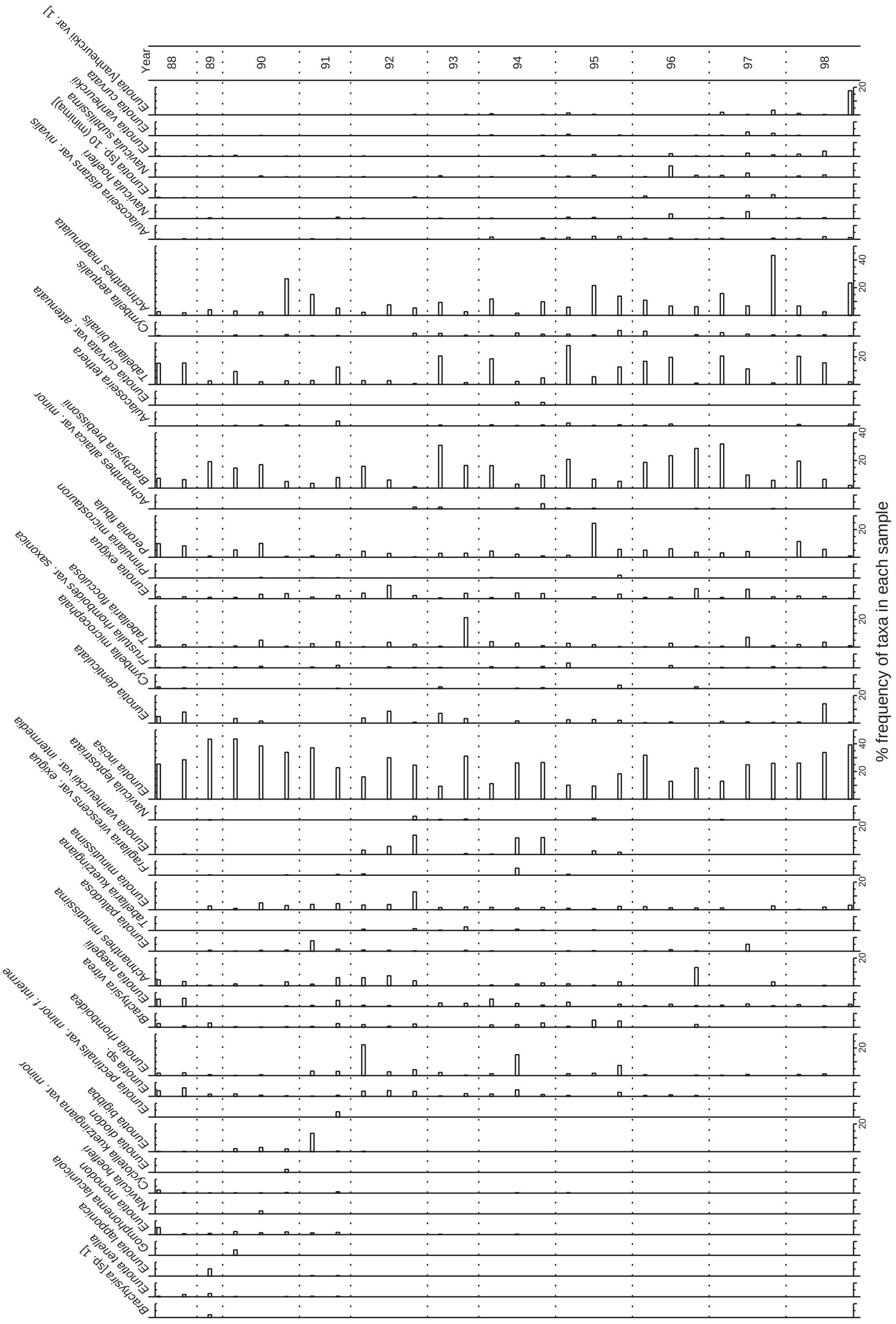


Figure 4.10.3

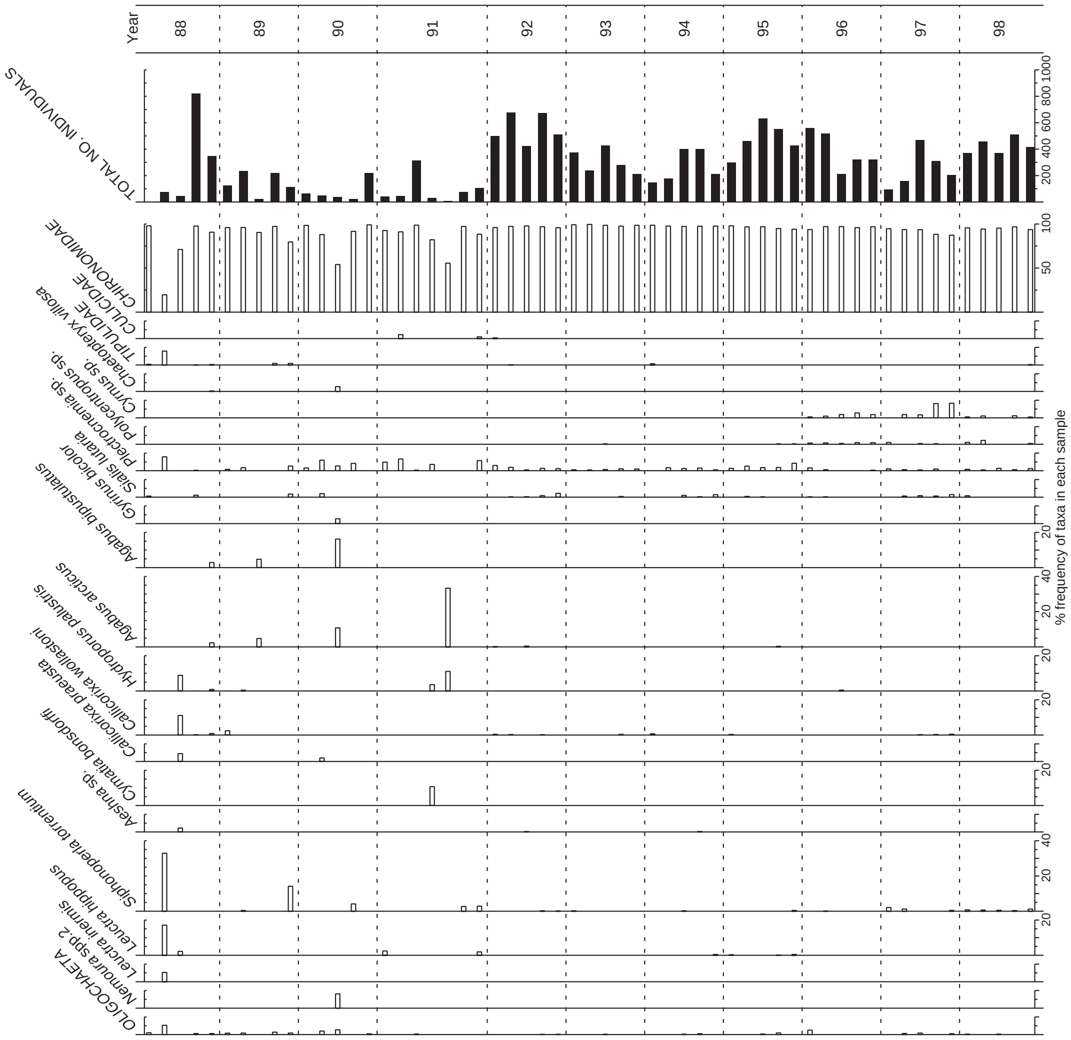
Scoat Tarn: summary of epilithic diatom data (1988 - 1998)

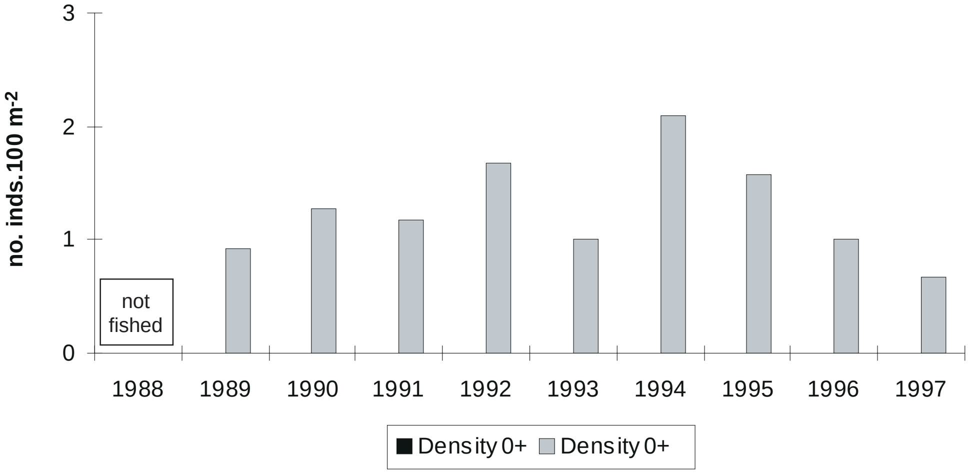
Percentage frequency of all taxa occurring at >2% abundance in any one sample

Figure 4.10.4

Scoat Tarn: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples




(a) Density

(b) Condition (0+)

no 0+ fish caught

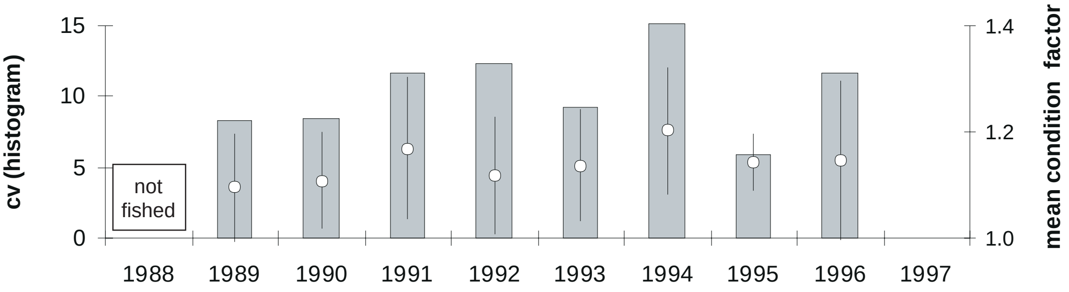

Condition (0+)

Figure 4.10.5

Scoat Tarn: summary of fish data (1989 - 1997)

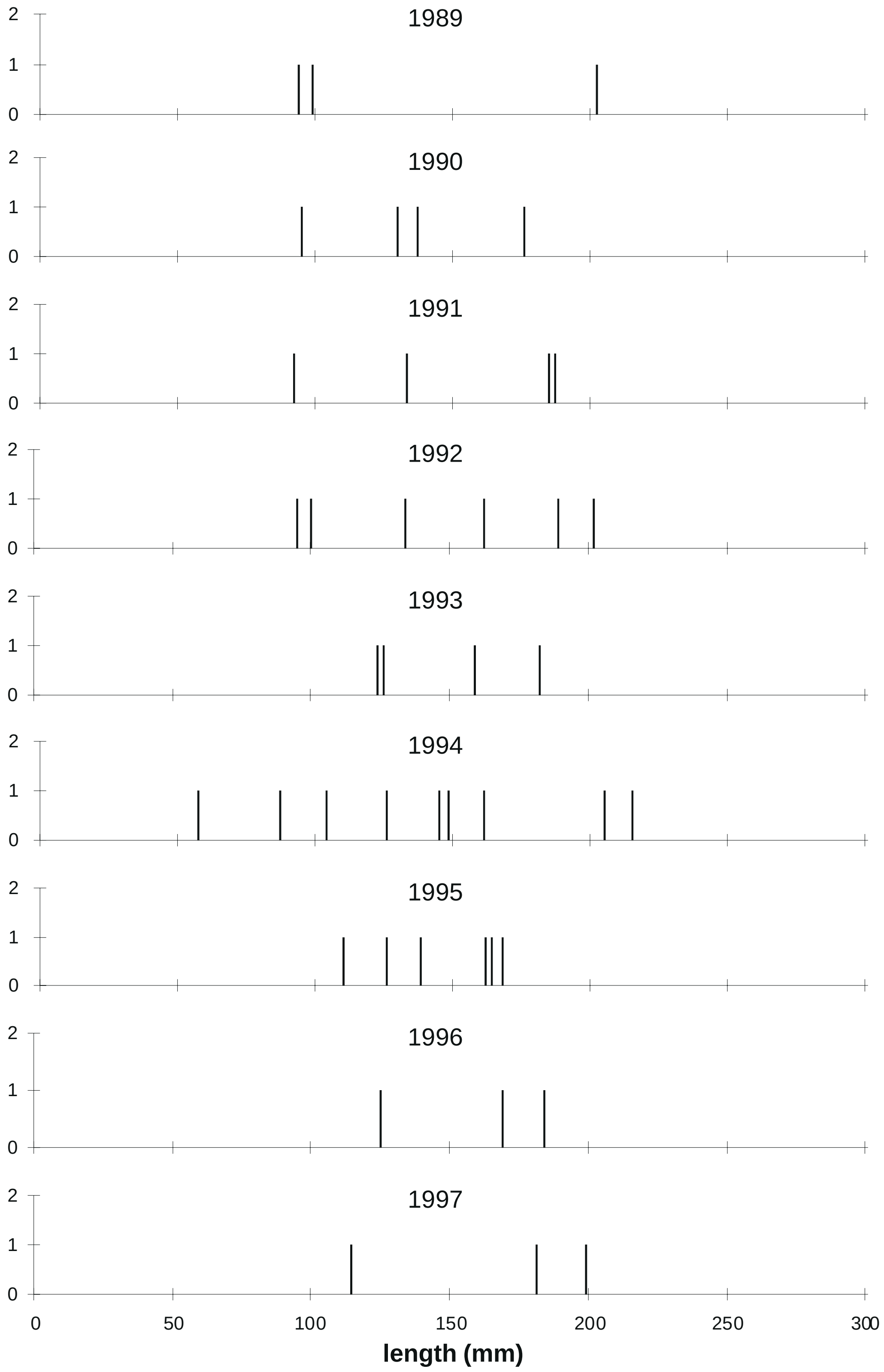
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

Figure 4.10.5

Scoat Tarn: summary of fish data

(c) Trout length frequency summaries (1989 - 1997)



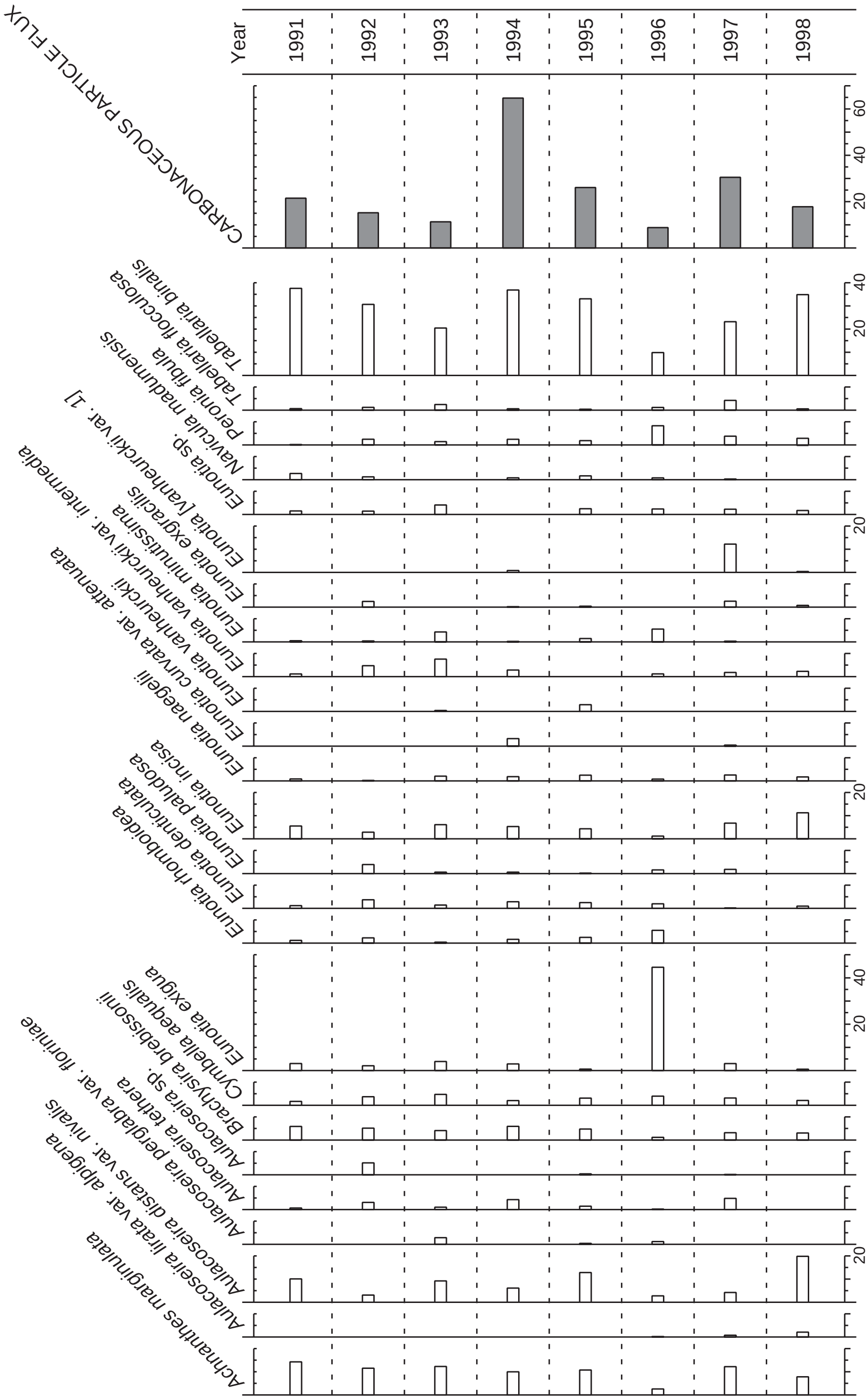


Figure 4.10.6

Scoat Tarn: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year

4.11 Burnmoor Tarn

■ Site Review

In contrast to the neighbouring and highly acidic Scoat Tarn, Burnmoor Tarn benefits from a more weatherable catchment geology and is relatively alkaline. Diatom based pH reconstruction of a sediment core indicates that the site became slightly more acid around the turn of the 20th century (Patrick *et al.*, 1995). Recently however it was observed that at particularly high flows, the more acid Hardrigg Beck can spill over into the outflow end of the Tarn and this may occasionally have an large impact on the chemistry of the Tarn outflow and possibly on the main basin. Catchment vegetation is subject to more intensive grazing than at most other sites and cattle are likely to provide localised nutrient enrichment and physical disturbance of the littoral zone. There is no indication of any major change in the grazing regime or other catchment disturbance since the onset of monitoring in 1988.

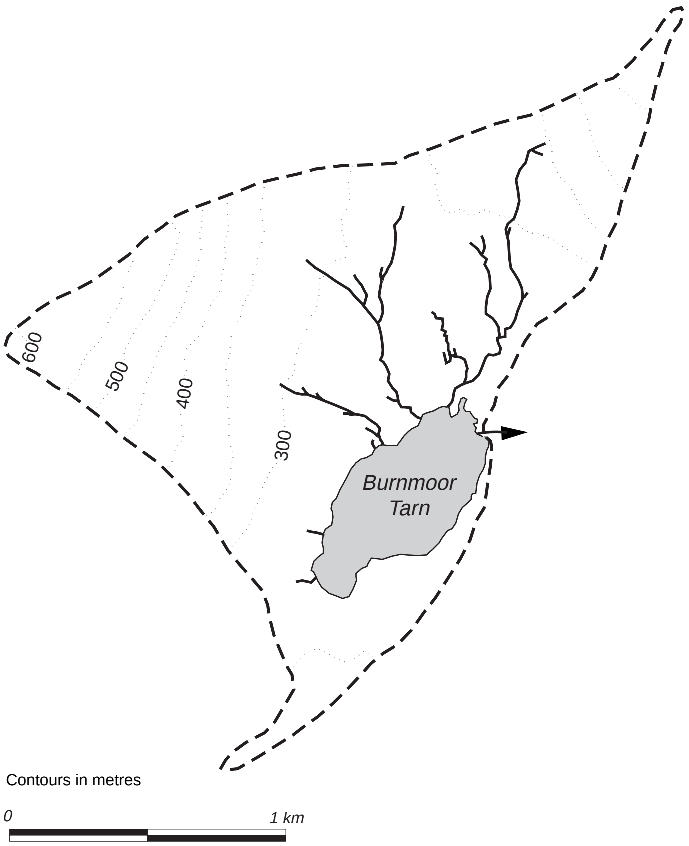


Figure 4.11.1

Burnmoor Tarn: catchment

Table 4.11.1

Burnmoor Tarn: site characteristics

Grid reference	*NY 184044*
Lake altitude	*252 m*
Maximum Depth	*13 m*
Mean Depth	*5.1 m*
Volume	*8.9 x* 10^5 m^3
Lake Area	*24 ha*
Catchment area (excl. lake)	*226 ha*
Catchment: Lake area ratio	*9.4*
Catchment Geology	*andesite lava and granite*
Catchment Soils	*podsols, shallow peat, rankers*
Catchment vegetation	*moorland - 100%*
Net Relief	*350 m*
Mean annual rainfall	*2210 mm*
1996 deposition	
Total S	*25 kg* ha^{-1} yr^{-1}
non-marine S	*21 kg* ha^{-1} yr^{-1}
Oxidised N	*9 kg* ha^{-1} yr^{-1}
Reduced N	*19 kg* ha^{-1} yr^{-1}

Table 4.11.2

Burnmoor Tarn: summary of chemical determinands, June 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*6.48*	*6.99*	*4.38*
Alkalinity	µeq l^{-1}	*47.8*	*96.0*	*-44.0*
Ca	µeq l^{-1}	*89.5*	*118.5*	*32.0*
Mg	µeq l^{-1}	*65.0*	*83.3*	*33.3*
Na	µeq l^{-1}	*192.2*	*243.5*	*126.1*
K	µeq l^{-1}	*8.5*	*15.4*	*2.6*
SO_4	µeq l^{-1}	*81.5*	*118.8*	*56.3*
xSO_4	µeq l^{-1}	*59.4*	*102.3*	*38.3*
NO_3	µeq l^{-1}	*5.0*	*12.9*	*<1.4*
Cl	µeq l^{-1}	*209.9*	*287.3*	*129.6*
Soluble Al	µg l^{-1}	*8.1*	*42.0*	*<2.5*
Labile Al	µg l^{-1}	*3.0*	*14.0*	*<2.5*
Non-labile Al	µg l^{-1}	*6.9*	*35.0*	*<2.5*
DOC	mg l^{-1}	*2.0*	*4.7*	*0.9*
Conductivity	µS cm^{-1}	*41.6*	*54.0*	*23.0*

Water Chemistry

(Figure 4.11.2, Tables 4.11.2-3)

Burnmoor Tarn is a well-buffered site, with the second highest mean pH and alkalinity in the Network. Al concentrations are generally low, with labile Al commonly below detection limits, and Ca concentrations are high with a mean of 90 µeq l^{-1}. NO_3 concentrations are low (mean 5 µeq l^{-1}), although they exhibit strong seasonality.

Time series for Burnmoor Tarn (Figure 4.11.2) are dominated by a very severe episode in late 1993, when pH dropped from an antecedent value of 6.75 to 4.38, and alkalinity from 67 to -44 µeq l^{-1}. Strong concurrent increases were observed in xSO_4 and labile Al, as well as a decrease in Ca. It is thought that this extreme episode may be the due to the unusual hydrology of the site, with Hardrigg Beck partially diverting into the outflow end of the tarn at high flows. Whereas the catchment of Burnmoor Tarn is predominantly low-lying, with thick soils and till deposits, Hardrigg Beck drains the steep, high-elevation slopes of Scafell. It is therefore likely to have chemical characteristics closer to that of Scoat Tarn, and water from this source entering the lake during episodes could cause the major changes observed. It is uncertain whether such episodes are a regular feature of the site, although a second, less severe episode was recorded in the winter of 1991-1992, and, given the quarterly sampling frequency, it is possible that other episodes occurred but were not recorded.

To some extent, the 1993 episode masks other trends at this site. However, the cyclical variations in marine ions clearly match those at Scoat Tarn and the Galloway sites, with a peak in 1991 (Figure 4.11.2). Declining trends are consequently observed for Cl, Na, Mg and Ca (Table 4.11.3).

No clear trends are observed for pH, alkalinity, xSO_4 or NO_3, but significant increases are again identified for DOC (1.8 mg l^{-1} over ten years) and non-labile Al.

Epilithic diatoms

(Figure 4.11.3, Table 4.11.4)

Burnmoor Tarn is dominated by species typical of mildly acid lakes. The more dominant taxa, *Achnanthes minutissima* and *Brachysira vitrea* vary considerably in relative abundance throughout the last decade. Abundance of the latter species (pH optima 5.9) was reduced from 1989-1991 while that of *Tabellaria flocculosa* (pH optima 5.4) was elevated. The planktonic species, *Cyclotella kuetzingiana* var. *minor* was relatively abundant in the early years of monitoring, declined to low levels by 1994 and

Table 4.11.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
Cl	µeq l^{-1}	*-6.17***	-
Na	µeq l^{-1}	*-5.13****	*-4.96**
Mg	µeq l^{-1}	*-1.48****	*-1.42**
Ca	µeq l^{-1}	*-2.15**	-
DOC	mg l^{-1}	*+0.11****	*+0.18***
Non-labile Al	µg l^{-1}	-	*+0.25**

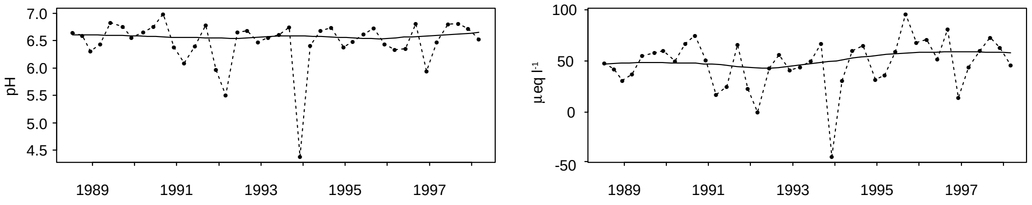
** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

Figure 4.11.2

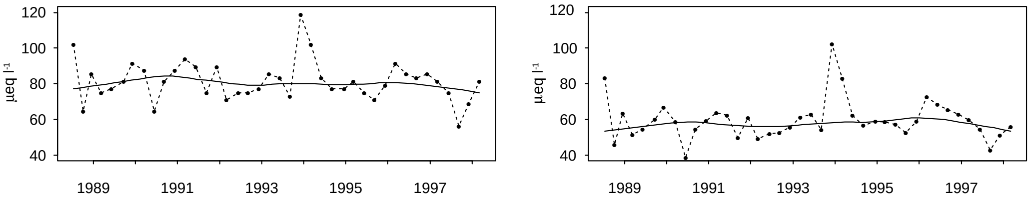
Burnmoor Tarn: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

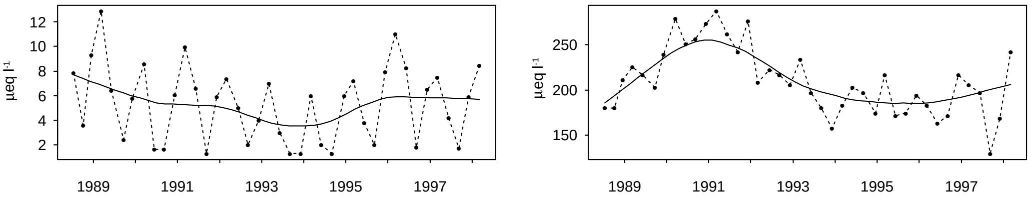
(a) pH (b) Alkalinity



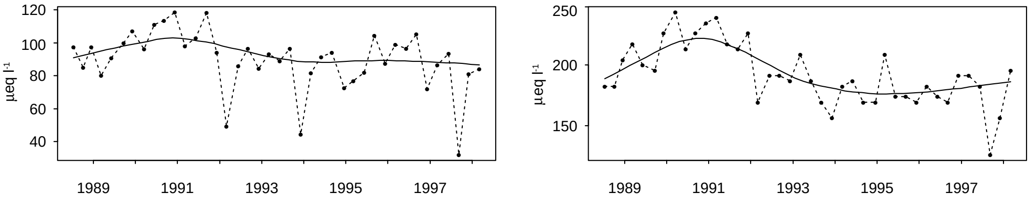
(c) Sulphate (d) Non-marine Sulphate



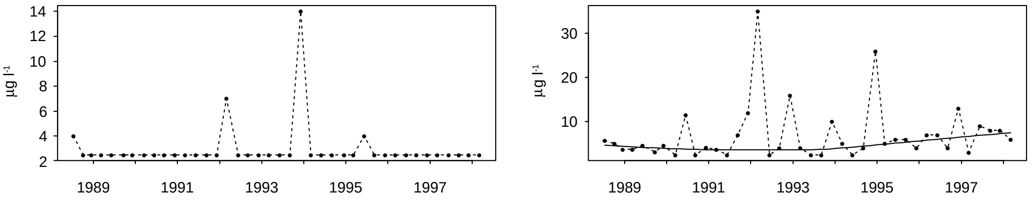
(e) Nitrate (f) Chloride



(g) Calcium (h) Sodium



(i) Labile Al (j) Non-labile Al



(k) Total Soluble Al (l) Dissolved Organic Carbon

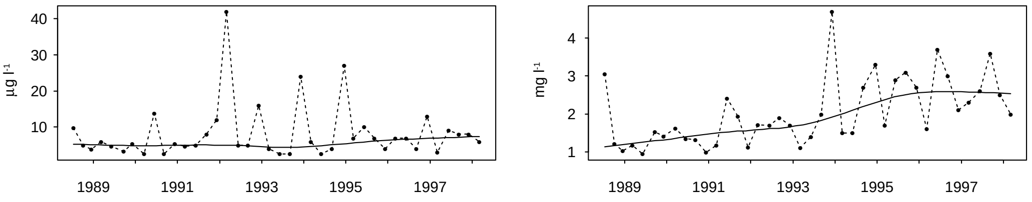


Table 4.11.4

Burnmoor Tarn: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*300*	*142*	*6.5*	*0.73*	*0.63*
Macrophytes	*20*	*15*	*9.1*	*0.38*	*0.38*
Invertebrates	*895*	*39*	*3.1*	*0.67*	*0.50*

Variance explained (%)	within year	between years	linear trend	p unrestricted	p restricted
Epilithic diatoms	*43.0*	*57.0*	*10.6*	*<0.01*	*<0.01*
Macrophytes	*	*	*14.2*	*0.46*	*0.39*
Invertebrates	*60.7*	*39.3*	*11.6*	*<0.01*	*<0.01*

has since increased again. Several rare taxa have increased in relative abundance since about 1993, including *Denticula tenuis*, *Navicula subtilissima*, *Cymbella cesatii* and *Synedra acus.* These changes appear to account for the significant linear trend according to RDA and associated permutation test. Diatom inferred pH, derived from weighted averaging, is indicative of a general improvement in conditions since 1992 (see Section 7.2.1) and this is evident in the spring/summer water chemistry. However, given the well buffered nature of this site it seems most likely that the changes reflect climatic variations, particularly as they affect the rainfall regime at this time of year. The diatom assemblage collected by sediment trap contains a larger proportion of *C. kuetzingiana* var. *minor* and its representation increased steadily since traps were first emptied in 1992 until 1997, before falling back slightly in 1998.

■ Macroinvertebrates

(Figure 4.11.4, Table 4.11.4)

Burnmoor Tarn is characterised by a typically oligotrophic, slightly acid fauna. The first three years of the monitoring period were dominated by chironomids and oligochaetes. From 1991, acid tolerant Leptophlebid mayflies increased in abundance and became the dominant taxon. Other acid tolerant species, including Polycentropodid caddisflies *Plectrocnemia spp.*, *Polycentropus* spp. and *Cyrnus spp.,* have all occurred sporadically in low numbers. Other characteristic species include the acid tolerant freshwater bivalve *Pisidium* spp., the moderately acid tolerant leech *Erpobdella octoculata,* and the acid sensitive crustacean *Gammarus lacustris*, which was recorded in highest densities in 1996. The mayfly *Caenis horaria*, which first occurred in 1996, had its greatest abundance most recently in 1998. Time as a linear trend is significant at the 0.01 level according to RDA and associated permutation test. The trend appears to be largely influenced by the appearance and disappearance of several species of water beetle and an increase in abundance of Leptophlebiidae in recent years. These changes are not indicative of a change in water chemistry.

■ Fish

(Figure 4.11.5)

The outflow of Burnmoor Tarn has been electrofished since 1989. Population density is low and although densities of 0+ fish rose between 1989 and 1991 they crashed in 1992, since when there has only been one successful

Table 4.11.5

Burnmoor Tarn: relative abundance of aquatic macrophyte flora (1988 - 1997)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Nitella flexilis[1]	3	3	4	3	3	3	3	3
Myriophyllum alterniflorum[2]	2	2	2	2	2	2	2	2
Utricularia sp.[2]	1	0	2	2	0	0	2	1
Drepanocladus fluitans[4]	0	0	1	0	0	0	0	0
Sphagnum auriculatum[4]	1	0	0	1	0	1	0	0
Juncus bulbosus var. *fluitans*[4]	3	3	3	3	3	3	3	3
OTHER SUBMERGED OR FLOATING SPECIES								
Filamentous green algae	2	2	3	3	4	3	2	2
Fontinalis sp.	1	1	1	1	1	1	1	0
Rhytidiadelphus squarrosus	0	0	0	1	0	0	0	1
Isoetes lacustris	3	3	3	3	3	3	3	3
Elatine hexandra	0	0	0	0	0	0	1	0
Littorella uniflora	2	2	2	2	2	2	2	2
Lobelia dortmanna	5	5	5	5	4	4	4	4
Ranunculus flammula	1	1	2	2	2	2	2	1
Juncus effusus	1	1	1	1	1	1	1	1
Juncus acutifloris/articulatus	2	2	2	2	2	2	2	2
Potamogeton polygonifolius	1	1	1	1	1	1	2	1
Scirpus fluitans	1	1	1	1	1	1	1	1
TOTAL NUMBER OF SPECIES	15	13	15	16	13	14	15	14

recruitment (1995). Population densities of >0+ fish declined between 1989 and 1992 and only two fish were caught in each of the following three years. However, since then they have shown some recovery. The length frequency graphs show the abnormal structure of the population at this site. Neither the mean condition factor nor its coefficient of variation, for either age class, shows any temporal trend over the years, although there has been a general decline in the condition factor of 0+ fish since 1991 with a possible improvement in the last two years. It is interesting to note that the years of recruitment failure generally coincide with the years with highest soluble labile Al concentrations. It is possible that, for the hydrological reasons given in the chemistry section, trout populations in the outflow are sensitive to occasional extreme spates of acidity and high Al levels despite the generally well buffered chemistry of the lake.

■ Aquatic macrophytes

(Tables 4.11.4-5)

Burnmoor Tarn contains a relatively diverse submerged aquatic macrophyte flora which is typical for a well buffered oligotrophic lake. The acid tolerant isoetid species *Isoetes lacustris*, *Littorella uniflora* and *Lobelia dortmanna* are all common at the site, while more sensitive species such as the charophyte *Nitella flexilis*, *Utricularia* sp., and *Myriophyllum alterniflorum* are present at lower abundances. A single specimen of the six-stamened waterwort *Elatine* *hexandra* was recovered in a grab sample in 1995. RDA and associated permutation test shows time to be insignificant as a linear variable at the 0.01 level.

■ Summary

Although not normally acidic, the outflow and possibly the main basin of Burnmoor Tarn experience infrequent, but extremely severe acidic episodes. These are thought to result from the overflow of water from the adjacent Hardrigg Beck, which drains a more acid-sensitive catchment, into the tarn during high flows. Few trends are observed at the site, although DOC and non-labile Al appear to have risen since 1988. As at Scoat Tarn and the Galloway sites, cyclical variations in marine ions have occurred during this time. Changes in epilithic diatoms and fish populations may relate to the occasional acid episodes, but the linear trend in macroinvertebrates is more difficult to explain.

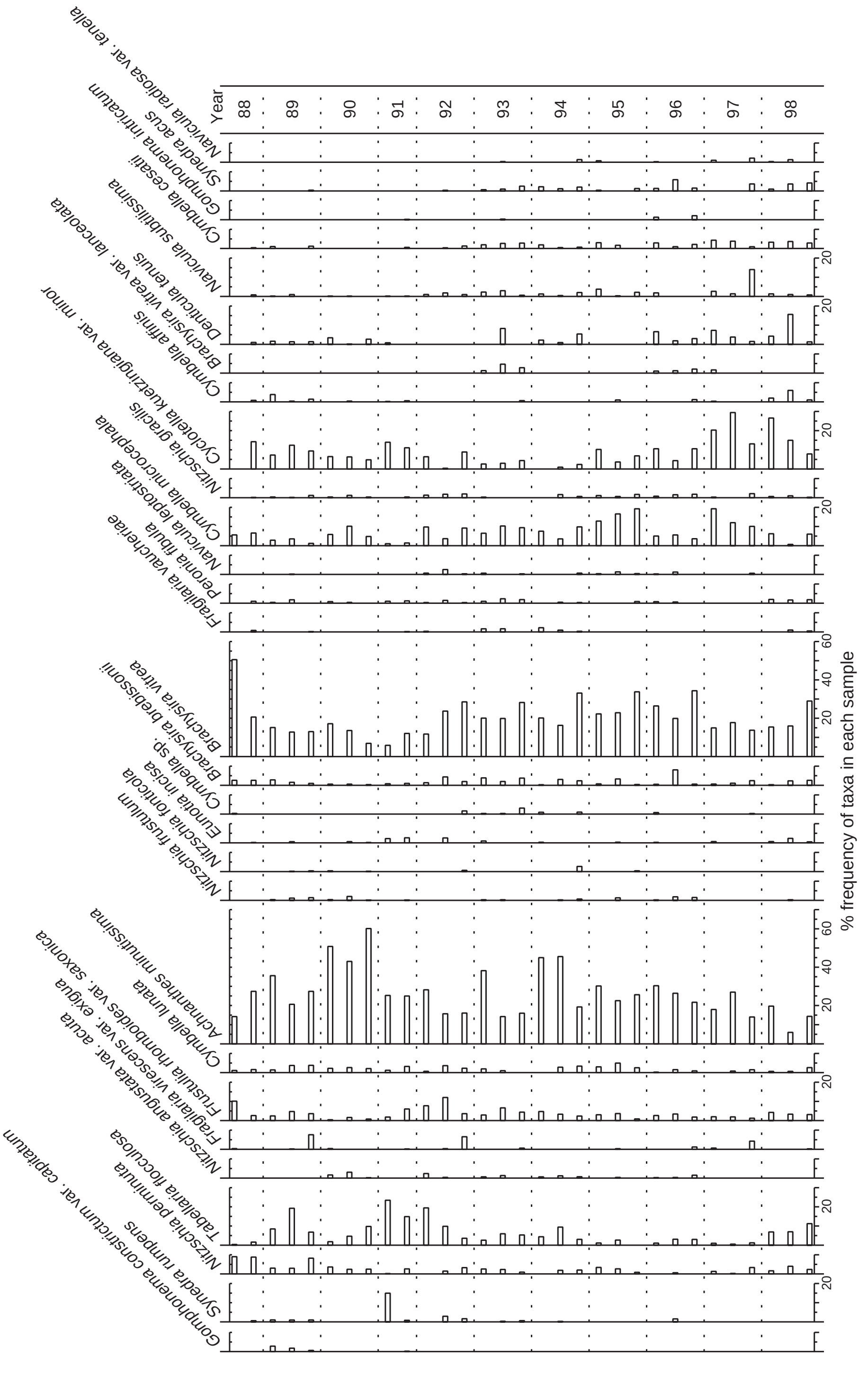


Figure 4.11.3

Burnmoor Tarn: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

Figure 4.11.4

Burnmoor Tarn: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

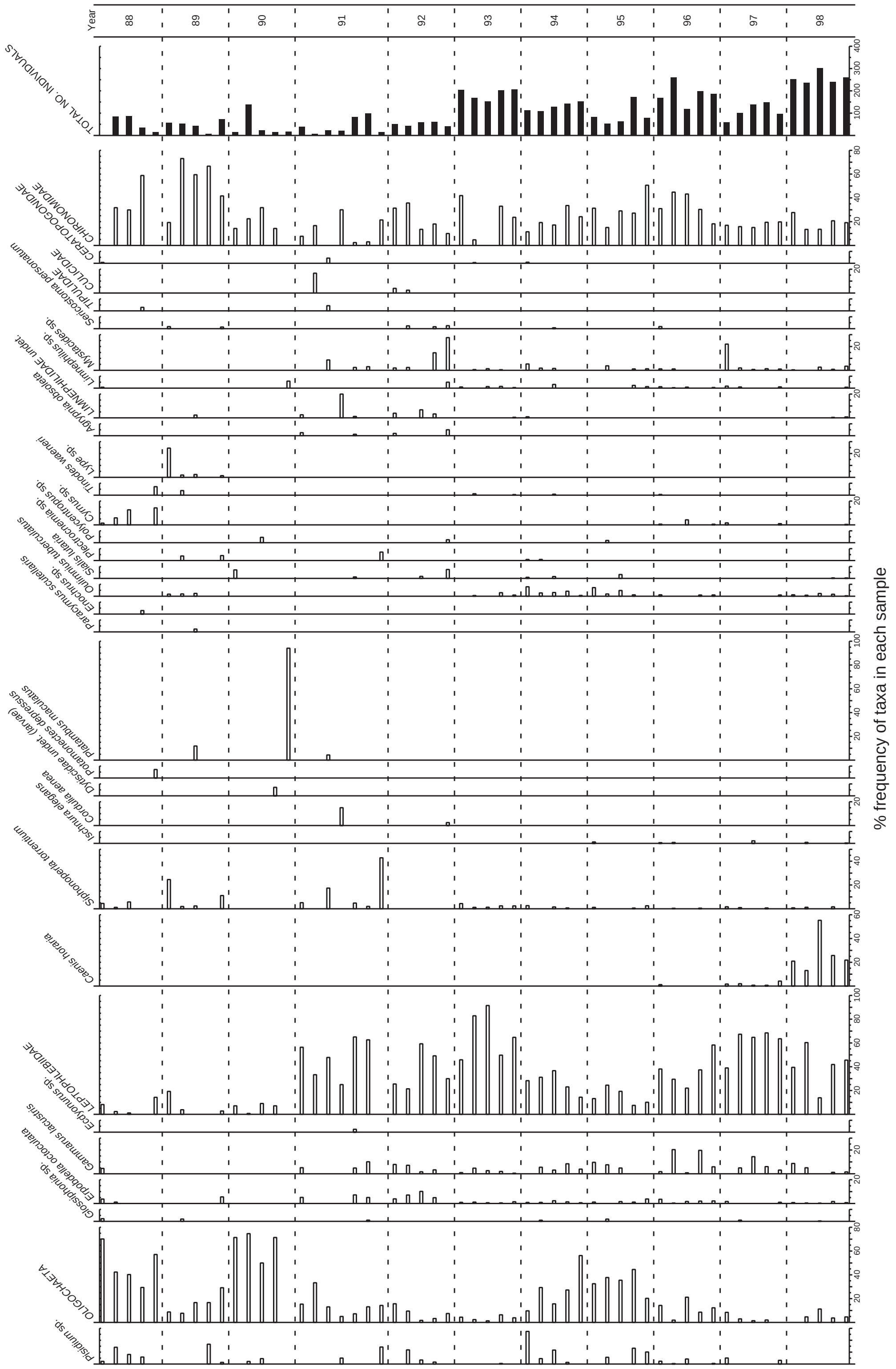
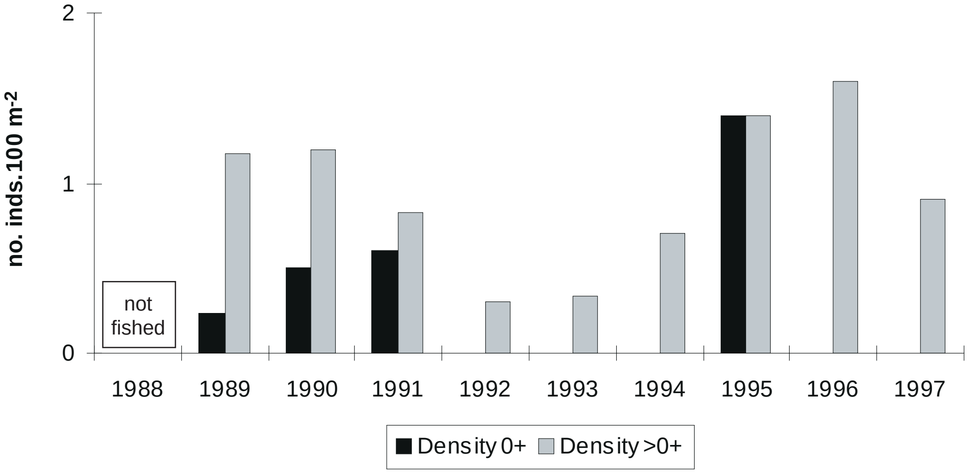


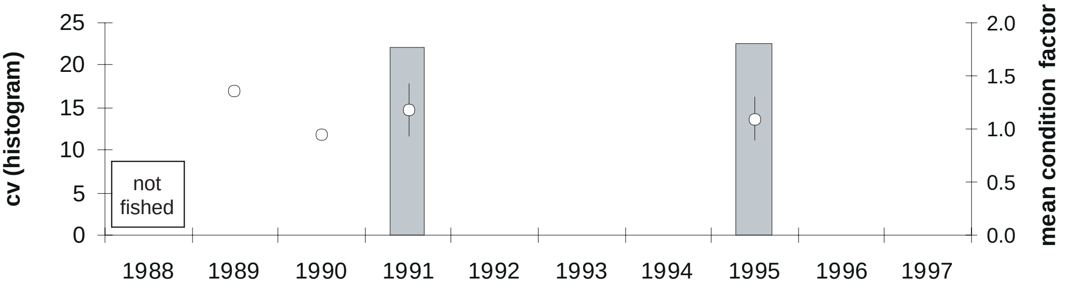
Figure 4.11.5

Burnmoor Tarn: summary of fish data (1989 - 1997)
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})
(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

(a) Density



(b) Condition (0+)



Condition (>0+)

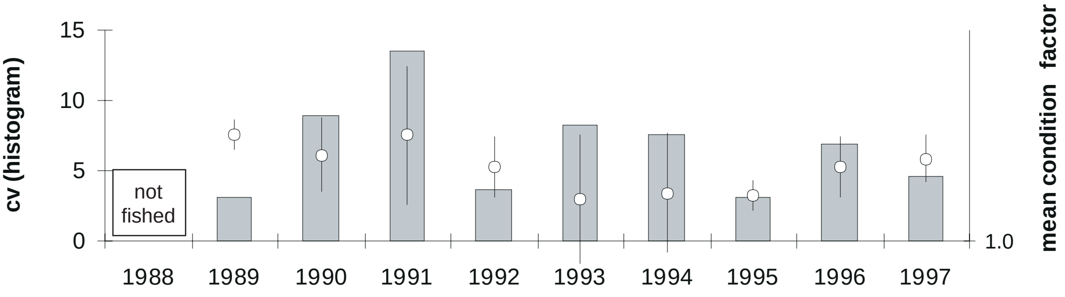


Figure 4.11.5

Burnmmor Tarn: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries

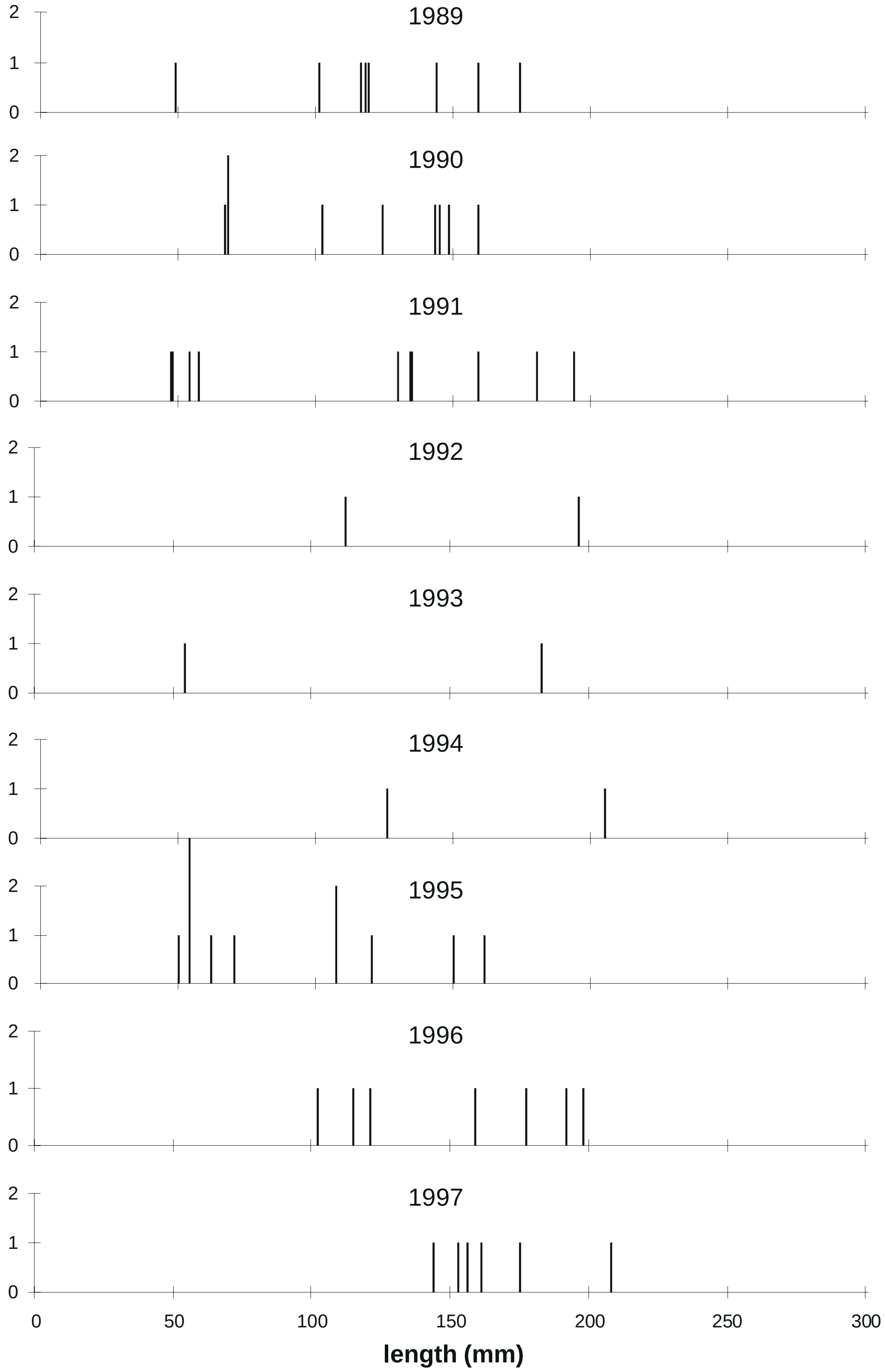
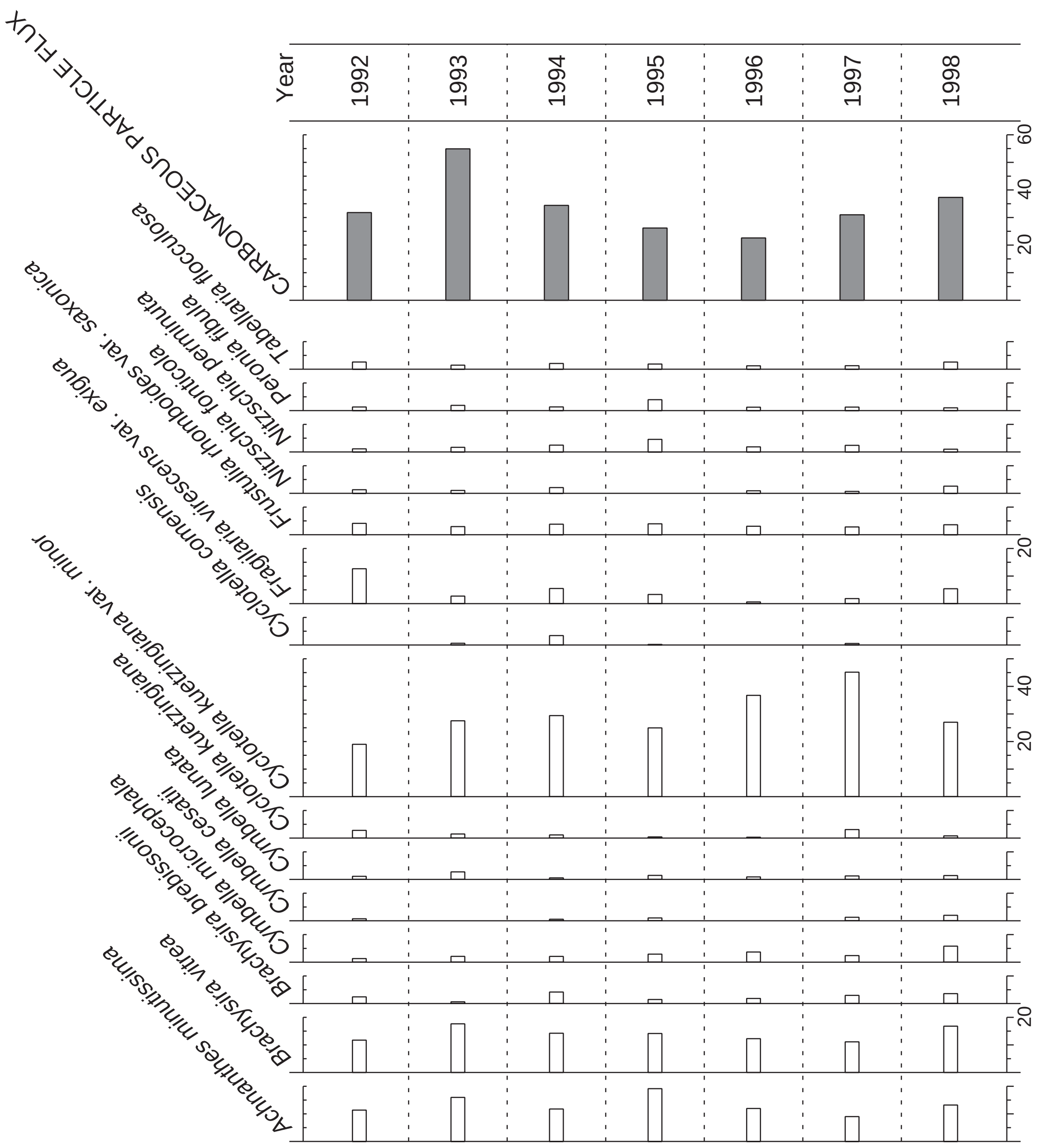


Figure 4.11.6

Burnmmor Tarn: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year



4.12 River Etherow

Site Review

The River Etherow flows into the Woodhead reservoir to the east of Manchester in the southern Pennines. This severely deposition impacted site has been subject to considerable hydro-chemical and hydro-biological research (e.g. Say *et al.*, 1981; Harding *et al.*, 1981; Evans & Jenkins, 2000) and detailed studies of catchment nitrogen dynamics are currently ongoing (Curtis, pers. comm.). It is likely that the water chemistry is occasionally influenced by road-salt, blown or washed in from the nearby A628 trunk road.

Water Chemistry

(Figure 4.12.2, Tables 4.12.2-3)

The South Pennines region, which is close to major industrial centres such as Manchester, receives some of the highest S and N deposition in the UK

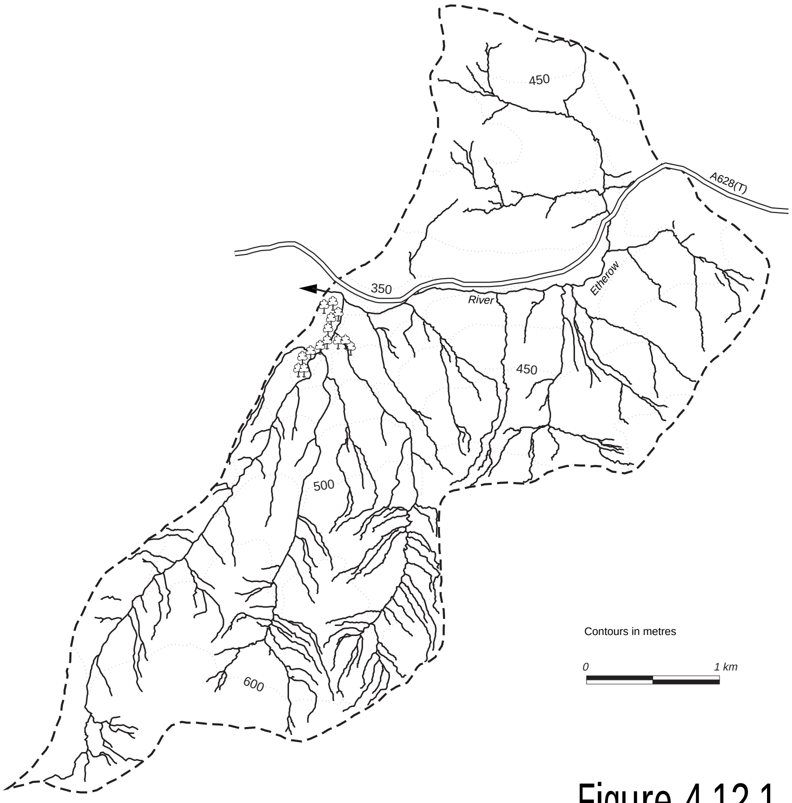


Figure 4.12.1

River Etherow: catchment

Table 4.12.1

River Etherow: site characteristics

Grid reference	*SK 116996*
Catchment area	*1300 ha*
Minimum catchment altitude	*280 m*
Maximum catchment altitude	*633 m*
Catchment Geology	*millstone grit*
Catchment Soils	*peaty podsols, blanket peat*
Catchment vegetation	*moorland - 100%*
Mean annual rainfall	*1572 mm*
1996 deposition	
Total S	39 kg ha^{-1} yr^{-1}
non-marine S	38 kg ha^{-1} yr^{-1}
Oxidised N	14 kg ha^{-1} yr^{-1}
Reduced N	25 kg ha^{-1} yr^{-1}

Table 4.12.2

River Etherow: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		5.48	7.22	3.79
Alkalinity	µeq l^{-1}	7.2	231.0	-165.0
Ca	µeq l^{-1}	172.0	350.0	40.0
Mg	µeq l^{-1}	165.8	291.7	25.0
Na	µeq l^{-1}	302.2	647.8	100.0
K	µeq l^{-1}	19.0	64.6	2.6
SO_4	µeq l^{-1}	272.3	408.3	85.4
xSO_4	µeq l^{-1}	239.6	372.9	73.5
NO_3	µeq l^{-1}	48.6	90.7	7.1
Cl	µeq l^{-1}	310.1	704.2	112.7
Soluble Al	µg l^{-1}	143.7	580.0	<2.5
Labile Al	µg l^{-1}	66.3	394.0	<2.5
Non-labile Al	µg l^{-1}	77.8	238.0	<2.5
DOC	mg l^{-1}	5.28	34.00	0.30
Conductivity	µS cm^{-1}	85.0	161.0	33.0

(RGAR, 1997). This is reflected in surface water chemistry with mean concentrations of xSO_4 (240 µeq l^{-1}) and NO_3 (49 µeq l^{-1}) the highest in the network. NO_3 concentrations are high throughout the year, with little seasonal variation, indicative of Stage 3 (i.e. complete) N saturation (Stoddard, 1994). Nevertheless, because xSO_4 levels are so high, the mean ratio of $NO_3/(NO_3+xSO_4)$ is only 0.17, implying that NO_3 is proportionally a less important contributor to acidity than at Scoat Tarn.

The mean Ca concentration of 172 µeq l^{-1} indicates that this site is relatively well buffered, and mean alkalinity (7 µeq l^{-1}) and pH (5.5) are therefore higher than might be expected given the high acid anion concentrations. However, the river is highly episodic, and much of the base cation buffering capacity is lost due to dilution at high flows. As a result, alkalinity and pH minima (-165 µeq l^{-1} and 3.79 respectively) are substantially lower than at any other site in the Network (lowest values recorded elsewhere -86 µeq l^{-1} and 4.1). Labile Al concentrations are high, peaking at almost 400 µg l^{-1}, with the non-labile fraction also significant due to high DOC levels.

The River Etherow is one of the few sites in the UKAWMN showing a clear decrease in sulphate levels, with both SO_4 and xSO_4 exhibiting large and significant declining trends over the last ten years. It is estimated that the reduction in xSO_4 has been approximately 60-80 µeq l^{-1} since 1988, a decrease of around 25-30% on the first year mean. Time series and LOESS curves (Figures 4.12.2c,d) show that decreases occurred fairly steadily over the monitoring period. Due to analytical problems prior to a laboratory change in April 1991 (Section 3), the early part of the alkalinity record is missing, and no clear trends are observed in the remaining data. The pH record, although complete, also shows no trend. This may be due to the masking effect of extreme short-term variability (Figure 4.12.2a); clear rising trends in pH have been observed at a number of reservoir sites in the south Pennine region (Evans & Jenkins, 2000), but it is also possible that changes in other ions are offsetting the reduction in xSO_4. Declining trends in both Ca and Mg, identified using regression, suggest that with reduced acid inputs, the leaching of base cations from soil exchange sites has also decreased. This base cation response to reduced acid deposition corresponds to that predicted by Reuss *et al.* (1987). In addition, there is a significant upward trend in NO_3, which has risen by an estimated 15-21 µeq l^{-1} since 1988. NO_3 is thus becoming increasingly significant as a contributor to the acid anion total, and a Seasonal Kendall analysis of $NO_3/(NO_3+xSO_4)$ gave a highly significant estimated increase of 0.04 over the ten year period.

As noted above, road salt may provide a source of Na and Cl at the Etherow. This, and the inland

Table 4.12.3

Significant trends in chemical determinands (July 1988 - March 1998)

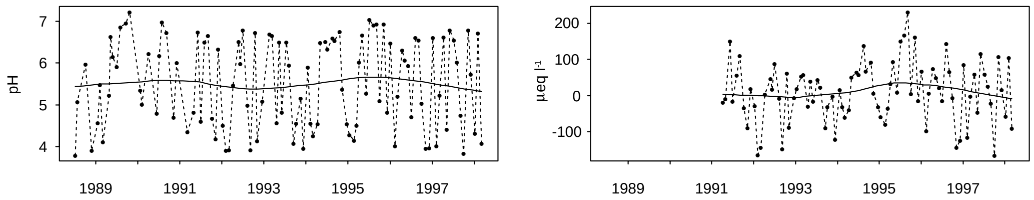
Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
SO_4	µeq l^{-1}	-8.15***	-5.56*
xSO_4	µeq l^{-1}	-8.04***	-5.85*
Mg	µeq l^{-1}	-3.25**	-
Ca	µeq l^{-1}	-2.85*	-
NO_3	µeq l^{-1}	+2.07***	+1.50*
DOC	mg l^{-1}	+0.48*	+0.27***
Non-labile Al	µg l^{-1}	+4.27*	+5.00**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

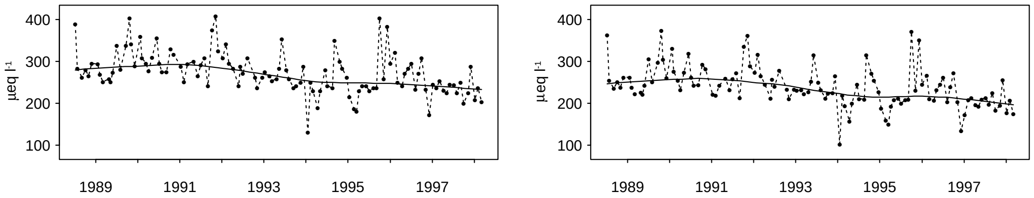
Figure 4.12.2

River Etherow: summary of major chemical determinands (September 1988 - March 1998)

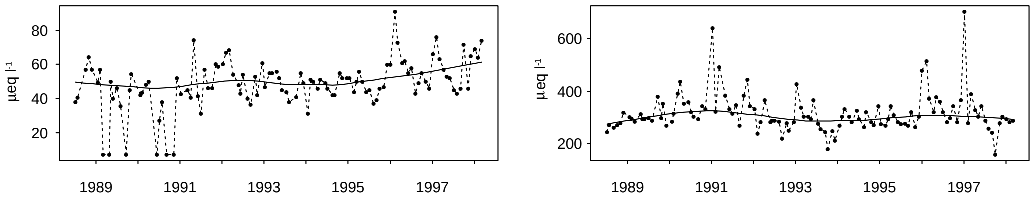
Smoothed line represents LOESS curve (Section 3.1.2)


(a) pH

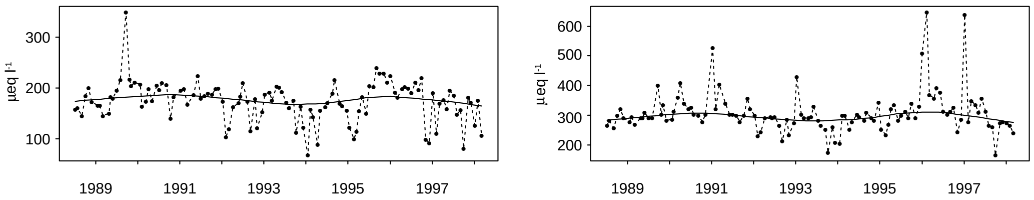
(b) Alkalinity


(c) Sulphate

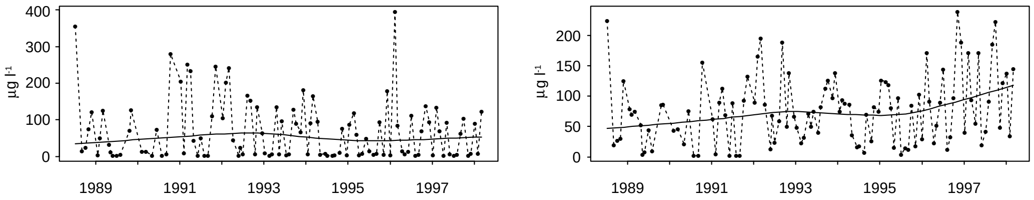
(d) Non-marine Sulphate


(e) Nitrate

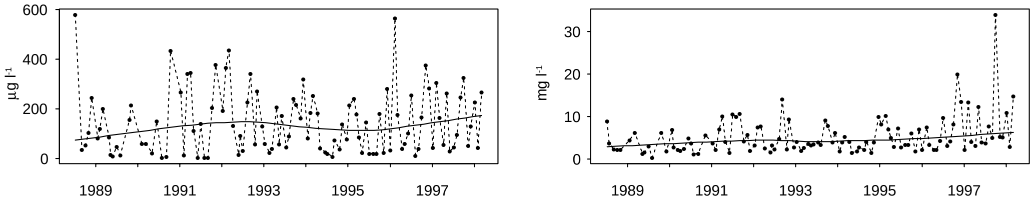
(f) Chloride


(g) Calcium

(h) Sodium


(i) Labile Al

(j) Non-labile Al


(k) Total Soluble Al

(l) Dissolved Organic Carbon

Table 4.12.4

River Etherow: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	318	66	3.1	0.11	0.11
Macrophytes	2	5	1.0	1.82	0.65
Invertebrates	346	29	3.5	0.54	0.43

Variance				p	
explained (%)	**within year**	**between years**	**linear trend**	**unrestricted**	**restricted**
Epilithic diatoms	23.0	77.0	4.4	0.21	0.70
Macrophytes	*	*	63.3	0.01	<0.01
Invertebrates	29.7	70.3	17.7	<0.01	0.06

location, may explain the low variability in these ions relative to most other sites. Nevertheless, the time series for Cl (Figure 4.12.2f) does appear to show a small peak in 1990, comparable to those observed elsewhere, and there may therefore be some climatic influence. A highly significant DOC increase has occurred at this site, with concentrations having risen by 2.7 mg l^{-1} since 1988 based on the SKT trend estimate. This increase largely appears to have come from higher peak concentrations (Figure 4.12.21). An associated, although less significant, increase is identified for non-labile Al.

■ Epilithic diatoms

(Figure 4.12.3, Table 4.12.4)

The epilithic diatom assemblage of the River Etherow has undergone large inter-annual variation, with the abundance of the most dominant species, *Achnanthes minutissima* (pH optima 6.3) and *Eunotia exigua* (pH optima 5.1) shifting markedly between years. In 1993 both these species occurred in relatively low abundance and the samples were relatively diverse, with elevated representation of the acidophilous species *Frustulia rhomboides* var. *saxonica*, *Brachysira brebissonii*, *B. vitrea* and *Eunotia rhomboidea*. *Pinnularia divergentissima* was recorded for the first time in 1997 and was again present in 1998. Floristic differences between years appear to be associated with variation in hydrological characteristics of the River Etherow and therefore with variation in climate. Years in which *A.minutissima* dominates are generally characterised by prolonged periods of elevated pH (at least according to monthly spot samples) in the spring and early summer, e.g. 1989, 1994 and 1995. Rainfall data for the nearby Meteorological Station (Emley Moor) demonstrates that spring and early summer in these years were relatively dry, resulting in relatively alkaline, base-flow dominated conditions. *E. exigua* is most abundant in the wetter years which exhibit more episodic chemical characteristics, resulting from the increased influence of acidic surface runoff. The link between summer rainfall and the diatom community is illustrated by the relationship between diatom inferred pH (using weighted averaging) and June-July rainfall data (Section 7.3.1). RDA and associated permutation test show that time is not significant at the 0.01 level.

■ Macroinvertebrates

(Figure 4.12.4, Table 4.12.4)

The macroinvertebrate community of the River Etherow has undergone a considerable increase in species richness over the past decade. The site

Table 4.12.5

River Etherow: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	88	89	90	91	92	93	95	96	97
SUBMERGED SPECIES									
Filamentous green algae	<0.1	1.2	<0.1	<0.1	1.0	0.0	0.0	<0.1	<0.1
Atrichum crispum	0.0	0.0	<0.1	0.0	0.0	0.0	0.0	0.0	0.0
Mnium hornum	<0.1	<0.1	0.0	0.0	0.0	0.0	0.0	<0.1	0.0
Polytrichum sp.	0.0	0.0	0.0	0.0	<0.1	<0.1	<0.1	<0.1	0.0
Scapania undulata	18.7	18.5	14.8	14.9	9.0	6.3	6.7	12.6	3.6
Juncus bulbosus var. *fluitans*	<0.1	<0.1	<0.1	0.0	0.0	0.0	0.0	<0.1	0.0
EMERGENT SPECIES									
Juncus effusus	<0.1	<0.1	<0.1	<0.1	0.0	<0.1	<0.1	0.0	<0.1
total macrophyte cover excluding filamentous algae	18.7	18.5	14.8	14.9	9.0	6.3	6.7	12.6	3.6
TOTAL NUMBER OF SPECIES	5	5	5	3	3	2	2	5	3

is dominated by acid tolerant detritivorous stoneflies. *Leuctra inermis* was the dominant stonefly throughout and occurred in very high numbers while *Amphinemura sulcicollis* and *Protonemura* spp. were both numerous. *Brachyptera risi* showed an increase in abundance in the last five years of the survey. The predatory stonefly *Siphonoperla torrentium* was present throughout, with the exception of 1992 which was an impoverished year both in species richness and abundance. Of the mayflies, *Ameletus inopinatus* was recorded in relatively high numbers throughout while the acid sensitive *Baetis* spp. first appeared in 1992, was absent between 1994 and 1996 and reappeared in 1997. Other characteristic species include *Rhyacophila* spp., *Plectrocnemia* spp., Tipulids and chironomids. Possible causes for the apparent increase in diversity are unclear as there is no evidence to suggest improvements in acidity status. However, it is interesting to note that - inter-annual variation in species richness is well correlated with that for the majority of the other streams in the Network (Section 7.4.2) and it is therefore possible that climatic factors, and particularly spring rainfall/flow, may be important. Despite these changes the species composition does not show a linear trend with time according to RDA and associated restricted permutation test.

■ Fish

On sampling in 1989 this site was found to be fishless. As it is situated above a fishless reservoir which prohibits any possibility of fish colonising the reach from downstream, no further sampling has been carried out.

■ Aquatic macrophytes

(Tables 4.12.4-5)

The ubiquitous and highly acid tolerant liverwort species, *Scapania undulata*, has been the only consistent representative of the aquatic macrophyte flora over the past decade. The cover of this species in the survey stretch has declined since 1988. Given its broad chemical tolerance it seems most likely that its reduction results from physical scouring associated with storm events. Alternatively, it is possible that the large increase in DOC at the site has restricted its available habitat through the effect of light limitation. Reduction in the cover of *S.undulata* appears to drive the significant time trend in species cover identified by RDA and associated restricted permutation test.

Summary

The River Etherow has the highest xSO_4 and NO_3 concentrations in the UKAWMN, due to high deposition levels. Mean pH and alkalinity are not as low as might be expected, due to a large internal supply of base cations, but the site is extremely episodic, with chemistry at high flows the most acidic in the UKAWMN. Consistent with the regional pattern of deposition reductions, the Etherow is one of the few sites to have shown clear reduction in xSO_4 (by 25-30%) since 1988. This has not yet been accompanied by identifiable recovery in either pH or alkalinity, possibly due to limitations in the data and high short-term variability, although it also appears that other ionic changes are offsetting the reduction in xSO_4. In particular, NO_3 has risen significantly, and is becoming an increasingly important contributor to site acidity. The considerable inter-annual variation in the epilithic diatom species assemblage, the increase in the number of macroinvertebrate species with time, and the reduction in cover of aquatic liverworts, may be primarily related to changes in the rainfall regime, through its influence on episodes and physical scouring at high flow.

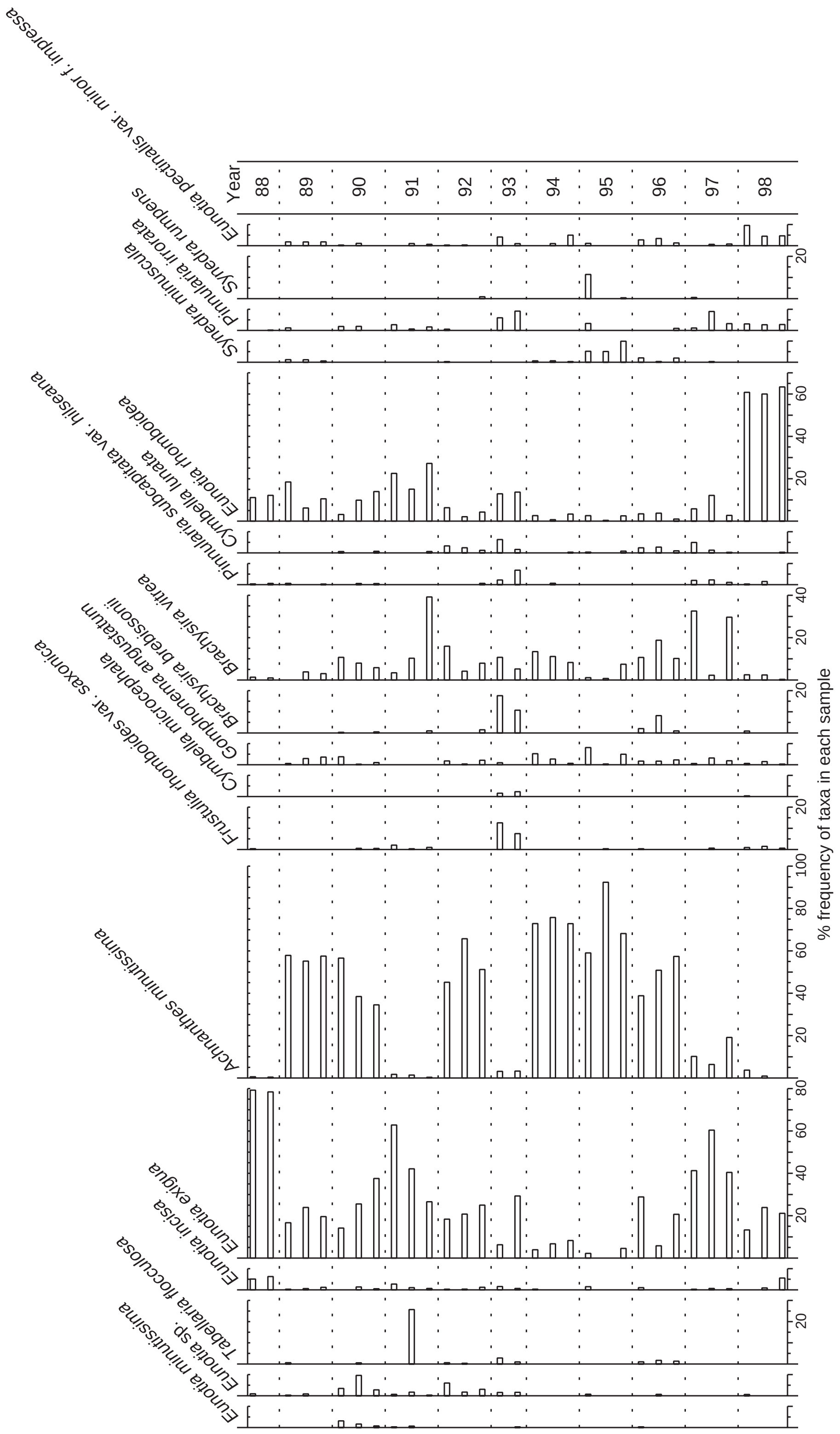


Figure 4.12.3

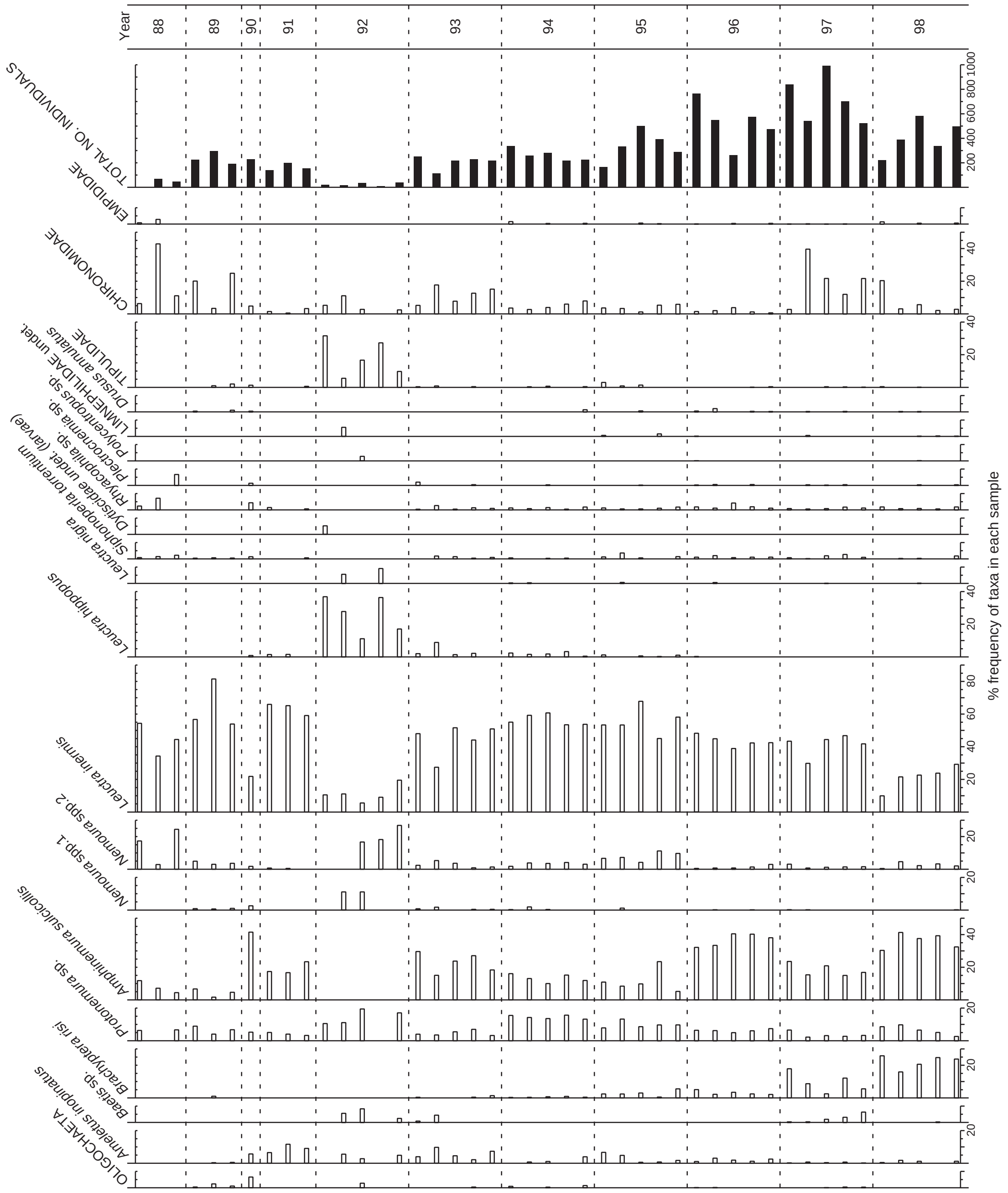
River Etherow: summary of epilithic diatom data (1988 - 1998)

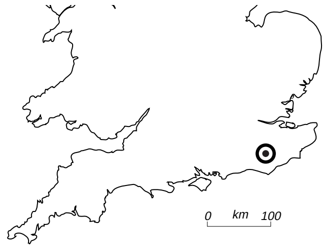
Percentage frequency of all taxa occurring at >2% abundance in any one sample

Figure 4.12.4

River Etherow: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples





4.13 Old Lodge

Site Review

Situated on the Ashdown sands, within the Ashdown Forest, the Old Lodge catchment is the only UKAWMN site in southeast England. The survey sections are prone to occasional wind-blow of large beech trees, and while fallen timber is generally removed in the course of Reserve maintenance, physical changes have resulted from the accumulation of old wood and other debris in some reaches and from changes in the extent of shading. Otherwise there has been no major physical disruption within the catchment over the course of the last decade.

Water Chemistry

(Figure 4.13.2, Table 4.13.2-3)

Old Lodge is the most chronically acidic site in the UKAWMN, with a mean pH of 4.59, a mean alkalinity of -30 µeq l^{-1}, and a mean labile Al

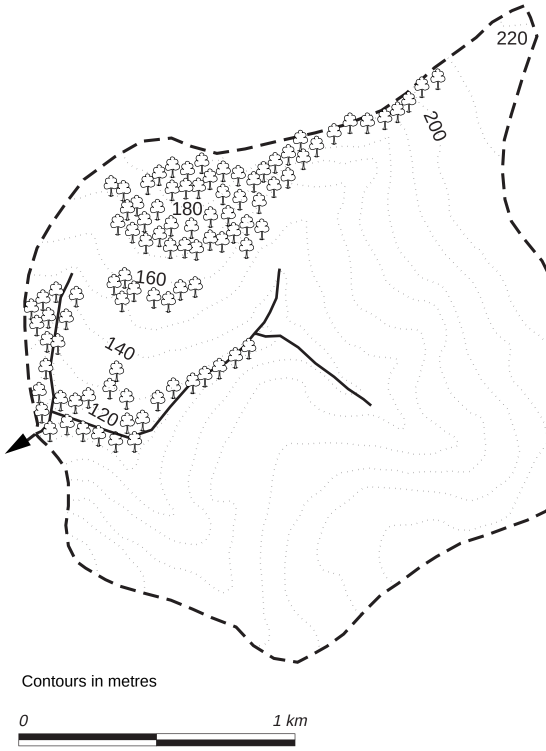


Figure 4.13.1

Old Lodge: catchment

Table 4.13.1

Old Lodge: site characteristics

Grid reference	*TQ 456294*
Catchment area	*240 ha*
Minimum catchment altitude	*94 m*
Maximum catchment altitude	*198 m*
Catchment Geology	*Ashdown sands*
Catchment Soils	*podsols*
Catchment vegetation	*heathland 80%* *deciduous woodland 15%* *conifers15%*
Mean annual rainfall	*872 mm*
1996 deposition	
Total S	*14 kg ha^{-1} yr^{-1}*
non-marine S	*11 kg ha^{-1} yr^{-1}*
Oxidised N	*5 kg ha^{-1} yr^{-1}*
Reduced N	*9 kg ha^{-1} yr^{-1}*

Table 4.13.2

Old Lodge: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*4.59*	*4.95*	*4.10*
Alkalinity	µeq l^{-1}	*-30.0*	*-9.0*	*-86.0*
Ca	µeq l^{-1}	*152.0*	*354.5*	*91.5*
Mg	µeq l^{-1}	*144.2*	*358.3*	*66.7*
Na	µeq l^{-1}	*463.0*	*813.0*	*269.6*
K	µeq l^{-1}	*20.0*	*110.3*	*7.7*
SO_4	µeq l^{-1}	*252.7*	*818.8*	*64.6*
xSO_4	µeq l^{-1}	*192.7*	*731.5*	*-17.5*
NO_3	µeq l^{-1}	*7.1*	*25.0*	*< 1.4*
Cl	µeq l^{-1}	*571.0*	*1036.6*	*304.2*
Soluble Al	µg l^{-1}	*239.9*	*533*	*36.2*
Labile Al	µg l^{-1}	*194.7*	*530.5*	*22.4*
Non-labile Al	µg l^{-1}	*45.0*	*310.0*	*< 2.5*
DOC	mg l^{-1}	*5.0*	*15.0*	*1.7*
Conductivity	µS cm^{-1}	*105.9*	*202.0*	*63.0*

concentration of 195 µeq l^{-1} (maximum 531 µeq l^{-1}). Alkalinity has remained negative, and pH below 5.0, throughout the monitoring period, and several large episodic decreases have been recorded for both determinands (Figure 4.13.2a,b). Major ion concentrations are generally high at this site, with mean Cl, Na, Mg, Ca and K concentrations the highest in the Network, and xSO_4 second only to the Etherow. These high concentrations result partly from the warmer and drier climate, and hence higher evaporation, at this southeast England site compared to the rest of the Network. They are also a function of high marine ion deposition from the nearby English Channel, and high pollutant inputs from upwind emission sources, relative to the low rainfall. DOC concentrations are also high, with large episodic increases, but NO_3 concentrations are low (mean 7 µeq l^{-1}), indicating that the catchment retains the capacity to immobilise large N inputs.

Trend analyses at Old Lodge are hindered by analytical problems prior to a laboratory change in April 1991 (Section 3.1.1), and data for the first three years are missing for pH, alkalinity and NO_3. Absence of significant trends in pH and alkalinity is therefore unsurprising, although there appears to have been a peak in 1994 and 1995 (Figure 4.13.2a,b). Regression analysis does however indicate that NO_3 has risen significantly since 1991, by approximately 7 µeq l^{-1}, although the relatively short period analysed must be taken into consideration. Also identified by regression are declining trends in SO_4, xSO_4, Na, Mg and Ca, and an increase in DOC. The DOC change, of around 3 mg l^{-1} over the decade, is also identified by SKT, and appears to represent a fairly steady increase. The other regression trends are not observed using SKT, however, and are therefore less certain. Inspection of time series in Figure 4.13.2 suggests that changes have occurred erratically for these determinands over time. It is therefore possible that climatic factors have influenced changes over the decade, and apparently cyclical variations in Cl and Na (Figures 4.13.2f,h) support this hypothesis. In fact, despite the difference in geographical location, there are striking similarities between marine ion variations at Old Lodge and those at west coast sites, with a pronounced peak around 1990. Nevertheless, some underlying decline in SO_4, xSO_4 and Ca is suggested by time series (Figure 4.13.2c,d,g), perhaps indicating a catchment response to deposition reductions.

Table 4.13.3

Significant trends in chemical determinands (July1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
SO_4	*µeq 1^{-1}*	*-10.12***	-
xSO_4	*µeq 1^{-1}*	*-8.81**	-
Na	*µeq 1^{-1}*	*-9.30***	-
Mg	*µeq 1^{-1}*	*-4.42***	-
Ca	*µeq 1^{-1}*	*-4.90****	-
NO_3	*µeq 1^{-1}*	*+0.71**	-
DOC	*mg 1^{-1}*	*+0.35****	*+0.28***
labile Al	*µg 1^{-1}*	*-5.98**	-

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$. Trend for nitrate based on 1991-1998 only*

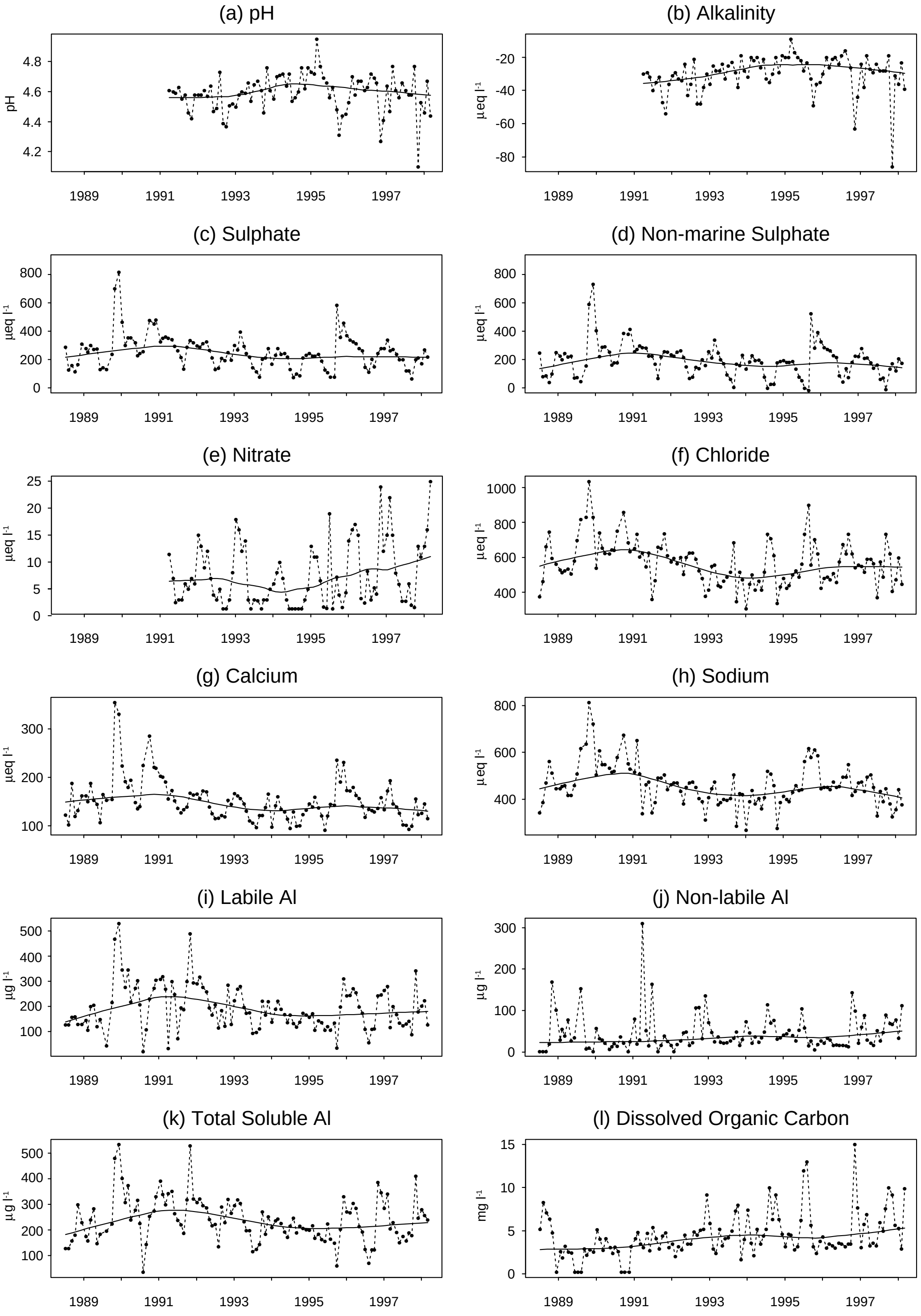


Figure 4.13.2

Old Lodge: summary of major chemical determinands (July 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.13.4

Old Lodge: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of taxa	Mean N_2 diversity	λ_1RDA/I_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	176.0	87	2.5	0.30	0.28
Macrophytes	1.1	3	1.3	0.14	0.12
Invertebrates	351.0	23	3.3	0.50	0.41

Variance explained (%)	within year	between years	linear trend	p unrestricted	p restricted
Epilithic diatoms	42.2	57.8	8.4	0.01	0.13
Macrophytes	-	-	11.6	0.38	0.52
Invertebrates	26.9	73.1	12.6	<0.01	0.08

Table 4.13.5

Old Lodge: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

(% cover of 50 m survey stretch)

Year	88	89	90	91	92	93	95	96	97
SUBMERGED SPECIES									
Filamentous green algae	9.4	63.0	<0.1	1.3	22.8	0.0	0.0	<0.1	<0.1
Scapania undulata	0.6	2.0	3.2	2.6	2.4	1.9	1.1	0.5	1.3
Glyceria fluitans	<0.1	<0.1	0.1	<0.1	0.0	0.2	<0.1	0.0	0.0
Juncus bulbosus var. *fluitans*	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	0.1	<0.1	<0.1
EMERGENT SPECIES									
Juncus effusus	0.0	0.0	<0.1	0.0	0.0	0.1	0.1	<0.1	<0.1
total macrophyte cover excluding filamentous algae	0.6	2.0	3.3	2.6	2.4	2.4	1.3	0.5	1.3
TOTAL NUMBER OF SPECIES		3	3	4	3	2	4	4	3

■ Epilithic diatoms

(Figure 4.13.3, Table 4.13.4)

As at several other stream sites, the epilithon of Old Lodge has varied markedly from year to year, although the relatively narrow range of pH optima of the dominant species emphasises the restricted, permanently strongly acid pH fluctuations of this site. The acidophilous *Eunotia* species, *E. exigua*, *E. incisa* and *E. rhomboidea*, are the three most abundant taxa and the former was dominant in most years, with the exception of 1993 when *E.incisa* was relatively common. *Achnanthes minutissima*, which has a higher pH optima (6.3) was relatively abundant in 1989, appearing to reflect a period of relatively elevated pH in the summer of this year. However, unlike the majority of stream sites there is no relationship between the diatom inferred pH, using weighted averaging, and summer rainfall. RDA and associated restricted permutation test shows that "sampling year" is not significant at the 0.01 level.

Macroinvertebrates

(Figure 4.13.4, Table 4.13.4)

The impoverished macroinvertebrate fauna of Old Lodge is typical of an acid stream, characterised by acid tolerant detritivorous stoneflies and the predatory caddisfly *Plectrocnemia* spp. Of the stoneflies, *Nemoura* spp. and *Leuctra nigra* dominate. *Leuctra hippopus* occurred in high densities in 1992 only, while *Nemurella pictetii* was present intermittently in low numbers during the first half of the study period, but has shown increasing abundance during the last three years. *Siphonoperla torrentium* was present in low numbers in the second half of the monitoring period. Other characteristic fauna include the freshwater Bivalve *Pisidium* spp., the acid tolerant Amphipod *Niphargus aquilex*, and the alderfly *Sialis fuliginosa*. *Baetis* spp. occurred intermittently in low numbers, the highest density being recorded in 1993. Inter-annual variation in species richness is similar to that observed at several other UKAWMN stream sites. This suggests that climatic factors, particularly as they relate to the flow regime, may have an important influence (Section 7.4.2). RDA and associated permutation test show no significant time trend in the species assemblage at the 0.01 level.

Fish

(Figure 4.13.5)

Old Lodge has been electrofished since 1989. For the first three years samples were characterised by the absence of any 0+ trout and extremely low numbers of >0+ trout. However, in 1992 a significant increase in density occured with an influx of 0+ trout. Since then recruitment has occurred in all years except 1996. Mean condition factor of 0+ fish was highest in both the high recruitment year of 1992 and the low recruitment year of 1994. Length frequency graphs show clearly the recruitment peak in 1992. They also show that this was not accompanied by a strong cohort of fish progressing through the population in subsequent years. It is interesting to note that the first three years of monitoring, during which there was no recrutiment, were also characterised by particularly elevated concentrations of soluble labile alumium. These data are therefore consistent with a response to declining levels of acidity.

Aquatic macrophytes

(Tables 4.13.4-5)

The aquatic macrophyte flora of Old Lodge is dominated by the ubiquitous and acid tolerant liverwort, *Scapania undulata*, although occasionally this has been covered by a considerable growth of filamentous algae. The rush *Juncus bulbosus* var. *fluitans* and the grass *Glyceria fluitans*, both relatively opportunistic, have occurred sporadically over the decade in silty locations. The macrophyte survey stretch has undergone considerable physical change during the monitoring period as the result of wind-blown trees which have caused temporary damming and siltation. In addition, canopy shading has reduced substantially in places. Despite these changes there is no evidence of any trend in cover or species representation over the monitoring period and time is insignificant as a linear trend according to RDA and restricted permutation test.

Summary

Old Lodge is severely acidified, with a continuously negative alkalinity. Major ion concentrations are generally higher than at other UKAWMN sites, due to a combination of high pollutant and marine deposition and higher evaporation, although most incoming NO_3 continues to be retained. Shortened data series for some determinands makes trend analysis difficult, but it appears that xSO_4 and Ca may have declined, and NO_3 and DOC risen. Marine ions have exhibited large fluctuations over the monitoring period, possibly having a significant impact on stream acidity. Trout data indicate a general improvement in conditions, but this is not apparent for other biological groups and suggestions of signs of “biological recovery” are perhaps premature at this stage.

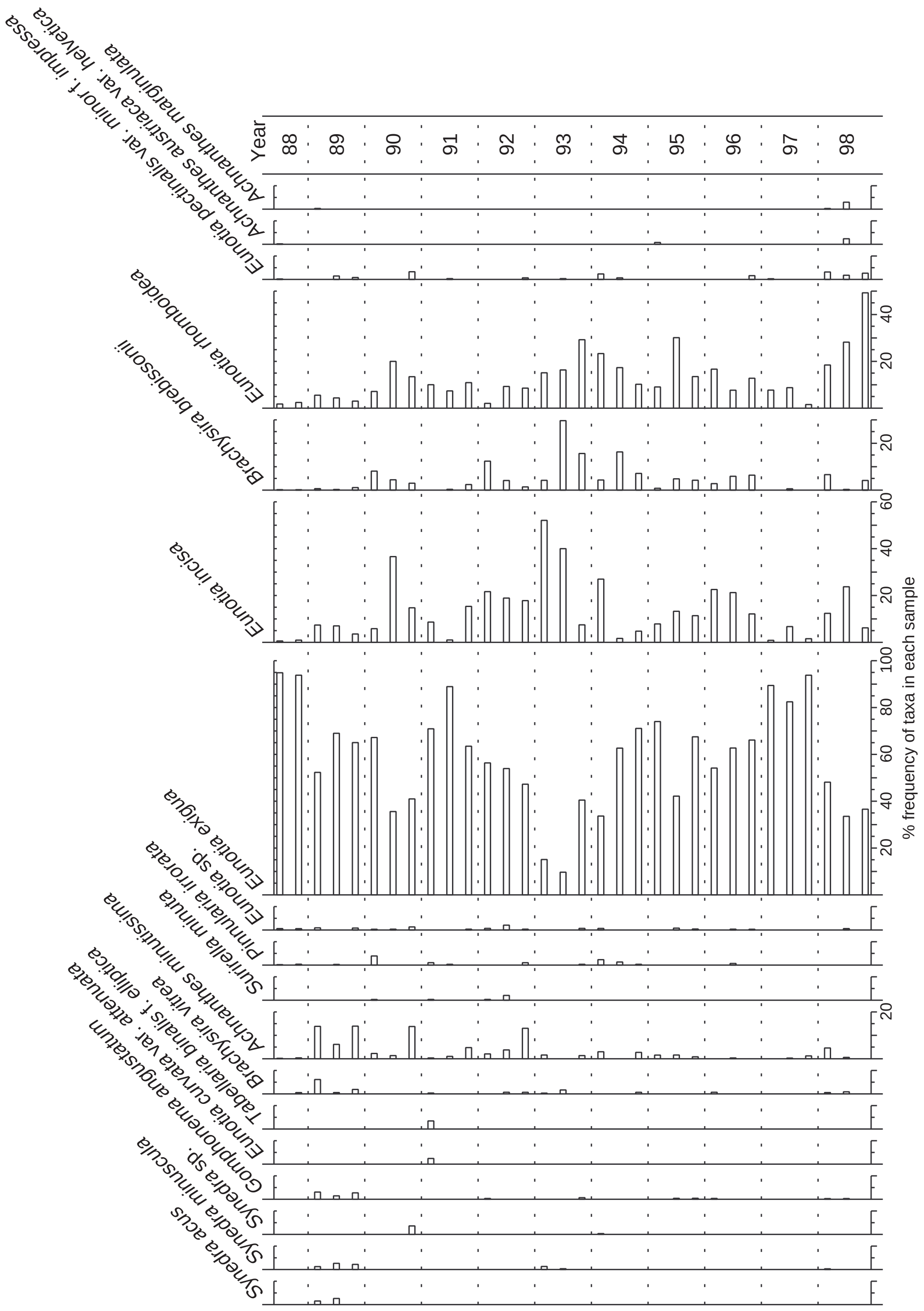


Figure 4.13.3

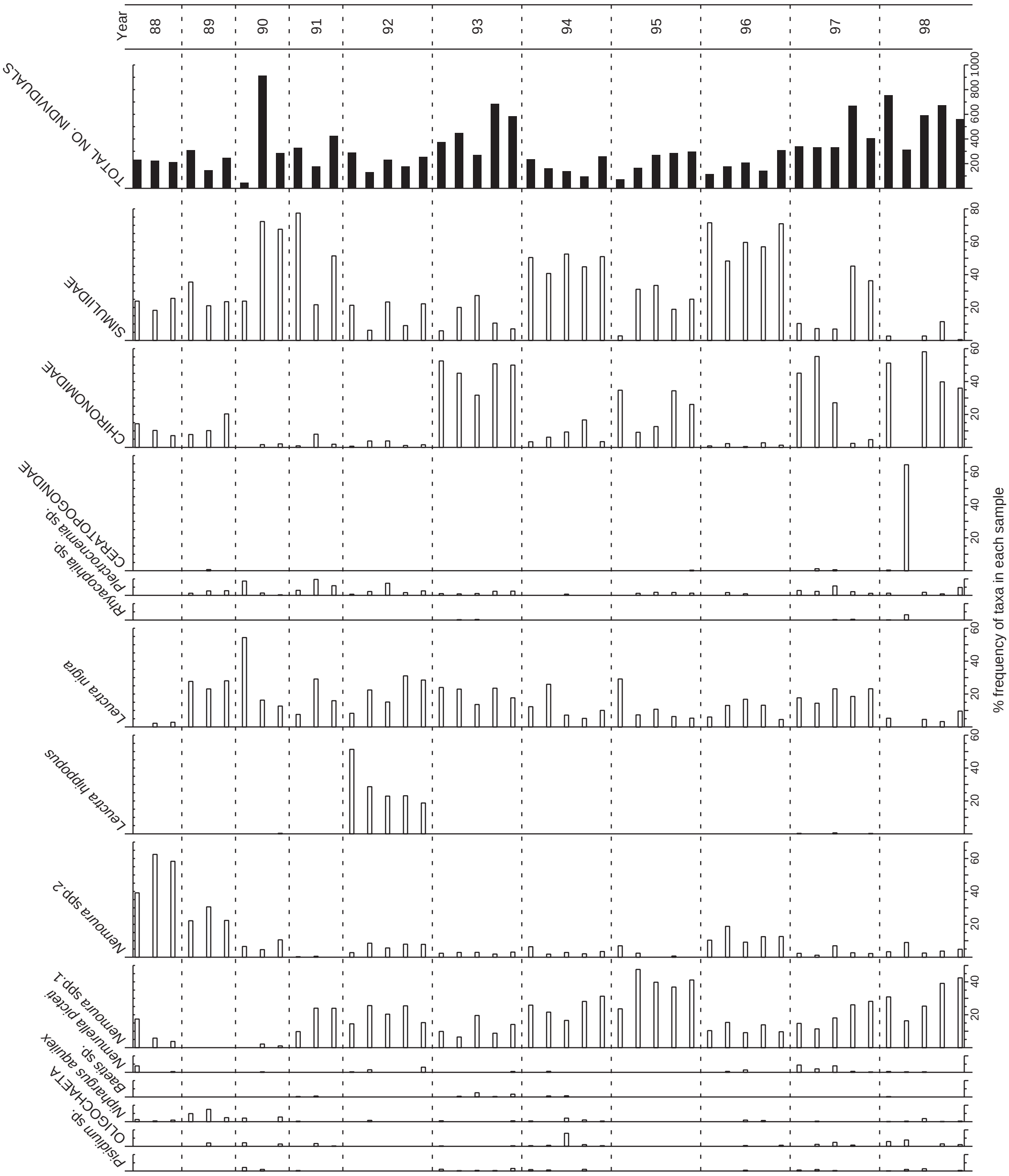
Old Lodge: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

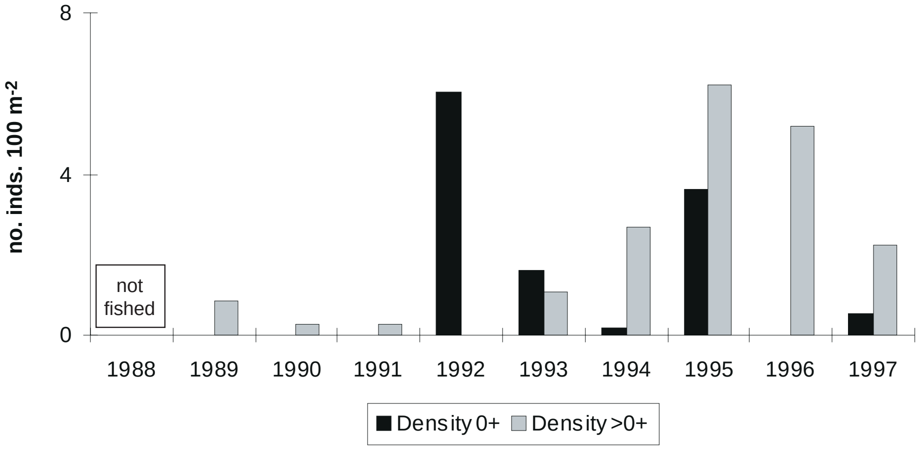
Figure 4.13.4

Old Lodge: summary of macroinvertebrate data (1988 - 1998)

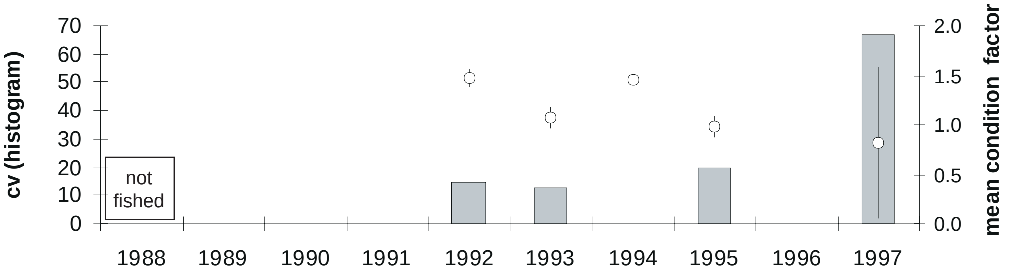
Percentage frequency of taxa in individual samples



(a) Density



(b) Condition (0+)



Condition (>0+)

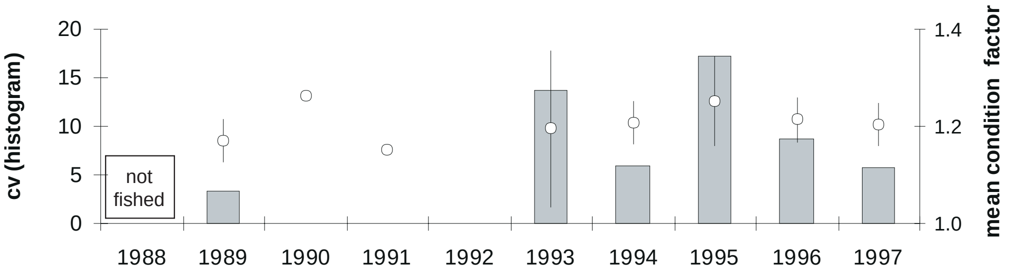


Figure 4.13.5

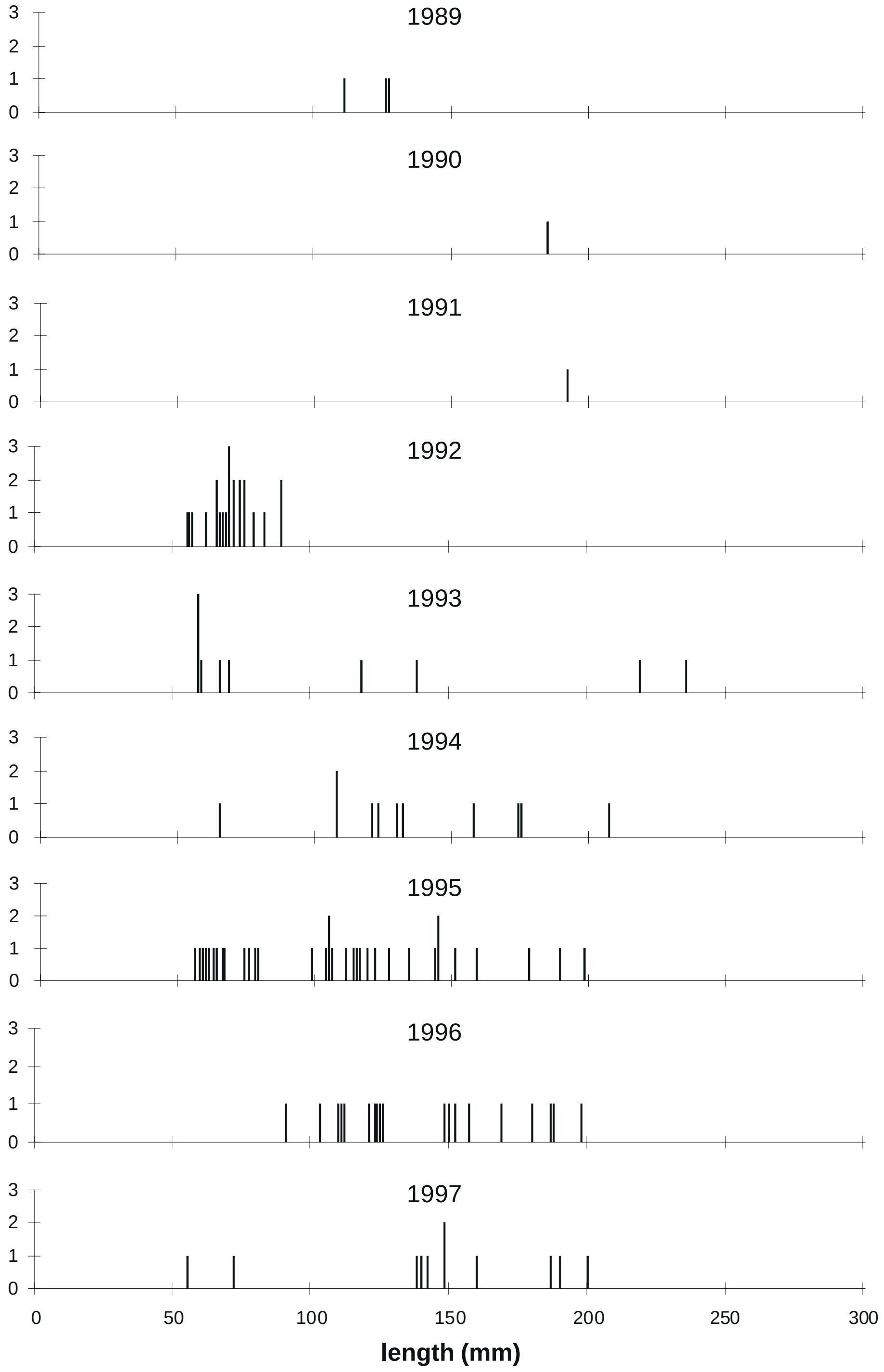
Old Lodge: summary of fish data (1989 - 1997)

(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

Figure 4.13.5

Old Lodge: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries



4.14 Narrator Brook

■ Site Review

Narrator Brook, which feeds the Burrator Reservoir within the Dartmoor National Park, is the only representative site for southwest England. The water chemistry sampling point was moved upstream in 1991 following a period of felling in the lower part of the catchment. This has led to a step change in the concentration of some chemical determinands and as a result trend analysis has only been carried out on the last 7 years of data. Low intensity grazing around the 50 m long macrophyte survey stretch has recently been restricted following the introduction of new fencing. However, this has had little impact on the bank-side vegetation to date. Otherwise, there are no indications of physical changes within the catchment over the past decade.

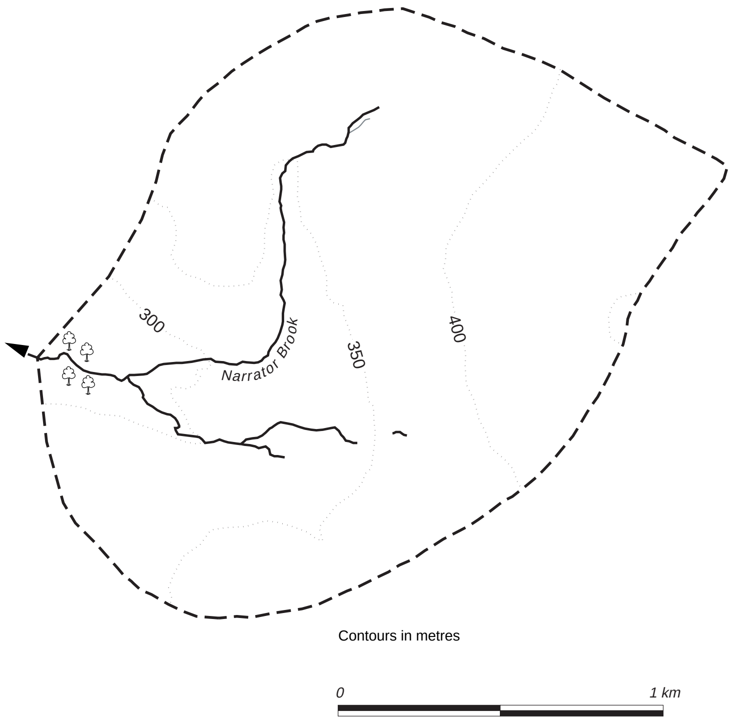


Figure 4.14.1

Narrator Brook: catchment

Table 4.14.1

Narrator Brook: site characteristics

Grid reference	*SX 568692*
Catchment area	*253 ha*
Minimum catchment altitude	*225 m*
Maximum catchment altitude	*456 m*
Catchment Geology	*granite*
Catchment Soils	*iron pan stagnopodsols, brown podsols*
Catchment vegetation	*moorland and acid grassland 98%, deciduous woodland 2%*
Mean annual rainfall	*1819 mm*
1996 deposition	
Total S	22 kg ha^{-1} yr^{-1}
non-marine S	15 kg ha^{-1} yr^{-1}
Oxidised N	9 kg ha^{-1} yr^{-1}
Reduced N	20 kg ha^{-1} yr^{-1}

Table 4.14.2

Narrator Brook: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.77*	*6.37*	*4.93*
Alkalinity	µeq l^{-1}	*15.6*	*58.4*	*-11.0*
Ca	µeq l^{-1}	*34.5*	*69.5*	*17.5*
Mg	µeq l^{-1}	*65.0*	*100.0*	*50.0*
Na	µeq l^{-1}	*253.5*	*334.8*	*208.7*
K	µeq l^{-1}	*20.0*	*28.2*	*15.4*
SO4	µeq l^{-1}	*73.8*	*85.4*	*62.5*
xSO4	µeq l^{-1}	*45.0*	*57.7*	*22.7*
NO3	µeq l^{-1}	*6.4*	*15.7*	*<1.4*
Cl	µeq l^{-1}	*273.8*	*478.9*	*219.7*
Soluble Al	µg l^{-1}	*60.0*	*236.0*	*11.0*
Labile Al	µg l^{-1}	*26.6*	*166.0*	*<2.5*
Non-labile Al	µg l^{-1}	*33.6*	*156.0*	*<2.5*
DOC	mg l^{-1}	*1.4*	*5.8*	*0.3*
Conductivity	µS cm^{-1}	*42.9*	*58.0*	*29.0*

Water Chemistry

(Figure 4.14.2, Tables 4.14.2-3)

Narrator Brook has a mean pH of 5.77, and a mean alkalinity of 16 µeq l^{-1}. Al concentrations are low, and divided equally between labile and non-labile forms. Low Ca concentrations (mean 35 µeq l^{-1}) suggest that this is a sensitive catchment, and it becomes acidic (pH <5.0, alkalinity <0 µeq l^{-1}) during episodes. NO_3 concentrations are low, with a mean of 6 µeq l^{-1}, whilst marine ion concentrations are high owing to the near-coastal location.

The change of sampling point in April 1991 led to a step change in a number of determinands (Patrick *et al.* 1995). Data collected prior to this are not included in trend analyses. The 1991-1998 dataset exhibits a number of significant trends (Table 4.14.3). Cl has declined significantly since 1991 according to both analytical methods, and this is clearly observable in the time series (Figure 4.14.2f). It is thought that this represents part of a similar cyclical Cl variation to that observed at many other sites across the UK, and this is supported by pre-1991 data at Narrator Brook. Although not comparable to post-1991 data in absolute terms, Cl levels clearly rose during the first three years of sampling to a peak in winter 1990-1991. Given high marine cation concentrations and the subsequent sea-salt effect during the early 1990s, pH and alkalinity may have been depressed at this time. This would explain the subsequent increases in these determinands identified by regression analysis, rather than a recovery due to reduced acid deposition reduction. This conclusion is supported by the fact that SO_4 and xSO_4 appear actually to have risen since 1991. Reasons for this increase are uncertain; it is possible that xSO_4 deposition has also risen in this region over the last decade (Vincent *et al.*, 1998), but an alternative cause may be the variation in marine inputs. It has been proposed by Evans *et al.* (in press) that during periods of high sea-salt deposition, higher SO_4 concentration in soil water leads to increased SO_4 adsorption on to the soil, which in turn leads to an effective reduction in xSO_4 (ie. a reduction in the ratio of total SO_4 to Cl). This mechanism is discussed in more detail in Section 5.3.3. The rise in xSO_4 from 1991 onwards may therefore represent the desorption of this stored SO_4.

Although Narrator Brook exhibits limited episodicity, two major episodes were sampled in the latter part of the record. The first, in November 1996, appears to have been a standard base cation dilution event, with Ca falling to its lowest recorded level. In contrast, the January 1998 event was the result of a major sea-salt storm, and led to the highest observed Cl and Na concentrations. The resulting sea-salt effect generated a severe acidic episode, with the

Table 4.14.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
pH		*+0.053***	-
Alkalinity	µeq l^{-1}	*+1.86***	-
SO_4	µeq l^{-1}	*+0.65***	*+0.52**
xSO_4	µeq l^{-1}	*+1.02****	*+1.08**
Cl	µeq l^{-1}	*-3.55**	*-5.63**
Labile Al	µg l^{-1}	*+2.92**	-

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

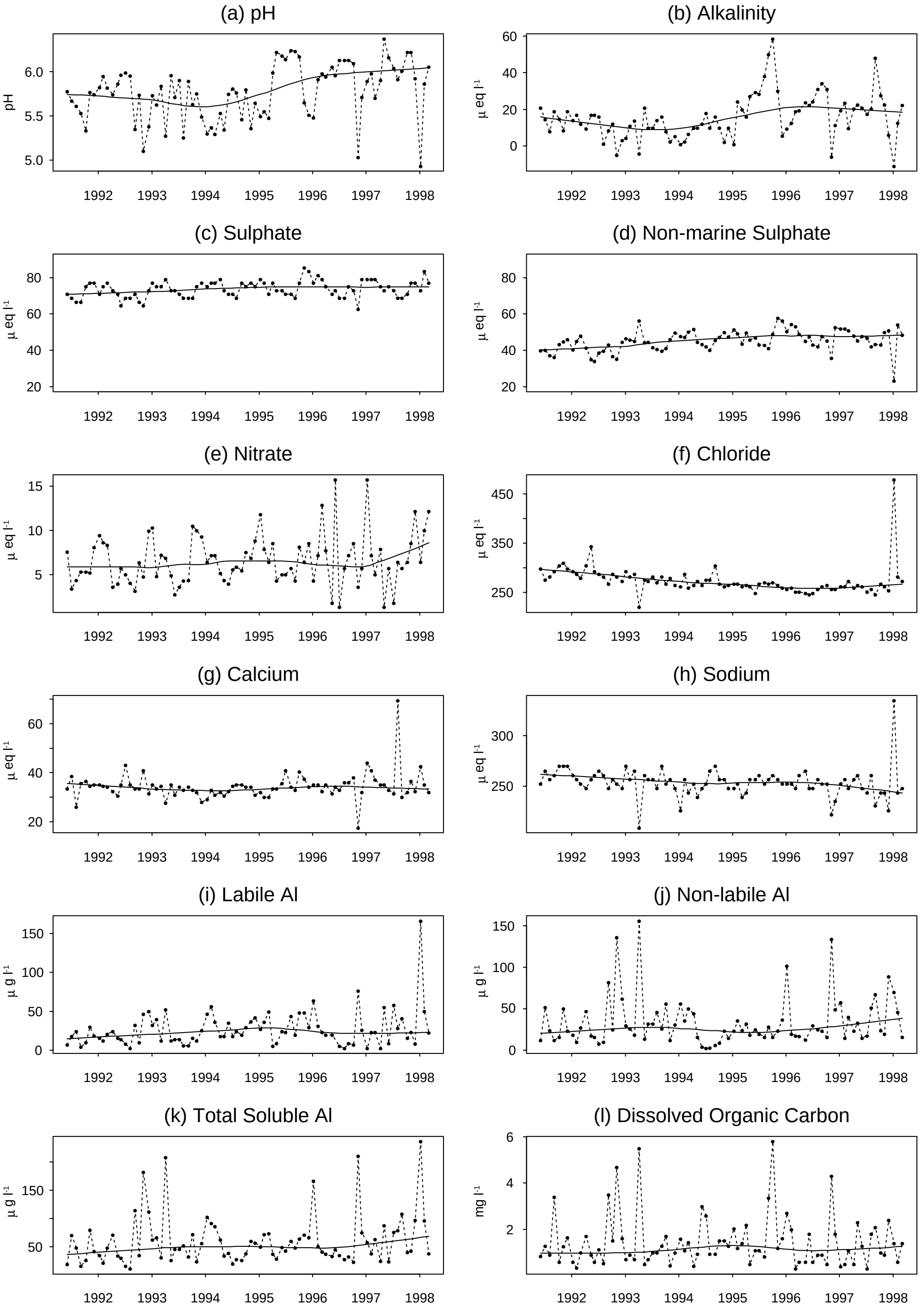


Figure 4.14.2

Narrator Brook: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.14.4

Narrator Brook: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*333*	*88*	*3.1*	*0.20*	*0.20*
Macrophytes	*5*	*13*	*2.1*	*0.84*	*0.57*
Invertebrates	*436*	*46*	*5.6*	*0.30*	*0.29*

Variance explained (%)	within year	between years	linear trend	p unrestricted	 restricted
Epilithic diatoms	*44.4*	*55.6*	*4.3*	*0.17*	*0.64*
Macrophytes	*	*	*30.3*	*0.04*	*0.06*
Invertebrates	*54.1*	*45.9*	*6.1*	*<0.01*	*0.09*

lowest pH and alkalinity, and highest labile Al, observed during the monitoring period. Additionally, there was a sharp decline in xSO_4, supporting the hypothesis of marine SO_4 retention described above.

■ Epilithic diatoms

(Figure 4.14.3, Table 4.14.4)

Although the epilithon of Narrator Brook is dominated by *Achnanthes minutissima* and *Fragilaria vaucheriae*, species typical of mildly acid streams, samples in some years have also contained taxa with lower pH preferences. *Eunotia vanheurckii* var. *intermedia* (pH optima 5.3) was particularly abundant in 1991 and 1993, while Eunotia [sp. 10 (minima)] (pH optima 4.9) occurred at >5% frequency in 1997 and 1998. Increases in both taxa appear to be balanced by a reduction in *A. minutissima*, suggesting more acid conditions during these periods. These findings are consistent with changes in the water chemistry for this site. For example, *A. minutissima* was particularly abundant in 1992 and 1995 when pH of samples was consistently elevated during the spring and summer, probably as a result of low rainfall (as recorded by the nearby Princetown Meteorological Station) and base-flow dominance of the stream hydrology. As with several other UKAWMN stream sites, diatom inferred pH (derived from weighted averaging), is inversely correlated with June-July rainfall over the period (Section 7.4.1). RDA and associated permutation test show that time is not a significant variable at the 0.01 level.

■ Macroinvertebrates

(Figure 4.14.4, Table 4.14.4)

This is the most diverse stream in the Network. After the Chironomidae, the fauna is dominated by a diverse community of stoneflies, characterised by *Leuctra inermis* and the predators *Isoperla grammatica* and *Siphonoperla torrentium*. Other abundant stoneflies include *Protonemura* spp., which had its highest density in 1998 and *Brachyptera risi*. Several species intolerant of low pH have been recorded (e.g. *Baetis* spp., *Hydropsyche siltalai* and *Limnius volckmari*). Caddisfly species are also numerous, although several have appeared in the last 5 years (notably *Lepidostoma hirtum*, *Drusus annulatus* and *Adicella reducta*). The first five years were rather impoverished in abundance, with 1992 being a particularly poor year. Since 1993 there has been an increase in both species richness and

Table 4.14.5

Narrator Brook: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**96**	**97**
INDICATOR SPECIES									
Lemanaea sp.[1]	*0.0*	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*	*0.3*	*0.0*
Brachythecium plumosum[2]	*0.8*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
Fontinalis squamosa[2]	*3.9*	*5.2*	*2.4*	*2.5*	*2.8*	*1.5*	*2.5*	*2.6*	*0.4*
Hyocomium armoricum[2]	*4.9*	*4.6*	*2.4*	*2.9*	*1.3*	*1.5*	*2.8*	*3.8*	*1.9*
Rhyncostegium riparioides[1]	*19.2*	*14.1*	*18.3*	*13.9*	*9.4*	*7.5*	*18.3*	*12.6*	*7.3*
Nardia compressa[3]	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
OTHER SUBMERGED SPECIES									
Filamentous green algae	*0.0*	*0.3*	*<0.1*	*0.7*	*<1.0*	*0.0*	*0.0*	*0.0*	*0.0*
Juncus bulbosus var. *fluitans*	*0.0*	*0.1*	*<0.1*	*0.1*	*0.2*	*<0.1*	*0.0*	*0.0*	*0.0*
Polytrichum commune	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*	*<0.1*	*<0.1*	*1.4*	*<0.1*
Scapania undulata	*<0.1*	*0.9*	*0.5*	*0.7*	*0.5*	*0.2*	*0.6*	*1.0*	*0.8*
Sphagnum sp.	*0.0*	*0.0*	*0.0*	*0.0*	*0.7*	*0.0*	*0.0*	*<0.1*	*0.0*
EMERGENT SPECIES									
Glyceria fluitans	*<0.1*	*0.3*	*<0.1*	*0.0*	*0.0*	*<0.1*	*0.1*	*0.0*	*0.0*
Juncus effusus	*0.0*	*<0.1*	*<0.1*	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*	*0.1*
Ranunculus flammula	*0.0*	*<0.1*	*<0.1*	*0.1*	*<0.1*	*0.0*	*0.1*	*0.1*	*<0.1*
Ranunculus omiophyllus	*<0.1*	*0.1*	*<0.1*	*0.0*	*<0.1*	*0.0*	*0.3*	*0.0*	*0.1*
total macrophyte cover excluding filamentous algae	*28.8*	*25.3*	*23.6*	*20.2*	*14.9*	*10.7*	*24.7*	*21.8*	*10.6*
TOTAL NUMBER OF SPECIES	*8*	*11*	*10*	*8*	*9*	*8*	*8*	*8*	*8*

abundance. This may reflect an improvement in conditions, although similar temporal patterns have been observed in macroinvertebrate diversity at several other stream sites and it seems likely that climatic factors, particularly those relating to spring flow conditions have an important influence (Section 7.4.2). Time as a linear trend is not significant in explaining changes in species composition using RDA and associated permutation test at the 0.01 level.

■ Fish

(Figure 4.14.5)

Narrator Brook has been electrofished since 1988. Mean trout densities are the second highest found in the Network and reflect the relatively high water quality of this site. Population density of both 0+ and >0+ fish show no trends over the ten years, although the density of >0-group fish was lower between 1991 and 1994 than in other years. Similarly, no time trends are apparent for condition factor statistics for either age class, although they do show remarkably smooth and synchronous oscillatory patterns which appear independent of density. The length frequency histograms indicate a healthy population structure at the site although a somewhat higher proportion of 0+ fish might have been expected.

■ Aquatic macrophytes

(Tables 4.14.4-5)

The particularly diverse aquatic macrophyte flora of the Narrator Brook survey stretch appears to reflect the relatively alkaline water chemistry, and the incised nature of the channel which provides a habitat for a number of emergent species. Throughout the decade the stretch has been dominated by the acid sensitive moss *Rhyncostegium ripariodes*, while two other moss species, *Fontinalis squamosa* and *Hyocomium armoricum* have also been relatively abundant. There has been a general reduction in overall cover over the decade. However, as this has not been accompanied by relative changes in species representation, it most likely represents effects of physical disturbance, or possibly an increase in shading of the survey stretch by bank-side vegetation, rather than any response to changing water chemistry. RDA and associated permutation test show that the change in species cover with time is insignificant at the 0.01 level.

■ Summary

Narrator Brook is moderately acidic, with occasional dilution or sea-salt driven episodes causing alkalinity to fall below zero. Trend analysis is only possible on data for 1991-1998, during which time chemical changes have been dominated by recovery from a marine ion peak in 1990-1991. Apparently contradictory increases in xSO_4 and pH/alkalinity may both be due to the effects of marine ions, while inter-annual variation in the macroinvertebrate and epilithic diatom communities may both be linked to variations in flow at particular times of the year.

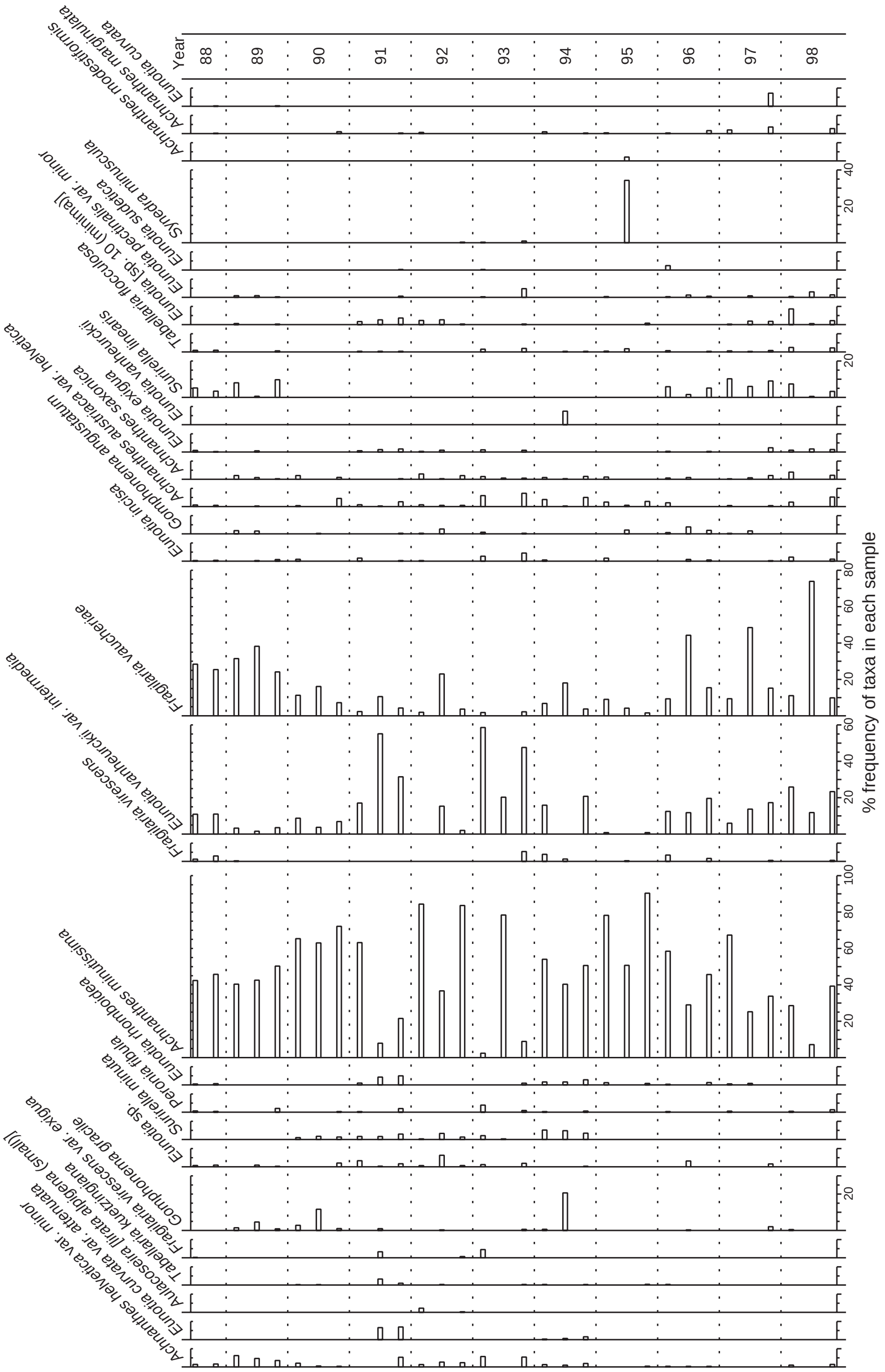


Figure 4.14.3

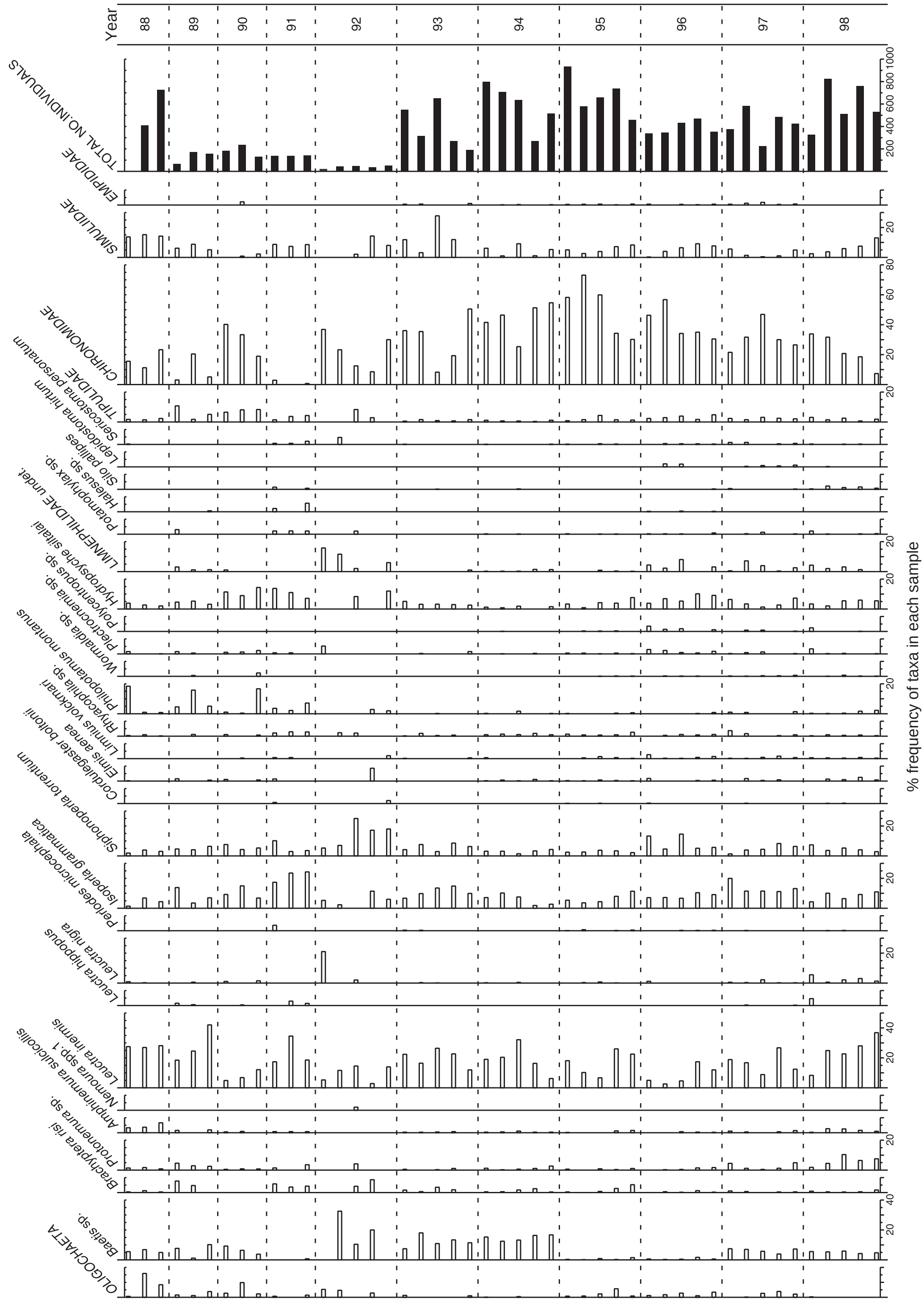
Narrator Brook: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

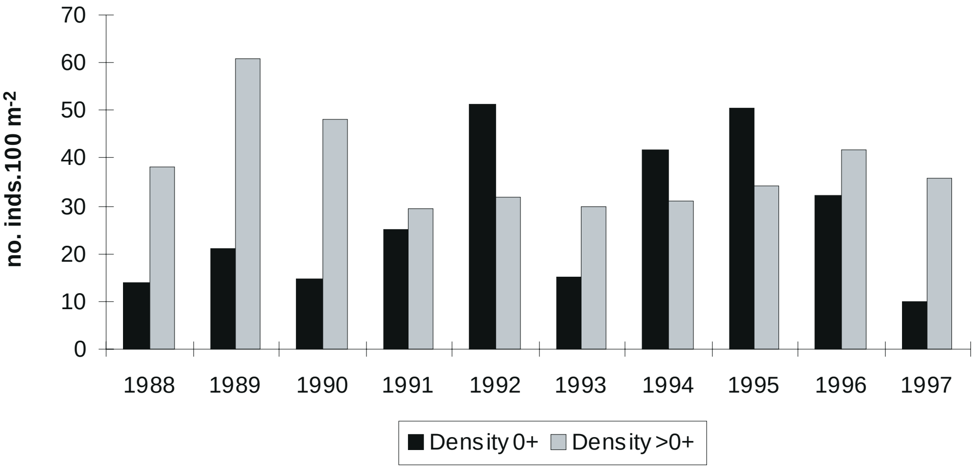
Figure 4.14.4

Narrator Brook: summary of macroinvertebrate data (1988 - 1998)

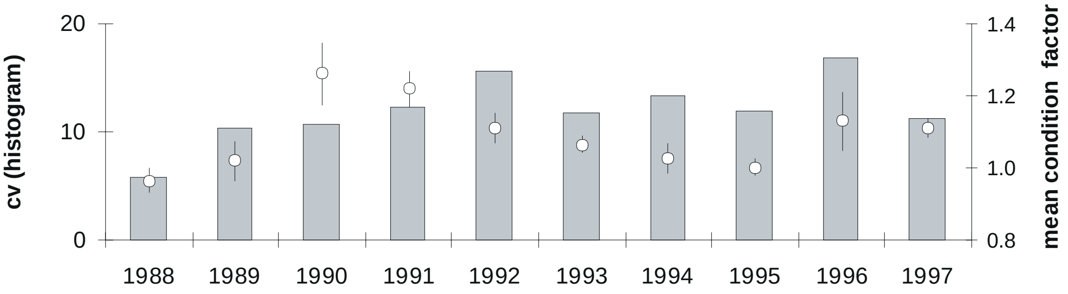
Percentage frequency of taxa in individual samples



(a) Density



(b) Condition (0+)



Condition (>0+)

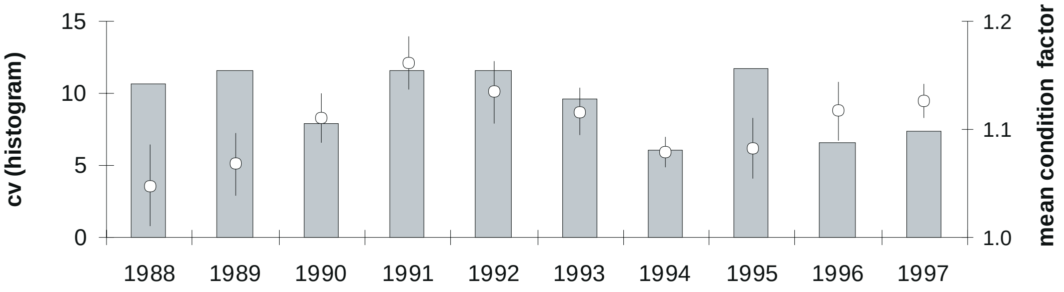


Figure 4.14.5

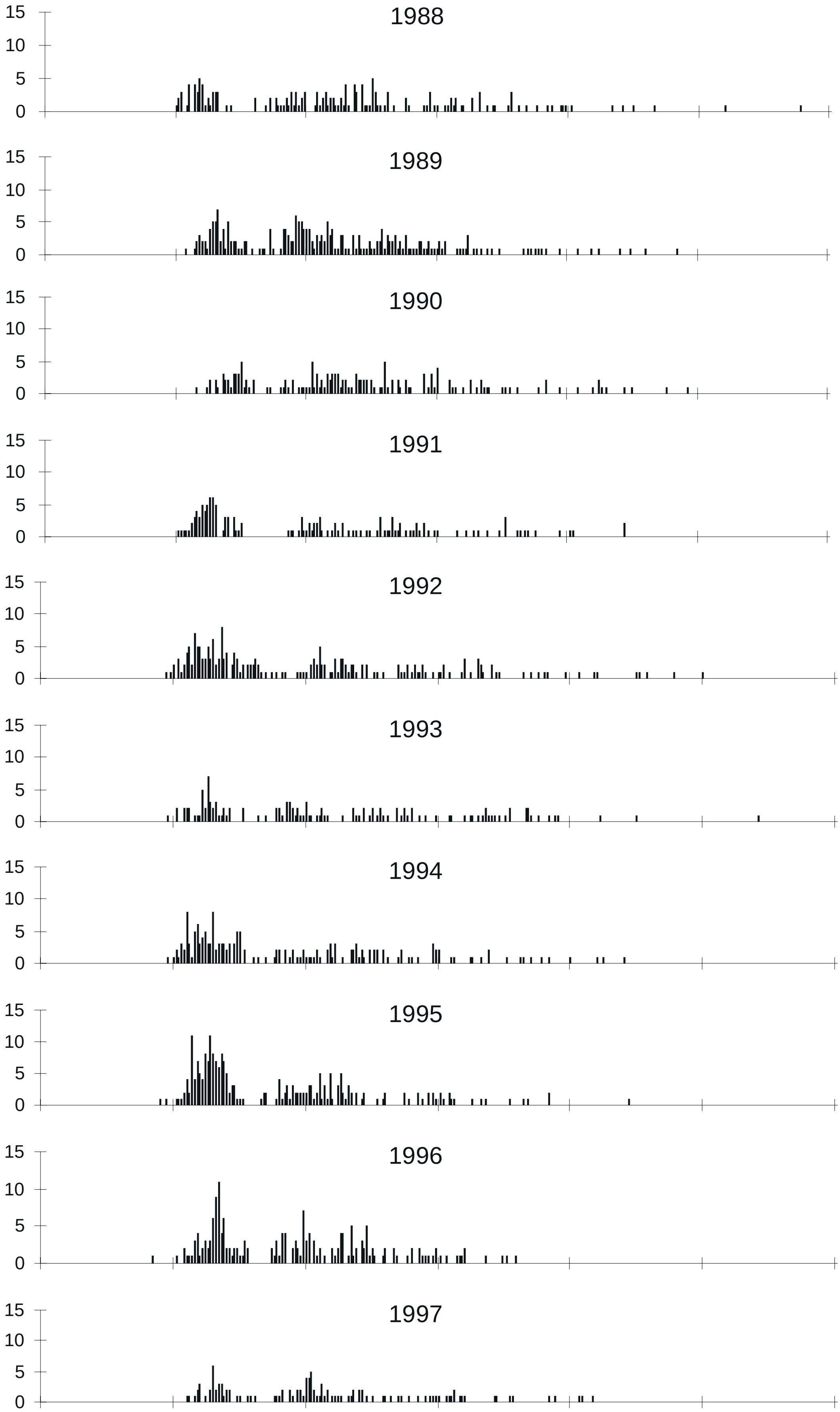
Narrator Brook: summary of fish data (1988 - 1997)

(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

Figure 4.14.6

Narrator Brook: summary of fish data (1988 - 1997)
(c) Trout length frequency summaries



4.15 Llyn Llagi

Site Review

Llyn Llagi lies at an altitude of 380 m in the Snowdonia National Park. Changes in the fossil diatom assemblage of a sediment core from the site indicate that the lake has acidified progressively from at least the mid-nineteenth century (diatom inferred pH 6.0) to around pH 4.6 by the mid 1980s (Patrick *et al.*, 1995). The uppermost levels of the sediment core suggested a slight improvement (i.e. recovery) from this time to the top of the core (1990). There has been no physical disturbance or change in the land management regime (low intensity sheep grazing) in the catchment over the last decade. Recently the site has been included in the UK Acid Deposition Monitoring Network, and

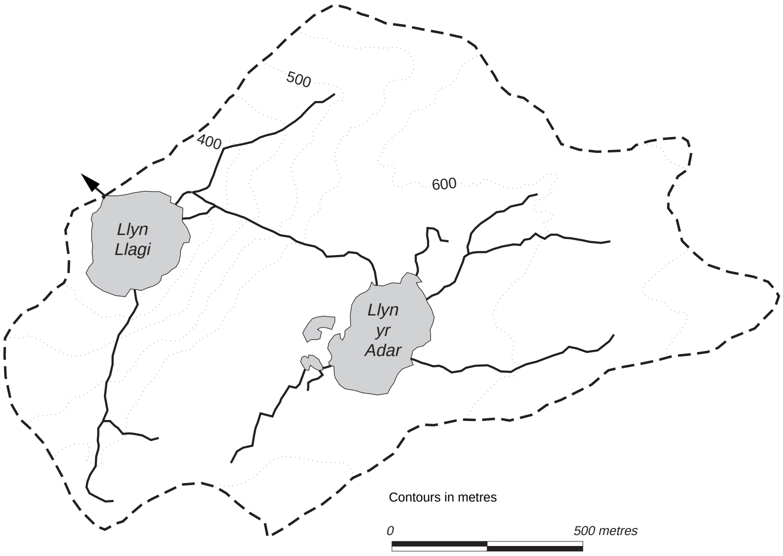


Figure 4.15.1

Llyn Llagi: catchment

Table 4.15.1

Llyn Llagi: site characteristics

Grid reference	*SH 649483*
Lake altitude	*380 m*
Maximum depth	*16.5 m*
Mean depth	*5.8 m*
Volume	3.3×10^5 *m*^{3}
Lake area	*5.67 ha*
Catchment area (excl. lake)	*157 ha*
Catchment: Lake area ratio	*27.7*
Catchment Geology	*ordivcian slates and shales, dolerite and volcanic intrusions*
Catchment Soils	*stagnopodsols, stagnohumic gleys, blanket peat*
Catchment vegetation	*moorland 100%*
Net relief	*298 m*
Mean annual rainfall	*2941 mm*
1996 deposition	
Total S	*24 kg ha*$^{-1}$ *yr*$^{-1}$
non-marine S	*18 kg ha*$^{-1}$ *yr*$^{-1}$
Oxidised N	*9 kg ha*$^{-1}$ *yr*$^{-1}$
Reduced N	*18 kg ha*$^{-1}$ *yr*$^{-1}$

Table 4.15.2

Llyn Llagi: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.34*	*6.30*	*4.78*
Alkalinity	µeq l^{-1}	*5.6*	*33.4*	*-8.0*
Ca	µeq l^{-1}	*52.5*	*94.0*	*31.0*
Mg	µeq l^{-1}	*46.7*	*75.0*	*25.0*
Na	µeq l^{-1}	*168.7*	*291.3*	*100.0*
K	µeq l^{-1}	*6.2*	*19.2*	*2.6*
SO_4	µeq l^{-1}	*61.0*	*81.3*	*39.6*
xSO_4	µeq l^{-1}	*40.6*	*67.9*	*17.1*
NO_3	µeq l^{-1}	*10.0*	*38.6*	*2.1*
Cl	µeq l^{-1}	*193.8*	*377.5*	*98.6*
Soluble Al	µg l^{-1}	*74.1*	*193.0*	*5.0*
Labile Al	µg l^{-1}	*39.7*	*159.0*	*<2.5*
Non-labile Al	µg l^{-1}	*35.6*	*80.0*	*<2.5*
DOC	mg l^{-1}	*2.4*	*5.50*	*<0.10*
Conductivity	µS cm^{-1}	*31.2*	*58.0*	*13.0*

this should allow a more thorough comparison of the temporal relationship between deposition and surface water chemistry in the catchment in future years.

Water Chemistry

(Tables 4.15.2-3, Figure 4.15.2)

Llyn Llagi is a moderately acidic site with a mean pH of 5.34 and a mean alkalinity of 6 μeq l^{-1}. Al concentrations are fairly low, with approximately equal concentrations of labile and non-labile forms. Large seasonal variations are observed for a number of determinands, with alkalinity generally becoming negative during winter. Although mean NO_3 levels are low (mean 10 μeq l^{-1}), large winter peaks have been recorded, at which times concentrations have approached those of xSO_4 (mean 41 μeq l^{-1}).

Trend analyses show that little net change has occurred in lake chemistry at this site since 1988. A trend is identified in pH, using SKT (Table 4.15.3), but as this is not accompanied by significant changes in either alkalinity or acid anions it is difficult to attribute to genuine chemical recovery. Peaks in Cl and Na during 1990-1991 are remarkably similar to those observed in the Galloway and the Lake District, supporting the hypothesis of a wide-ranging climatic influence. On the chemical evidence alone it is therefore more likely that the pH trend and cyclical variation in Ca, primarily result from climatic effects (Figure 4.15.2g) (however, see epilithic diatom Section). Non-marine sulphate rose during the early part of the record but may now have begun to decline, as in Galloway and the Lake District.

Epilithic diatoms

(Figure 4.15.3, Table 4.15.4)

The epilithic diatom assemblage of Llyn Llagi has undergone highly significant linear change, according to RDA and associated permutation test. “Sample year” can account for 17.6 % of all variance between samples while the maximum variance which can be explained by one axis in PCA is only 22.9%. The most striking change observed is the dramatic reduction in acidophilous *Tabellaria quadriseptata* (pH optima 4.9) between 1995-1996. As at Loch Grannoch there has been an abrupt change in the relative abundance of this species, although at Loch Grannoch it has become more abundant. Its decline appears to be reciprocally related to increases in species with higher pH optima including *Nitzschia perminuta* (pH optima 5.7), *Peronia fibula* (pH optima 5.3) and *Brachysira vitrea* (pH optima 5.9). Diatom inferred pH (derived from weighted averaging) shows that the species assemblage is indicative of gradually increasing pH during the decade (Figure 7.3a). Similar species changes are apparent in the sediment trap samples (Figure 4.15.6) although in these there is a steadier increase in *E.incisa.* Generally therefore, changes in both the epilithon and sediment traps are consistent with an increase in pH observed in the more recent years of monitoring and also appear to follow the

Table 4.15.3

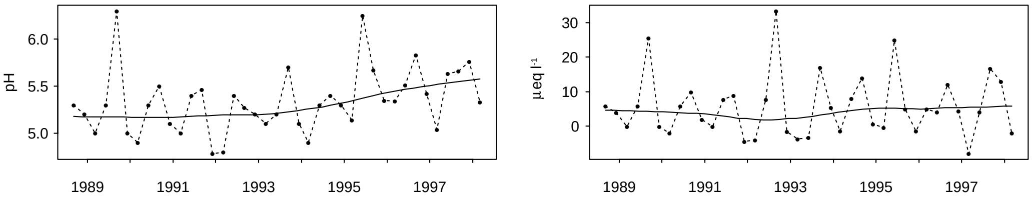
Significant trends in chemical determinands (July 1988 -1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
pH		*+0.049**	-

** Trend significant at p < 0.05; ** trend significant at p < 0.01; *** trend significant at p < 0.001*

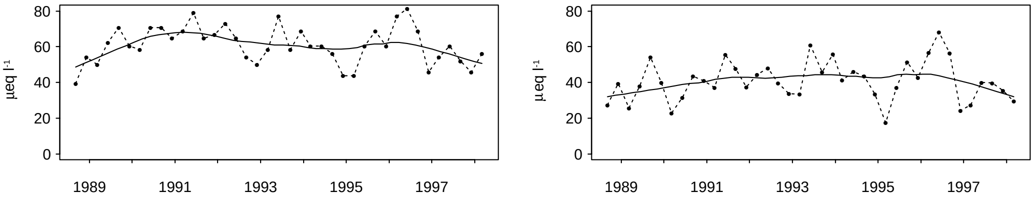
(a) pH

(b) Alkalinity



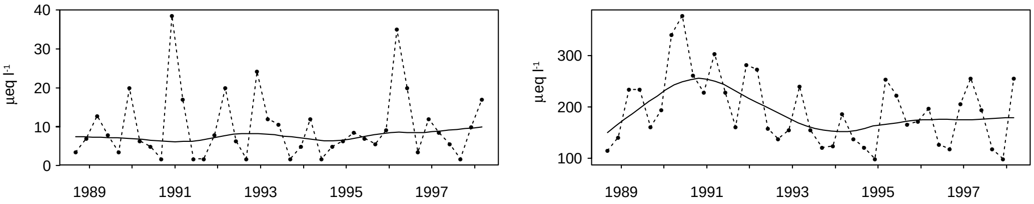
(c) Sulphate

(d) Non-marine Sulphate



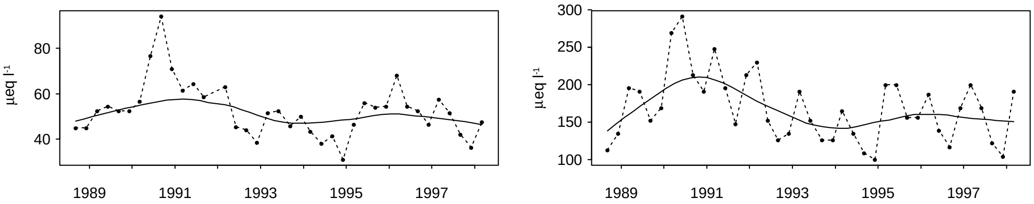
(e) Nitrate

(f) Chloride



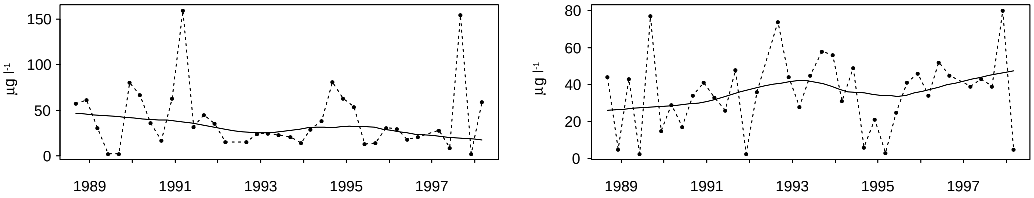
(g) Calcium

(h) Sodium



(i) Labile Al

(j) Non-labile Al



(k) Total Soluble Al

(l) Dissolved Organic Carbon

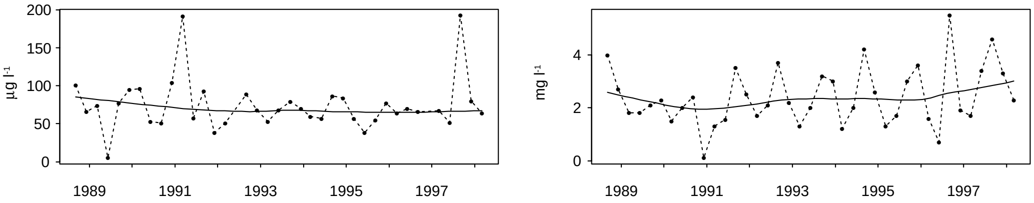


Figure 4.15.2

Llyn Llagi: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.15.4

Llyn Llagi: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*376*	*135*	*8.0*	*1.28*	*0.77*
Macrophytes	*39.8*	*21*	*11.9*	*1.01*	*0.70*
Invertebrates	*771*	*36*	*3.0*	*0.69*	*0.46*

Variance				p	
explained (%)	within year	between years	linear trend	unrestricted	restricted
Epilithic diatoms	*43.4*	*56.6*	*17.6*	*<0.01*	*<0.01*
Macrophytes	*	*	*27.6*	*0.02*	*0.12*
Invertebrates	*42.0*	*58.0*	*11.5*	*<0.01*	*<0.01*

apparent recovery trend identified in the uppermost levels of the sediment core taken in 1990 (Patrick *et al.*, 1995) (Section 7.2.5). These observations provide the most convincing evidence of real biological “recovery” seen at any UKAWMN site. However, due to the clear sensitivity of the chemistry of Llyn Llagi to climatic effects, further monitoring is essential to ascertain whether these changes are sustained.

■ Macroinvertebrates

(Figure 4.15.4, Table 4.15.4)

Llyn Llagi is dominated by chironomids and the acid tolerant mayfly family, the Leptophlebiidae. The first few years were characterised by acid tolerant stoneflies (*Nemoura* spp.) and caddisflies (*Plectrocnemia* spp., *Limnephilus* spp.). The second half of the survey showed an increase in the number of Coleopterans, particularly *Oulimnius tuberculatus*. Of the Polycentropodid caddisflies, *Polycentropus* spp. was the most abundant and ocurred in all years except 1990, *Plectrocnemia* spp. was recorded in low numbers and was absent in 1998, while *Holocentropus* spp. and *Cyrnus* spp. were both recorded intermittently. The Hydroptilid caddisfly, *Oxyethira* spp. was first recorded in 1993 and was present in very high numbers in 1995. Time as a linear trend is significant at the 0.01 level according to RDA and restricted permutation test. There seems to have been a change in species composition from a community characterised by acid tolerant stoneflies in the early years to one with fewer stoneflies and some moderately acid sensitive beetles and caddisflies.

■ Fish

(Figure 4.15.5)

The outflow stream from Llyn Llagi has been electrofished since 1989. Mean trout densities are in the middle range of those found in the Network sites. Densities of 0+ trout have fluctuated over the years and overall show a pattern of decline although there is not a statistically significant linear relationship with time. Densities of >0+ fish and the mean condition factor for both age groups show no pattern over the years. The coefficient of variation of the condition factor for the >0 group is particularly elevated in 1990. The length frequency graphs show the variation in recruitment together with the subsequent impact upon the numbers of >0+ fish present in the following year.

Table 4.15.5

Llyn Llagi: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Myriophyllum alterniflorum[2]	1	1	1	1	1	2	1	1
Sphagnum auriculatum[4]	1	2	2	3	3	3	3	3
Juncus bulbosus[4]	0	1	1	1	1	1	2	2
OTHER SUBMERGED SPECIES								
Batrachospermum sp.	2	2	2	2	2	3	2	2
Filamentous green algae	4	5	5	5	5	5	5	5
Amblystegium sp.	1	2	0	1	2	2	2	1
Drepanocladus sp.	1	1	0	0	0	0	0	1
Fontinalis sp.	1	1	2	2	2	2	2	1
Polytrichum sp.	0	0	1	0	0	0	0	0
Rhytidiadelphus squarrosus	0	1	0	0	1	0	1	1
Marsupella emarginata	0	1	1	1	1	1	1	1
Nardia compressa	0	1	2	2	1	0	1	1
Plectocolea obovata	1	1	1	1	0	0	0	0
Scapania undulata	1	2	2	2	0	1	0	1
Isoetes echinospora	1	1	2	2	2	1	2	2
Isoetes lacustris	5	5	5	5	5	5	5	5
Littorella uniflora	2	2	3	3	3	3	3	3
Lobelia dortmanna	4	4	4	4	4	4	4	4
Subularia aquatica	0	0	0	0	0	1	0	0
Potamogeton polygonifolius	0	0	1	1	1	2	1	1
Sparganium angustifolium	1	2	2	2	2	2	2	2
EMERGENT SPECIES								
Juncus effusus	2	2	2	2	2	2	2	2
Juncus acutifloris/articulatus	5	5	5	5	5	5	5	5
TOTAL NUMBER OF SPECIES	16	20	19	19	18	18	18	20

Aquatic macrophytes

(Tables 4.15.4-5)

Llyn Llagi is characterised by an aquatic macroflora typical of moderately acid lakes. The submerged flora is dominated by the isoetid species, *Lobelia dortmanna,* in the shallows, and *Isoetes lacustris,* which forms a dense sward in deeper water. At the time of summer sampling, *I. lacustris* plants support a thick bloom of filamentous algae. *Littorella uniflora* occurs in association with these species but at a lower frequency. The relatively acid sensitive species *Myriophyllum alterniflorum* is limited to two locations close to stream inflows. According to survey maps, the cover of the acidophilous species *Juncus bulbosus* var. *fluitans*, which was not recorded until 1989, has since gradually increased in several littoral areas. This is surprising, given the gradual amelioration in acidity observed for Llyn Llagi, and requires further attention. *Callitriche hamulata*, which was recorded at the site by Wade in 1980 (Wade

1980), has not been seen over the monitoring period. With the exception of the increase in *J.bulbosus* var. *fluitans* there is no other evidence of floristic change over the decade and "sample year" is insignificant as a linear variable according to RDA and restricted permutation test.

■ Summary

Llyn Llagi has an intermediate pH, alkalinity and xSO_4 concentration, and a relatively low NO_3 concentration. Linear regression shows pH to have increased over the decade although there is no accompanying downward trend in acid anion concentration. Pronounced cyclical variations have been observed in marine ion concentrations which could account for cyclical change in Ca, and climatic effects may also have influenced the pH trend. However, changes in the relative abundance of diatom species, both in epilithon and sediment trap samples appear to follow the apparent "recovery" trend identified in the uppermost layers of a sediment core taken in 1990. These provide strong evidence that long term chemical and biological recovery from acidification is underway. Improvements have also been observed in the macroinvertebrate community. It is therefore possible that the last decade of data for Llyn Llagi demonstrate the effects of climatic variation superimposed on a longer term recovery trend. It is essential that monitoring is maintained at this site, first to determine whether recent chemical and biological improvements are sustained, and second, to see whether this apparent response at a low trophic level will eventually be accompanied by improvements further up the food chain.

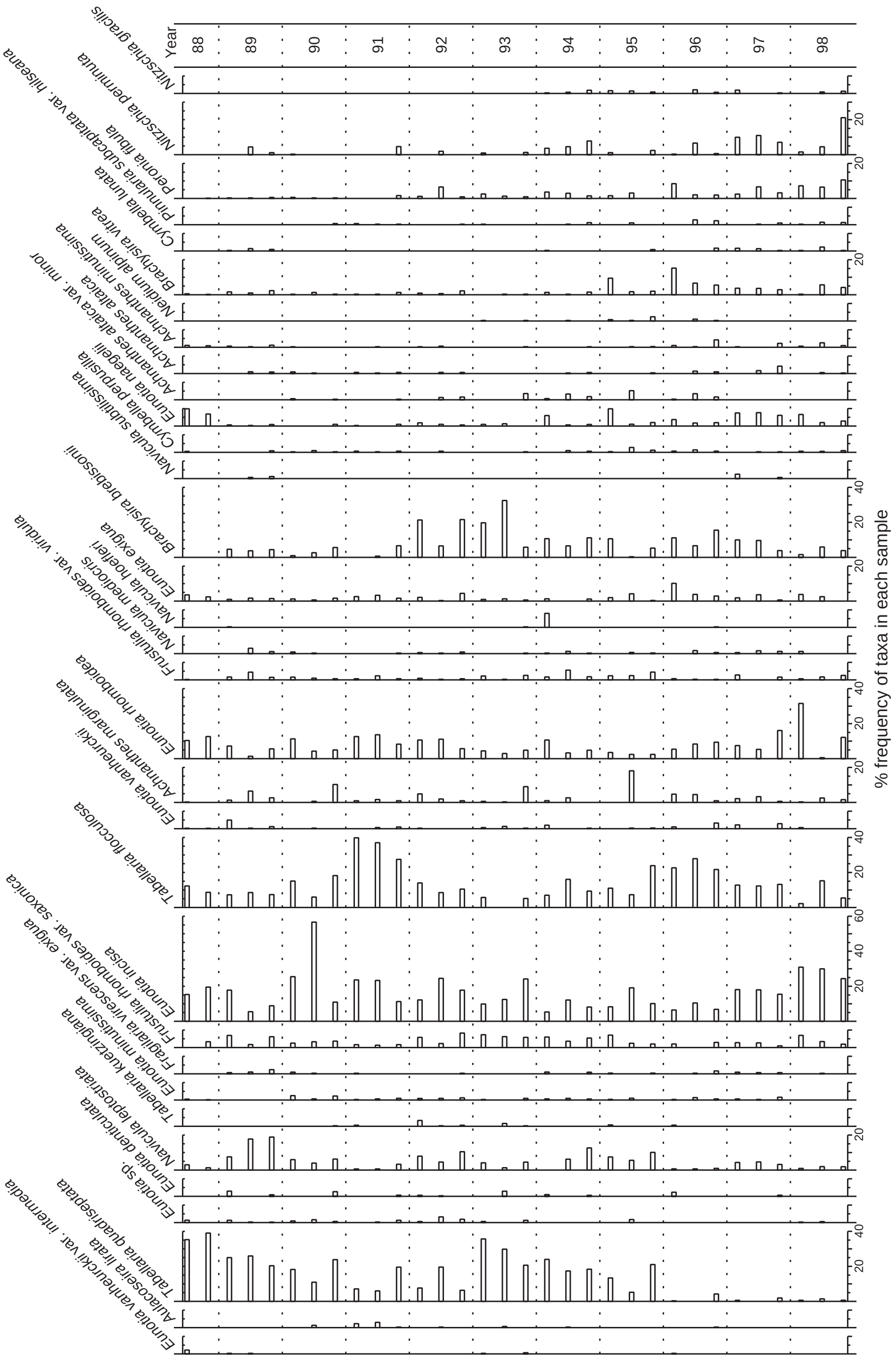


Figure 4.15.3

Llyn Llagi: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

Figure 4.15.4

Llyn Llagi: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

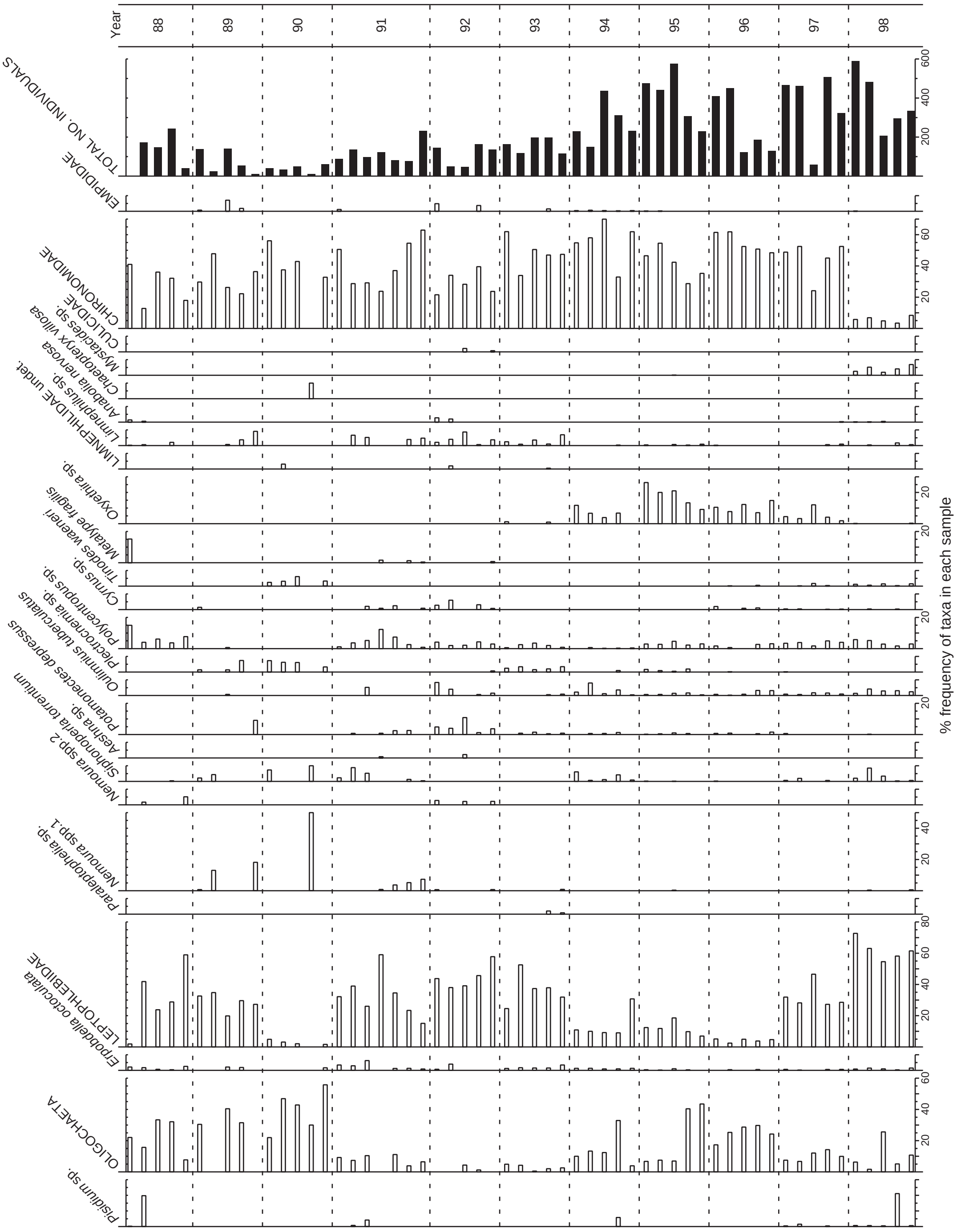


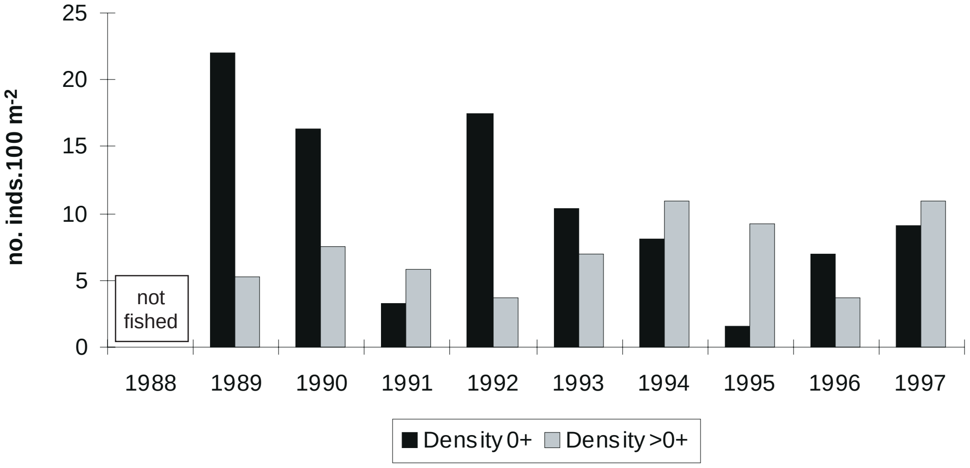
Figure 4.15.5

Llyn Llagi: summary of fish data (1988 - 1997)

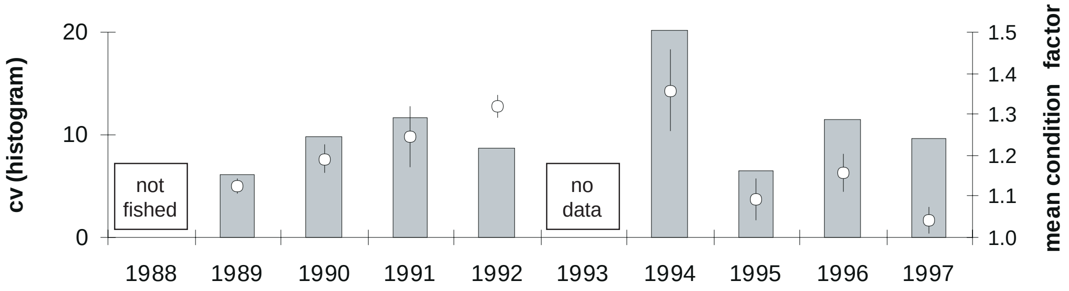
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

(a) Density



(b) Condition (0+)



Condition (>0+)

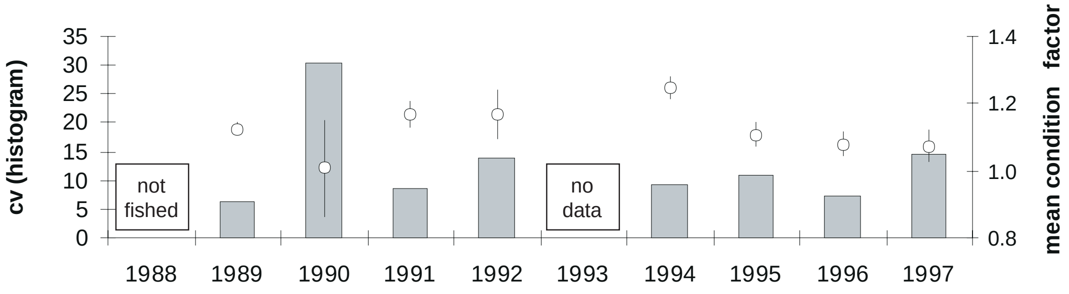
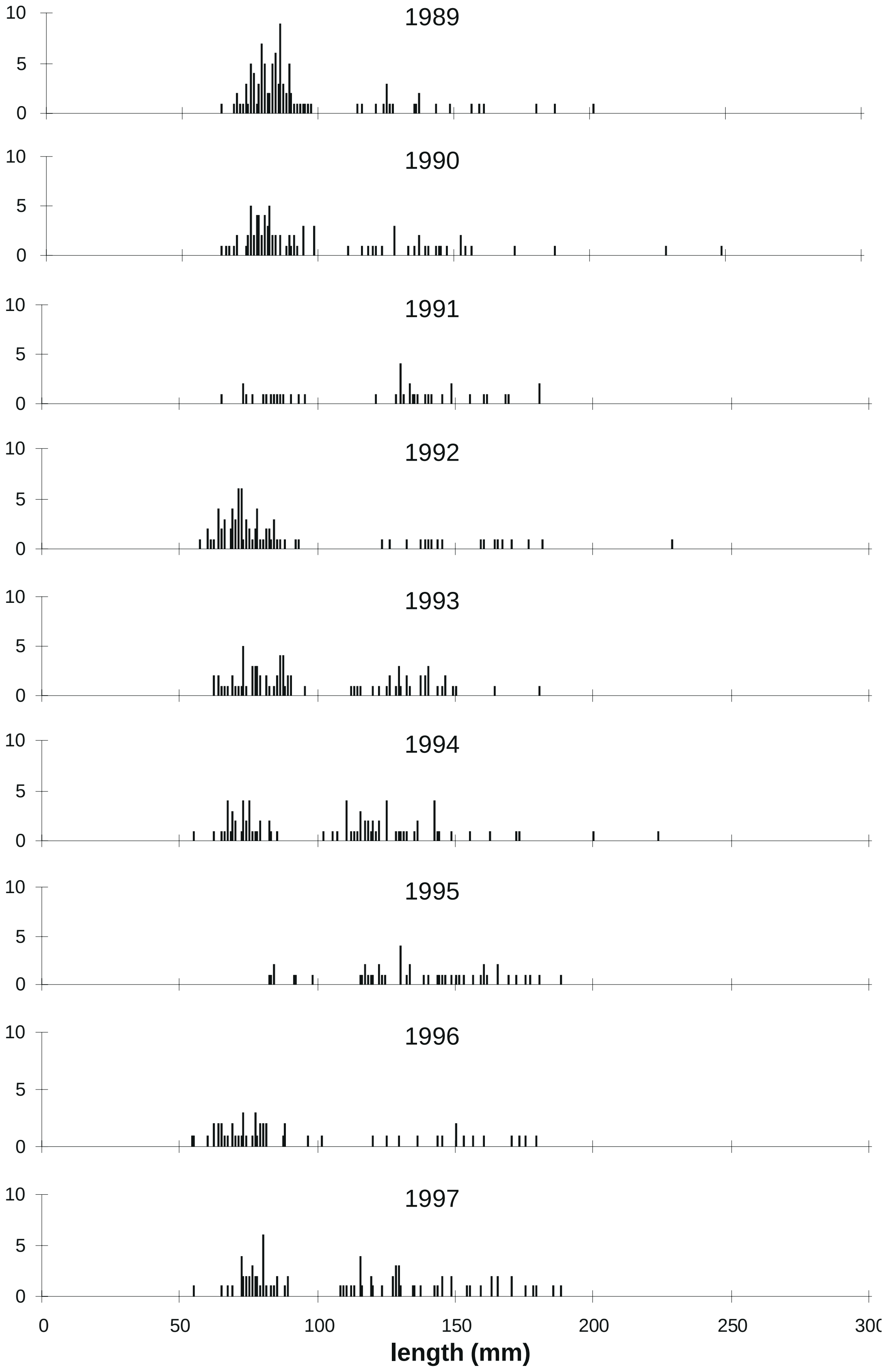


Figure 4.15.5

Llyn Llagi: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries



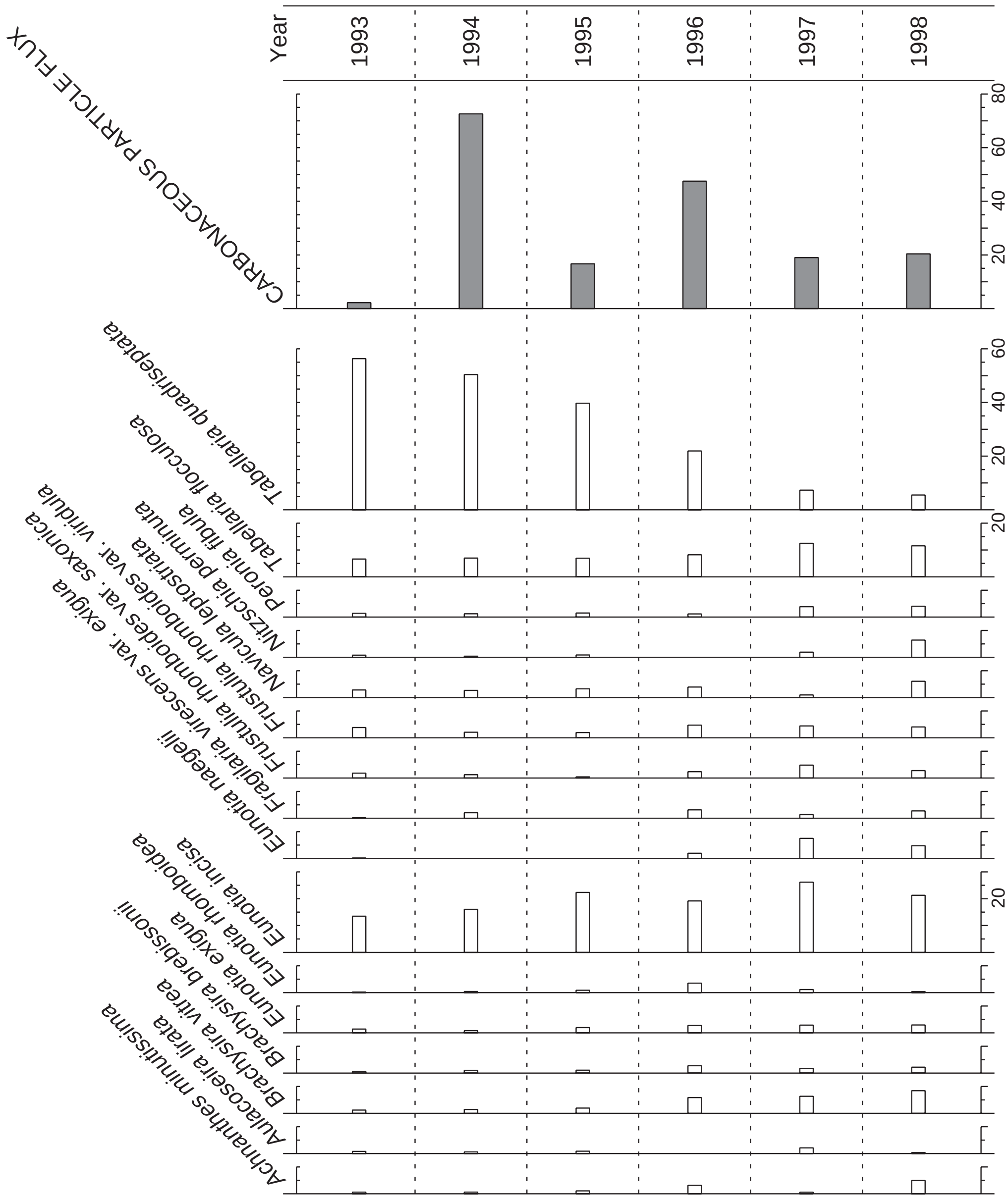
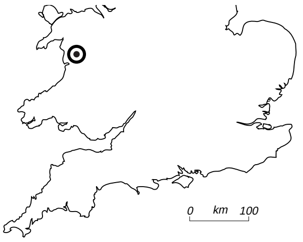


Figure 4.15.6

Llyn Llagi: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year



4.16 Llyn Cwm Mynach

■ Site Review

The catchment of Llyn Cym Mynach, in the Rhinog mountains of north Wales, includes a substantial proportion of mature forest. According to diatom based pH reconstruction, using a sediment core taken in 1990, Llyn Cwm Mynach has undergone relatively recent acidification, with pH declining from 5.8 at the turn of the century to 5.4 by the onset of the monitoring period. Over the past four years some thinning of the forest has been carried out but the overall land cover has remained unchanged. The main lake basin has been affected by the blue-green alga *Plectonema* which has blanketed large areas and out-competed submerged vascular aquatic macrophytes. As a result, the littoral strand-line has become increasingly choked

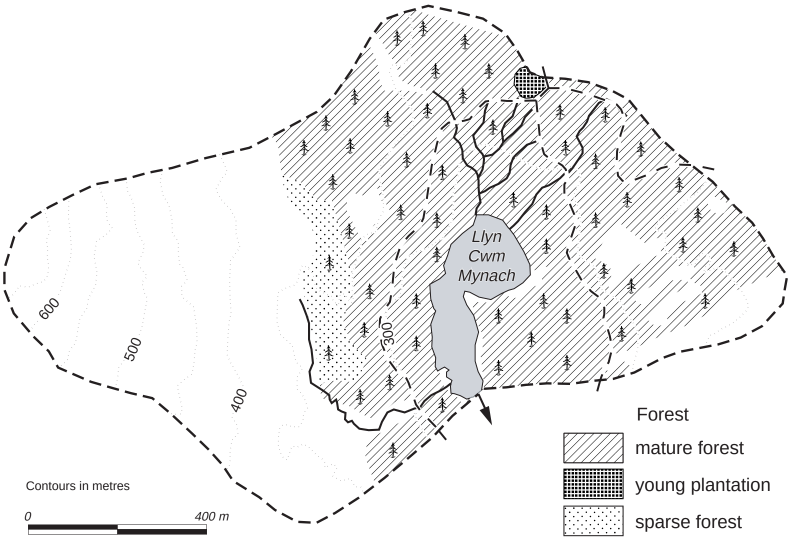


Figure 4.16.1

Llyn Cwm Mynach: catchment

Table 4.16.1

Llyn Cwm Mynach: site characteristics

Grid reference	*SH 678238*
Lake altitude	*285 m*
Maximum depth	*11.0 m*
Mean depth	*0.9 m*
Volume	*5 x 10^4 m^3*
Lake area	*5.9 ha*
Catchment area (excl. lake)	*152.5 ha*
Catchment: lake area ratio	*25.9*
Catchment Geology	*Cambrian sedimentary*
Catchment Soils	*blanket peats, acid rankers*
Catchment vegetation	*conifers 55%, moorland 45%*
Net relief	*395 m*
Mean annual rainfall	*2197 mm*
1996 deposition	
Total S	*19 kg ha^{-1} yr^{-1}*
non-marine S	*14 kg ha^{-1} yr^{-1}*
Oxidised N	*7 kg ha^{-1} yr^{-1}*
Reduced N	*13 kg ha^{-1} yr^{-1}*

Table 4.16.2

Llyn Cwm Mynach: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.37*	*6.30*	*4.70*
Alkalinity	μeq l^{-1}	*4.6*	*34.4*	*-21.0*
Ca	μeq l^{-1}	*70.0*	*128.0*	*21.5*
Mg	μeq l^{-1}	*63.3*	*100.0*	*33.3*
Na	μeq l^{-1}	*268.3*	*404.3*	*173.9*
K	μeq l^{-1}	*5.6*	*9.7*	*2.6*
SO_4	μeq l^{-1}	*86.0*	*154.2*	*58.3*
xSO_4	μeq l^{-1}	*54.2*	*110.4*	*32.9*
NO_3	μeq l^{-1}	*10.0*	*30.7*	*2.1*
Cl	μeq l^{-1}	*304.2*	*518.3*	*143.7*
Soluble Al	μg l^{-1}	*117.3*	*378.0*	*5.0*
Labile Al	μg l^{-1}	*65.2*	*291.0*	*<2.5*
Non-labile Al	μg l^{-1}	*52.3*	*158.0*	*<2.5*
DOC	mg l^{-1}	*2.6*	*10.7*	*<0.1*
Conductivity	μS cm^{-1}	*46.0*	*72.0*	*24.0*

by dead vegetation and the availability of macroinvertebrate littoral habitats may have been affected.

Water Chemistry

(Figure 4.16.2, Tables 4.16.2-3)

This is a moderately acidic site, with a mean pH and alkalinity of 5.37 and 5 µeq l^{-1} respectively. Alkalinity frequently becomes negative during winter, and soluble Al concentrations are relatively high (mean 117 µg l^{-1}, maximum 348 µg l^{-1}), with the labile fraction on average slightly exceeding the non-labile fraction. Mean xSO_4 is 54 µeq l^{-1}, significantly higher than at Llyn Llagi in the same region, and this possibly results from the enhancement of deposition by forestry. Despite these differences the acidity of the two sites is very similar, since Ca concentrations are also higher at Cwm Mynach, implying that this catchment has a greater base cation weathering supply. NO_3 concentrations are low, with a mean of 10 µeq l^{-1}, although concentrations are higher during the acidic winter period.

As at Llyn Llagi, this site exhibits few clear trends over the last ten years (Table 4.16.3). The most notable feature of the time series (Figure 4.16.2) is again a very strong cyclical variation in Cl, Na and perhaps also Ca. An apparent decrease in Cl identified by regression analysis is certainly a consequence of this variation. Non-marine SO_4 appears to have risen to a peak in the mid-1990s, and subsequently to have declined (Figure 4.16.2d). An increasing trend is identified by both regression and SKT for non-labile Al, which is consistent with increases observed elsewhere, although it is not matched by a rising trend in DOC. The LOESS curve for DOC (Figure 4.16.2l) does suggest a small increase over the decade, but this is masked to some extent by a very high, and possibly anomalous, DOC value early in the record.

Epilithic diatoms

(Figure 4.16.3, Table 4.16.4)

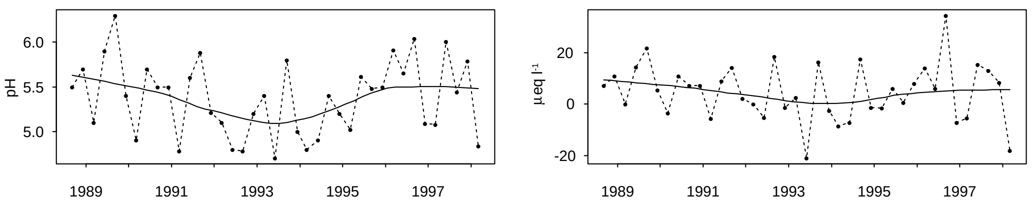
Epilithic diatom species representation has been relatively stable at Llyn Cwm Mynach compared to other sites in the Network. However, subtle shifts in the proportions of some species have occurred and a time trend is significant at the 0.01 level according to RDA and associated permutation test. The clearest changes have been a decline in *Eunotia incisa* (pH optima 5.1) from maximum abundances in the early 1990s, and increases in *Navicula leptostriata* (pH optima 5.1), *N. tenuicephala* (pH optima 5.3) and *Brachysira vitrea* (pH optima 5.9). These changes are indicative of a small increase in pH at this site and although not strongly supported by water chemistry data, there is evidence for a general increase in pH since 1993. Diatom inferred pH (derived from weighted averaging) illustrates the gradual shift to species with higher pH optima (Figure 7.3a).

Table 4.16.3

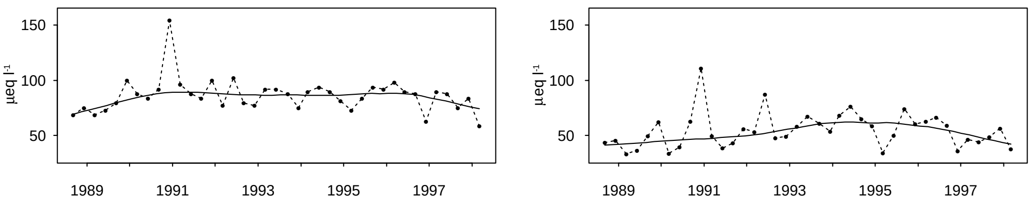
Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
Cl	µeq l^{-1}	*-10.1**	-
Na	µeq l^{-1}	*-7.0**	-
Ca	µeq l^{-1}	*-2.45**	-
Non-labile Al	µg l^{-1}	*+4.77**	*+5.25***

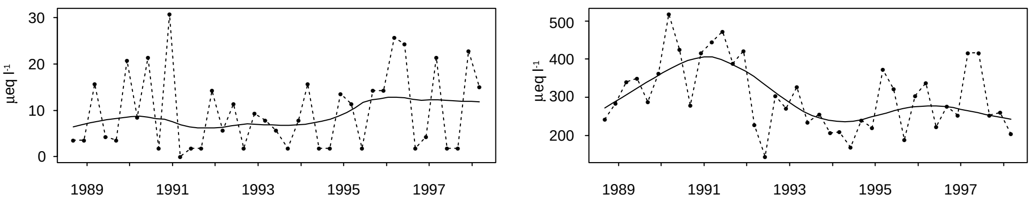
** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*


(a) pH

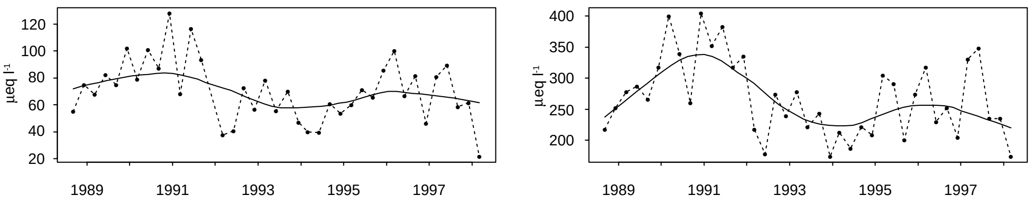
(b) Alkalinity


(c) Sulphate

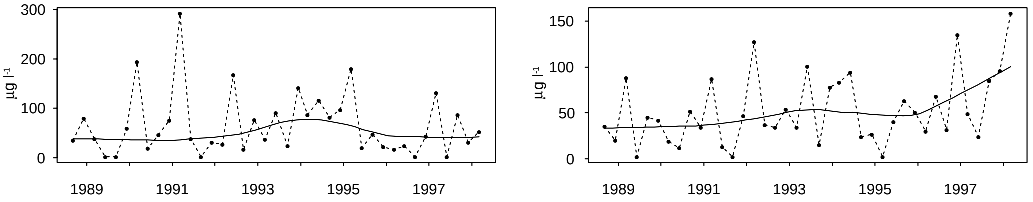
(d) Non-marine Sulphate


(e) Nitrate

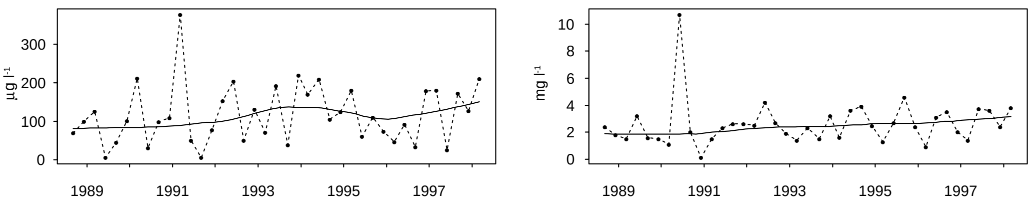
(f) Chloride


(g) Calcium

(h) Sodium


(i) Labile Al

(j) Non-labile Al


(k) Total Soluble Al

(l) Dissolved Organic Carbon

Figure 4.16.2

Llyn Cwm Mynach: summary of major chemical determinands (September 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.16.4

Llyn Cwm Mynach: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*418*	*123*	*10.1*	*0.68*	*0.53*
Macrophytes	*43*	*28*	*17.7*	*1.02*	*0.74*
Invertebrates	*832*	*40*	*2.5*	*0.86*	*0.55*

Variance explained (%)	within year	between years	linear trend	p unrestricted	p restricted
Epilithic diatoms	*55.2*	*44.8*	*13.0*	*<0.01*	*<0.01*
Macrophytes	*	*	*32.2*	*0.03*	*0.07*
Invertebrates	*57.1*	*42.9*	*12.1*	*<0.01*	*<0.01*

■ Macroinvertebrates

(Figure 4.16.4, Table 4.16.4)

Llyn Cwm Mynach has a relatively species poor fauna dominated by acid tolerant mayflies (Leptophlebiidae) and chironomids. Leptophlebid numbers have declined over the monitoring period, while chironomid numbers appear to have increased. The stonefly community, which is composed of acid tolerant detritivores (*Nemoura* spp.), has become impoverished in recent years. Of the caddisflies, *Plectrocnemia* spp. and *Polycentropus* spp. were both numerous in the first half of the survey but declined after 1993. *Holocentropus* spp. appeared in 1995. Other characteristic species include several corixids, of which *Sigara scotti* is the most numerous, and the relatively acid tolerant alderfly *Sialis lutaria*, which was most abundant in 1997. Time as a linear trend is significant at the 0.01 level using RDA and associated permutation test. The time trend appears to be driven by the decrease in Leptophlebid mayflies and disappearance of some other acid tolerant species. These species however have not been replaced by acid sensitive ones and it should be noted that this site is one of only three in the Network where species richness has declined over the decade. At the other two (Loch Grannoch and Lochnagar), there is evidence for a recent increase in acidity, but similar chemical change has not been experienced here. However, parts of the littoral zone of Llyn Cwm Mynach have become progressively inundated with decaying plant matter (see aquatic macrophyte section). These alterations in littoral habitat and, possibly, food supply, could account for some of the observed changes.

■ Fish

(Figure 4.16.5)

The outflow stream from Llyn Cwm Mynach has been electrofished since 1989. Mean trout densities are the fifth highest found in the Network. Mean population levels of 0+ trout declined between 1989 to 1994, peaked in 1995 and 1996 and were again reduced in 1997 when recruitment was the lowest observed in the nine years of monitoring. Densities of >0+ group have shown a general increase since 1990. Due to problems with weighing fish in 1989 and 1993 insufficient data are available for condition factor trend analysis. Mean condition factor of both age groups was highly variable in the early years of monitoring but has remained relatively constant for the past three years.

Table 4.16.5

Llyn Cwm Mynach: relative abundance of aquatic macrophyte flora (1988 - 1997) (see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES								
Nitella flexilis[1]	*1*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
Myriophyllum alterniflorum[2]	*3*	*3*	*3*	*3*	*3*	*3*	*2*	*2*
Utricularia sp.[2]	*3*	*3*	*4*	*4*	*4*	*4*	*4*	*4*
Plectonema sp. [4]	*2*	*2*	*3*	*3*	*3*	*4*	*4*	*4*
Drepanocladus fluitans[4]	*0*	*1*	*0*	*0*	*0*	*0*	*0*	*1*
Sphagnum auriculatum[4]	*2*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Juncus bulbosus var. *fluitans*[4]	*5*	*5*	*5*	*5*	*5*	*5*	*4*	*4*
OTHER SUBMERGED SPECIES								
Batrachospermum sp.	*1*	*1*	*2*	*3*	*3*	*3*	*3*	*2*
Filamentous green algae	*3*	*4*	*4*	*4*	*4*	*3*	*4*	*2*
Amblystegium sp.	*1*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
Fontinalis sp.	*1*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
Marsupella emarginata	*1*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
Nardia compressa	*0*	*0*	*0*	*0*	*0*	*2*	*1*	*0*
Scapania undulata	*0*	*0*	*0*	*0*	*0*		*1*	*0*
Littorella uniflora	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Lobelia dortmanna	*2*	*2*	*3*	*3*	*3*	*3*	*2*	*2*
Nuphar lutea	*3*	*3*	*3*	*3*	*3*	*2*	*3*	*2*
Nymphaea alba	*3*	*3*	*3*	*3*	*3*	*2*	*3*	*2*
Glyceria fluitans	*1*	*1*	*1*	*1*	*1*	*0*	*0*	*1*
Potamogeton berchtoldii	*1*	*1*	*0*	*0*	*0*	*0*	*0*	*1*
Potamogeton natans	*2*	*2*	*2*	*2*	*2*	*3*	*2*	*2*
Potamogeton polygonifolius	*1*	*2*	*2*	*2*	*2*	*1*	*1*	*1*
EMERGENT SPECIES								
Equisetum fluviatile	*4*	*4*	*4*	*4*	*4*	*4*	*4*	*4*
Hydrocotyle vulgaris	*1*	*1*	*2*	*2*	*2*	*2*	*2*	*2*
Menyanthes trifoliata	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Ranunculus flammula	*2*	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Carex rostrata	*2*	*2*	*3*	*3*	*3*	*3*	*3*	*3*
Eleocharis palustris	*1*	*1*	*1*	*1*	*1*	*0*	*1*	*1*
Juncus effusus	*2*	*2*	*4*	*4*	*4*	*4*	*4*	*4*
Juncus acutifloris/articulatus	*3*	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Scirpus lacustris ssp. *lacustris*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
TOTAL NUMBER OF SPECIES	*28*	*25*	*23*	*23*	*23*	*22*	*24*	*23*

Aquatic macrophytes

(Tables 4.16.4-5)

The oligotrophic macrophyte flora of the main basin of Llyn Cwm Mynach has been affected by the increase in the cover of the mat forming blue-green alga, *Plectonema* sp., described in the site review, although no species seems to have been lost completely as a result. The development of blue-green algal mats in acidifying lakes has been described for Scandinavia and the United States (e.g. Hendrey & Vertucci, 1980) but there is no evidence for this in other UKAWMN lakes, and the reasons for its recent expansion in Llyn Cwm Mynach are not understood. Plants which grow in deeper water locations, such as *Juncus bulbosus* var. *fluitans* and *Myriophyllum alterniflorum* appear to have been directly out-competed by the alga, while the littoral habitat of *L. dortmanna* has been reduced as a result of the accumulation of decaying plant material (mainly composed of *J. bulbosus*) originating from the deeper water. A small specimen of the acid sensitive charophyte *Nitella flexilis* was recovered from the site in the first year of monitoring but this species has not been recorded since, and this suggests that the lake was still in the process of acidifying around the onset of monitoring in 1988. *Potamogeton berchtoldii*, which was considered to have been lost after the first five years, has more recently been recorded again. There is no evidence of floristic changes in the shallow basin which leads to the outflow and overall RDA shows “sample year” to be insignificant as a linear variable in explaining changes in the DAFOR abundance data.

Summary

Llyn Cwm Mynach is a moderately acidic site, at which likely enhancement of acid deposition by forestry (Section 5.5) is partly ameliorated by a relatively high internal base cation supply. Few clear changes in lake chemistry have taken place during the last ten years. Fluctuations in marine ion concentrations have been the major cause of chemical variation. This is possibly the main influence on the linear change in the epilithic diatom community which is indicative of gradually improving pH. Vascular aquatic macrophyte cover has been reduced as a result of an increase in a mat forming blue-green alga, and the subsequent increase in dead plant material along the shoreline may have influenced the habitat and food supply of macroinvertebrate species.

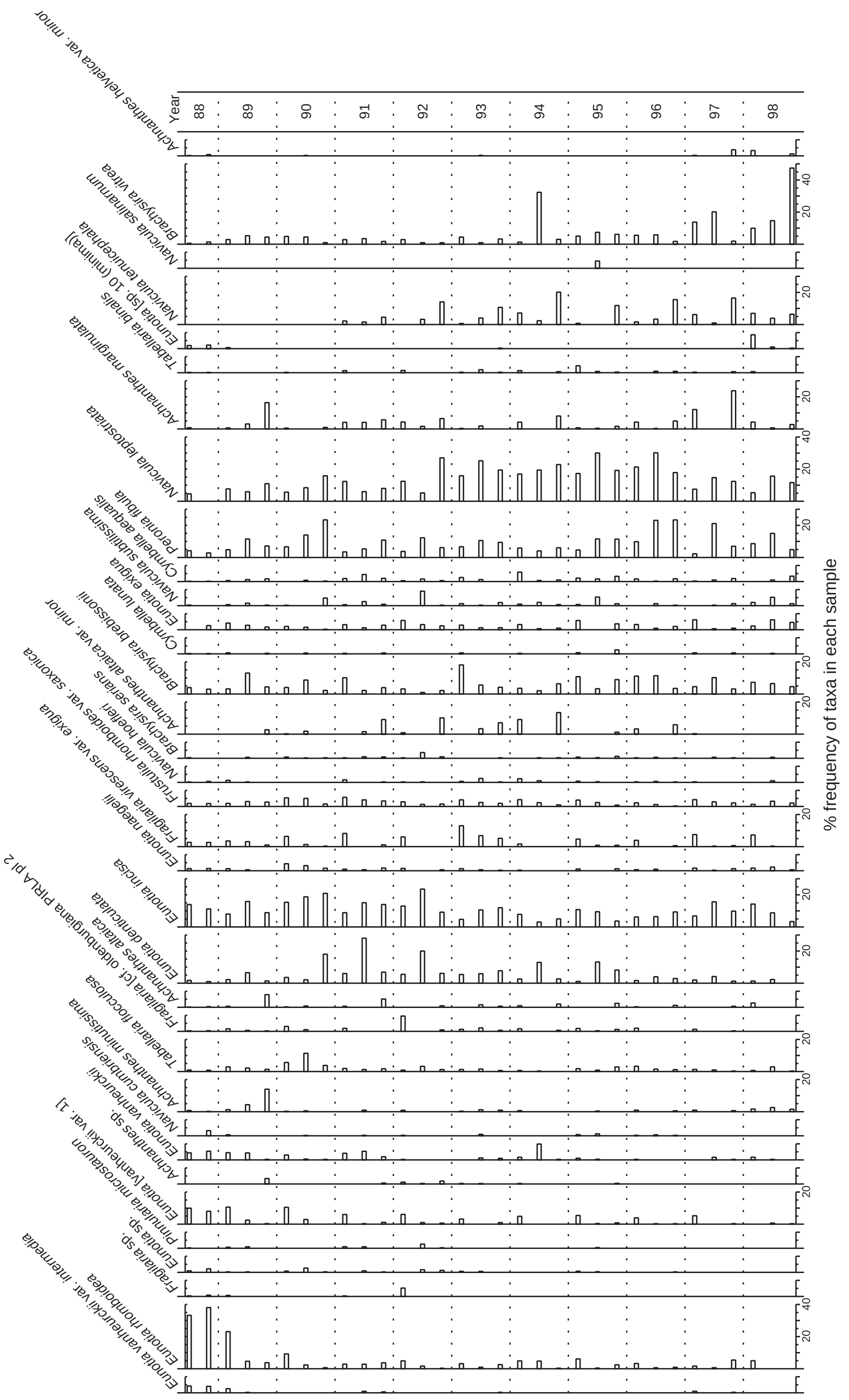


Figure 4.16.3

Llyn Cwm Mynach: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample

Figure 4.16.4

Llyn Cwm Mynach: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

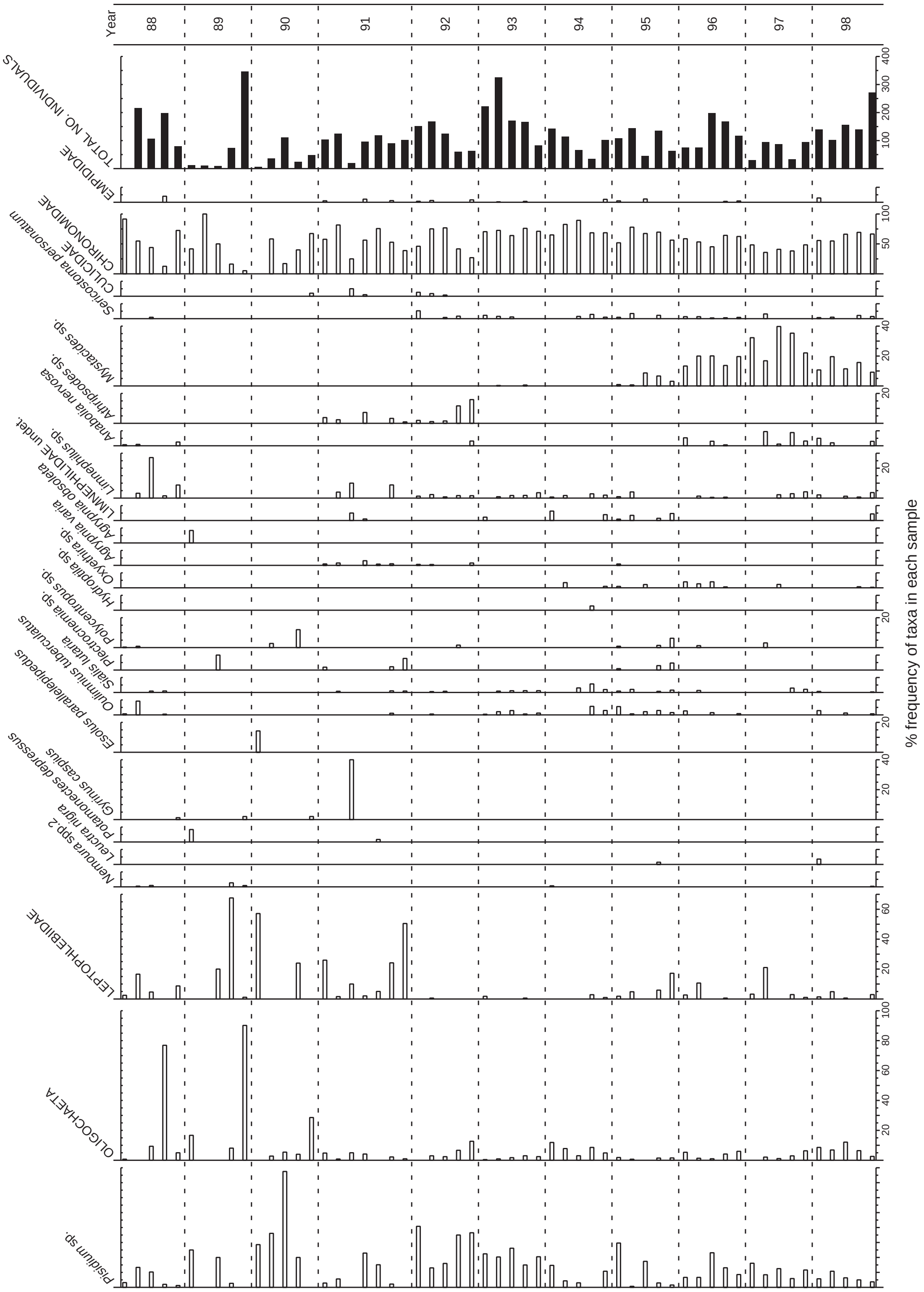


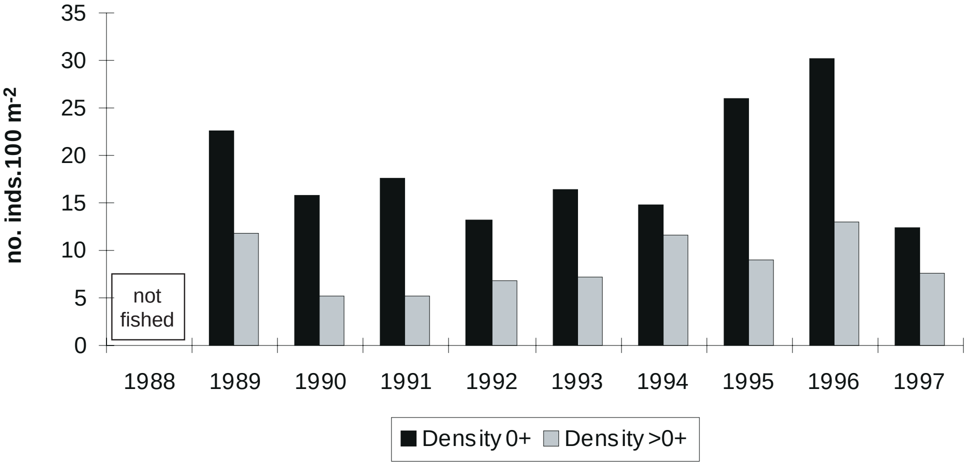
Figure 4.16.5

Llyn Cwm Mynach: summary of fish data (1989 - 1997)

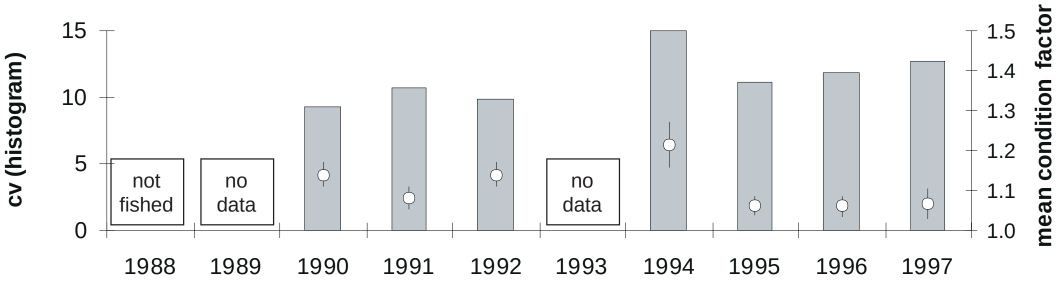
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

(a) Density



(b) Condition (0+)



Condition (>0+)

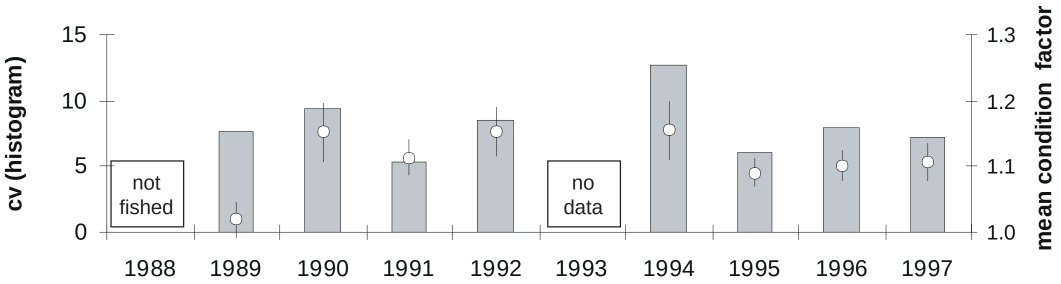
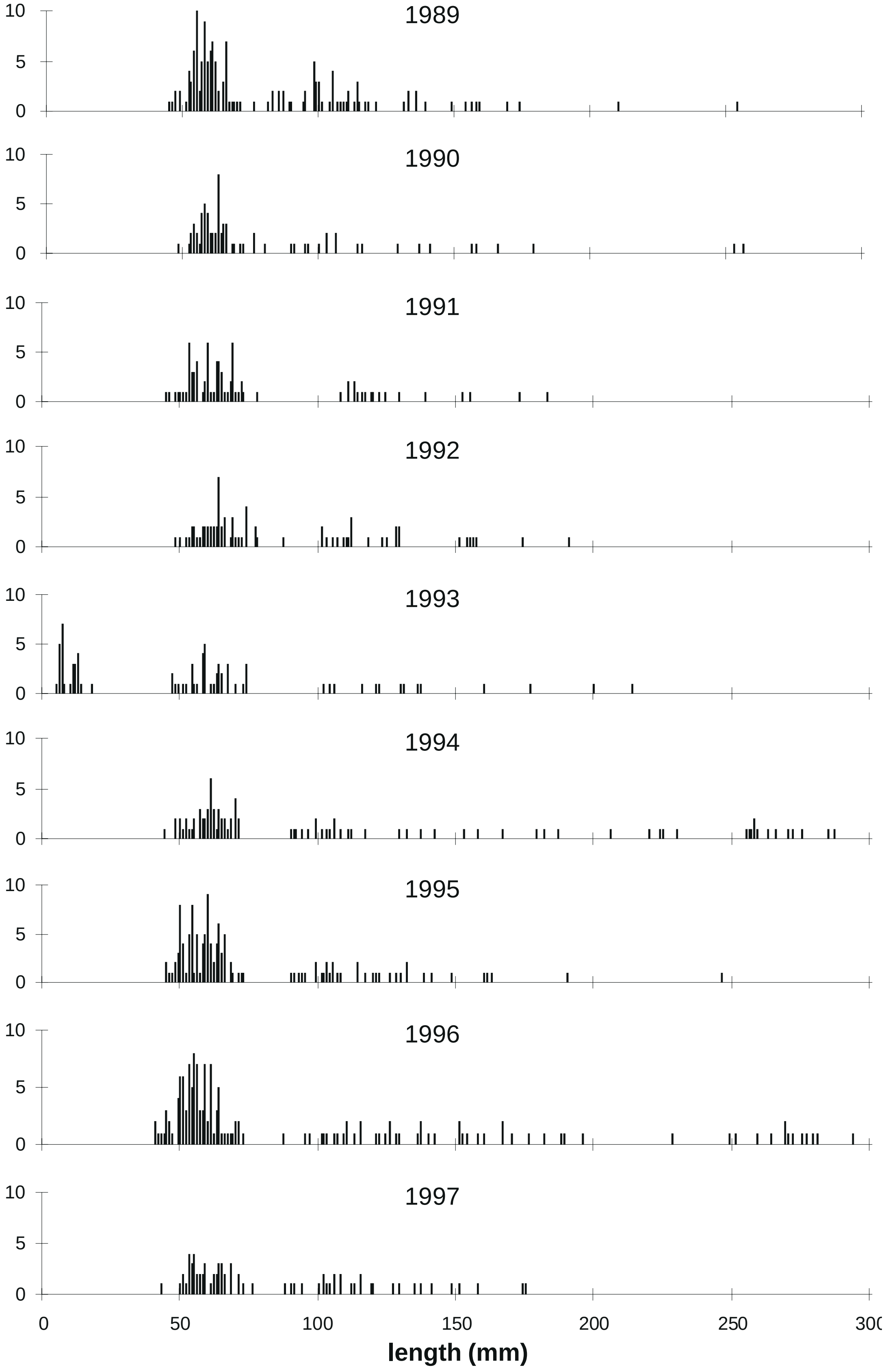


Figure 4.16.5

Llyn Cwm Mynach: summary of fish data (1989 - 1997)
(c) Trout length frequency summaries



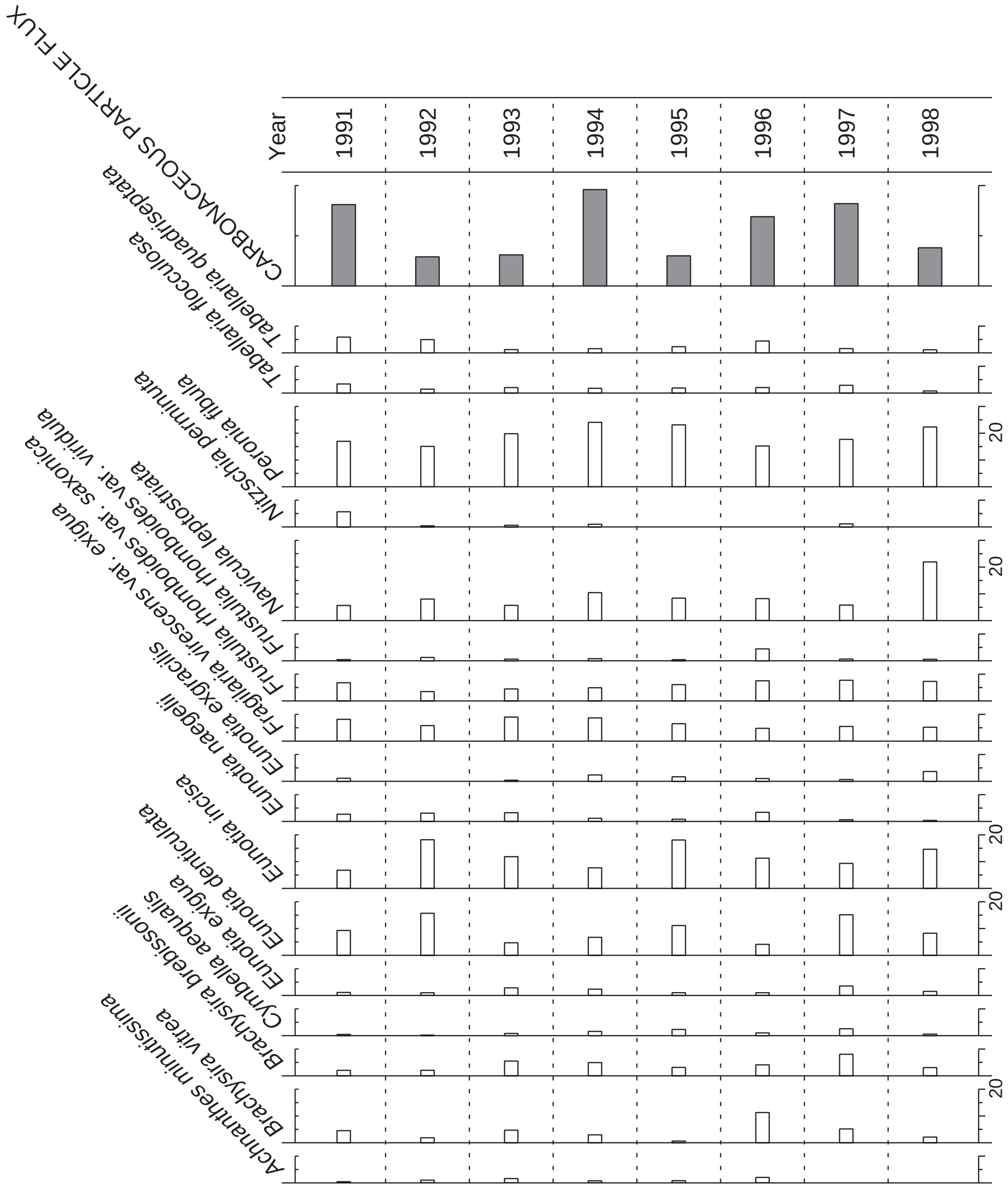
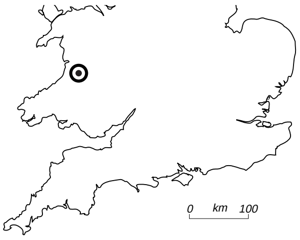


Figure 4.16.5

Llyn Cwm Mynach: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year



4.17 Afon Hafren

Site Review

The hydrology and ecology of the Afon Hafren, a headwater of the River Severn at Plynlimon, has received considerable scientific attention since the early 1980s due to its inclusion in Plynlimon catchment studies (e.g. Neal *et al.* 1997, Gee & Smith, 1997). Over the course of the last decade the coniferous forest within the catchment has been thinned, but clear-felling, which is now underway, had not been instigated within the period of analysis covered by this report.

Water Chemistry

(Figure 4.17.2, Tables 4.17.2-3)

The Afon Hafren has a mean pH of 5.37 and a mean alkalinity of 6 µeq l^{-1}. Mean xSO_4 (60 µeq l^{-1}) is high for the region, probably due to forest

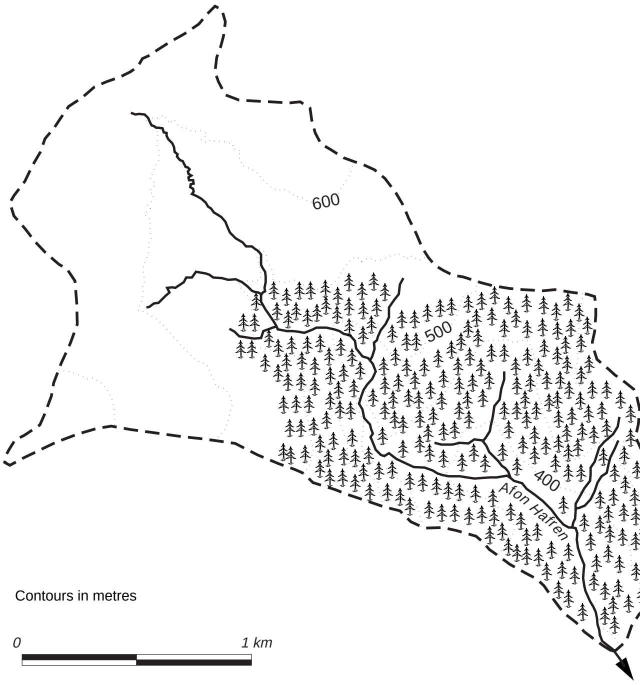


Figure 4.17.1

Afon Hafren: catchment

Table 4.17.1

Afon Hafren: site characteristics

Grid reference	*SH 844876*
Catchment area	*358 ha*
Minimum Catchment altitude	*355 m*
Maximum Catchment altitude	*690 m*
Catchment Geology	*Ordovician and silurian sedimentary*
Catchment Soils	*Podsols and organic peats*
Catchment vegetation	*conifers 50%,* *moorland 50%*
Mean annual rainfall	*2468 mm*
1996 deposition	
Total S	*30 kg* ha^{-1} yr^{-1}
non-marine S	*20 kg* ha^{-1} yr^{-1}
Oxidised N	*10 kg* ha^{-1} yr^{-1}
Reduced N	*17 kg* ha^{-1} yr^{-1}

Table 4.17.2

Afon Hafren: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.37*	*6.60*	*4.31*
Alkalinity	µeq l^{-1}	*6.0*	*75.6*	*-42.0*
Ca	µeq l^{-1}	*45.0*	*102.5*	*7.0*
Mg	µeq l^{-1}	*65.8*	*91.7*	*41.7*
Na	µeq l^{-1}	*191.7*	*304.3*	*134.8*
K	µeq l^{-1}	*5.9*	*15.4*	*2.6*
SO_4	µeq l^{-1}	*81.9*	*139.6*	*58.3*
xSO_4	µeq l^{-1}	*60.0*	*113.3*	*35.0*
NO_3	µeq l^{-1}	*20.7*	*62.9*	*<1.4*
Cl	µeq l^{-1}	*209.3*	*349.3*	*152.1*
Soluble Al	µg l^{-1}	*172.5*	*550.0*	*5.0*
Labile Al	µg l^{-1}	*99.1*	*372.0*	*<2.5*
Non-labile Al	µg l^{-1}	*74.7*	*245.0*	*<2.5*
DOC	mg l^{-1}	*1.9*	*8.1*	*<0.1*
Conductivity	µS cm^{-1}	*38.1*	*112.0*	*20.0*

deposition enhancement, and NO_3 concentrations (mean 21 µeq l^{-1}) are also the highest among the Welsh UKAWMN sites. The site has a low buffering capacity, with a mean Ca concentration of 45 µeq l^{-1}, and experiences severe episodic acidification with recorded pH and alkalinity minima of 4.31 and -42 µeq l^{-1} respectively.

Significant declining trends are observed using linear regression, for Cl, Na, Mg and Ca (Table 4.17.3). However, inspection of time series (Figure 4.17.2) suggests that these can all be linked to the same marine ion cycles that have already been described at many other sites. The 1991 peak appears more subdued than at the north Wales lakes, although this is partly due to the large episodic fluctuations superimposed on the longer term variation. There are no clear trends in pH, alkalinity or NO_3, but as at the north Wales lakes xSO_4 appears to have decreased following a peak in the mid-1990s (Figure 4.17.2d). A significant upward trend is identified for DOC using SKT, although this does not appear particularly strong (Figure 4.17.2l). The estimated increase of 0.67 mg l^{-1} over the ten years is less than at most other sites in the Network where DOC is rising.

A previous trend analysis for the Hafren, for the period 1983-1993, has been presented by Robson & Neal (1996). They also found few significant trends, with no clear changes in acidity, xSO_4 or NO_3. However, DOC was found to have increased by an estimated 0.7 mg l^{-1} over the ten years, which is extremely close to the value obtained in the present analysis. Longer term data for the Hafren are discussed in Chapter 6.

■ Epilithic diatoms

(Figure 4.17.3, Table 4.17.4)

Typically, for stream sites in the Network, epilithic diatom species relative abundance varies substantially between years. *Eunotia exigua* (pH optima 5.1) is dominant in nearly all samples, reflecting the extremely acidic conditions of this site. However, in 1990 *Achnanthes helvetica* var. *minor* (pH optima 5.4) was more abundant. Since 1990 the relative frequency of *E. exigua* has increased, and recent years have also seen a small increase in *Tabellaria flocculosa* (pH optima 5.4). These changes with time are significant at the 0.01 level according to RDA and associated restricted permutation test. Interesting parallels are apparent between the diatom flora and its observed inter-annual variation at this site and that of the Afon Gwy (see section 4.18). Unlike the majority of stream sites, variation in summer rainfall and the associated flow regime does not appear to have had a strong influence on species composition.

Table 4.17.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
Cl	µeq l^{-1}	*-2.93**	-
Na	µeq l^{-1}	*-2.87****	*-2.91**
Mg	µeq l^{-1}	*-0.58**	-
Ca	µeq l^{-1}	*-1.05***	-
DOC	mg l^{-1}	*+0.07**	-

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

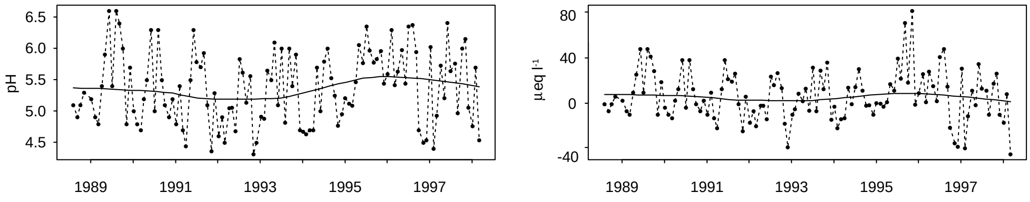
Figure 4.17.2

Afon Hafren: summary of major chemical determinands (September 1989 - March 1997)

Smoothed line represents LOESS curve (Section 3.1.2)

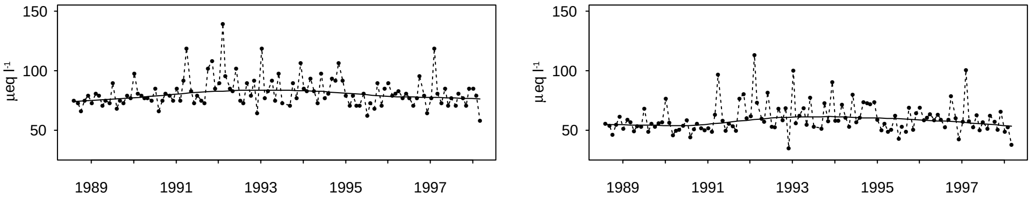
(a) pH

(b) Alkalinity



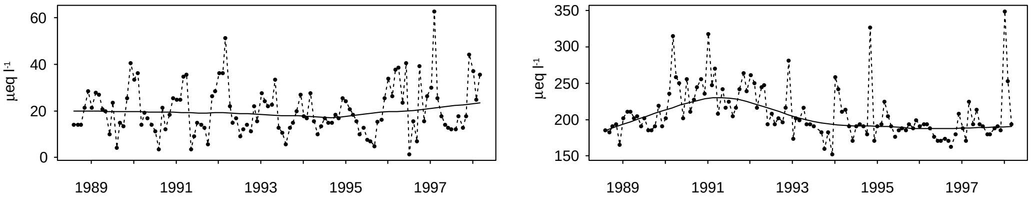
(c) Sulphate

(d) Non-marine Sulphate



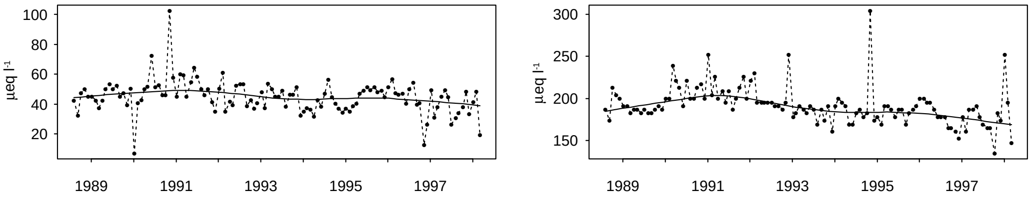
(e) Nitrate

(f) Chloride



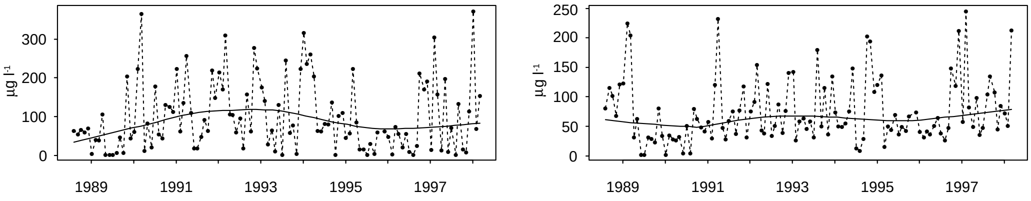
(g) Calcium

(h) Sodium



(i) Labile Al

(j) Non-labile Al



(k) Total Soluble Al

(l) Dissolved Organic Carbon

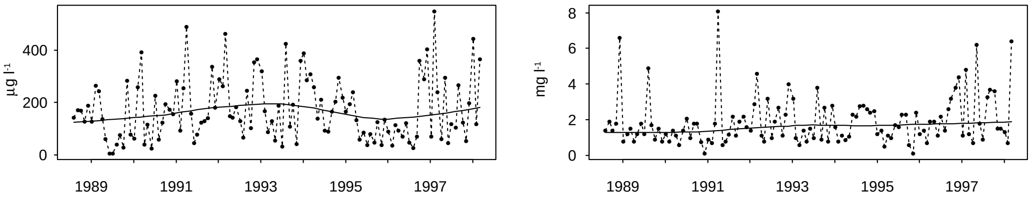


Table 4.17.4

Afon Hafren: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*154*	*59*	*1.8*	*1.13*	*0.62*
Macrophytes	*1.8*	*7*	*1.2*	*0.51*	*0.34*
Invertebrates	*191*	*270*	*2.9*	*0.26*	*0.25*

Variance				**p**	
explained (%)	**within year**	**between years**	**linear trend**	**unrestricted**	**restricted**
Epilithic diatoms	*35.7*	*64.3*	*6.2*	*<0.01*	*<0.01*
Macrophytes	*	*	*33.0*	*0.09*	*<0.01*
Invertebrates	*45.1*	*54.9*	*7.7*	*<0.01*	*0.09*

■ Macroinvertebrates

(Figure 4.17.4, Table 4.17.4)

The macroinvertebrate fauna is characterised by acid tolerant detritivorous stoneflies typical of acid waters. Two species of stonefly, *Brachyptera risi* and *Leuctra inermis* dominated the fauna, with *Amphinemura sulcicollis*, *Siphonoperla torrentium* and *Protonemura* spp. occurring at lower densities. Of the caddisflies, *Rhyacophila* spp. and *Plectrocnemia* spp. were present throughout the monitoring period, while one individual of the genus Polycentropus was recorded in 1993. Only the most acid tolerant mayfly family, the Leptophlebiidae, have been found at this site, and then only two individuals recorded in 1996. Other characteristic fauna include the Dipterans, Chironomidae and Simulidae. There are no apparent changes in species abundance and diversity over the monitoring period and there is no significant time trend.

■ Fish

(Figure 4.17.5)

No fish were caught in surveys conducted during the first few years of monitoring. However, following recent reports that a small population of trout were known to be present nearby (Crisp & Beaumont 1996), the electrofishing survey stretch was changed in 1995 to cover the lower end of this reach (Beaumont pers. comm). Small numbers of fish were caught on this and subsequent surveys. The three years of data available are insufficient for detailed analysis.

■ Aquatic macrophytes

(Tables 4.17.4-5)

In common with the other most acid streams in the Network, the aquatic macrophyte flora of the Afon Hafren is comprised almost exclusively of the ubiquitous and acid tolerant liverwort *Scapania undulata*. The cover of this species has remained at a consistent level over the decade. In contrast however, cover of filamentous algae has varied markedly between years, and since this is included in the estimate of the overall cover score for each survey stretch, may have led to bias in the liverwort cover estimate in some years. The total number of species, most of which have only ever occured at very low cover, has declined over the monitoring period. These temporal changes are deemed significant by RDA and associated permutation test, but can not be attributed to changes in water chemistry.

Table 4.17.5

Afon Hafren: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**96**	**97**
INDICATOR SPECIES									
Nardia compressa[3]	*0.0*	*<0.1*	*<0.1*	*<0.1*	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*
OTHER SUBMERGED SPECIES									
Atrichum sp.	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
Filamentous green algae	*0.3*	*36.7*	*<0.1*	*<0.1*	*0.3*	*<0.1*	*0.4*	*6.9*	*1.4*
Juncus bulbosus var. fluitans	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*
Juncus effusus	*<0.1*	*<0.1*	*<0.1*	*0.0*	*0.0*	*<0.1*	*0.0*	*<0.1*	*<0.1*
Polytrichum commune	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*<0.1*
Racomitrium aciculare	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*<0.1*	*0.0*	*<0.1*	*0.0*
Ranunculus omiophyllus	*<0.1*	*<0.1*	*<0.1*	*0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
Scapania undulata	*3.1*	*12.8*	*3.5*	*2.5*	*2.7*	*3.2*	*3.0*	*2.7*	*1.5*
total macrophyte cover excluding filamentous algae	*3.1*	*12.8*	*3.5*	*2.5*	*2.7*	*3.2*	*3.0*	*2.7*	*1.5*
TOTAL NUMBER OF SPECIES	*8*	*8*	*8*	*7*	*4*	*6*	*4*	*5*	*4*

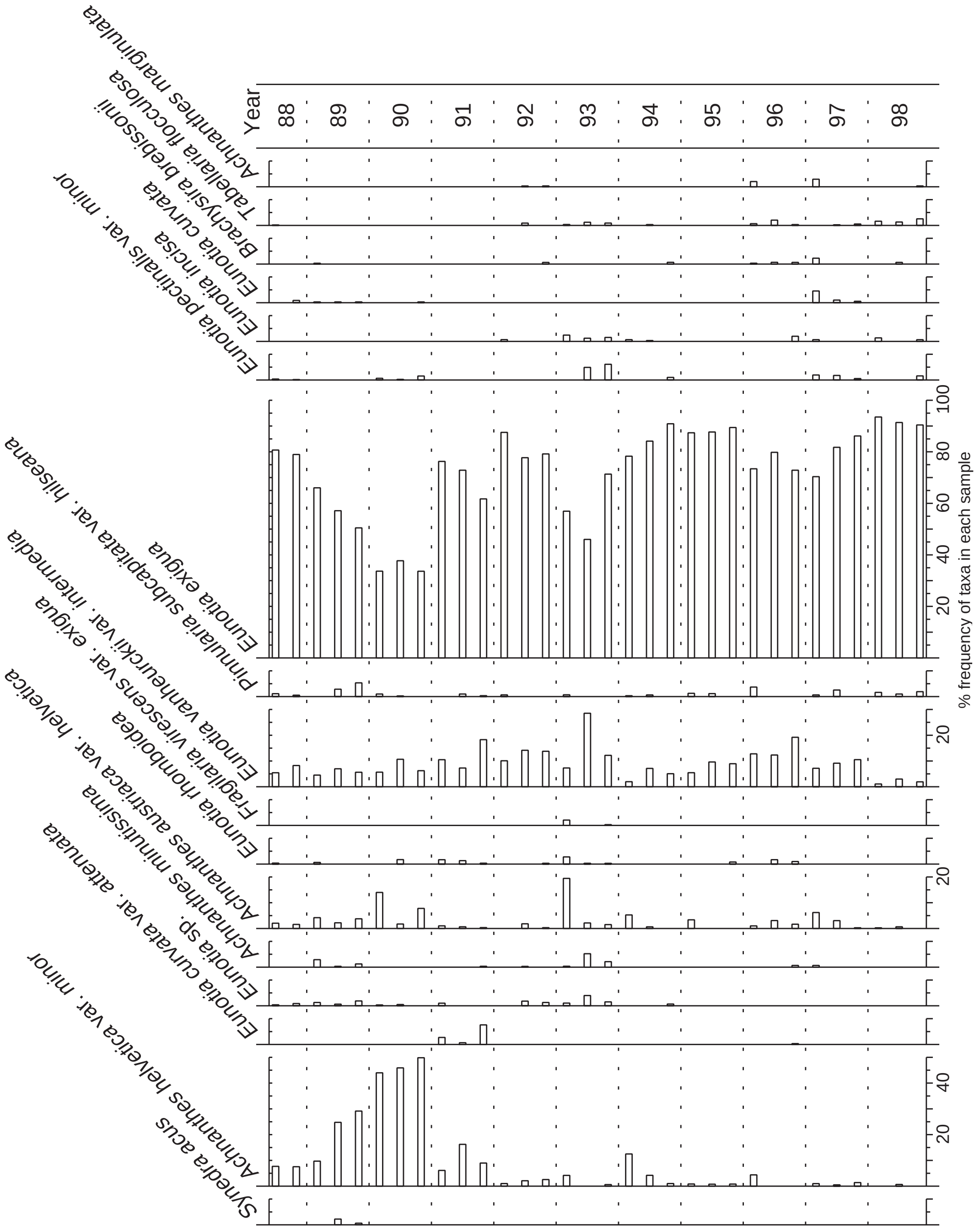
■ Summary

The Afon Hafren is a moderately acidic site, which has seemingly been adversely affected by forestry (Section 5.5). Variations in marine ions match those observed at other sites, but apart from this stream chemistry has exhibited few significant changes over the last decade. There have been few changes in water chemistry apart from a possible increase in DOC. Linear changes in the composition of the epilithic diatom flora and the reduction in rare macrophyte species are difficult to explain at this stage, while the macro-invertebrate assemblage remains fairly stable, although in an impoverished state. Trout density is low, but since the survey stretch has only recently been moved it is not possible to comment on trends.

Figure 4.17.3

Afon Hafren: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



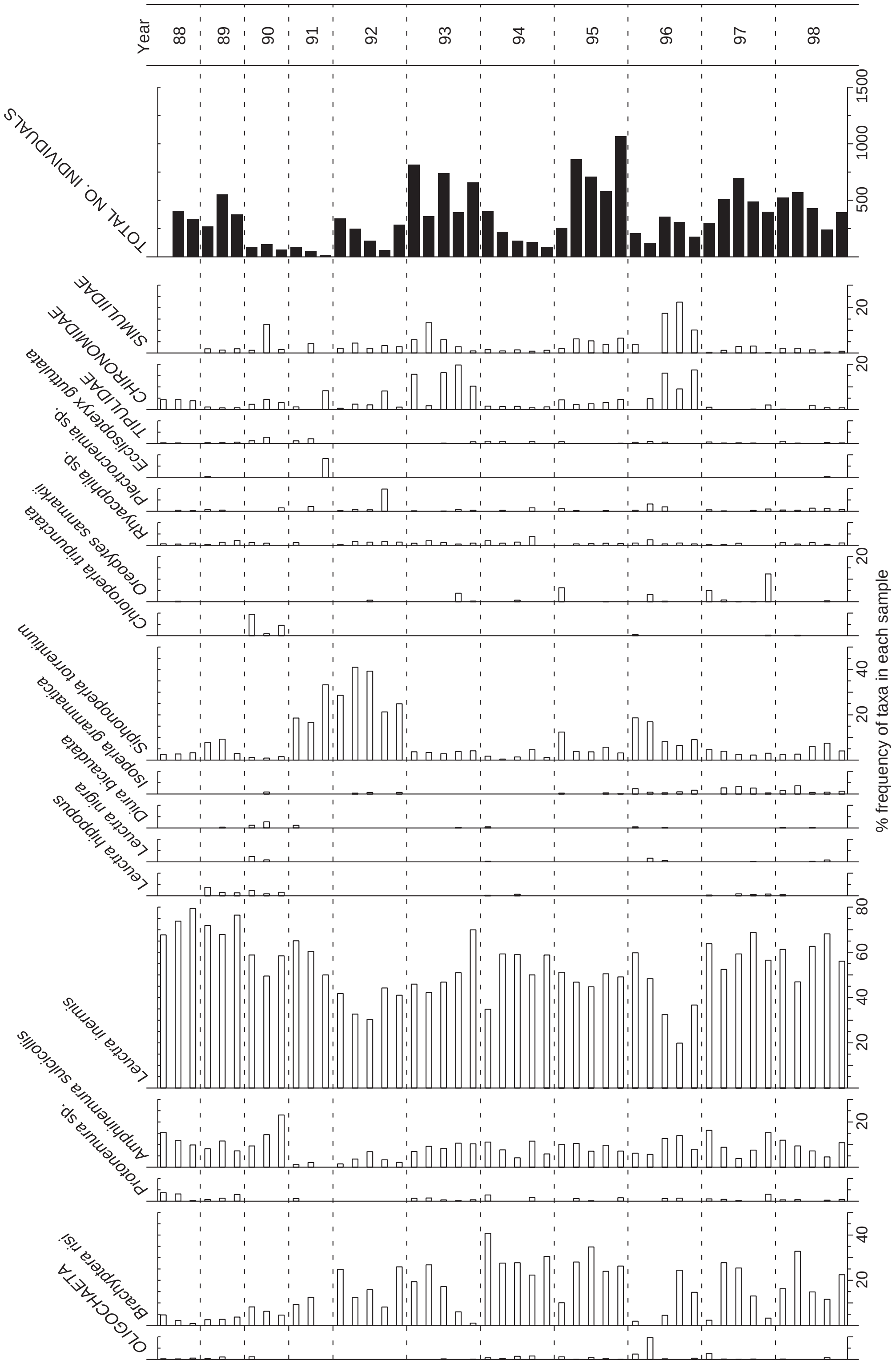


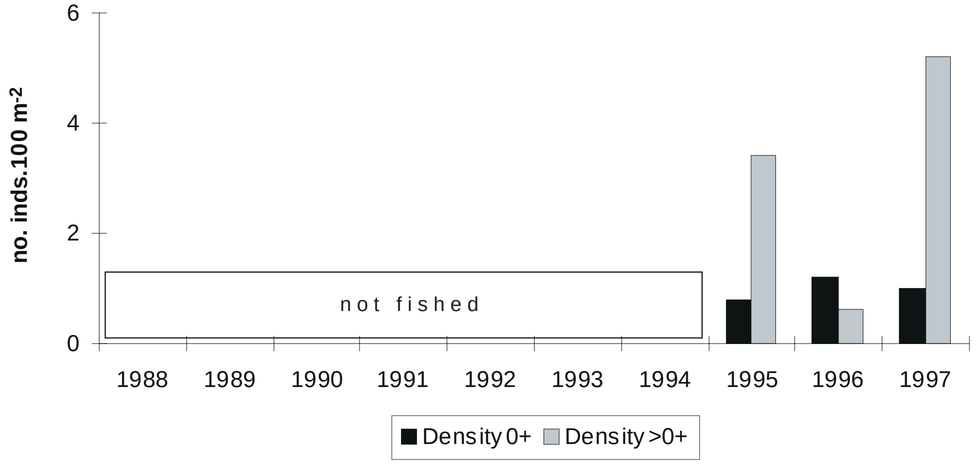
Figure 4.17.4

Afon Hafren: summary of macroinvertebrate data (1988 - 1998)

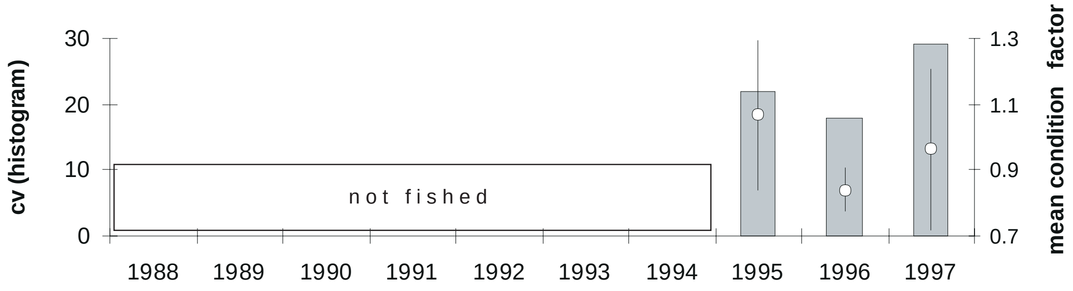
Percentage frequency of taxa in individual samples

Figure 4.17.5

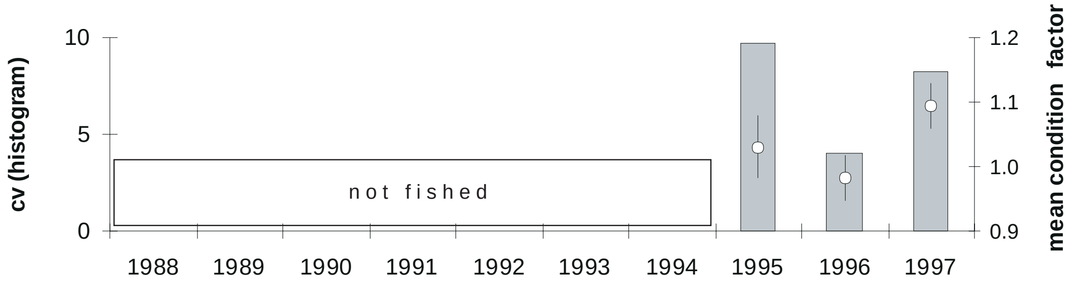
Afon Hafren: summary of fish data (1995 - 1997)
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})
(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)



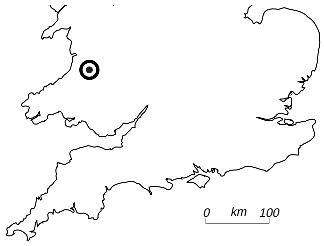
(a) Density



(b) Condition (0+)



Condition (>0+)



4.18 Afon Gwy

Site Review

Monitoring of the moorland Afon Gwy within the UKAWMN only began in 1991, although like the neighbouring site, the Afon Hafren, longer chemical time series records exist due to its inclusion in the Plylimon catchment studies which commenced in 1983 (Section 6.5). In close proximity to the Afon Hafren, these two sites provide an excellent forested/control pair (Section 5.5). There is no evidence of disturbance within the catchment of the Afon Gwy since the onset of monitoring.

Water Chemistry

(Figure 4.18.2, Tables 4.18.2-3)

The Afon Gwy is less acidic than the adjacent forested catchment, the Afon Hafren, with a mean pH of 5.55 and a mean alkalinity of 12 µeq l^{-1}.

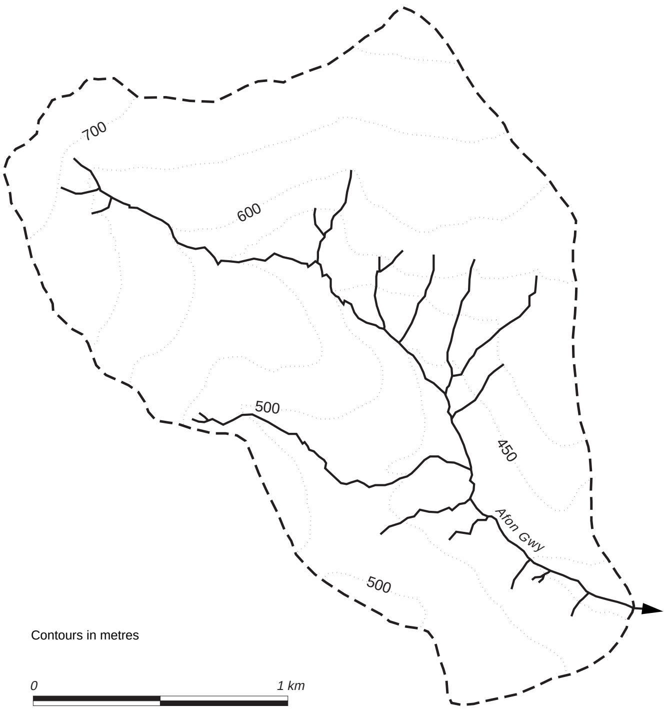


Figure 4.18.1

Afon Gwy: catchment

Table 4.18.1

Afon Gwy: site characteristics

Grid reference	*SN 842854*
Catchment area	*389 ha*
Minimum Catchment altitude	*440 m*
Maximum Catchment altitude	*730 m*
Catchment Geology	*lower palaeozoic sedimentary*
Catchment Soils	*peats, peaty podsols*
Catchment vegetation	*moorland 100%*
Mean annual rainfall	*2599 mm*
1996 deposition	
Total S	*30 kg ha^{-1} yr^{-1}*
non-marine S	*20 kg ha^{-1} yr^{-1}*
Oxidised N	*10 kg ha^{-1} yr^{-1}*
Reduced N	*17 kg ha^{-1} yr^{-1}*

Table 4.18.2

Afon Gwy: summary of chemical determinands, July 1988 - March 1998

Determinand		Mean	Max	Min
pH		*5.55*	*6.40*	*4.50*
Alkalinity	µeq l^{-1}	*11.8*	*65.4*	*-22.6*
Ca	µeq l^{-1}	*39.5*	*63.5*	*8.5*
Mg	µeq l^{-1}	*54.2*	*91.7*	*25.0*
Na	µeq l^{-1}	*146.1*	*239.1*	*113.0*
K	µeq l^{-1}	*4.6*	*16.2*	*2.6*
SO_4	µeq l^{-1}	*64.4*	*106.3*	*37.5*
xSO_4	µeq l^{-1}	*47.7*	*90.0*	*22.9*
NO_3	µeq l^{-1}	*10.7*	*71.4*	*<1.4*
Cl	µeq l^{-1}	*158.6*	*338.0*	*104.2*
Soluble Al	µg l^{-1}	*112.2*	*336.0*	*5.0*
Labile Al	µg l^{-1}	*56.2*	*249.0*	*<2.5*
Non-labile Al	µg l^{-1}	*57.1*	*170.0*	*<2.5*
DOC	mg l^{-1}	*2.12*	*6.30*	*<0.10*
Conductivity	µS cm^{-1}	*27.5*	*44.0*	*16.0*

Although internal base cation supply appears to be similar, xSO_4 is significantly lower, with a mean of 48 µeq l^{-1}. NO_3 concentrations are also lower (mean 11 µeq l^{-1}) and fall below detection limits during summer. Acidic episodes are observed during winter high flows, with alkalinity frequently falling below zero and pH below 5.0. Aluminium levels are moderate (mean 112 µg l^{-1}) and divided approximately equally between labile and non-labile fractions.

The Afon Gwy was not included in the UKAWMN until April 1991, and trend analyses at this site are therefore of limited value. The rising pH trend identified by regression (Table 4.18.3) could be spurious, since it is not supported by the LOESS fit to the data (Figure 4.18.2a), or by changes in any other ions. The DOC increase (1 mg l^{-1} per decade) identified by SKT must also be treated with caution, although it does appear to have occurred steadily over the study period (Figure 4.18.2l), and corresponds to that observed at the Afon Hafren and at other UKAWMN sites. Given the shorter dataset it is also difficult to assess changes in marine ions, but it seems likely that variations are similar to those at the Afon Hafren, and this is supported by apparently higher Cl, Na and Ca concentrations at the Gwy in 1991-1992 (Figure 4.18.2f-h). A pulse of very high Cl and Na at the end of the record corresponds to the sea-salt episode identified at Narrator Brook, and this also appears in the Hafren data (Figure 4.18.2f and h). Unlike at Narrator Brook, however, this large sea-salt input did not generate a major acidic episode at either of the Plynlimon streams. Finally, although xSO_4 has not shown any overall trend during the seven years of monitoring, concentrations appear to have declined sharply since 1996. Additional monitoring will be required to establish whether this is part of a sustained, deposition-driven decrease.

Trends in data collected at the Afon Gwy between 1980 and 1996 were analysed by Reynolds *et al.* (1997). Using SKT they observed a decline in SO_4 by an estimated 0.3 µeq l^{-1} yr^{-1}, and a rise in pH by 0.025 pH units yr^{-1}. These trends are consistent with recovery at the site, but accompanying time series indicate that most of the overall change took place prior to the onset of UKAWMN sampling in 1991. A rising trend in DOC was also observed over the longer time period, with a rate of increase identical to that identified in the present study. (Section 6.5).

Epilithic diatoms

(Figure 4.18.3, Table 4.18.4)

The epilithic diatom flora of the Afon Gwy has similar characteristics to that of the Afon Hafren, reflecting its similar acidic nature. *Eunotia exigua* was again dominant in nearly all samples. Greater diversity is apparent in samples from 1993, 1996 and 1998, when *Tabellaria flocculosa* and *Eunotia incisa* were relatively abundant. Interestingly, *T. flocculosa* also reached higher abundances in the Afon Hafren assemblages during these years, suggesting that both sites are sensitive to the same environmental influences. Rainfall data from the nearby Cymystyth Meteorological Station suggests that flows would have been relatively high and

Table 4.18.3

Significant trends in chemical determinands (July 1988 - March 1998)

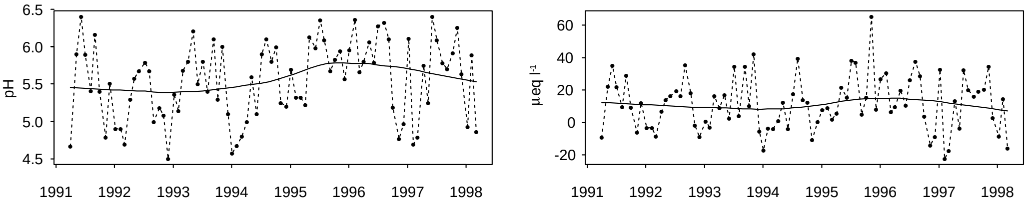
Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
pH	-	*+0.05**	-
DOC	mg l^{-1}	-	*+0.10**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

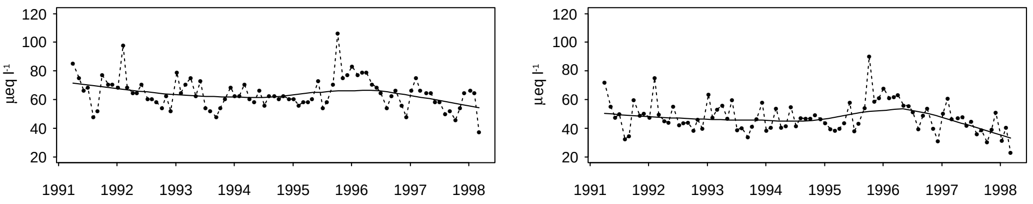
Figure 4.18.2

Afon Gwy: summary of major chemical determinands (September 1991 - March 1998)

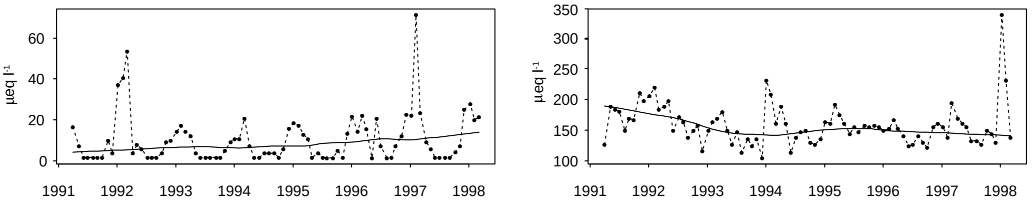
Smoothed line represents LOESS curve (Section 3.1.2)


(a) pH

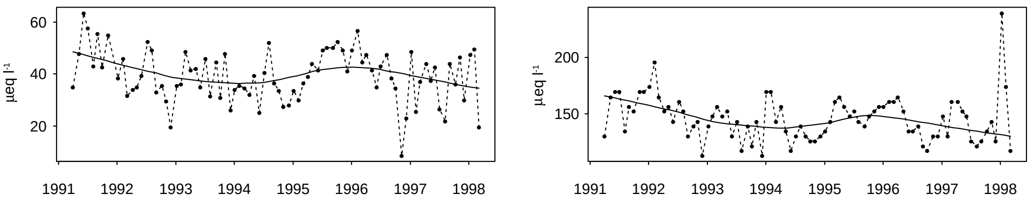
(b) Alkalinity


(c) Sulphate

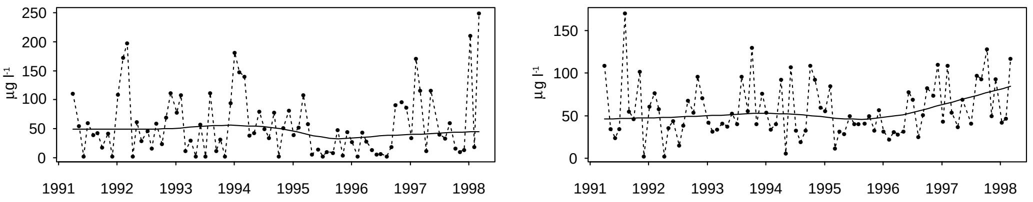
(d) Non-marine Sulphate


(e) Nitrate

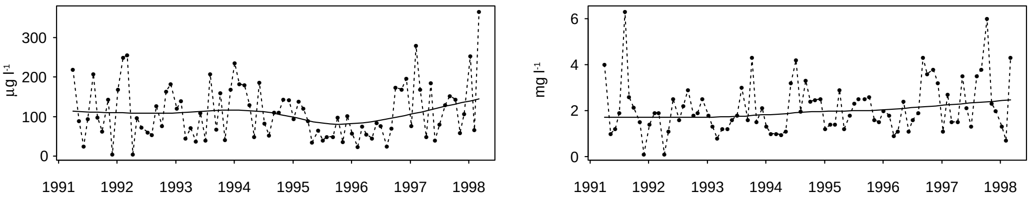
(f) Chloride


(g) Calcium

(h) Sodium


(i) Labile Al

(j) Non-labile Al


(k) Total Soluble Al

(l) Dissolved Organic Carbon

Table 4.18.4

Afon Gwy: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	**Number of Taxa**	**Mean N_2 diversity**	**λ_1RDA/λ_2RDA**	**λ_1RDA/λ_1PCA**
Epilithic diatoms	*135*	*57*	*4.6*	*0.45*	*0.44*
Macrophytes	*3*	*4*	*1.9*	*1.11*	*0.57*
Invertebrates	*369*	*26*	*3.9*	*0.39*	*0.32*

Variance explained (%)	**within year**	**between years**	**linear trend**	**p**	
				unrestricted	**restricted**
Epilithic diatoms	*	*	*12.0*	*<0.01*	*0.12*
Macrophytes	*	*	*37.9*	*0.13*	*0.16*
Invertebrates	*55.7*	*44.3*	*8.8*	*<0.01*	*0.04*

probably more episodic during the summer of these years and this could account for the inter-annual variation, through effects of flow on pH depression. RDA and associated restricted permutation test show that “sample year” is not significant at the 0.01 level for this relatively short time series (1991-1998). Given the possible sensitivity to the flow regime and the time restricted dataset it is not possible to infer signs of recovery in the Afon Gwy to date.

■ Macroinvertebrates

(Figure 4.18.4, Table 4.18.4)

This site is very similar to the Afon Hafren in species composition. Chironomids and a diverse community of acid tolerant stoneflies characterise the benthic fauna. The predatory stonefly *Siphonoperla torrentium* is the most abundant, while the detritivores *Leuctra inermis* and *Amphinemura sulcicollis* are also common. *Leuctra hippopus* was abundant in the early years but numbers have declined more recently. Of the caddisflies, *Plectrocnemia* spp. was present throughout the monitoring period with the exception of 1997; *Polycentropus* spp. was only recorded in the last three years and *Rhyacophila* spp. occurred intermittently in low numbers. The Coleopterans *Oreodytes sanmarkii* and *Limnius volckmari* both appeared after 1995. Only four individual mayflies have been recorded in the eight year monitoring period, *Ameletus inopinatus*, *Baetis* spp. and a member of the Leptophlebidae. Time as a linear trend was not significant at the 0.01 level according to RDA and associated restricted permutation test.

■ Fish

(Figure 4.18.5)

The Afon Gwy has been electrofished since 1991. With only seven years of data available to date there are no significant linear trends in population or condition factor statistics. Population levels of $>0^+$ fish are generally low, although 1993 and 1995 were years of good recruitment. The two highest densities of $>0^+$ fish (associated with relatively low condition factors) have occured within the last three years. Length frequency graphs clearly show the sparseness of the fish population at this site.

■ Aquatic macrophytes

(Tables 4.18.4-5)

The Afon Gwy survey stretch is dominated by two acid tolerant liverwort species, *Scapania undulata* and *Nardia compressa*. The moss *Racomitrium aciculare* is present in patches

Table 4.18.5

Afon Gwy: relative abundance of aquatic macrophyte flora (1991 - 1998)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	91	92	93	95	96	97
INDICATOR SPECIES						
Nardia compressa[3]	5.4	1.5	0.7	<0.1	0.7	0.5
OTHER SUBMERGED SPECIES						
Filamentous green algae	10.4	0.7	9.8	0.3	19.7	2.0
Polytrichum sp.	1.0	<0.1	<0.1	<0.1	<0.1	<0.1
Racomitrium aciculare	0.3	<0.1	<0.1	<0.1	<0.1	0.2
Scapania undulata	0.9	1.7	2.0	1.0	5.8	0.9
EMERGENT SPECIES						
Juncus effusus	0.0	0.0	0.0	0.0	0.0	<0.1
total macrophyte cover excluding filamentous algae	7.6	3.2	2.7	1.0	6.5	1.6
TOTAL NUMBER OF SPECIES	5	5	5	5	5	6

above the normal water level. There is no evidence of any trend in species cover since the onset of monitoring in 1991 and “sample year” is insignificant as a linear variable according to RDA and associated restricted permutation test.

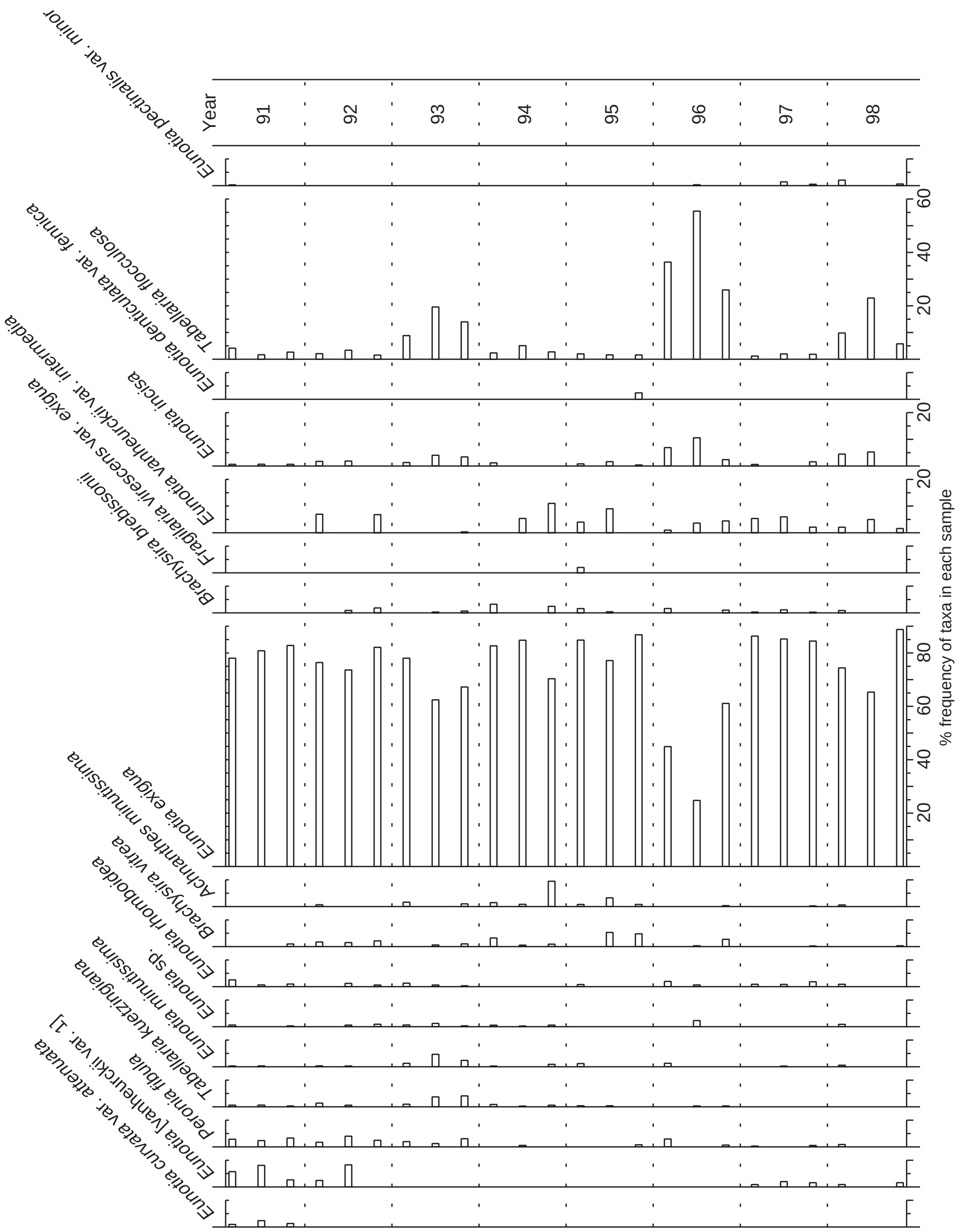
■ Summary

The Afon Gwy is the least acidic of the Welsh UKAWMN sites, although differences between sites are small, and the stream is subject to acid episodes during high flows. NO_3 and xSO_4 concentrations are lower than at the nearby Afon Hafren, and this is likely to reflect the impact of forestry at the latter. The two Welsh stream sites also demonstrate similarities in their aquatic flora and fauna. Trend analyses for the Gwy are limited by the absence of data for the first three years, but there appears to have been an increase in DOC since 1991. There has been a sharp decline in xSO_4 since 1996, but it remains to be seen whether this represents a sustained recovery at the site.

Figure 4.18.3

Afon Gwy: summary of epilithic diatom data (1991 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



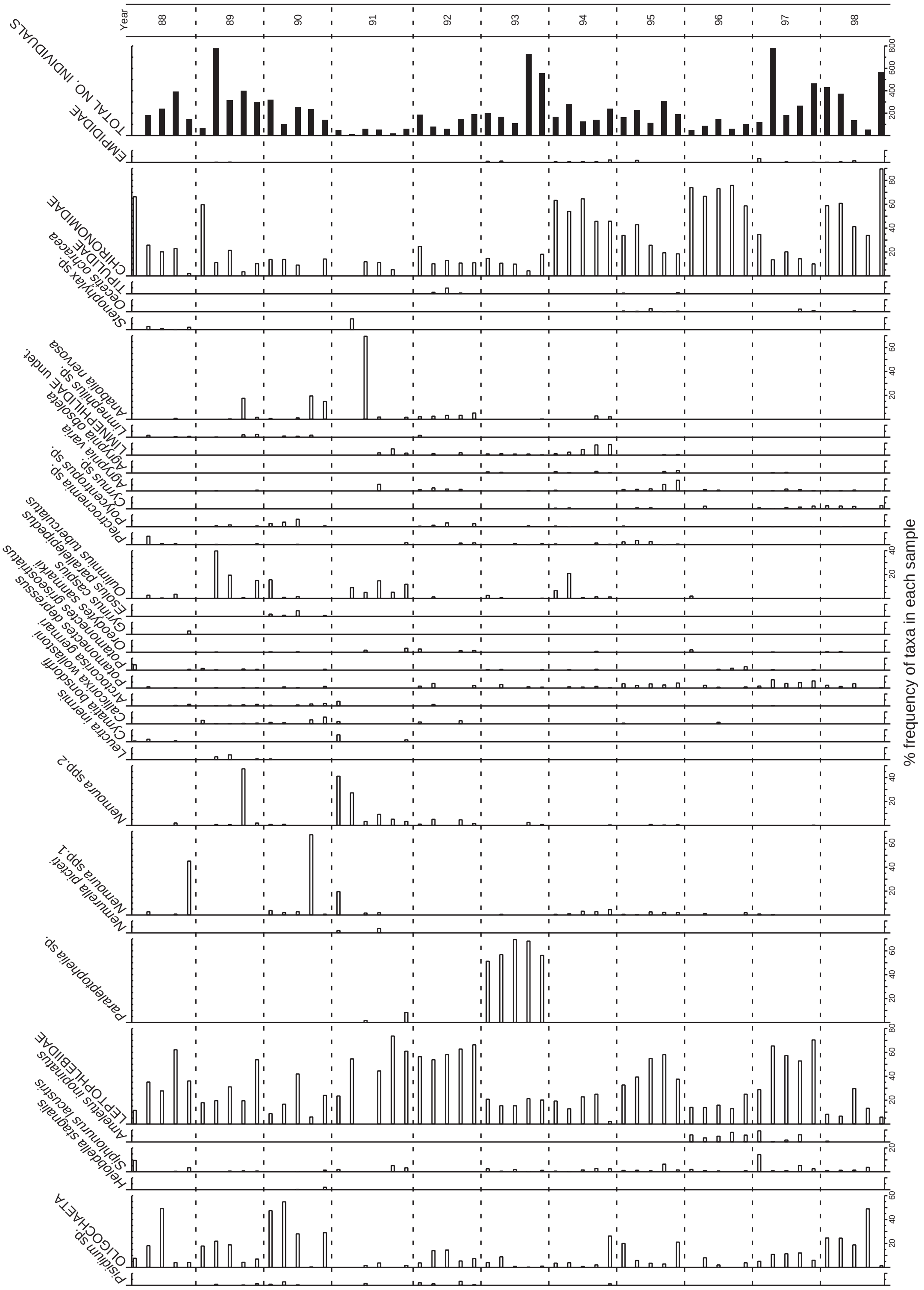


Figure 4.18.4

Afon Gwy: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

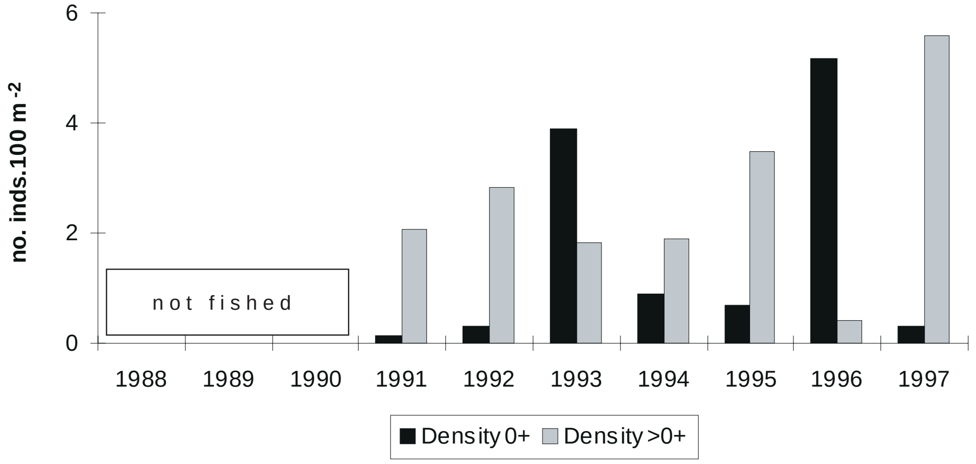
Figure 4.18.5

Afon Gwy: summary of fish data (1991 - 1997)

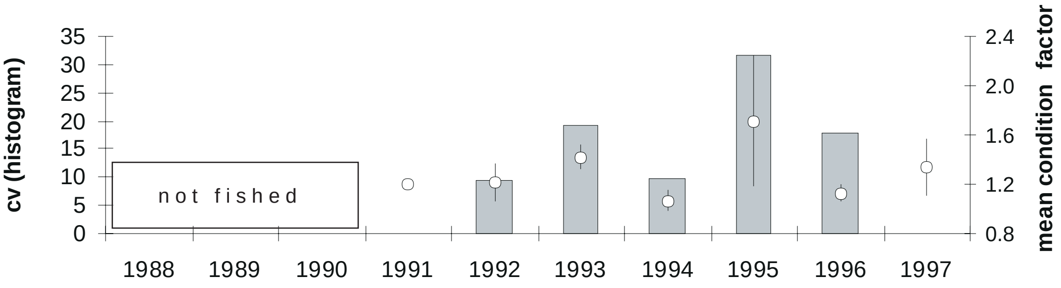
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

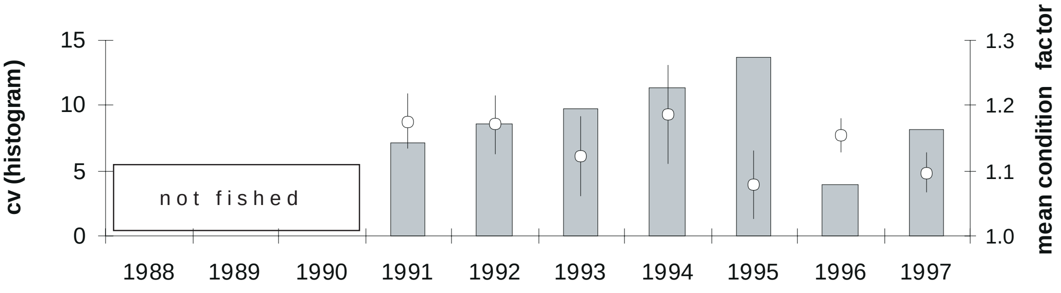
(a) Density



(b) Condition (0+)



Condition (>0+)



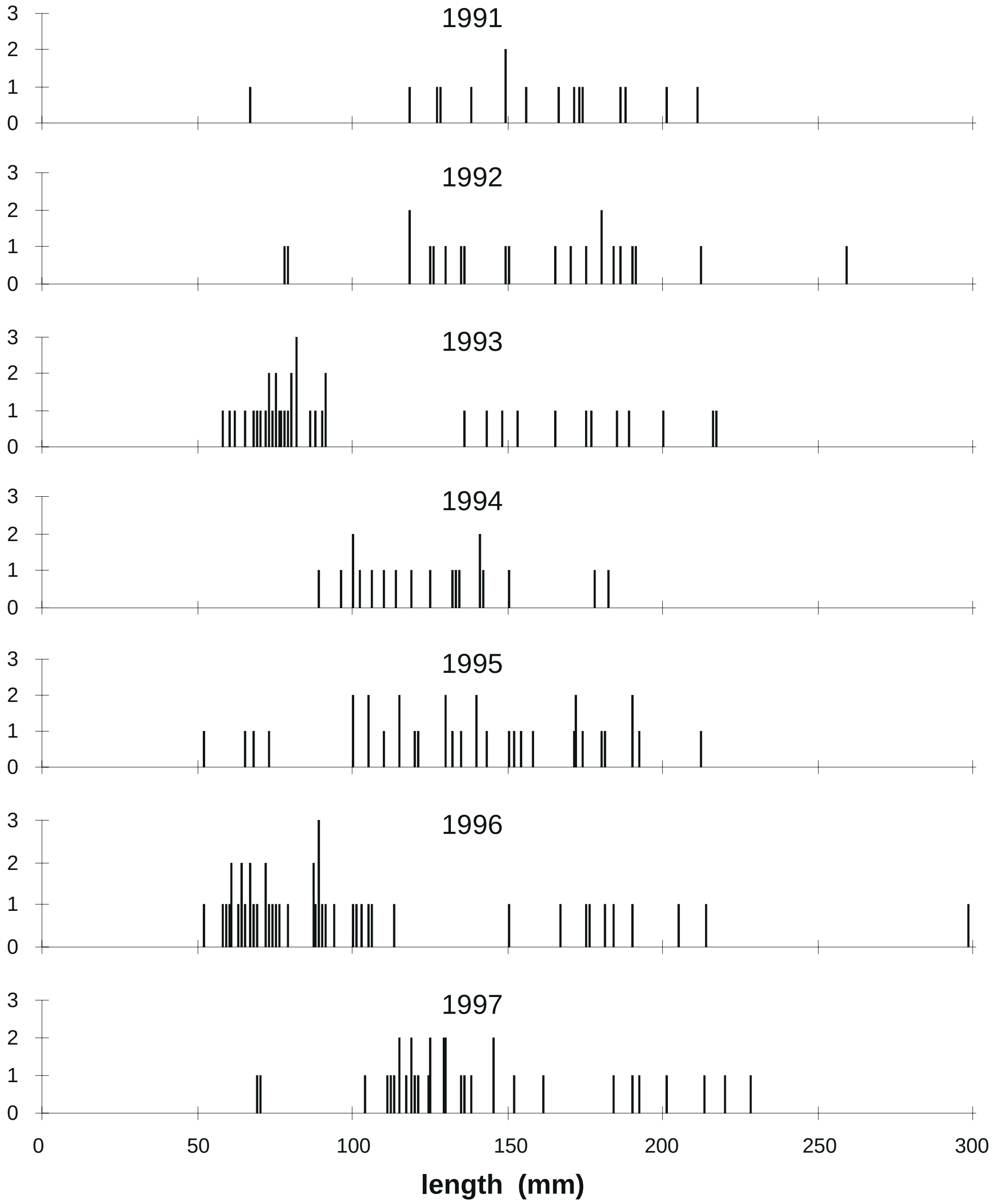


Figure 4.18.5

Afon Gwy: summary of fish data (1991 - 1997)
(c) Trout length frequency summaries

4.19 Beagh's Burn

Site Review

Beagh's Burn lies in the Glens of Antrim in north east Northern Ireland. The site was subject to a major storm event during 1991 which redistributed substrate and sharply reduced the bryophyte cover of the stream bed. Recent work carried out by a local farm, involving improvements to a wall and sheep pen, are all beneath the water sample point and biological survey stretches. There is no evidence of any physical disturbance within the catchment over the survey period.

Water Chemistry

(Tables 4.19.2-3, Figure 4.19.2)

Beagh's Burn is not strongly acidic, having a mean alkalinity of 44 μeq l^{-1}. However, the range of

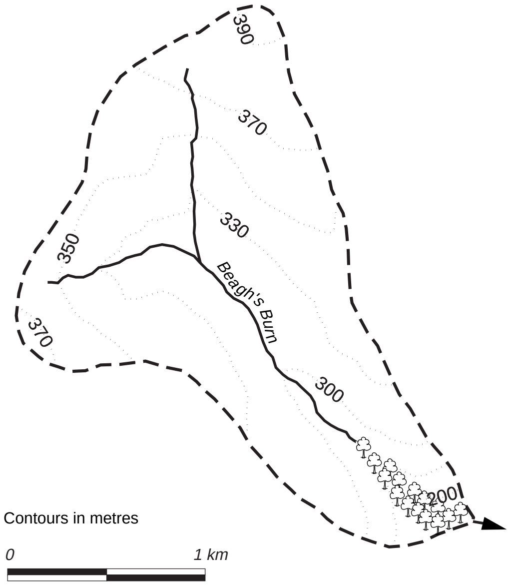


Figure 4.19.1

Beagh's Burn: catchment

Table 4.19.1

Beagh's Burn: site characteristics

Grid reference	*D 173297*
Catchment area	*303 ha*
Minimum Catchment altitude	*150 m*
Maximum Catchment altitude	*397 m*
Catchment Geology	*schists*
Catchment Soils	*blanket peats*
Catchment vegetation	*moorland >99%,* *deciduous trees <1%*
Mean annual rainfall	*1608 mm*
1996 deposition	
Total S	*16 kg ha^{-1} yr^{-1}*
non-marine S	*13 kg ha^{-1} yr^{-1}*
Oxidised N	*6 kg ha^{-1} yr^{-1}*
Reduced N	*14 kg ha^{-1} yr^{-1}*

Table 4.19.2

Beagh's Burn: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.76*	*7.18*	*4.31*
Alkalinity	μeq l^{-1}	*44.4*	*240.0*	*-58.0*
Ca	μeq l^{-1}	*102.5*	*218.5*	*35.5*
Mg	μeq l^{-1}	*111.7*	*183.3*	*50.0*
Na	μeq l^{-1}	*302.2*	*443.5*	*204.3*
K	μeq l^{-1}	*10.5*	*23.1*	*2.6*
SO_4	μeq l^{-1}	*72.5*	*275.0*	*27.1*
xSO_4	μeq l^{-1}	*37.5*	*243.1*	*0.0*
NO_3	μeq l^{-1}	*3.6*	*15.7*	*<1.4*
Cl	μeq l^{-1}	*336.6*	*619.7*	*191.5*
Soluble Al	μg l^{-1}	*55.6*	*106.0*	*<2.5*
Labile Al	μg l^{-1}	*10.2*	*60.0*	*<2.5*
Non-labile Al	μg l^{-1}	*45.9*	*92.0*	*<2.5*
DOC	mg l^{-1}	*11.1*	*30.0*	*3.1*
Conductivity	μS cm^{-1}	*59.4*	*96.0*	*39.0*

observed values is high, from –58 to 240 µeq l^{-1}. Mean pH (5.76) is low relative to alkalinity, probably due to high levels of weak organic acidity; Beagh's Burn has the highest mean DOC concentrations in the Network. Na and Cl concentrations are also extremely high, whereas xSO_4 and NO_3 concentrations are both low (means 38 µeq l^{-1} and 4 µeq l^{-1} respectively). In general these characteristics resemble those of the coastal north and central Scotland UKAWMN sites, with very high marine ion deposition and low pollutant deposition. Beagh's Burn also has a relatively high Ca concentration (mean 102 µeq l^{-1}) and therefore a low sensitivity to acid deposition.

A strong correlation between Ca and alkalinity ($R^2 = 0.57$, $p< 0.0001$, Figure 4.19.2b,g) suggests a simple hydrological control on stream acidity, with low flows dominated by Ca-rich, alkaline groundwater, and dilution generating acidic episodes at high flows. Marine ion inputs also generate some acid episodes through the "sea-salt effect". Both processes can be considered natural, although neither would be expected to cause negative alkalinity in the absence of anthropogenic SO_4 and NO_3. However, a small number of SO_4 and NO_3 pulses are also observed at this stream, and the January 1996 NO_3 peak in particular (Figure 4.19.2e) appears to have caused significant episodic acidification. A concurrent and more pronounced peak observed at Coneyglen Burn (Site 22) is discussed in greater detail below.

Trend analyses for Beagh's Burn show few changes in stream chemistry during the last decade (Table 4.19.3). A decreasing trend in labile Al obtained using regression can be linked to a small, possibly anomalous group of high values during 1990-1991, and no changes were observed in alkalinity, pH, xSO_4 or NO_3. LOESS curves suggest some inter-annual variability in Na and Cl, but this is small relative to UK mainland sites. The only major change in stream chemistry appears to have been an increase in DOC, highly significant using both analytical methods, of around 6 mg l^{-1} over the decade. Most of this increase appears to have occurred since 1993, with both spring minima and autumn maxima having risen.

■ Epilithic diatoms

(Figure 4.19.3, Table 4.19.4)

The composition of the epilithic diatom assemblage of Beagh's Burn has fluctuated markedly beween years and no species has been consistently dominant. The earlier years are characterised by relatively diverse samples, dominated by species with relatively acid preferences including *Eunotia exigua* (pH optima 5.1), *Gomphonema angustatum* [agg.](pH optima 5.8) and *Pinnularia subcapitata* var. *hilseana* (pH optima 5.0). *Achnanthes minutissima* (pH optima 6.3) and *Synedra minuscula* (pH optima 6.0) comprised >80% of the assemblage of all samples in 1994 and 1995 respectively since when *G. angustatum*, and *P. subcapitata* var. *hilseana* have again been abundant. The substantial differences between years in the pH preference of the dominant taxa are likely to relate to the varying hydrological regime. Summer rainfall

Table 4.19.3

Significant trends in chemical trends (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
DOC	mg l^{-1}	*+0.65****	*+0.60***
labile Al	µg l^{-1}	*-0.93**	-

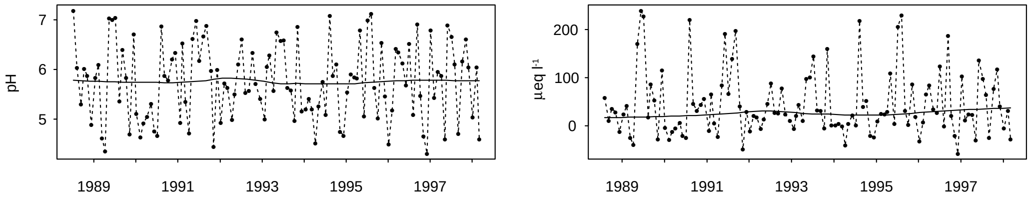
** Trend significant at p < 0.05; ** trend significant at p < 0.01; *** trend significant at p < 0.001*

Figure 4.19.2

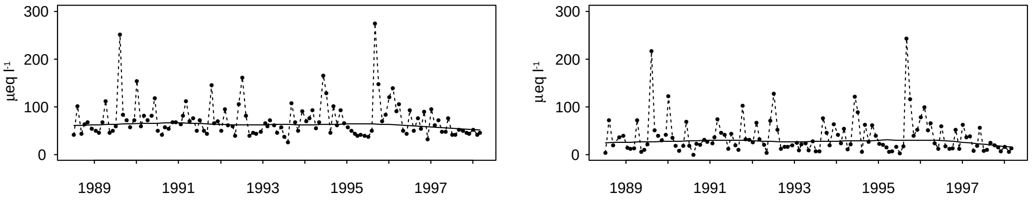
Beagh's Burn: summary of major chemical determinands (July 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

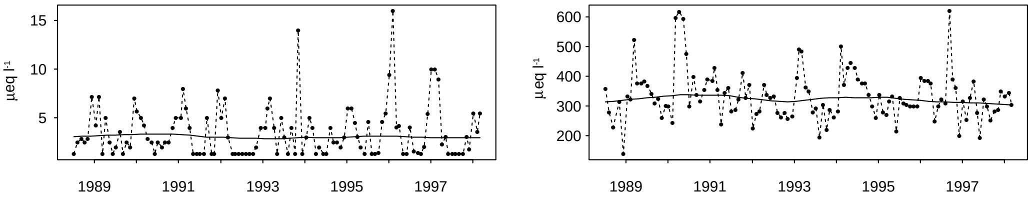
(a) pH
(b) Alkalinity



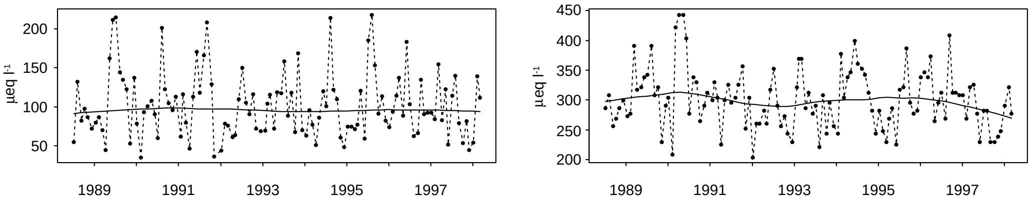
(c) Sulphate
(d) Non-marine Sulphate



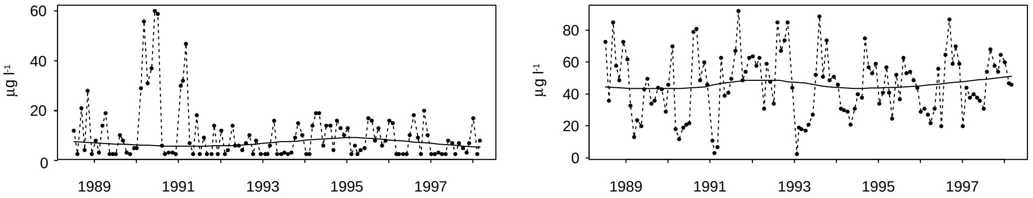
(e) Nitrate
(f) Chloride



(g) Calcium
(h) Sodium



(i) Labile Al
(j) Non-labile Al



(k) Total Soluble Al
(l) Dissolved Organic Carbon

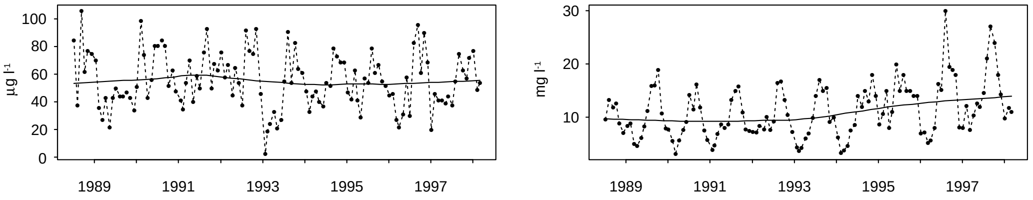


Table 4.19.4

Beagh's Burn: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	530	87	4.4	0.46	0.46
Macrophytes	9	5	1.7	0.26	0.21
Invertebrates	449	28	2.7	0.43	0.41

Variance explained (%)	within year	between years	linear trend	p unrestricted	p restricted
Epilithic diatoms	25.2	74.8	12.3	<0.01	0.07
Macrophytes	*	*	19.5	0.25	0.50
Invertebrates	51.7	48.3	8.6	<0.01	0.02

(June-August) was particularly low in 1994 and 1995 at the nearby Ballypatrick Meteorological station and this is likely to have resulted in fewer and less intense flow related acid episodes. As at the majority of UKAWMN stream sites, diatom inferred pH, using weighted averaging, is significantly and inversely correlated with total June-July rainfall (Section 7.4.1). RDA and associated restricted permutation test shows that a time trend is insignificant at the 0.01 level.

■ Macroinvertebrates

(Figure 4.19.4, Table 4.19.4)

The macroinvertebrate community is characterised by very large numbers of Simuliidae, which in some years make up to 80% of the total species composition. Acid tolerant stoneflies form the largest part of the remaining benthic composition. *Siphonoperla torrentium* dominated most years and was accompanied by *Leuctra inermis*, *Protonemura* spp., *Amphinemura sulcicollis* and *Brachyptera risi*. 1998 saw a marked increase in stonefly abundance. The caddisflies *Rhyacophila* spp. and *Plectrocnemia* spp. were both common, the latter species being absent the years 1991-1993. Several species of the moderately acid sensitive family Hydropsychidae (mainly *Hydropsyche siltalai* and *Hydropsyche pellucidula*) have been recorded, with highest densities occurring after 1994. 1991 was the poorest year both in number of species and abundance, while 1995 was the richest. While acid tolerant stoneflies have been present throughout the monitoring period, some species which are intolerant of very acid conditions have only been recorded in more recent years, during which time minimum species richness has also increased (see Figure 7.11b). Despite this, time as a linear trend is not significant at the 0.01 level according to RDA and associated permutation test.

■ Fish

(Figure 4.19.5)

A full ten years of data are available for Beagh's Burn. Mean trout densities are low and 0+ trout recruitment is extremely sporadic with presence only recorded in three years (1989, 1990 and 1997). Population densities of >0+ trout are relatively stable, with a minimum recorded in 1992 and a maximum in 1996. The mean condition factor of >0+ trout has also remained relatively stable between years although the coefficient of variation of the condition factor has shown wide fluctuations. The lowest condition factor recorded was associated with the highest coefficient of variation (1988). Length frequency

Table 4.19.5

Beagh's Burn: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	88	89	90	91	92	93	95	96	97
SUBMERGED SPECIES									
Filamentous green algae	6.9	5.9	1.5	0.5	<0.1	<0.1	<0.1	<0.1	<0.1
Hyocomium armoricum	0.0	0.0	0.0	0.0	<0.1	0.0	0.0	0.1	0.0
Marsupella emarginata	<0.1	0.0	0.0	<0.1	0.0	0.0	0.0	0.0	0.0
Racomitrium aciculare	1.4	2.2	0.1	0.1	<0.1	<0.1	<0.1	0.4	<0.1
Rhytidiadelphus squarrosus	0.0	0.0	0.0	<0.1	0.0	0.0	0.0	0.0	0.0
Scapania undulata	11.2	10.5	7.6	0.1	0.6	<0.1	0.8	3.2	3.7
total macrophyte cover excluding filamentous algae	12.6	12.7	7.7	0.2	0.6	<0.1	0.8	3.7	3.7
TOTAL NUMBER OF SPECIES	4	3	3	5	4	3	3	4	3

graphs illustrate the sparse population, even in the three recruitment years, and the absence of all medium sized (c.150 mm) fish in 1992.

■ Aquatic macrophytes

(Tables 4.19.4-5)

The impoverished aquatic macrophyte flora of Beagh's Burn, which is limited almost entirely to the acid tolerant liverwort, *Scapania undulata,* reflects the more acid characteristics of the site during high flows, rather than mean conditions. *S.undulata* is the only species which has been consistently recorded in fully submerged locations, although the moss *Racomitrium aciculare* is present in patches above the normal water level. The cover of *S.undulata* was substantially reduced in 1991, probably as a result of a major storm event earlier in the year, and consequent physical scouring effects. Since then the abundance of this species has gradually increased again. Time is insignificant as a linear variable according to RDA and restricted permutation test.

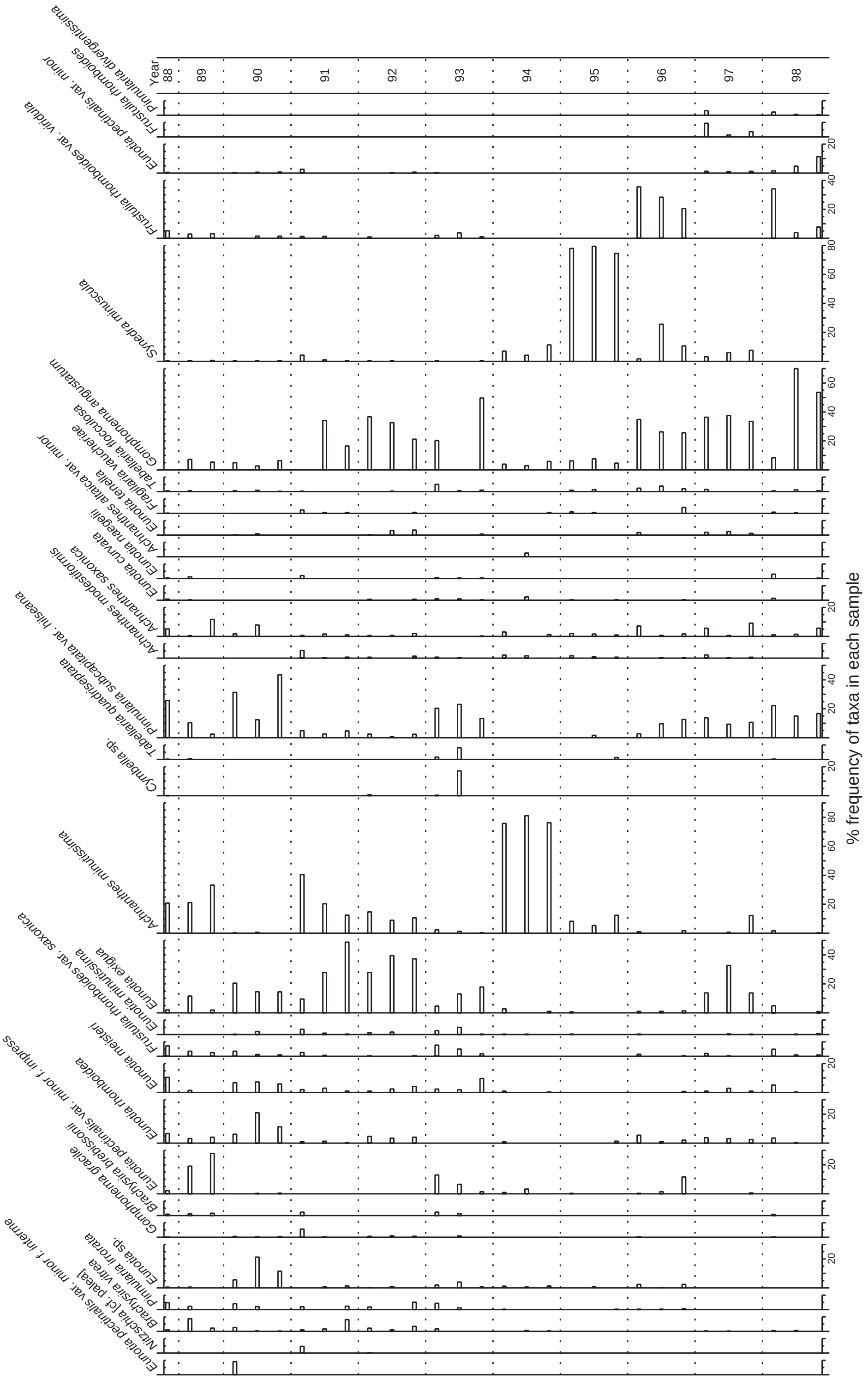
■ Summary

Beagh's Burn is a relatively unimpacted site, upwind of major emission sources, and is not severely acidified. The stream does however experience acidic episodes, driven by dilution of weathering-derived Ca during high flows, and by sea-salt cation exchange processes, and these, rather than mean conditions, appear to determine the nature of the aquatic biota. All biological groups demonstrate considerable inter-annual variability but there is no evidence of time trends in species composition. There has not been any change in major ion composition over the monitoring period, but DOC levels appear to have risen substantially from an already high baseline.

Figure 4.19.3

Beagh's Burn: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



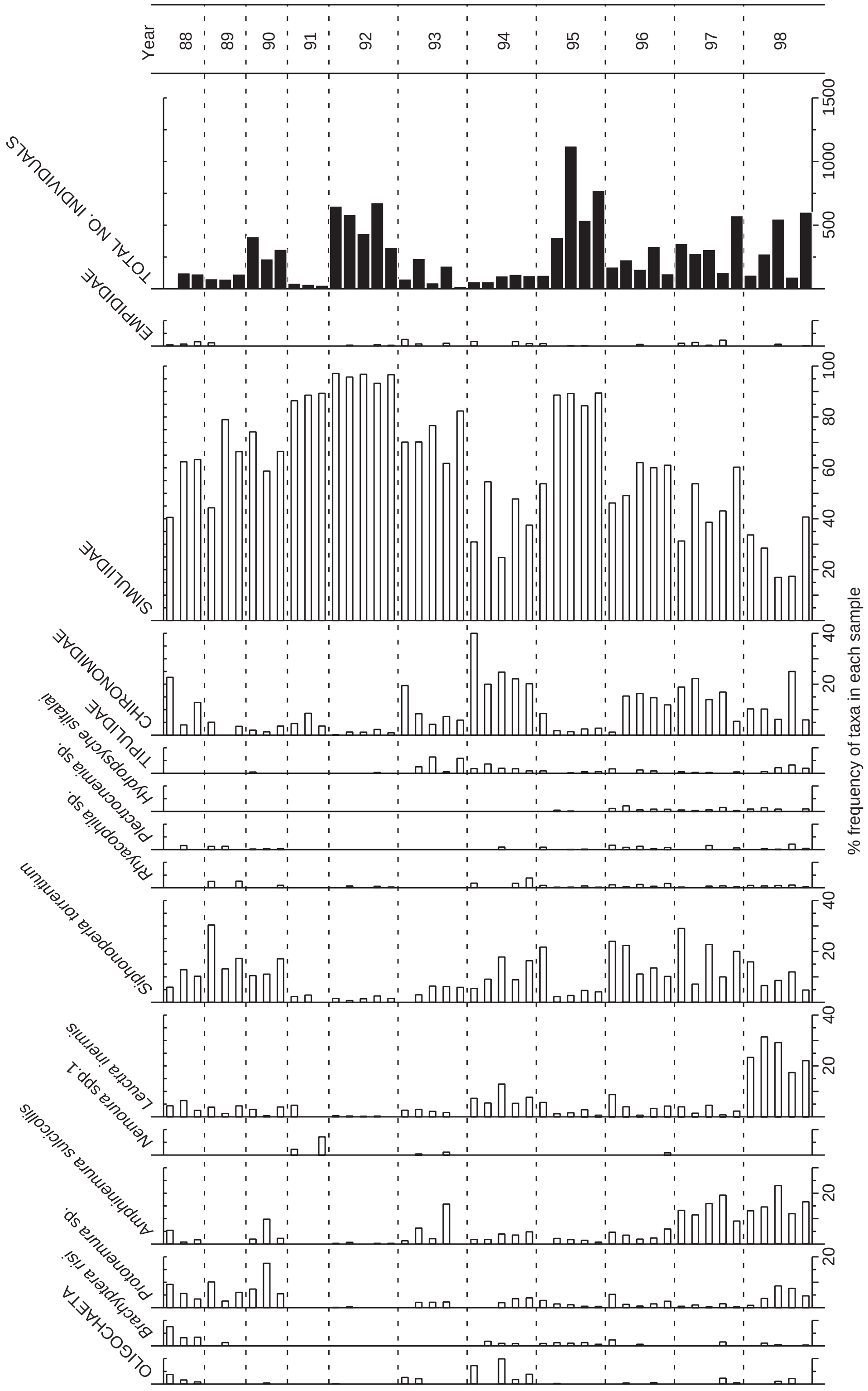


Figure 4.19.4

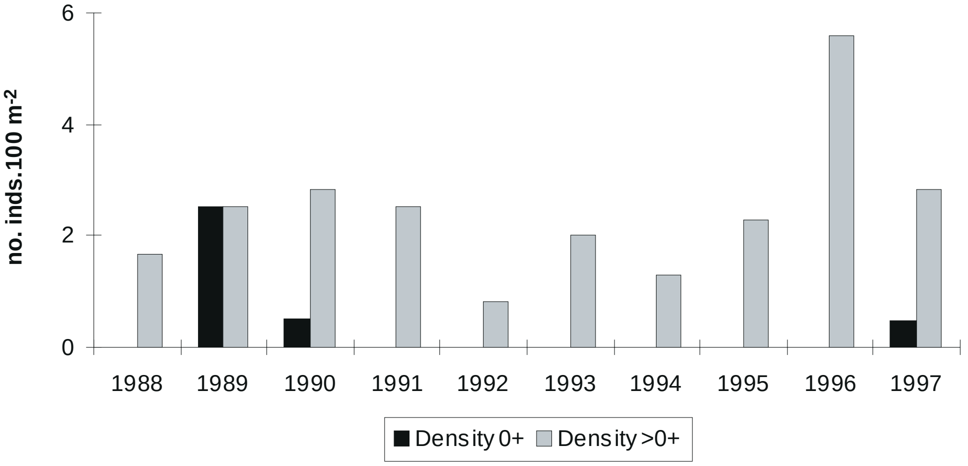
Beagh's Burn: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

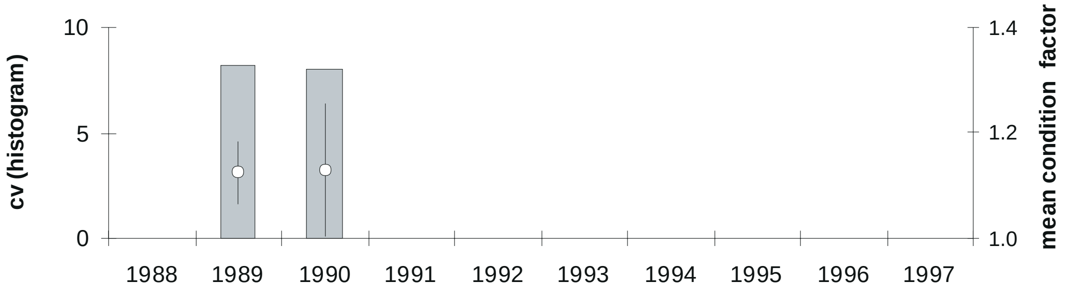
Figure 4.19.5

Beagh's Burn: summary of fish data (1988 - 1997)
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})
(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

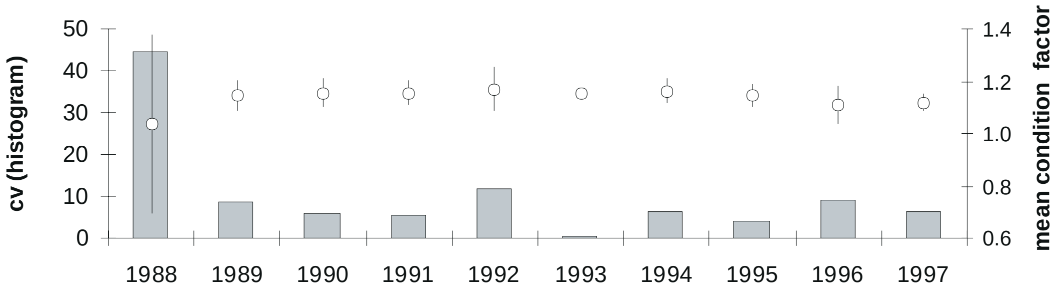
(a) Density



(b) Condition (0+)



Condition (>0+)



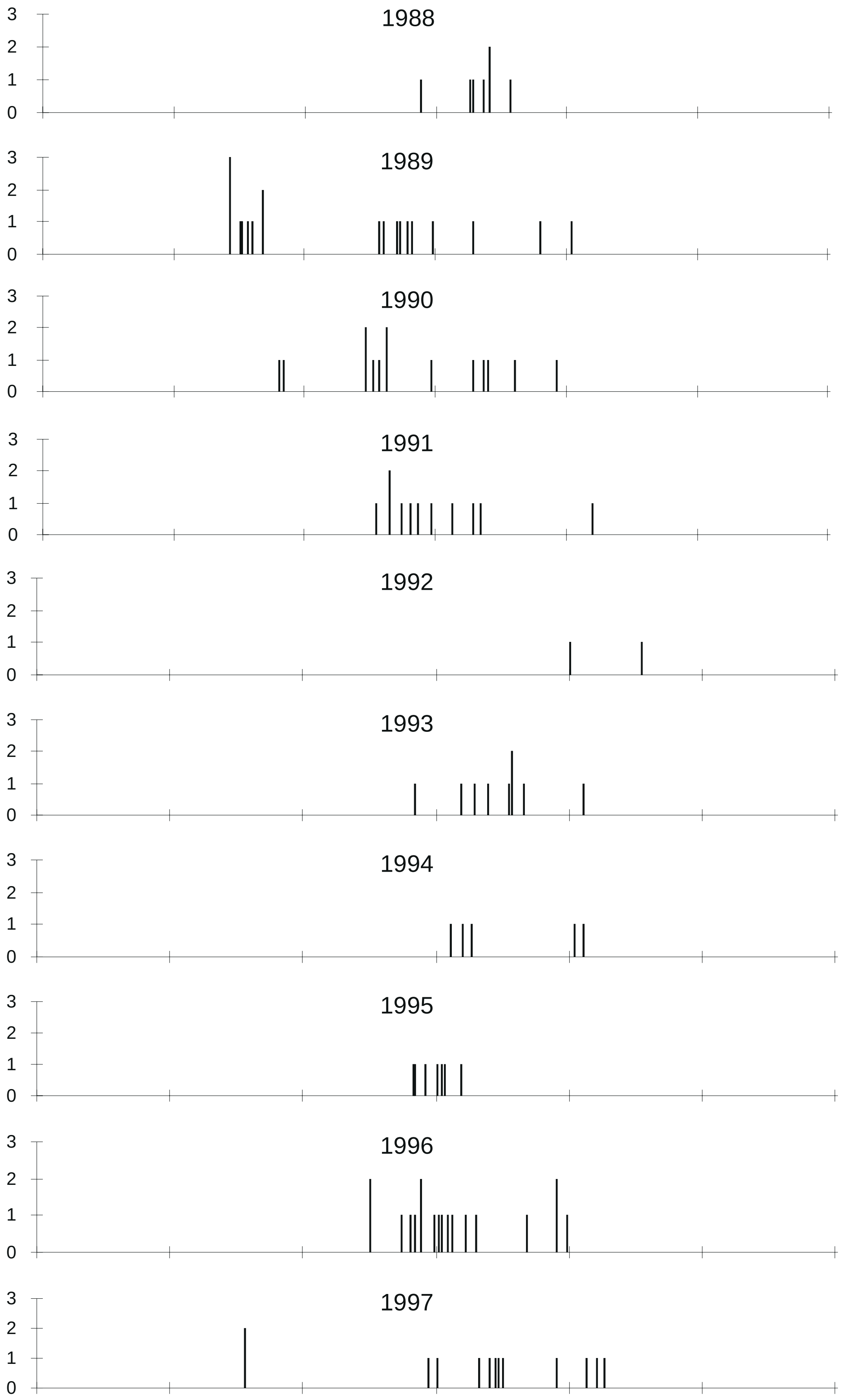


Figure 4.19.5

Beagh's Burn: summary of fish data (1988 - 1997)
(c) Trout length frequency summaries

4.20 Bencrom River

Site Review

The Bencrom River drains into the Silent Valley Reservoir in the Mourne Mountains of south eastern Northern Ireland. There has been no physical disturbance within the catchment since the onset of monitoring in 1988.

Water Chemistry

(Figure 4.20.2, Tables 4.20.2-3)

The Bencrom River is chronically acidic, with a mean alkalinity of –5 μeq l^{-1} and a mean pH of 5.19. Ca concentrations are low (mean 53 μeq l^{-1}), whilst Al concentrations are high and dominated by the labile fraction. The acidity of this stream can be attributed to high levels of xSO_4 (mean 67 μeq l^{-1}) and also to the second highest NO_3 concentrations in the UKAWMN (mean 29 μeq l^{-1}). NO_3 remained above detection limits throughout the monitoring

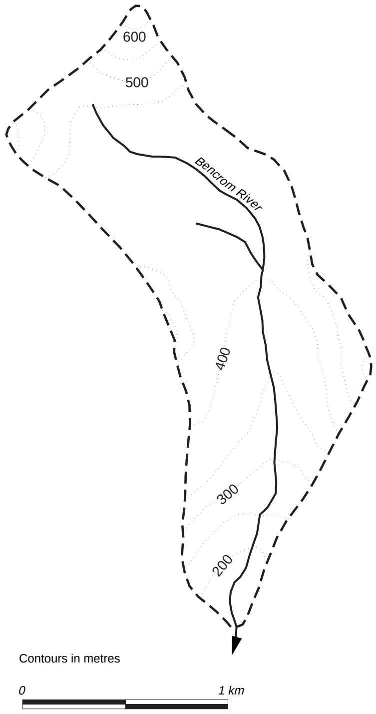


Figure 4.20.1

Bencrom River: catchment

Table 4.20.1

Bencrom River: site characteristics

Grid reference	*J 304250*
Catchment area	*216 ha*
Minimum Catchment altitude	*140 m*
Maximum Catchment altitude	*700 m*
Catchment Geology	*granite*
Catchment Soils	*blanket peat*
Catchment vegetation	*moorland 100%,*
Mean annual rainfall	*1768 mm*
1996 deposition	
Total S	*17 kg* ha^{-1} yr^{-1}
non-marine S	*15 kg* ha^{-1} yr^{-1}
Oxidised N	*7 kg* ha^{-1} yr^{-1}
Reduced N	*14 kg* ha^{-1} yr^{-1}

Table 4.20.2

Bencrom River: summary of chemical determinands, July 1988 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*5.19*	*6.27*	*4.38*
Alkalinity	μeq l^{-1}	*-5.4*	*37.0*	*-45.0*
Ca	μeq l^{-1}	*52.5*	*81.5*	*29.5*
Mg	μeq l^{-1}	*61.7*	*108.3*	*33.3*
Na	μeq l^{-1}	*263.5*	*352.2*	*178.3*
K	μeq l^{-1}	*11.0*	*25.4*	*5.1*
SO_4	μeq l^{-1}	*93.5*	*187.5*	*52.1*
xSO_4	μeq l^{-1}	*66.7*	*161.5*	*28.5*
NO_3	μeq l^{-1}	*28.6*	*77.1*	*5.7*
Cl	μeq l^{-1}	*255.5*	*371.8*	*138.0*
Soluble Al	μg l^{-1}	*202.1*	*400.0*	*9.0*
Labile Al	μg l^{-1}	*125.3*	*308.0*	*<2.5*
Non-labile Al	μg l^{-1}	*76.9*	*237.0*	*2.5*
DOC	mg l^{-1}	*4.1*	*15.5*	*1.2*
Conductivity	μS cm^{-1}	*50.4*	*80.0*	*36.0*

period, with some seasonal cyclicity evident, and peak concentrations exceeded 60 μeq l^{-1} during four separate winter/spring periods. In early 1996, NO_3 exceeded xSO_4 on an equivalent basis in two samples, and was thus the dominant acidifying anion at this time. It appears that NO_3 pulses, base cation dilution and sea-salt cation exchange all contribute to large episodic alkalinity and pH depressions at this site.

Rising trends have been observed at the Bencrom River for DOC using SKT and regression, and for NO_3 using regression only. (Table 4.20.3). The increase in NO_3 appears to be the result of climatically driven fluctuations, with higher concentrations at the beginning and end of the record (Figure 4.20.2e). No clear changes have taken place in pH, alkalinity or xSO_4, but there appears to be some cyclicity in Cl, Na and Ca (Figures 4.20.2f,h) with 1990-1991 and 1995-1996 peaks comparable to those at many UK mainland sites. However, in contrast to most other sites, the 1995-1996 peak was the larger at the Bencrom River. The DOC increase, which is highly significant using both methods, appears to have occurred linearly over the monitoring period (Figure 4.20.2l), with the overall change estimated between 1.4 at 2.1 mg l^{-1}.

■ Epilithic diatoms

(Figure 4.20.3, Table 4.20.4)

The epilithic diatom flora of the Bencrom River is typical for a permanently very acid stream and shows relative stability between years. The bulk of the assemblage was represented by *Eunotia naegelii* (pH optima 5.0) and *Brachysira brebissonii* (pH optima 5.3). The former was dominant in most samples and showed a general increase with time, although the latter was more frequent in 1990 and 1995. *Tabellaria quadriseptata*, which has a preference for particularly acid conditions (pH optima 4.9), commonly comprised over 5% of samples until 1994, since when it declined. The general increase in *E.naegelii* and reduction in *T. quadriseptata* is indicative of slight improvement in pH in recent years, and this is supported by LOESS plots for water chemistry data. However, as for the majority of UKAWMN stream sites, summer rainfall appears to be important in influencing species composition, and total June-July rainfall for the nearby Meteorological Station (Silent Valley) is inversely related to diatom infered pH using weighted averaging (Section 7.3.1). “Sample year” is not significant according to RDA and associated restricted permutation test.

■ Macroinvertebrates

(Figure 4.20.4, Table 4.20.4)

The Bencrom River is the most impoverished stream site of the Network. Species composition has remained relatively persistent through time although there is high within-year variation due to habitat patchiness. The fauna is dominated by two detritivorous stonefly species (*Amphinemura sulcicollis* and *Leuctra inermis*). Only one individual acid sensitive *Baetis* spp. was recorded in 1990. Other mayfly species, *Ameletus inopinatus* and *Siphlonurus lacustris*

Table 4.20.3

Significant trends in chemical determinands (July 1988 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
NO_3	μeq l^{-1}	*+1.00**	-
DOC	mg l^{-1}	*+0.21***	*+0.14**

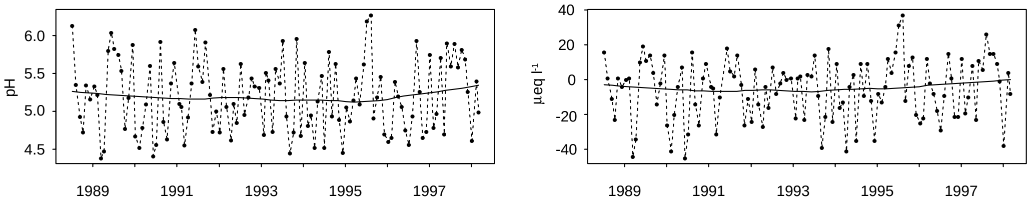
** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

Figure 4.20.2

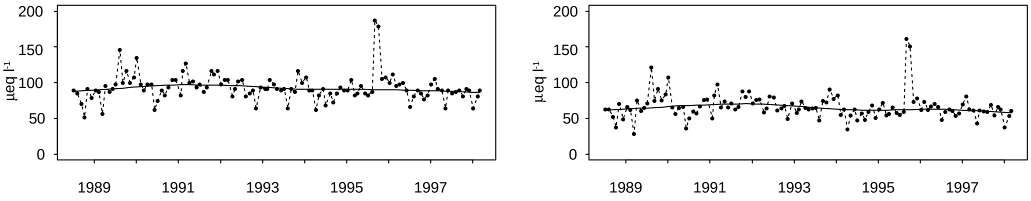
Bencrom River: summary of major chemical determinands (July 1988 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

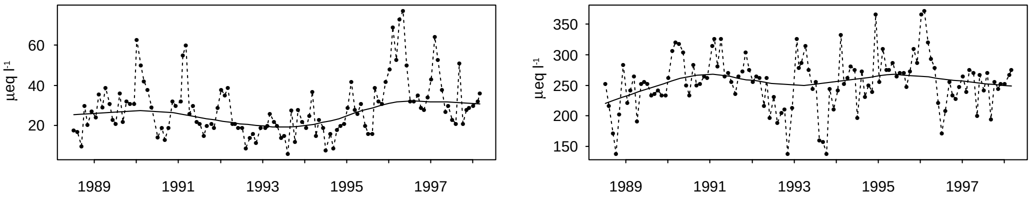
(a) pH (b) Alkalinity



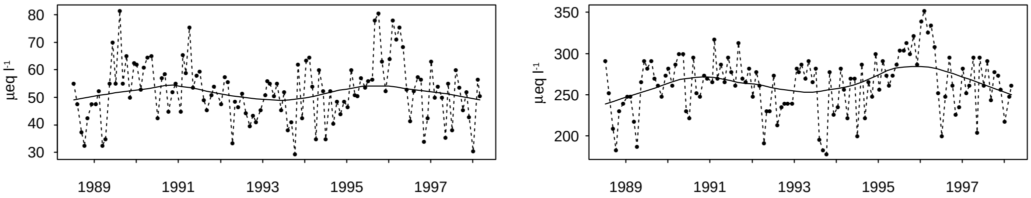
(c) Sulphate (d) Non-marine Sulphate



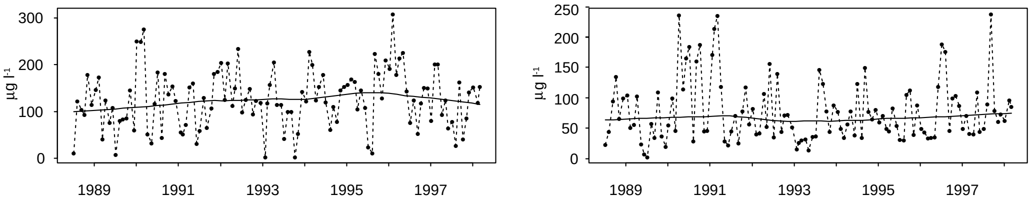
(e) Nitrate (f) Chloride



(g) Calcium (h) Sodium



(i) Labile Al (j) Non-labile Al



(k) Total Soluble Al (l) Dissolved Organic Carbon

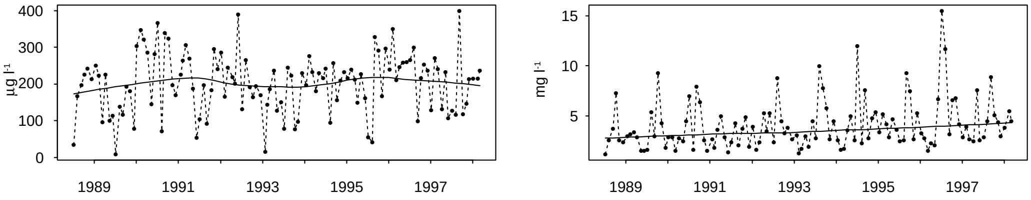


Table 4.20.4

Bencrom River: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1988 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*101*	*56*	*3.1*	*0.44*	*0.40*
Macrophytes	*3*	*5*	*1.1*	*0.67*	*0.40*
Invertebrates	*471*	*18*	*3.9*	*0.18*	*0.17*

Variance explained (%)	within year	between years	linear trend	p unrestricted	restricted
Epilithic diatoms	*44.6*	*55.4*	*9.3*	*<0.01*	*0.03*
Macrophytes	***	***	*38.0*	*0.06*	*0.23*
Invertebrates	*67.5*	*32.5*	*4.1*	*0.05*	*0.16*

were recorded intermittently in low numbers. Of the caddisflies, *Plectrocnemia* spp. was present in all years apart from 1989 and 1991, *Polycentropus* spp. appeared in 1997 and *Rhyacophila* spp. has been recorded on every survey since 1993. In common with other UKAWMN stream sites there has been a gradual increase in minimum species richness in more recent years (Section 7.3.2). However, RDA and associated permutation test show no significant linear trend between years.

■ Fish

(Figure 4.20.5)

This site has been electrofished since 1988 and trout densities have remained low. Mean population density of 0+ trout show some variation but no linear change over the ten years. Population density of >0+ trout seemed to show a decline between 1989 to 1995 but in 1996 and 1997 densities had returned to 1990 levels. Gaps in the data for fish weight make interpretation of the condition factor data difficult. However there has been a significant decline in condition factor of the >0+ fish ($p=<0.05$ df = 6) over the ten years indicative of a general worsening of conditions. No trend is apparent in the condition factor of the 0+ population.

■ Aquatic macrophytes

(Tables 4.20.4-5)

As for the other more acid UKAWMN stream sites, the permanently submerged flora of Bencrom River is largely restricted to a single liverwort species, in this case the acid tolerant, *Nardia compressa*. The abundance of filamentous algae and the red alga *Batrachospermum* sp. have varied considerably between years. Time is insignificant as a linear trend according to RDA and restricted permutation test.

■ Summary

The Bencrom River is severely acidified by a combination of high xSO_4 and NO_3 concentrations and this is reflected in its impoverished aquatic biology. NO_3 makes up a substantial part of the acid anion total, reaching levels comparpable to those of xSO_4 during the winter, when biological uptake within the catchment is minimal. The significant upward trend identified for NO_3 probably reflects differences in climate between the beginning and end of the monitoring period. Marine ions and NO_3 have both exhibited inter-annual variability during the monitoring period, but the only overall

Table 4.20.5

Bencrom River: relative abundance of aquatic macrophyte flora (1988 - 1997)
(see Section 3.2.3 for key to indicator values)

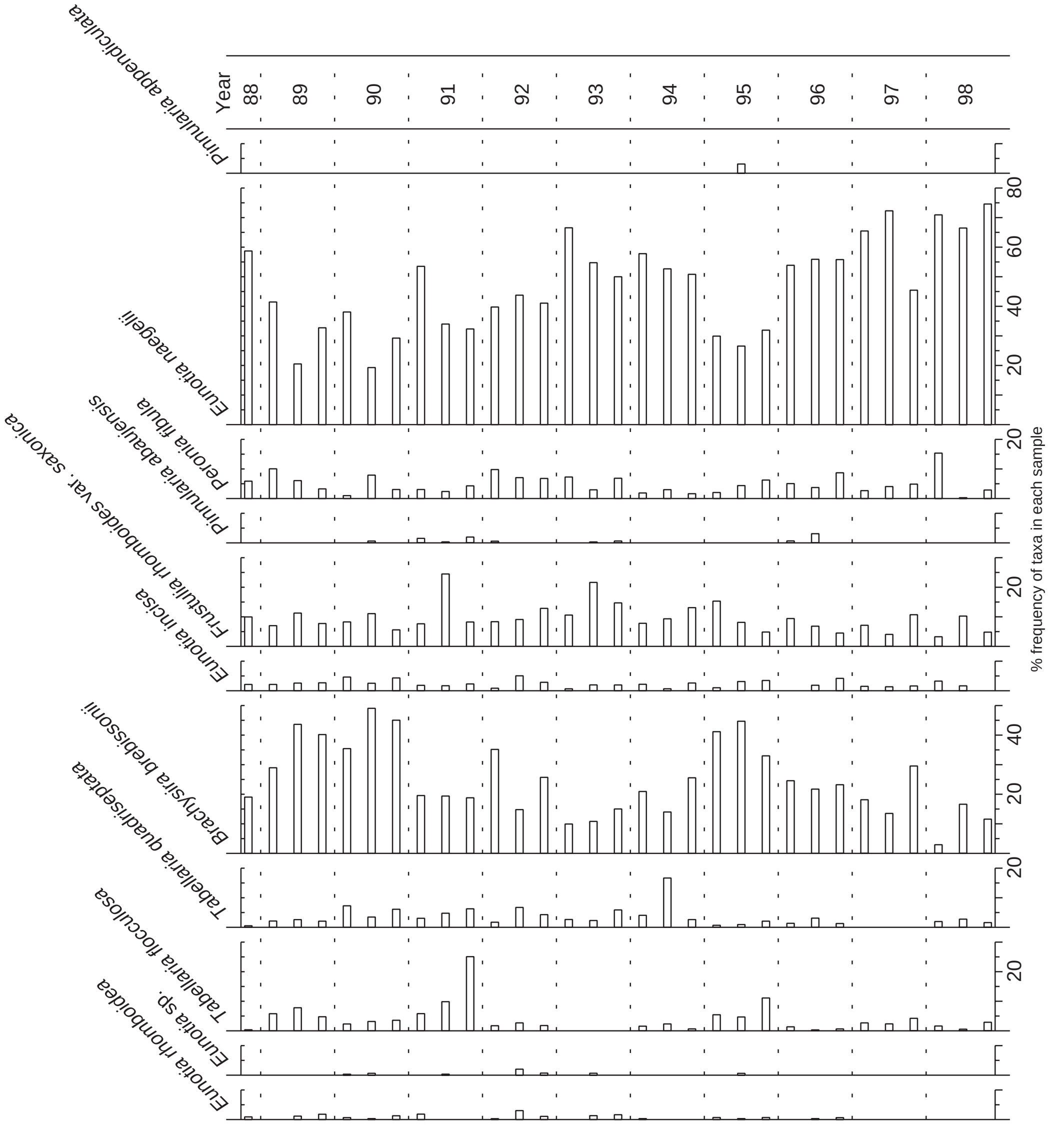
Abundance Taxon **Year**	**88**	**89**	**90**	**91**	**92**	**93**	**95**	**96**	**97**
INDICATOR SPECIES									
Nardia compressa[3]	*2.2*	*6.2*	*10.6*	*8.6*	*3.7*	*2.5*	*2.9*	*1.3*	*1.3*
OTHER SUBMERGED SPECIES									
Batrachospermum sp.	*0.0*	*0.0*	*<0.1*	*<0.1*	*<0.1*	*0.5*	*0.0*	*0.0*	*<0.1*
Filamentous green algae	*7.8*	*9.7*	*3.0*	*3.9*	*3.1*	*2.2*	*30.1*	*1.4*	*1.7*
Juncus bulbosus var. fluitans	*0.0*	*0.0*	*<0.1*	*<0.1*	*0.0*	*0.0*	*<0.1*	*0.0*	*0.0*
Pellia sp.	*0.0*	*<0.1*	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
Scapania undulata	*0.0*	*0.1*	*<0.1*	*<0.1*	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*
total macrophyte cover excluding filamentous algae	*2.2*	*6.3*	*10.6*	*8.6*	*3.7*	*2.5*	*2.9*	*1.3*	*1.3*
TOTAL NUMBER OF SPECIES	*2*	*4*	*6*	*5*	*3*	*4*	*3*	*2*	*3*

change during this time appears to have been an increase in DOC. Variation between years in the epilithic diatom and macroinvertebrate communities appear to be strongly influenced by flow conditions, and no linear trends were detected in the biological datasets.

Figure 4.20.3

Bencrom River: summary of epilithic diatom data (1988 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



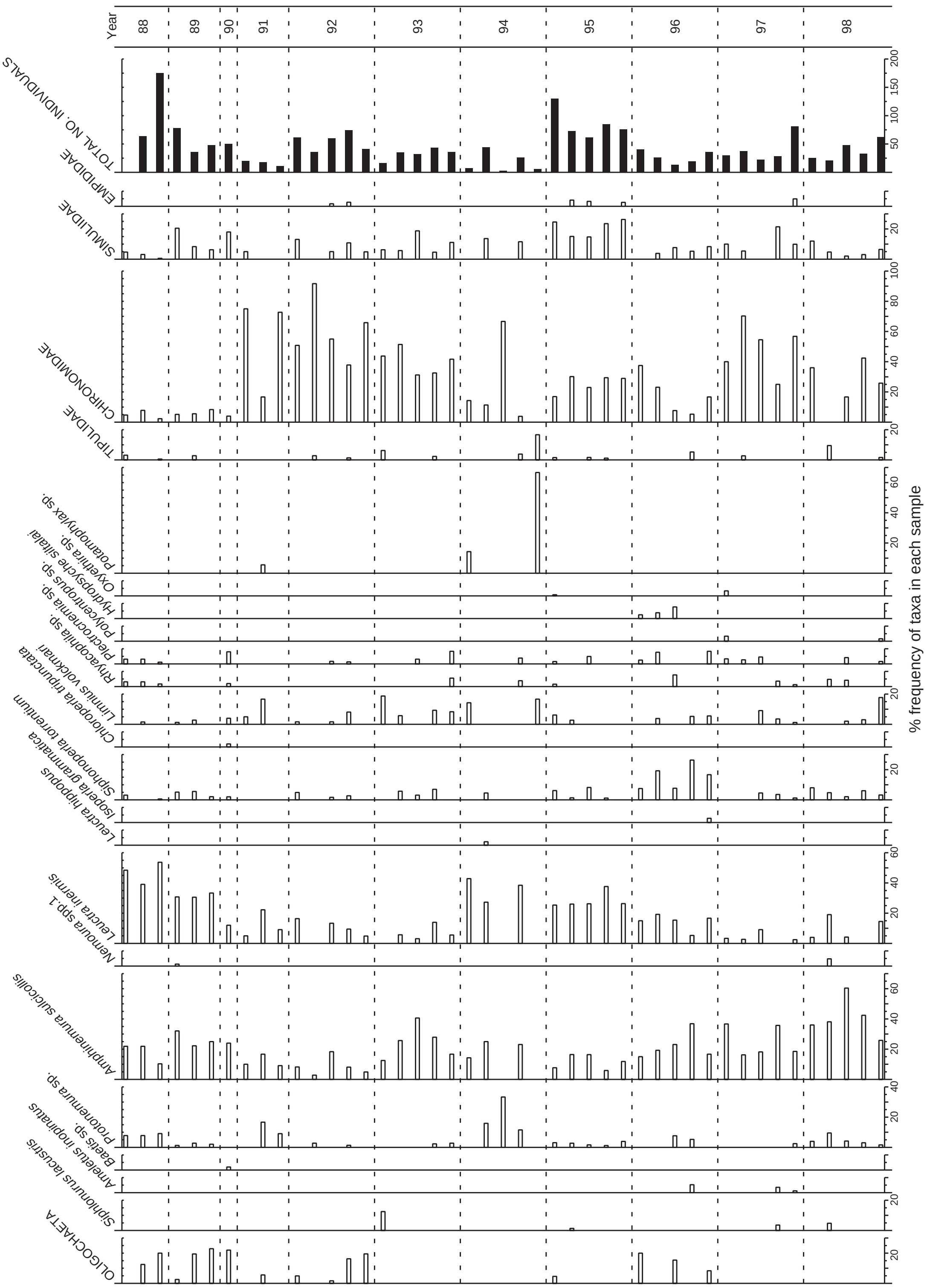


Figure 4.20.4

Bencrom River: summary of macroinvertebrate data (1988 - 1998)

Percentage frequency of taxa in individual samples

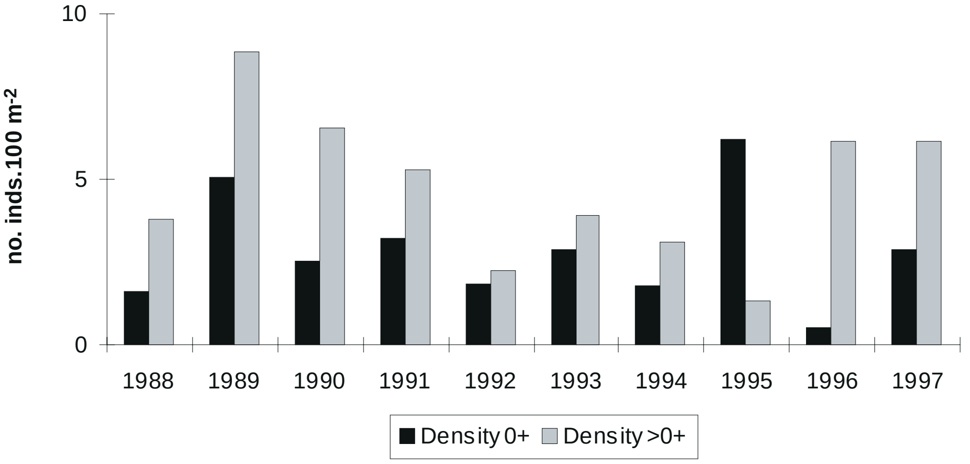
Figure 4.20.5

Bencrom River: summary of fish data (1988 - 1997)

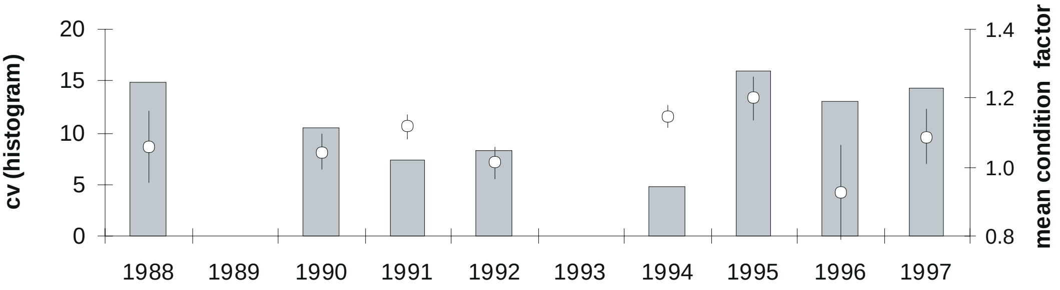
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})

(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

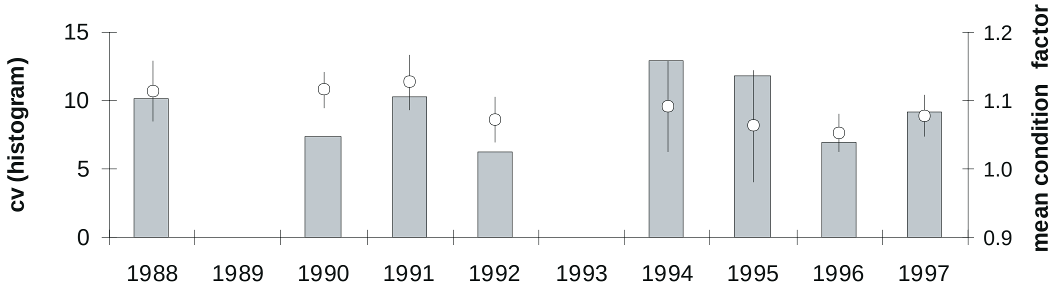
(a) Density



(b) Condition (0+)



Condition (>0+)



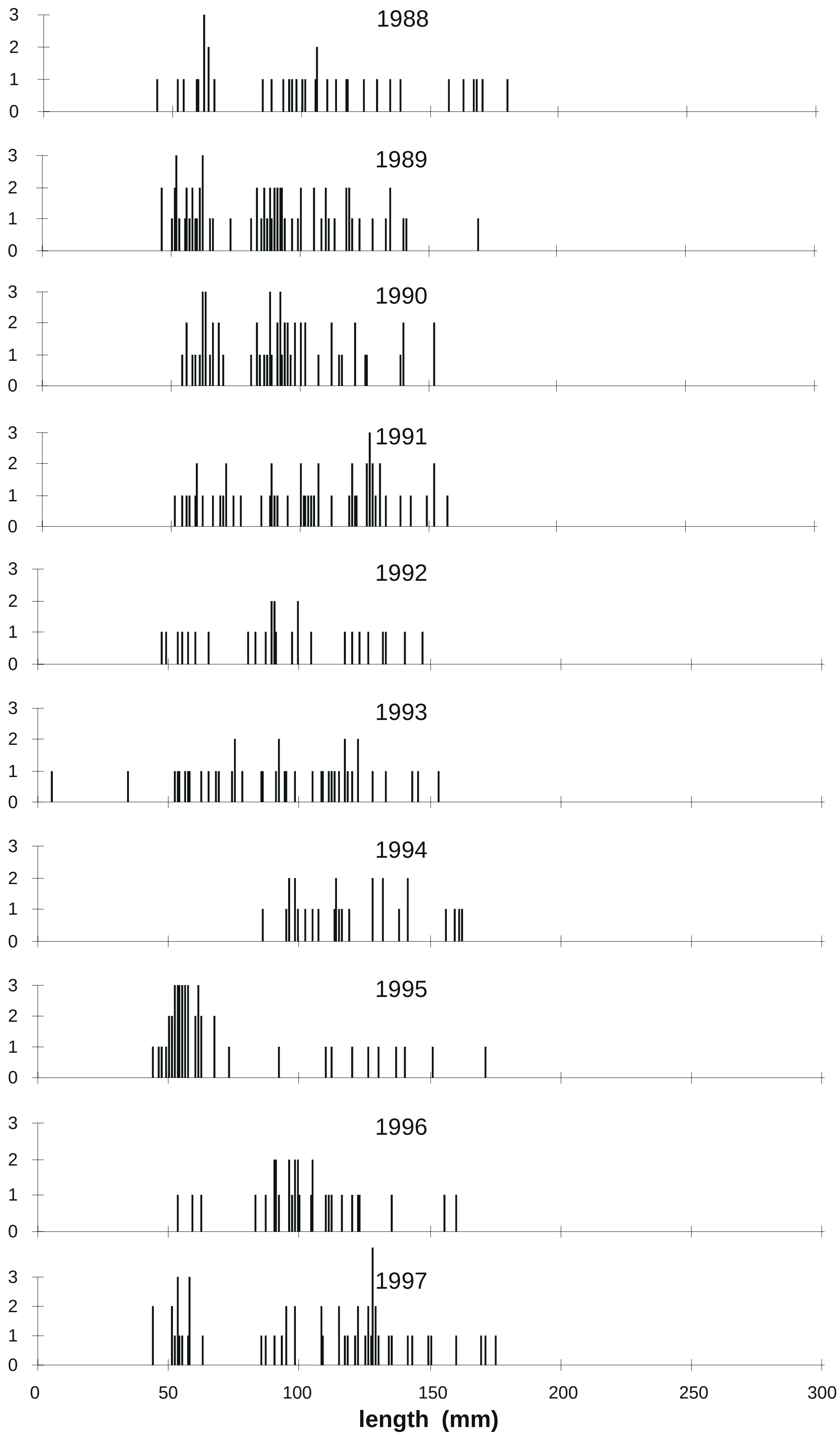


Figure 4.20.5

Bencrom River: summary of fish data (1988 - 1997)
(c) Trout length frequency summaries

4.21 Blue Lough

Site Review

Blue Lough lies in a col between the Silent Valley and the Annalong Valley in the Mourne Mountains, southeastern Northern Ireland. Diatom based pH reconstruction of a sediment core taken in 1992 suggest that the Lough has been acidic since at least the mid-nineteenth century (represented by the base of the core), but has acidified still further (i.e. pH 4.8 to 4.4) over the last one hundred years (Patrick *et al.* 1995). There is no evidence of land use change or any physical disruption within the catchment since the onset of monitoring in 1989.

Water Chemistry

(Figure 4.21.2, Tables 4.21.2-3)

Blue Lough is located just 2.3 km from the Bencrom River, and despite differences in catchment characteristics the two have remarkably

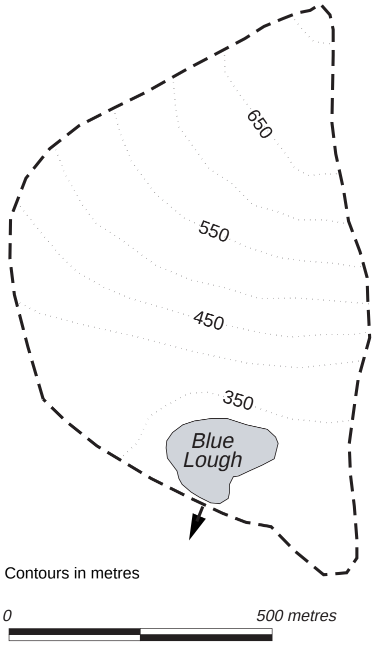


Figure 4.21.1

Blue Lough: catchment

Table 4.21.1

Blue Lough: site characteristics

Grid reference	*J 327252*
Lake altitude	*340 m*
Maximum depth	*5.0 m*
Mean depth	*1.7 m*
Volume	*3.6 x 10^4 m^3*
Lake area	*2.1 ha*
Catchment area (excl. lake)	*47.9 ha*
Catchment: lake area ratio	*19.9*
Catchment Geology	*granite*
Catchment Soils	*blanket peats*
Catchment vegetation	*moorland 100%,*
Net relief	*363 m*
Mean annual rainfall	*1629 mm*
1996 deposition	
Total S	*17 kg ha^{-1} yr^{-1}*
non-marine S	*15 kg ha^{-1} yr^{-1}*
Oxidised N	*7 kg ha^{-1} yr^{-1}*
Reduced N	*14 kg ha^{-1} yr^{-1}*

Table 4.21.2

Blue Lough: summary of chemical determinands, July 1990 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*4.69*	*5.11*	*4.51*
Alkalinity	µeq l^{-1}	*-22.8*	*-4.0*	*-33.0*
Ca	µeq l^{-1}	*40.0*	*98.0*	*16.5*
Mg	µeq l^{-1}	*60.0*	*91.7*	*33.3*
Na	µeq l^{-1}	*257.0*	*369.6*	*121.7*
K	µeq l^{-1}	*12.8*	*25.4*	*7.7*
SO_4	µeq l^{-1}	*94.8*	*118.8*	*35.4*
xSO_4	µeq l^{-1}	*66.3*	*87.3*	*19.4*
NO_3	µeq l^{-1}	*28.6*	*72.9*	*10.0*
Cl	µeq l^{-1}	*275.8*	*400.0*	*152.1*
Soluble Al	µg l^{-1}	*377.2*	*520.0*	*280.0*
Labile Al	µg l^{-1}	*286.9*	*470.0*	*72.0*
Non-labile Al	µg l^{-1}	*90.2*	*394.0*	*18.0*
DOC	mg l^{-1}	*3.5*	*6.8*	*1.4*
Conductivity	µS cm^{-1}	*55.9*	*73.0*	*36.0*

similar chemistry. Mean xSO_4 and NO_3 values at Blue Lough (66 meq l^{-1} and 29 meq l^{-1} respectively) are virtually identical to those at Bencrom, and marine ion concentrations are also very similar. Blue Lough is more acidic, however, with a mean alkalinity of –23 µeq l^{-1}, a mean pH of 4.69, and the highest mean labile Al concentrations in the Network. It appears that these more severe conditions can be attributed to differences in Ca concentrations, which are on average 13 µeq l^{-1} lower at Blue Lough. This may reflect the Lough's higher elevation (340 m compared to 140 m at the Bencrom River sampling point), with thinner, high-altitude soils and perhaps less weatherable geology generating a smaller internal supply of base cations.

Monitoring of Blue Lough only began in 1990, and the data are therefore of limited value for trend determination. Regression analyses suggest that pH and alkalinity have risen over the eight years of monitoring, although time series (Figures 4.21.2a,b) show that much of this increase may result from two unusually high values in 1997. Neither trend is identified using SKT. No accompanying trends are observed in SO_4 or xSO_4, but visual inspection of the LOESS curve for xSO_4 (Figure 4.21.2d) suggests that concentrations have been falling fairly steadily since 1992. This is consistent with data from the nearby Hillsborough Forest deposition monitoring site (Campbell *et al.* 1998), which shows a steady decline in wet deposited xSO_4 since the beginning of the decade. A number of determinands show evidence of cyclical concentration changes over the study period, including NO_3, Cl, Na, Ca, labile and total Al. These variations appear to coincide with those at the Bencrom River, with peaks in 1995-1996 and perhaps also 1990-1991. Similar climatic controls are therefore likely. The only determinand exhibiting a clear and apparently linear rising trend, as at the other Northern Ireland sites, is DOC.

■ Epilithic diatoms

(Figure 4.21.3, Table 4.21.4)

The dominance of *Tabellaria quadriseptata* (pH optima 4.9) in the epilithon of Blue Lough emphasises the extremely acidic nature of the site. However, there is evidence of an increase in the representation of species with higher pH optima, including *Frustulia rhomboides* var. *saxonica* (pH optima 5.2) and *Brachysira brebissonii* (pH optima 5.3) since 1993, while *Navicula hoefleri* (pH optima 4.9) has decreased, and "sample year" is significant as a linear trend according to RDA and associated restricted permutation test. These changes point to a recent increase in pH and alkalinity and are consistent with evidence from LOESS plots for pH and alkalinity. As these changes are accompanied by a long term reduction in xSO_4, it is possible that they represent early stages of biological recovery in response to reducing acid deposition. However, given the strong cyclicity in marine ions, further years of monitoring are required to verify whether this trend of improvement is sustainable. The diatom assemblage of sediment trap samples collected since 1992 do not show

Table 4.21.3

Significant trends in chemical determinands (July 1990 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
pH	-	*+0.018**	-
Alkalinity	µeq l^{-1}	*+1.18***	-
DOC	mg l^{-1}	*+0.18**	*+0.19**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

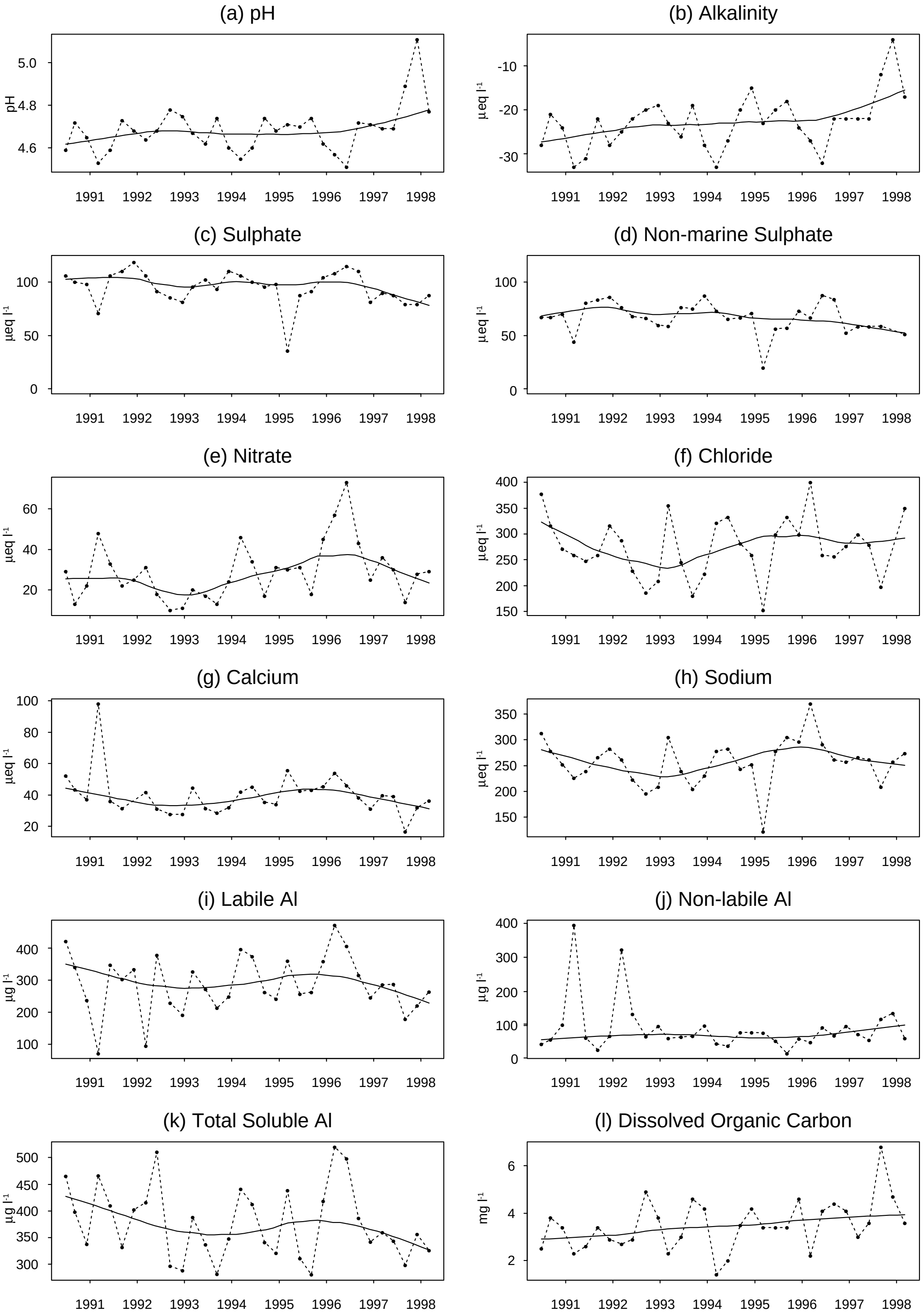


Figure 4.21.2

Blue Lough: summary of major chemical determinands (July 1990 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.21.4

Blue Lough: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1990 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*192*	*87*	*3.7*	*0.53*	*0.50*
Macrophytes	*6*	*11*	*6.4*	*0.41*	*0.34*
Invertebrates	*813*	*17*	*2.4*	*0.68*	*0.52*

Variance				p	
explained (%)	within year	between years	linear trend	unrestricted	restricted
Epilithic diatoms	*52.5*	*47.5*	*10.8*	*<0.01*	*<0.01*
Macrophytes	*	*	*14.7*	*0.55*	*0.51*
Invertebrates	*47.2*	*52.8*	*14.4*	*<0.01*	*<0.01*

such clear trends with time (Figure 4.21.6).

Macroinvertebrates

(Figure 4.21.4, Table 4.21.4)

The impoverished fauna of Blue Lough is typical of an acid lake. Only the most acid tolerant mayfly family, the Leptophlebiidae are represented. Acid tolerant caddisflies *Plectrocnemia* spp. and *Polycentropus* spp. occurred in most years and the latter has increased in abundance over the last three years. The remaining benthos is composed of several species of Corixidae and water beetles, mainly *Arctocorisa germari*, *Callicorixa wollostoni* and *Potamonectes griseostriatus*. The Corixid *Glaenocorisa propinqua* was very abundant in 1997. Only one individual stonefly, *Leuctra hippopus* was recorded in 1994. There is a high turnover of species at this site, mainly driven by the highly mobile Corixidae and water beetles, which are aquatic both as adults and nymphs. “Sample year”, as a linear variable, accounts for 14% of the variance in the macroinvertebrate data according to RDA and is significant at the 0.01 level using the restricted permutation test. Despite recent small improvements in pH and alkalinity, the change in species composition cannot be attributed to changes in water chemistry.

Fish

(Figure 4.21.5)

Only three fish have been caught in the outflow of Blue Lough in the period monitored (1990-1997). It is not possible to ascertain the population status or any pattern in the data from these results. However, fears that the population had become extinct have been countered by the presence of one fish in the site in 1997. HABSCORE HQS values indicate that the site could potentially carry a reasonable density of fish.

Aquatic macrophytes

(Tables 4.21.4-5)

Blue Lough is characterised by a small number of acid tolerant species. *Isoetes lacustris* dominates the deeper water habitats, where the acidophilous moss *Sphagnum auriculatum* is also common. *Lobelia dortmanna* and *Juncus bulbosus* var. *fluitans* are the most abundant vascular species in shallow water, occuring in association with a

Table 4.21.5

Blue Lough: relative abundance of aquatic macrophyte flora (1989 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**89**	**90**	**91**	**92**	**93**	**95**	**97**
INDICATOR SPECIES							
Sphagnum auriculatum[4]	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Juncus bulbosus var. *fluitans*[4]	*2*	*2*	*2*	*2*	*2*	*2*	*2*
OTHER SUBMERGED SPECIES							
Batrachospermum sp.	*1*	*1*	*1*	*1*	*1*	*0*	*1*
Filamentous green algae	*3*	*3*	*2*	*3*	*3*	*2*	*2*
Cephalozia bicuspidata	*0*	*1*	*1*	*1*	*1*	*1*	*1*
Cladopodiella fluitans	*1*	*0*	*0*	*0*	*0*	*0*	*0*
Diplophyllum albicans	*0*	*1*	*0*	*0*	*0*	*0*	*0*
Jungermannia/Nardia sp.	*2*	*2*	*2*	*2*	*2*	*2*	*2*
Isoetes lacustris	*4*	*4*	*4*	*4*	*4*	*4*	*4*
Littorella uniflora	*0*	*0*	*0*	*1*	*1*	*0*	*0*
Lobelia dortmanna	*3*	*3*	*3*	*3*	*3*	*3*	*3*
Sparganium angustifolium	*0*	*1*	*1*	*1*	*0*	*1*	*1*
TOTAL NUMBER OF SPECIES	*8*	*10*	*9*	*10*	*9*	*8*	*9*

number of liverwort species. There is no evidence of any change in species presence/absence or abundance over the last decade and time is insignificant as a linear variable according to RDA and associated permutation test.

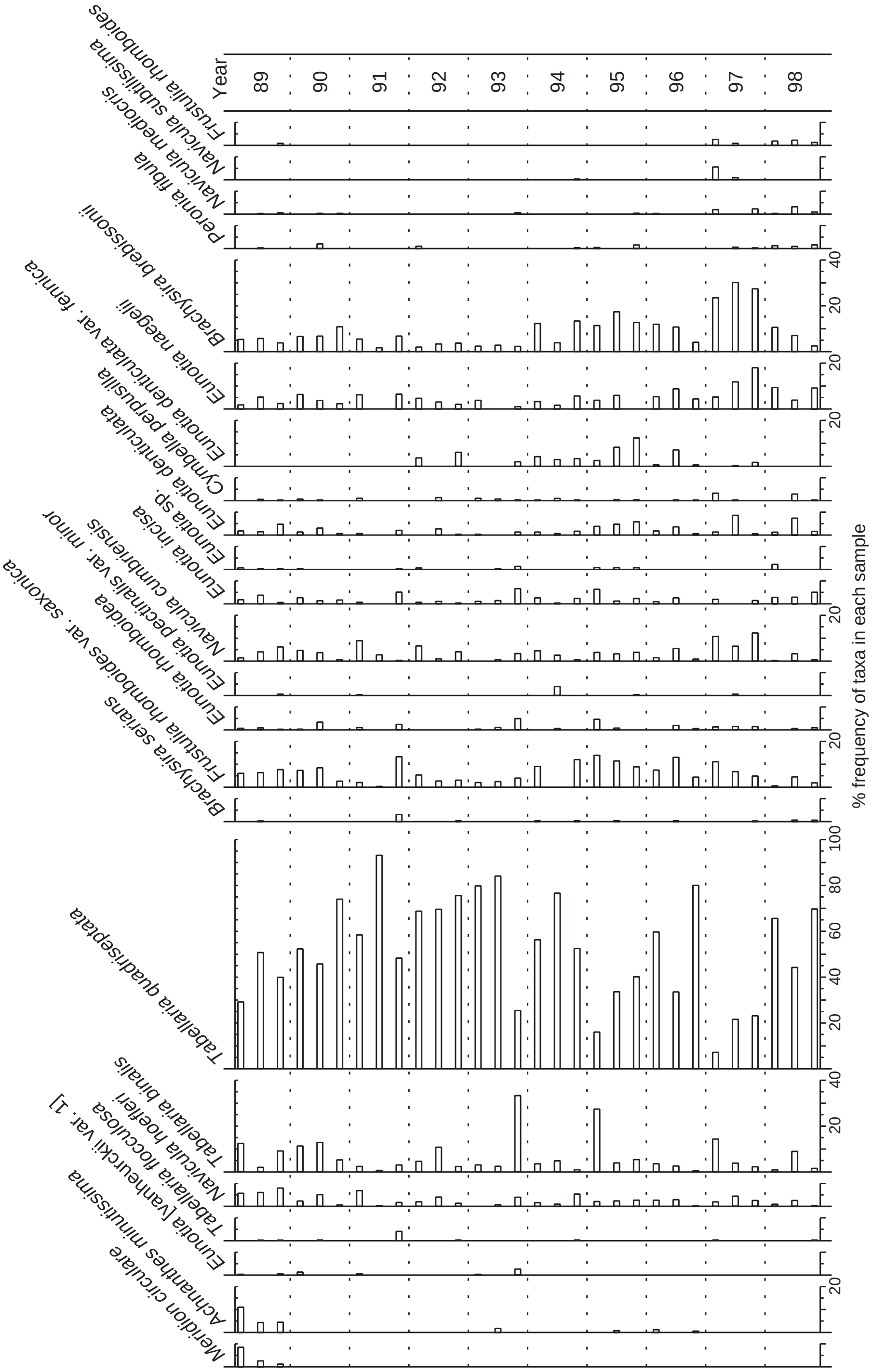
Summary

Blue Lough is highly acidic, with pollutant anion concentrations very similar to the nearby Bencrom River. NO_3 concentrations are high, and contribute significantly to the acidity of the Lough. Low pH and alkalinity relative to the Bencrom River can be attributed to a lower supply of base cations, in particular Ca, from internal sources. The only clear trend observed over eight years of monitoring is a rise in DOC, but there are some indications of falling xSO_4 and increasing pH and alkalinity in recent years, which could explain changes in the epilithic diatom community. The extent to which trends in the epilithic diatom and macroinvertebrate communities may represent sustainable recovery from acidification, as opposed to part of a climatic cycle, requires further monitoring for validation.

Figure 4.21.3

Blue Lough: summary of epilithic diatom data (1989 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



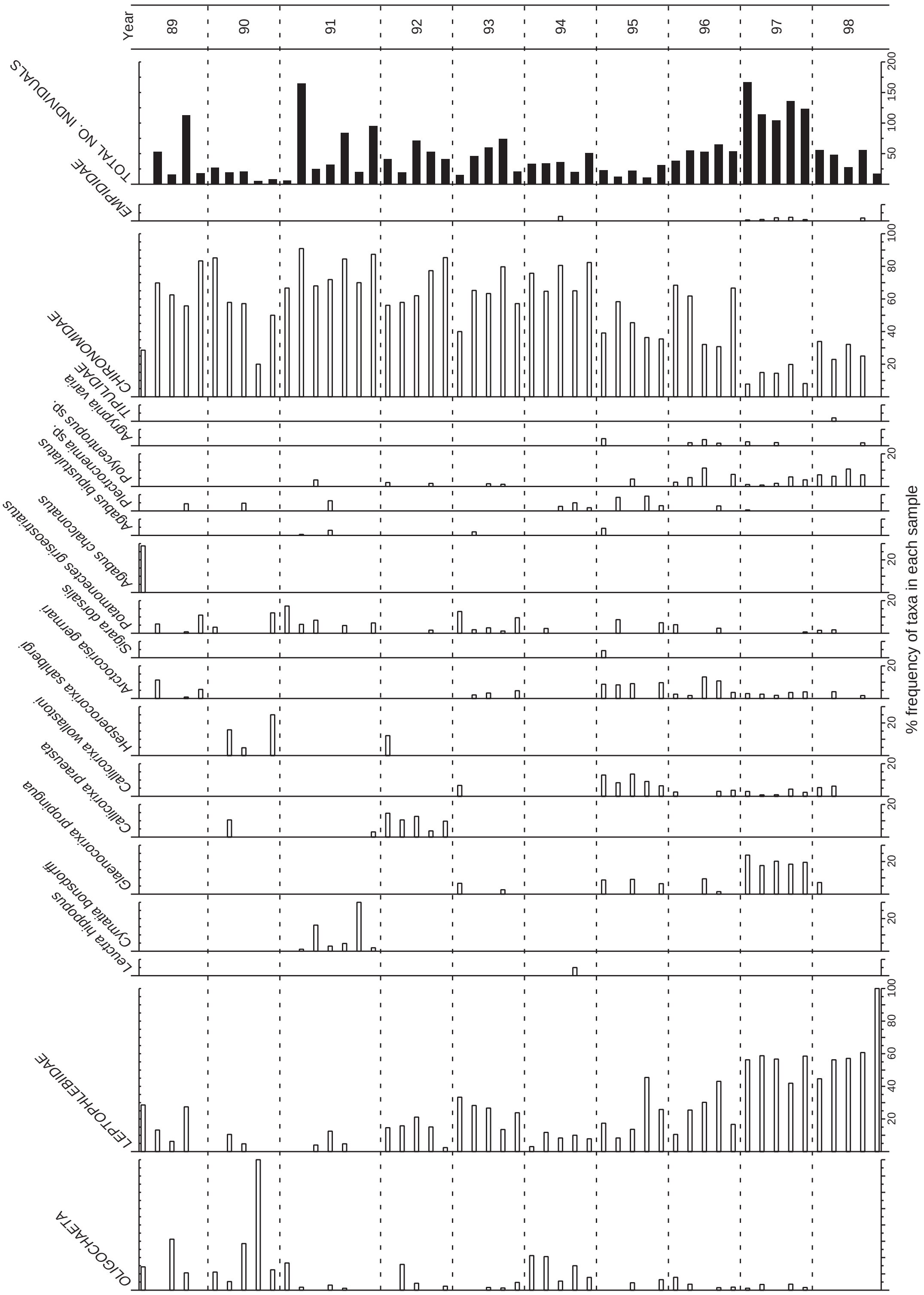


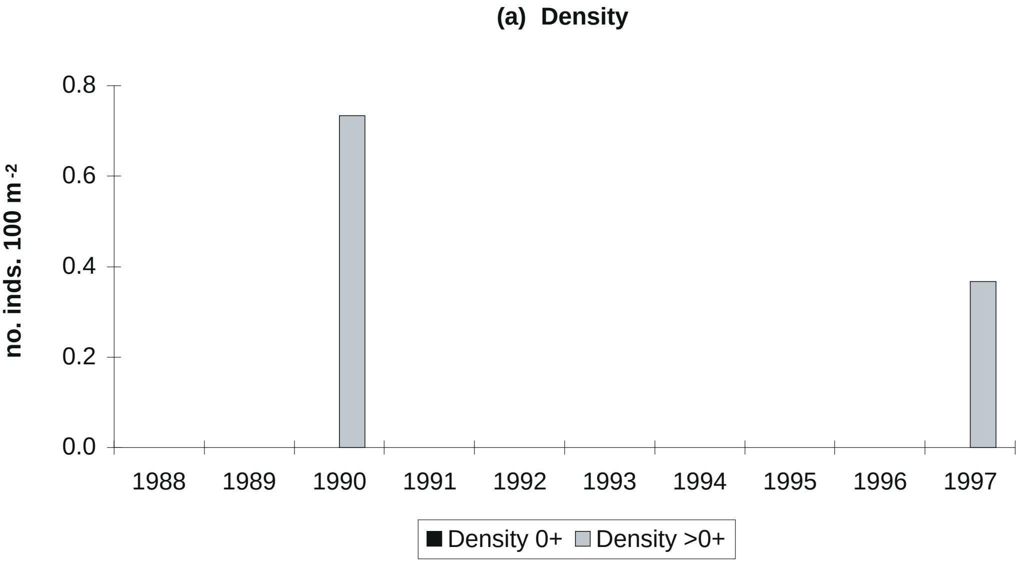
Figure 4.21.4

Blue Lough: summary of macroinvertebrate data (1989 - 1998)

Percentage frequency of taxa in individual samples

Figure 4.21.5

Blue Lough: summary of fish data (1990 - 1997)
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})
(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)



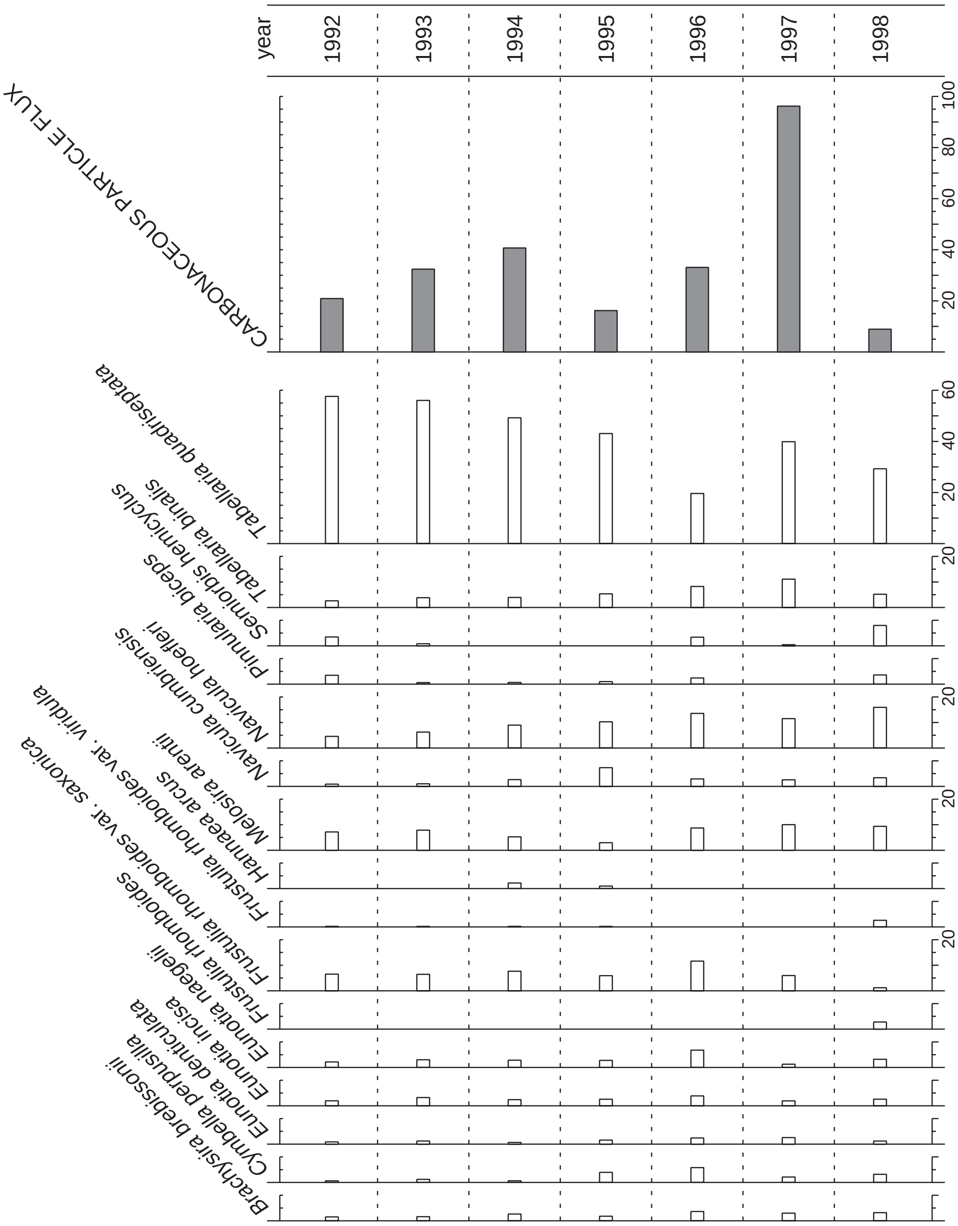


Figure 4.21.6

Blue Lough: summary of sediment trap data for diatoms and carbonaceous particles

Relative frequency of diatom taxa (>2% in at least one sample) at time of trap retrieval and estimated carbonaceous particle flux (no. trap^{-1} day^{-1}) for preceding year

4.22 Coneyglen Burn

Site Review

Coneyglen Burn, in the Sperrin Hills of Northern Ireland, drains a large area of moorland, although it is flanked by a relatively small area of coniferous forestry immediately upstream of the sampling stretches. The forest is approaching maturity but no felling has been carried out, and there is no other evidence of catchment disturbance since the onset of monitoring in 1989.

Water Chemistry

(Figure 4.22.2, Tables 4.22.2-3)

Coneyglen Burn has the highest mean pH and alkalinity of any UKAWMN site (6.51 and 161 μeq l^{-1} respectively). This is the result both of low levels of xSO_4 and NO_3 (means 30 μeq l^{-1} and 3 μeq l^{-1} respectively), consistent with the location of the catchment upwind of emission sources, and of

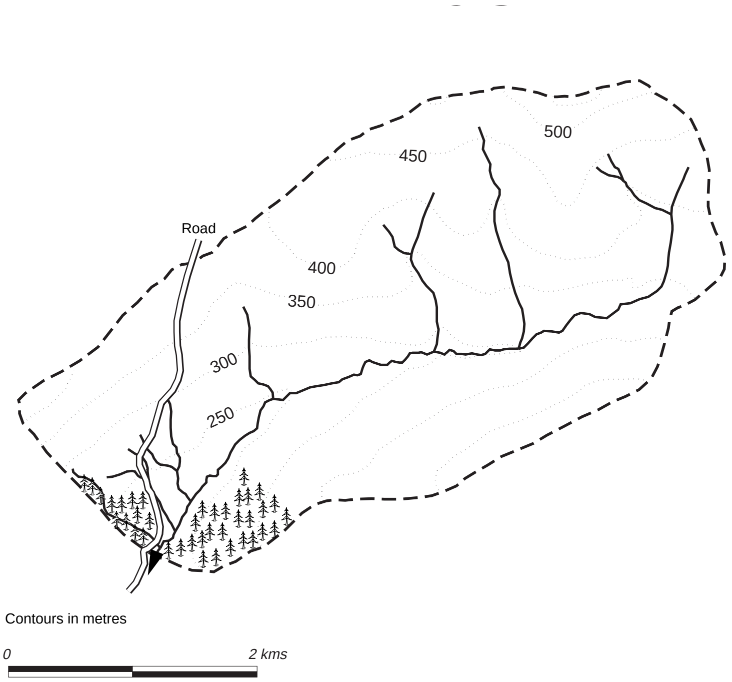


Figure 4.22.1

Coneyglen Burn: catchment

Table 4.22.1

Coneyglen Burn: site characteristics

Grid reference	*H 641884*
Catchment area	*1311 ha*
Minimum Catchment altitude	*230 m*
Maximum Catchment altitude	*562 m*
Catchment Geology	*schists*
Catchment Soils	*blanket peat*
Catchment vegetation	*moorland 95%,* *conifers 5%*
Mean annual rainfall	*1536 mm*
1996 deposition	
Total S	*15 kg ha^{-1} yr^{-1}*
non-marine S	*11 kg ha^{-1} yr^{-1}*
Oxidised N	*5 kg ha^{-1} yr^{-1}*
Reduced N	*13 kg ha^{-1} yr^{-1}*

Table 4.22.2

Coneyglen Burn: summary of chemical determinands, August 1990 - March 1998

Determinand		**Mean**	**Max**	**Min**
pH		*6.51*	*7.44*	*4.60*
Alkalinity	μeq l^{-1}	*160.6*	*461.0*	*-26.0*
Ca	μeq l^{-1}	*149.0*	*308.5*	*27.0*
Mg	μeq l^{-1}	*120.8*	*208.3*	*41.7*
Na	μeq l^{-1}	*239.1*	*373.9*	*139.1*
K	μeq l^{-1}	*10.3*	*23.1*	*5.1*
SO_4	μeq l^{-1}	*57.1*	*237.5*	*20.8*
xSO_4	μeq l^{-1}	*30.4*	*206.3*	*-0.8*
NO_3	μeq l^{-1}	*2.9*	*52.1*	*<1.4*
Cl	μeq l^{-1}	*255.5*	*495.8*	*104.2*
Soluble Al	μg l^{-1}	*40.5*	*264.0*	*6.0*
Labile Al	μg l^{-1}	*8.0*	*211.0*	*<2.5*
Non-labile Al	μg l^{-1}	*33.3*	*82.0*	*<2.5*
DOC	mg l^{-1}	*8.3*	*26.9*	*1.7*
Conductivity	μS cm^{-1}	*55.2*	*83.0*	*31.0*

buffering by relatively large internal base cation sources (mean Ca = 149 µeq l^{-1}, mean Mg = 121 µeq l^{-1}).

Stream chemistry at Coneyglen Burn is however subject to major episodic fluctuations, and alkalinity fell below zero on six occasions during the monitoring period. Most episodes appear to have been caused by base cation dilution, but in addition, an extremely large xSO_4 pulse was recorded in October 1995, followed by a similarly large NO_3 pulse in Febuary 1996 (Figure 4.22.2d,e). In the first pulse, xSO_4 rose from 25 to 206 µeq l^{-1}, after which concentrations took around a year to return to normal levels. The initial increase did not generate a major acidic episode, however, because base cation levels remained high. In contrast the increase in NO_3, from below detection limits to 52 µeq l^{-1}, concided with a large dilution of Ca. Alkalinity fell to –26 µeq l^{-1} and pH to 4.62, and the labile Al peak of 211 µg l^{-1} compares to a maximum of 28 µg l^{-1} for the remainder of the study period.

It is thought that the xSO_4 pulse at Coneyglen Burn was the result of a severe drought during the summer of 1995 (Marsh, 1996), at which time river flows in the area fell to their lowest levels in ten years (National River Flow Archive, Institute of Hydrology). De-saturation of peats at this time is likely to have allowed re-oxidation of stored reduced S, with the resulting SO_4 flushed to the stream as the soil re-wetted during autumn (Bayley *et al.*, 1986). Similar, albeit less pronounced xSO_4 peaks can also be detected in time series for Beagh's Burn and the Bencrom River, suggesting that this climatic effect covered a wide area. The NO_3 pulse is believed to result from a combination of drought and, subsequently, an unsually cold winter, both of which are likely to have reduced uptake, and increased the supply of dead biomass for mineralisation and nitrification (Reynolds *et al.* 1992; Monteith *et al.*, in press). Very high NO_3 peaks were observed throughout the UKAWMN in Spring 1996, and possible mechanisms are discussed in Section 5.4.

Regression trend analysis suggests an increase in NO_3 over the monitoring period (Table 4.22.3). This is partly a function of the 1996 peak, but NO_3 concentrations also rose above detection limits during the following two winters (Figure 4.22.2e). This could indicate a transition from Stage 0 to Stage 1 N saturation according to the classification of Stoddard (1994), but it is also possible that winter maxima are slowly returning to pre-1996 levels. A similar recovery over several years was observed at the C2 catchment at Plynlimon following a drought in 1984 (Reynolds *et al.* 1992). This issue should be resolved by further sampling. No trends are observed in other major ions, but an extremely large linear increase in DOC (approximately 8 mg l^{-1} over 10 years) and an accompanying rise in non-labile Al are identified by both SKT and regression (Table 4.22.3, Figures 4.22.2j,l).

■ Epilithic diatoms

(Figure 4.22.3, Table 4.22.4)

The epilithic diatom assemblage of samples from Coneyglen Burn has varied markedly between years. *Synedra minuscula* (pH optima 6.0) is the

Table 4.22.3

Significant trends in chemical determinands (August 1990 - March 1998)

Determinand	Units	Annual trend (Regression)	Annual trend (Seasonal Kendall)
NO_3	µeq l^{-1}	*+0.64***	-
DOC	mg l^{-1}	*+0.80****	*+0.78*
Non-labile Al	µg l^{-1}	*+1.86***	*+2.42**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$*

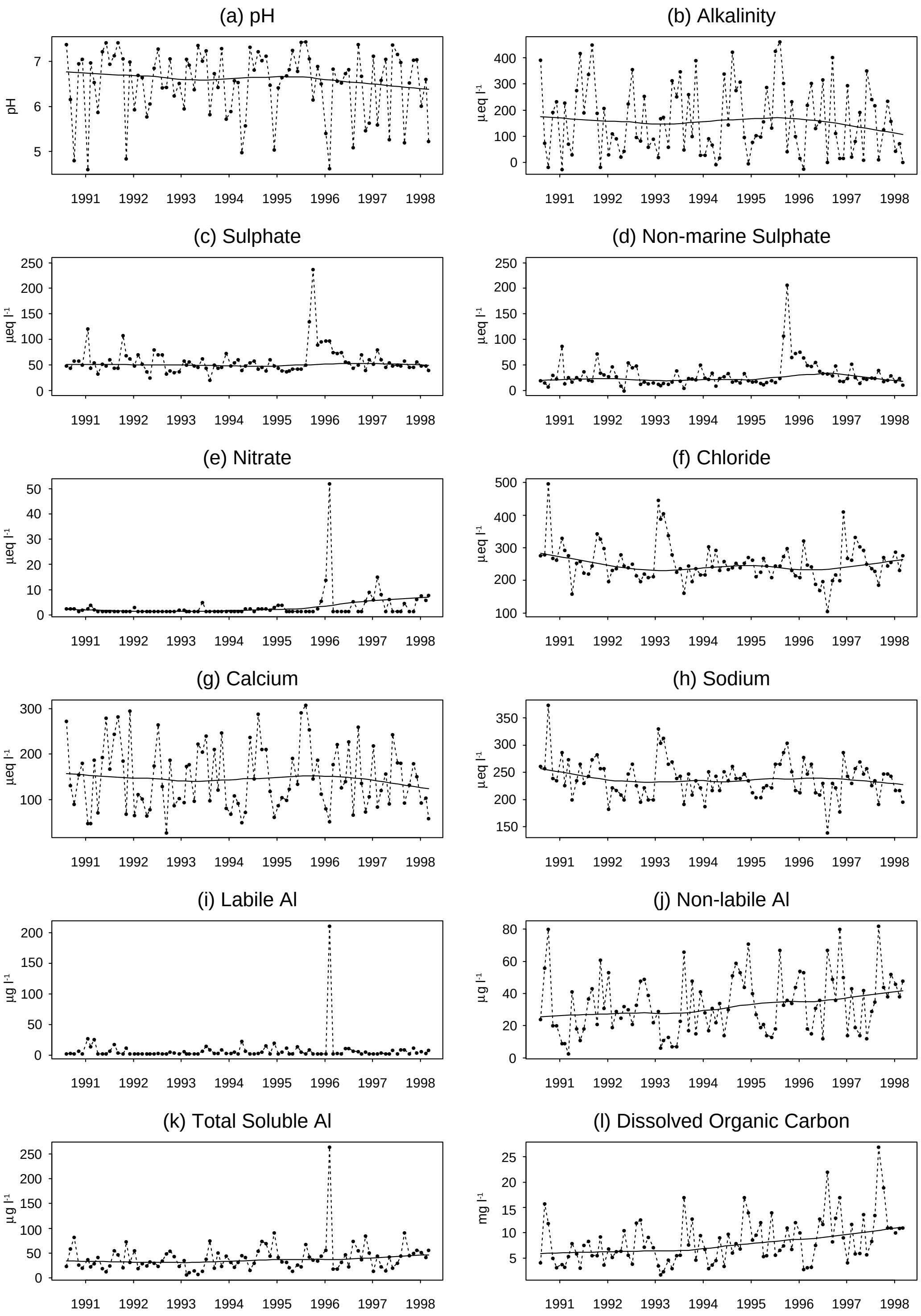


Figure 4.22.2

Coneyglen Burn: summary of major chemical determinands (August 1980 - March 1998)

Smoothed line represents LOESS curve (Section 3.1.2)

Table 4.22.4

Coneyglen Burn: trend statistics for epilithic diatom, macrophyte and macroinvertebrate summary data (1989 - 1998)

	Total sum of squares	Number of Taxa	Mean N_2 diversity	λ_1RDA/λ_2RDA	λ_1RDA/λ_1PCA
Epilithic diatoms	*448*	*110*	*5.1*	*0.60*	*0.49*
Macrophytes	*4*	*5*	*2.1*	*0.12*	*0.11*
Invertebrates	*357*	*32*	*2.6*	*0.68*	*0.49*

Variance explained (%)	within year	between years	linear trend	p unrestricted	 restricted
Epilithic diatoms	*29.5*	*70.5*	*13.4*	*<0.01*	*<0.01*
Macrophytes	*	*	*7.8*	*0.68*	*0.48*
Invertebrates	*44.9*	*55.1*	*13.9*	*<0.01*	*<0.01*

most abundant species in most samples. However, it was relatively scarce in 1992 and 1993, when several *Eunotia* taxa, and particularly *E.exigua* (pH optima 5.1), indicative of more acid conditions, were more abundant. Water chemistry data for Coneyglen Burn suggest that the summer months of 1992 and 1993 were unusually episodic. Rainfall data for the nearby Meteorological Station (Lough Fea) is incomplete for the summer of 1993 but demonstrates that July and August in 1992 were unusually wet. It is therefore possible that the hydrological regime has had a significant effect on the diatom flora of this site through the effect of variations in surface run-off relative to base-flow on pH. Over the nine year period (1989-1997) there has been a general decline in the relative abundance of *Achnanthes minutissima* (pH optima 6.3) and an increase in *Tabellaria flocculosa* (pH optima 5.4), which suggests the stream is becoming gradually more acidic. This is supported by LOESS plots which suggest a recent decline in pH. RDA and associated restricted permutation test show the time trend to be significant at the 0.01 level

■ Macroinvertebrates

(Figure 4.22.4, Table 4.22.4)

The fauna is dominated by the predatory stonefly *Siphonoperla torrentium* which was present in high densities throughout the study. Much of the benthos is characterised by detritivorous stoneflies (*Leuctra inermis*, *Brachyptera risi* and *Amphinemura sulcicollis*) and a relatively diverse community of water beetles. Three years, 1992, 1993 and 1997 had very large populations of Simuliidae larvae. 1994 was a poor year both in terms of number of species and abundance due to adverse sampling conditions. The caddisfly, *Hydropsyche siltalai*, which had been present in the first few years was absent during 1994 and 1995, and then reappeared in 1996. The acid sensitive mayfly *Baetis* spp. was first abundant in 1992 and 1993 then declined and has since reappeared in 1997. The mayfly *Heptagenia lateralis* also disappeared during the middle of the monitoring period then reappeared in 1998. The recent change in species composition is supported by a significant linear time trend at the 0.01 level according to RDA and associated permutation test and may indicate a general improvement in conditions.

■ Fish

(Figure 4.22.5)

Coneyglen Burn has been electrofished since 1990. Trout densities are in the middle range of those found in the Network sites. The population density of 0+ fish shows a general increase which is accompanied by a general decrease in

Table 4.22.5

Coneyglen Burn: relative abundance of aquatic macrophyte flora (1989 - 1997)
(see Section 3.2.3 for key to indicator values)

Abundance Taxon Year	**89**	**90**	**91**	**92**	**93**	**95**	**96**	**97**
INDICATOR SPECIES								
Hygrohypnum ochracheum[1]	*22.2*	*21.1*	*4.3*	*14.9*	*18.1*	*15.4*	*8.8*	*18.6*
Fontinalis squamosa[2]	*13.1*	*6.8*	*7.1*	*10.1*	*7.6*	*7.3*	*13.8*	*7.8*
OTHER SUBMERGED SPECIES								
Filamentous green algae	*13.5*	*<0.1*	*17.6*	*<0.1*	*<0.1*	*11.9*	*6.3*	*3.7*
Racomitrium aciculare	*<0.1*	*<0.1*	*<0.1*	*0.2*	*<0.1*	*<0.1*	*0.8*	*0.2*
Scapania undulata	*1.8*	*3.7*	*0.5*	*4.3*	*4.0*	*0.5*	*0.9*	*1.4*
Juncus bulbosus var. *fluitans*	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
EMERGENT SPECIES								
Juncus acutifloris	*0.0*	*<0.1*	*0.0*	*<0.1*	*<0.1*	*0.0*	*0.0*	*<0.1*
Juncus effusus	*0.0*	*<0.1*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
total macrophyte cover excluding filamentous algae	*37.1*	*31.6*	*11.9*	*29.5*	*29.7*	*23.2*	*24.3*	*28.0*
TOTAL NUMBER OF SPECIES	5	8	5	6	6	5	5	6

condition factor, although neither are statistically significant as linear trends over the eight years. The density of >0+ trout shows no notable trends over the sampling period but their mean condition factor shows a linear decline which in this case is statistically significant ($p = 0.05$ df = 6). The length frequency histograms show very poor recruitment in 1991 and 1992 but this did improve considerably in 1993 and there is evidence of this high recruitment following on in subsequent years. Unsurprisingly 1993 was a very poor year for >0+ trout.

■ Aquatic macrophytes

(Tables 4.22.4-5)

The composition and relatively high cover of the submerged aquatic macrophyte flora of Coneyglen Burn is indicative of the well buffered water chemistry of the site. The acid sensitive moss species, *Hygrohypnum ochraceum* and *Fontinalis squamosa* dominated the survey stretch, although the acid tolerant liverwort *Scapania undulata* was also abundant in patches. Considerable cover of filamentous green algae was also recorded in some years. Overall cover and relative species representation have remained very stable over the last eight years and time is insignificant as a linear variable using RDA and restricted permutation test.

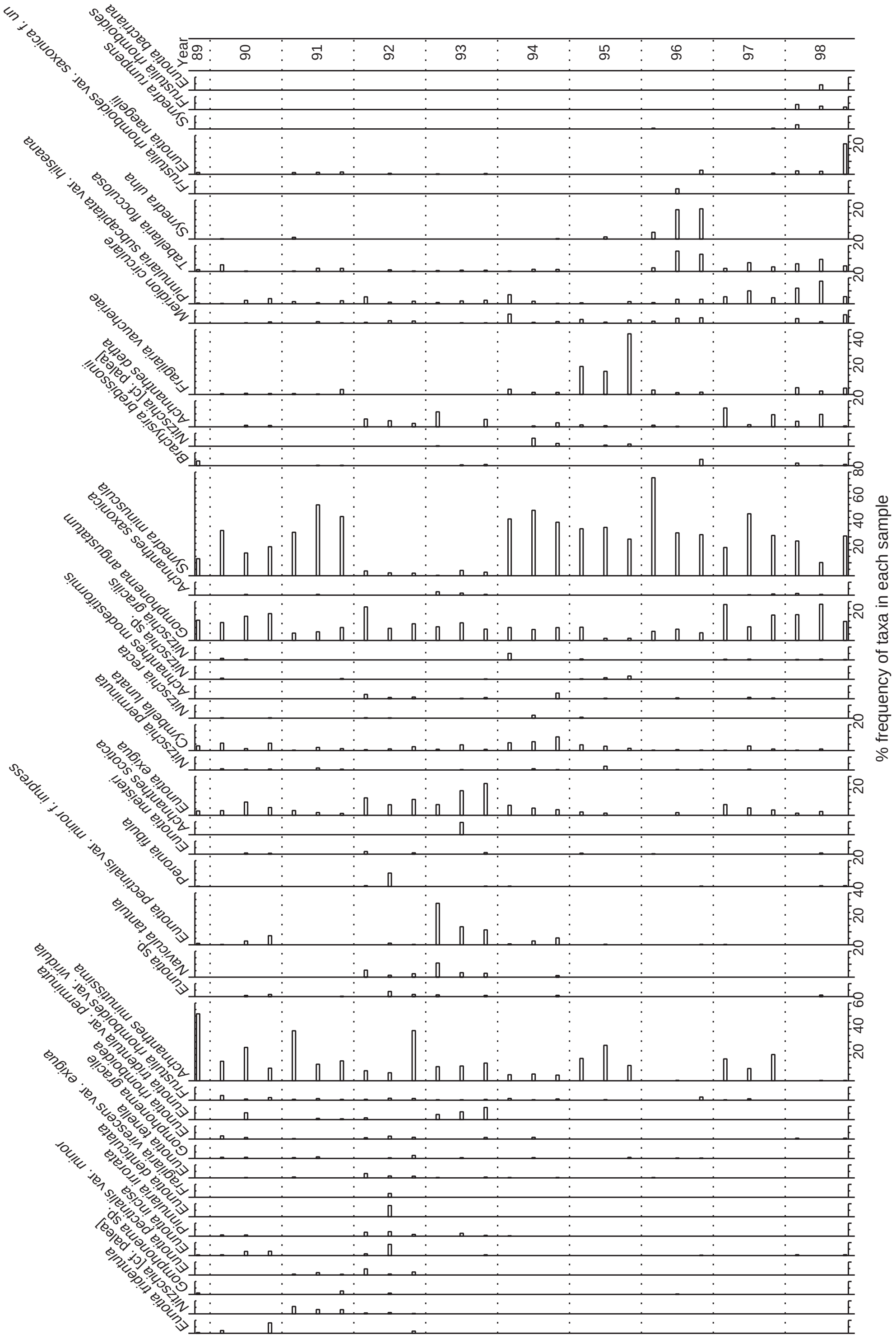
■ Summary

Coneyglen Burn is not chronically acidified, with relatively low pollutant anion and high base cation concentrations, but can become acidic during high flows. Time series are dominated by very large pulses of xSO_4 and NO_3 in 1995-1996 following a major drought and subsequent cold winter, the effects of which lasted for at least a year. The NO_3 peak in particular generated a severe acidic episode. The only overall changes in stream chemistry during the monitoring period have been increases in DOC and labile Al. The interpretation of the significant trends in epilithic diatoms and macroinvertebrate communities appear to conflict, with the former suggesting deterioration and the latter if anything, suggesting an ammelioration of acid conditions.

Figure 4.22.3

Coneyglen Burn: summary of epilithic diatom data (1989 - 1998)

Percentage frequency of all taxa occurring at >2% abundance in any one sample



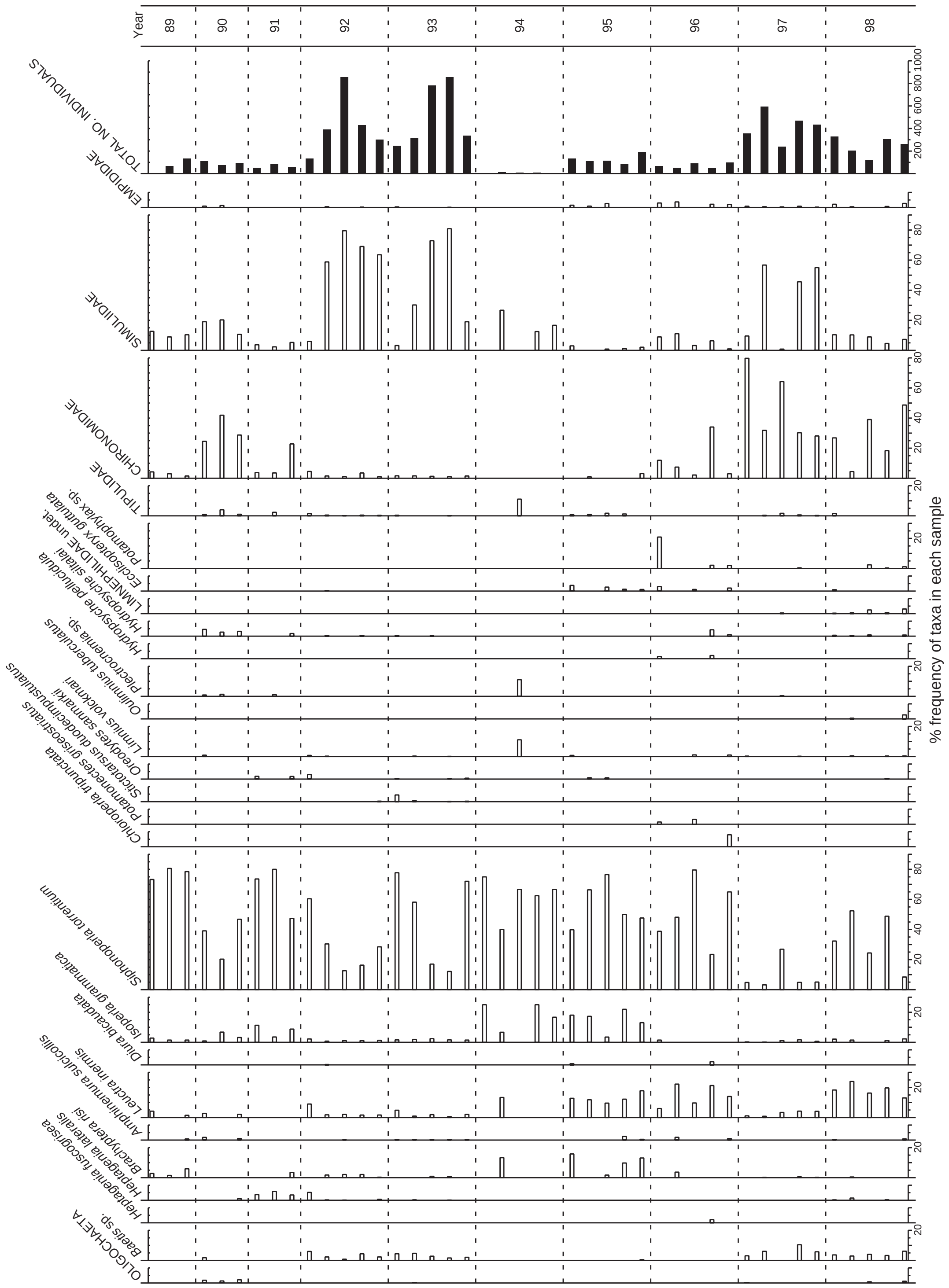


Figure 4.22.4

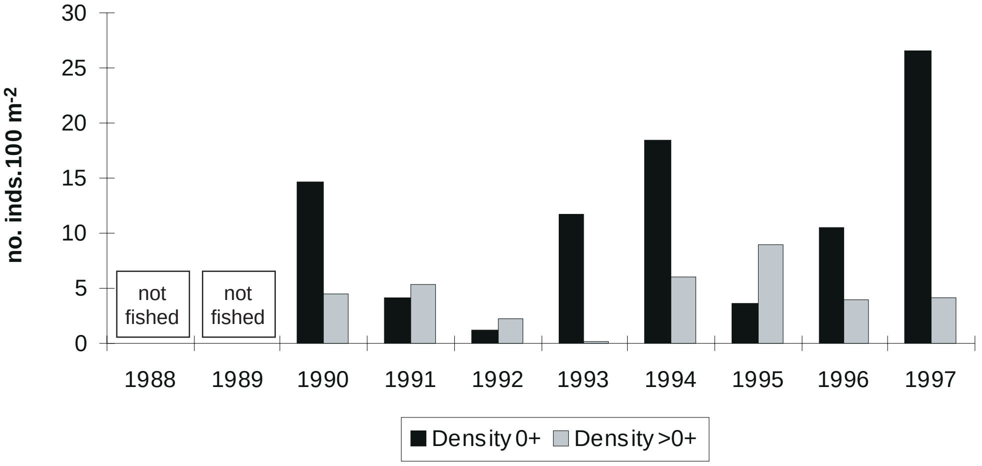
Coneyglen Burn: summary of macroinvertebrate data (1989 - 1998)

Percentage frequency of taxa in individual samples

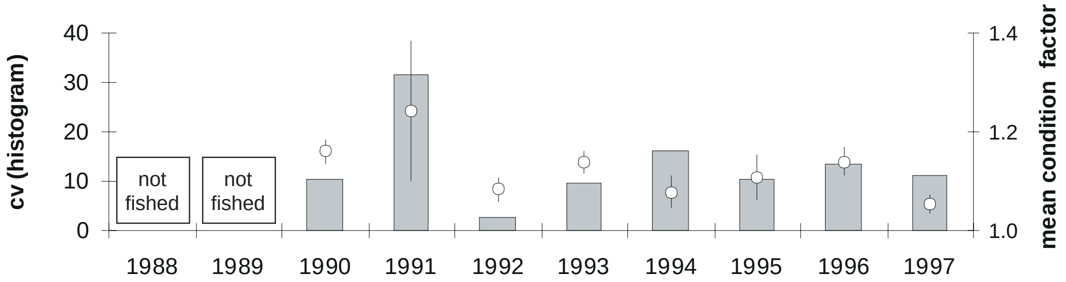
Figure 4.22.5

Coneyglen Burn: summary of fish data (1990 - 1997)
(a) Trout population density for 0+ and >0+ age classes (individuals 100 m^{-2})
(b) Mean condition factor (with standard deviation) of the trout population and its coefficient of variation (histogram)

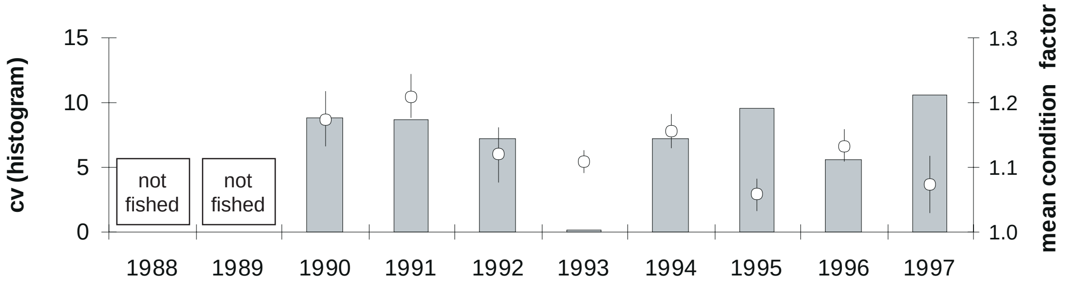
(a) Density



(b) Condition (0+)



Condition (>0+)



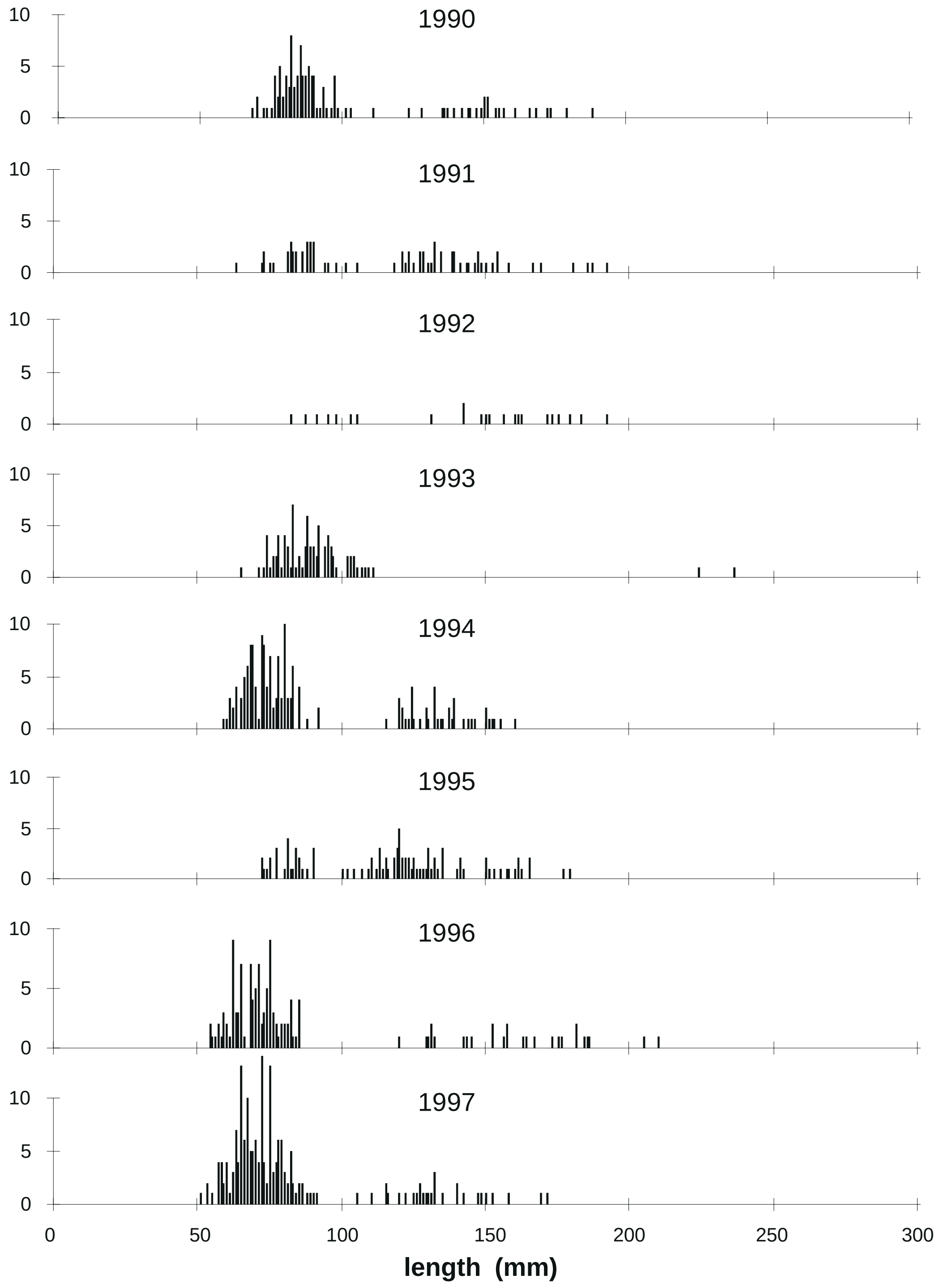


Figure 4.22.5

Coneyglen Burn summary of fish data (1990 - 1997)
(c) Trout length frequency summaries

5

Water Chemistry Discussion

Chris Evans
& Don Monteith

5.1 Regional Variability in Surface Water Chemistry

5.1.1 Acidity and Non-marine Sulphate

The UKAWMN, with only 22 sites in acid sensitive parts of the UK, was not designed to permit a statistically robust assessment of spatial variations in surface water chemistry across the UK. However, some general spatial patterns are observed, and maps showing mean values for a number of important variables are presented in Figure 5.1. Mean values for a wider range of determinands are given in Table 5.1.

Inter-site variability in mean alkalinity is actually quite low; with the exception of Coneyglen Burn (alkalinity 161 µeq l^{-1}), all site means fall within the range -30 to 48 µeq l^{-1}. However, this alkalinity band is associated with a wide range in pH, from 4.6 to 6.5, which in turn represents a variation in H^+ concentration of approximately two orders of magnitude (0.3 to 25 µeq l^{-1}). Similar variability is observed for labile Al (3 to 287 µg l^{-1}).

Mean Acid Neutralising Capacity (ANC) has been calculated as the sum of base cations minus the sum of acid anions. Although alkalinity, as a directly measured variable, was used in preference to ANC for trend analyses, ANC is widely used as an indicator of surface water acidity status and to relate water chemistry to biological status. Table 5.1 demonstrates a close relationship between alkalinity and ANC, with spatial variations in ANC largely replicating those for alkalinity. With the exception of Coneyglen Burn (204 µeq l^{-1}), ANC varies from –52 to 63 µeq l^{-1} between sites. This range is somewhat greater than for alkalinity.

Concentrations of xSO_4 (Figure 5.1a) generally increase across the mainland UK from northwest to southeast, with a similar gradient suggested from the sites within Northern Ireland. These patterns are consistent with measured emission and deposition variations across the UK (Chapter 2), although other factors such as forestry deposition enhancement, internal sulphur sources and evaporation (notably at Old Lodge) can also increase surface water concentrations to varying degrees. To a first approximation, sites with higher xSO_4 concentrations tend to be more acidic, in accordance with the role of xSO_4 as the main acidifying anion. However, this link is complicated by variations in catchment buffering capacity, represented in Table 5.1 by xCa. For example, Burnmoor Tarn has higher xSO_4 concentrations than nearby Scoat Tarn but, due primarily to higher xCa levels, is much less acidic. The importance of catchment buffering is reflected in the complex spatial variability observed for mean pH (Figure 5.1b).

5.1.2 Nitrate

Spatial variations in NO_3 (Figure 5.1c) show a reasonable correlation with N deposition; consistently low concentrations are observed in the relatively low deposition regions of northwest Scotland and northwest Northern Ireland, while maximum concentrations occur at the highly deposition impacted River Etherow. However, between these extremes there is significant inter-site variability which can be attributed to catchment specific conditions. Factors likely to enhance NO_3 concentrations at a given site include deposition enhancement at forested catchments (Section 5.5) and lower levels of biological uptake of N at high altitude sites such as Scoat Tarn and Lochnagar (Kernan & Allott, 1999). The mean proportional contribution of NO_3 to total anthropogenic acidity (i.e. NO_3 as a percentage of $[NO_3 + xSO_4]$) also varies widely, from 4% to 34% (Figure 5.1d). No clear spatial pattern is evident, with NO_3 contributing most significantly to acidity at Scoat Tarn, Blue Lough, the Bencrom River and the Afon Hafren, and least at the Allt a'Mharcaidh and Old Lodge. NO_3 is not the dominant cause of

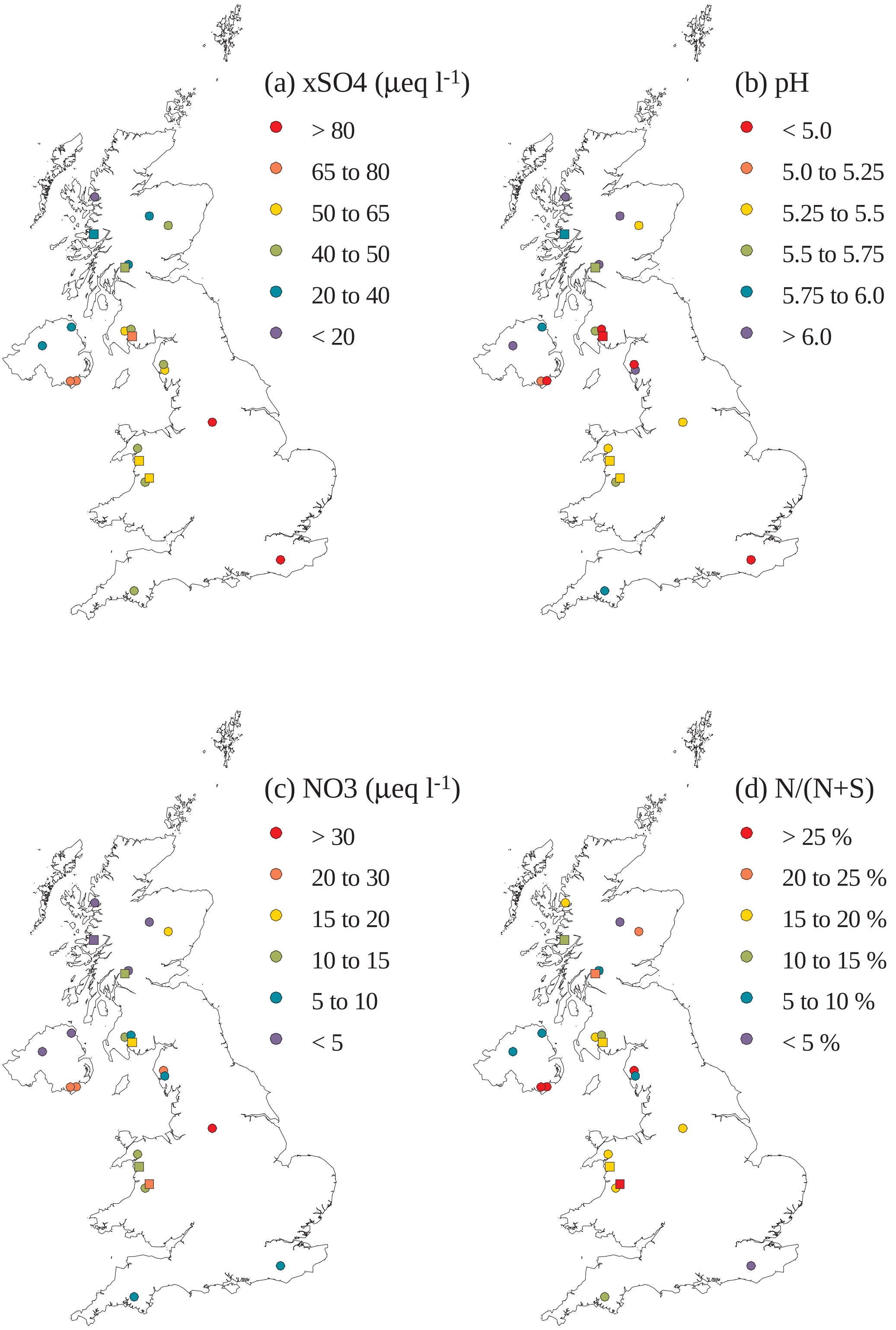


Figure 5.1

1988-1998 mean values for xSO_4, pH, NO_3 and N/(N+S) for UKAWMN sites

Table 5.1

Mean chemistry (1988 - 1998) of UKAWMN sites

All variables in µeq l^{-1} except labile Al (µg l^{-1}) and N% (NO_3 as a percentage of [NO_3 + xSO_4], measured in µeq l^{-1}).

SITE	Alkalinity	ANC	pH	labile Al	xSO_4	NO_3	N%	Cl	xCa
Loch Coire nan Arr	38	43	6.4	3	14	3	17%	258	32
Allt a'Mharcaidh	44	58	6.5	7	33	1	4%	110	38
Allt na Coire nan Con	22	34	5.9	17	30	4	12%	296	46
Lochnagar	1	1	5.3	26	48	16	25%	89	25
Loch Chon	10	20	5.6	20	49	12	20%	223	69
Loch Tinker	38	63	6.1	3	39	3	7%	163	78
Round Loch of Glenhead	-12	-9	4.9	60	47	7	13%	195	25
Loch Grannoch	-28	-14	4.6	225	72	17	19%	257	38
Dargall Lane	4	4	5.5	33	60	11	15%	186	42
Scoat Tarn	-8	-15	5.0	109	41	21	34%	186	25
Burnmoor Tarn	48	59	6.5	3	59	5	8%	210	81
River Etherow	7	29	5.5	66	240	49	17%	310	160
Old Lodge	-30	-52	4.6	195	193	7	4%	571	129
Narrator Brook	16	19	5.8	27	45	6	13%	274	24
Llyn Llagi	6	9	5.3	40	41	10	20%	194	45
Llyn Cwm Mynach	5	7	5.4	65	54	10	16%	304	58
Afon Hafren	6	-3	5.4	99	60	21	26%	209	37
Afon Gwy	12	11	5.6	56	48	11	18%	159	33
Beagh's Burn	44	114	5.8	10	38	4	9%	337	89
Bencrom River	-5	11	5.2	125	67	29	30%	255	42
Blue Lough	-23	-29	4.7	287	66	29	30%	276	29
Coneyglen Burn	161	204	6.5	8	30	3	9%	255	139

acidity at any site, although concentrations temporarily exceed those of xSO_4 during spring episodes at Scoat Tarn and the Bencrom River.

Whereas S inputs and outputs in most UK upland catchments are believed to be in long term balance (Jenkins *et al.*, 1997a), a significant proportion of incoming N deposition is retained or removed by the catchment biota through processes including vegetation uptake, microbial immobilisation and denitrification (Jenkins *et al.*, 1997b; Stoddard, 1994). In pristine environments nitrogen may be a limiting nutrient (Tamm, 1992), in which case virtually all N inputs are retained. However, it has been suggested (Skeffington & Wilson 1988; Aber *et al.*, 1989) that elevated atmospheric inputs from anthropogenic sources can lead to conditions of 'nitrogen saturation', allowing increasing release of NO_3 to surface waters with resultant acidification. Stoddard (1994) identified four stages of nitrogen saturation in upland systems. According to this scheme, Stage 0 is the unimpacted condition, in which strong ecosystem retention causes runoff concentrations to remain at or close to detection limits. At Stage 1, N supply exceeds demand during winter but catchments remain N-limited during summer, so that runoff concentrations vary seasonally, from near-zero during summer to maxima in late winter/early spring. Stage 2 saturation occurs when catchments cease to be N-limited at any time, causing summer minima to rise above detection limits, whilst at Stage 3, catchments are fully saturated throughout the year, with continuously high runoff concentrations and limited seasonality.

The quarterly sampling regime at UKAWMN lake sites may be considered insufficient for identification of saturation stages. Furthermore, seasonal N dynamics can be significantly altered by storage within larger lakes, for example by maintaining NO_3 above detection limits during summer (Momen *et al*., 1999), even though the terrestrial system may be N-limited at this time. Data for the monthly sampled UKAWMN streams are therefore considered to be more suitable for an assessment of catchment saturation status, and time series (Figure 5.2) appear to conform well to Stoddard's classification. According to the definitions given, the Allt a'Mharcaidh is clearly at Stage 0. Coneyglen Burn also appears to be at Stage 0 prior to a large episodic nitrate pulse in 1996 (Section 4.22). It is unclear as yet whether this event represents the onset of a permanent change in nitrogen status at this site, or simply a short term perturbation. Generally low concentrations but small winter peaks at Beagh's Burn, Allt na Coire nan Con and Narrator Brook suggest that these sites are transitional between Stages 0 and 1, whilst Old Lodge, the Afon Gwy and Dargall Lane all exhibit the strong seasonality and near-zero summer concentrations characteristic of Stage 1. The Afon Hafren and Bencrom River, with concentrations above detection limits at all times, appear to be at Stage 2, whilst the continously high concentrations and lack of seasonality at the Etherow indicate that this site is at Stage 3.

It appears then, that the full range of N leaching conditions are represented within the 11 streams of the UKAWMN, from full retention at low deposition locations to severe leaching in high deposition areas. The general correlation observed between N inputs and outputs at UKAWMN sites suggests that a space-for-time substitution similar to that used by Stoddard (1994) may be reasonable. This would suggest that sites currently at lower stages of N saturation would be likely, under increased or even continued current levels of N deposition, to move to more advanced saturation stages in the future.

■ 5.2 Temporal Trends in Surface Water Chemistry

5.2.1 Acidity and Non-marine Sulphate

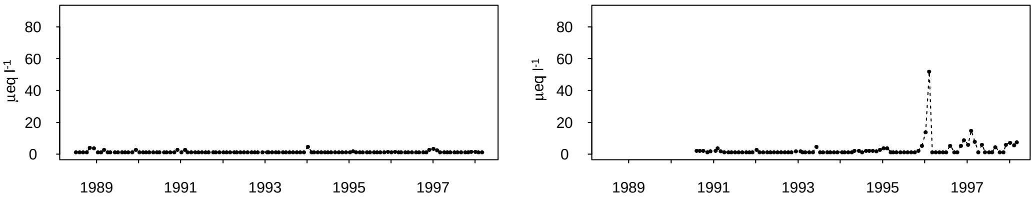
(i) Observed Changes, 1988-1998.

Trend analyses demonstrate increases in pH and alkalinity at six and four sites respectively, while four sites show trends in both. On initial assessment this provides encouraging evidence of chemical recovery. However, only three sites exhibit declines in xSO_4, while none show declines in NO_3, and no sites exhibit both reductions in acidity and declining trends in acid anion concentrations (Table 5.2). This is perhaps surprising given that decreases in UK sulphur emissions since the 1970s (RGAR, 1997) should in theory have led to reductions in surface water xSO_4 levels, and subsequently to reduced acidity. In the absence of decreasing xSO_4 trends, the observed pH and alkalinity increases cannot confidently be attributed to deposition reductions, and at some sites may instead be the result of variations in sea-salt inputs and/or rainfall (Section 5.3). The lack of clear widespread decreases in xSO_4 appears to be linked to several factors:

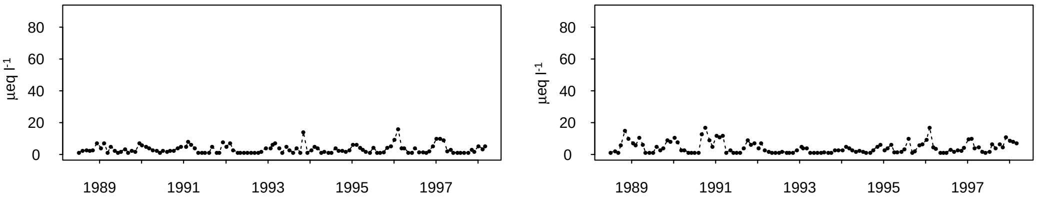
- *Reductions in sulphur deposition at many UKAWMN sites between 1988 and 1998 may have been relatively small.* As noted in Chapter 2, UK sulphur emissions have decreased by 55% between 1986-1997, and total deposition by around 50%. However, more of this reduction has been in dry deposition, which for the UK as a whole has declined by 61%, while wet deposition has only declined by 42%. In 1986 wet and dry deposition inputs were approximately equal, but in the remote, high-rainfall upland areas where most UKAWMN sites are located, wet deposition provides a greater proportion of the total input. Consequently, total deposition reductions in these regions have been much smaller than the national average, and at many sites no trend at all can be detected in wet deposition over the

Figure 5.2

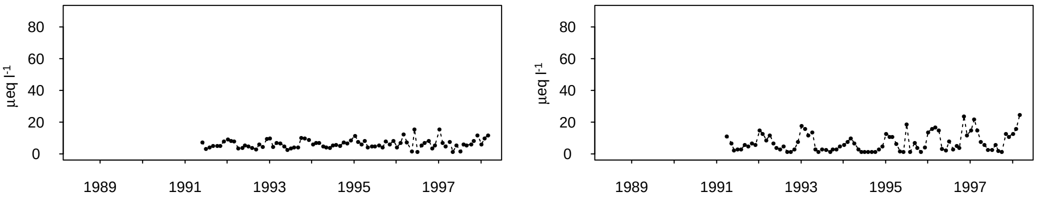
NO_3 time series (1988-1998) for UKAWMN streams


(a) Allt a'Mharcaidh

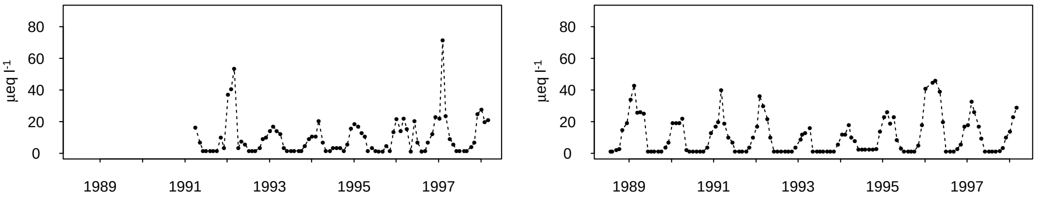
(b) Coneyglen Burn


(c) Beaghs Burn

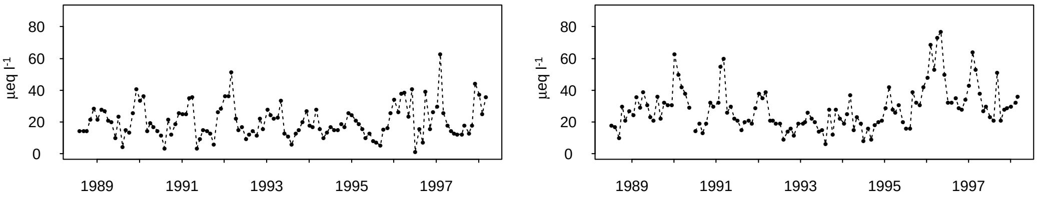
(d) Allt na Coire nan Con


(e) Narrator Brook

(f) Old Lodge


(g) Afon Gwy

(h) Dargall Lane


(i) Afon Hafren

(j) Bencrom River

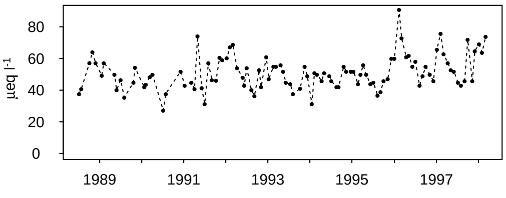

(k) River Etherow

Table 5.2

Sites with increasing alkalinity, increasing pH or decreasing xSO_4, for the period 1988-1998, according to trend analysis (SKT = Seasonal Kendal Test; REG = Linear regression)

	Alkalinity (μeq l^{-1})		pH		xSO_4 (μeq l^{-1})	
Site	**SKT**	**REG**	**SKT**	**REG**	**SKT**	**REG**
Loch Chon	*+1.0**	*+1.4**	*+0.044**	*+0.04**		
Blue Lough		*+1.2**		*+0.02**		
Narrator Brook		*+1.8**		*+0.06***		*+1.0***
Dargall Lane	*+0.9**					
Scoat Tarn			*+0.013**	*+0.02**		
Llyn Llagi			*+0.049**			
Afon Gwy				*+0.05**		
River Etherow					*-5.9***	*-7.9***
Lochnagar				*-0.02**	*-0.5**	*-1.0**
Old Lodge						*-8.8**

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$.*

last decade (Chapter 2). Lochnagar, the River Etherow and Old Lodge, which have central or eastern locations, receive proportionally higher dry deposition inputs, and have experienced greater total deposition reductions, and detectable reductions in surface water xSO_4 concentrations.

- *Short term variations are large relative to long term changes*. This problem is particularly severe at sites with relatively low xSO_4 concentrations. 13 of the UKAWMN sites have mean xSO_4 concentrations below 50 μeq l^{-1}. Even proportionally sizeable reductions at these sites are unlikely to be much larger than their mean standard deviation (of 13.1 μeq l^{-1}) over the decade. This demonstrates how even quite large trends may be difficult to detect By contrast, the observed decline in xSO_4 at the Etherow represents an absolute decrease of around 60 μeq l^{-1}, which is more readily identifiable.
- *The marine-ion correction, used to calculate xSO_4, is influenced by decadal-scale climatic variations at coastal sites*. There is evidence to suggest that soil retention and release of SO_4, driven by varying levels of sea-salt deposition, causes cyclicity in calculated xSO_4 concentrations which may mask anthropogenically driven changes. Unusually high levels of marine ion deposition during the first three years of monitoring appear to have suppressed xSO_4 estimates at this time, causing particular problems for trend detection. This subject is discussed further in Section 5.3.3.
- *Soils may be releasing stored sulphur*. Although UK soils are widely assumed to be saturated with respect to adsorbed SO_4, a reduction in deposition inputs may result in over-saturation, and therefore some S desorption. This may damp the effect of deposition reductions at some sites.

Even at the three sites with decreasing xSO_4 (Lochnagar, the River Etherow and Old Lodge), recovery in pH or alkalinity has not yet been observed. In Scandinavia and the United States, surface water chemistry recovery following xSO_4 reductions has been delayed by accompanying decreases in base cations (Stoddard *et al*., 1999). This can be attributed to reduced total cation export as mobile anion concentrations decline; as soil base saturation levels are re-stocked from primary weathering, surface water base cation

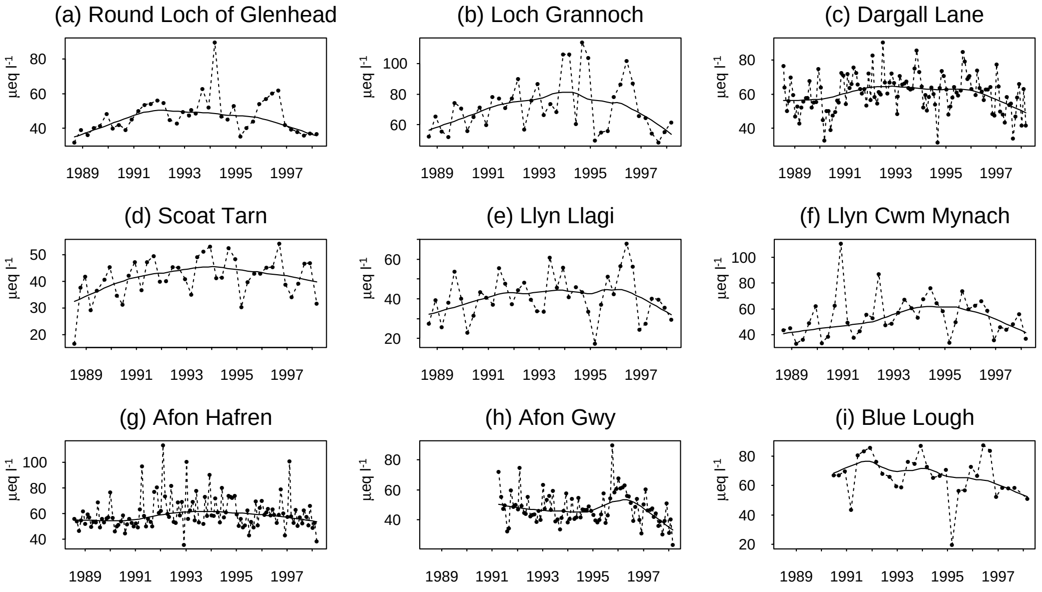


Figure 5.3

Non-marine SO_4 at sites showing recent downward trends

Smoothed line represents LOESS curve (Section 3.1.2)

concentrations can be expected to stabilise, permitting further recovery in pH and alkalinity (Galloway *et al*., 1983). Downward trends in Ca and Mg at the Etherow and Old Lodge (Tables 5.12.3, 5.13.3) suggest similar patterns here, although these trends are relatively weak, and detected only using regression analysis. At all three sites, however, there are strong indications that NO_3 concentrations have increased over the monitoring period. This appears to have offset the effects of decreasing xSO_4, and indeed at Lochnagar the rise in NO_3 has exceeded the fall in xSO_4, causing further acidification.

(ii) Prospects for future recovery

Although there has been little indication of recovery at the UKAWMN sites during the last decade, this should become evident with continued monitoring. As noted above, the apparent increase in xSO_4 at many sites during the early part of the monitoring period may have been the result of a very high sea-salt deposition period 1989-1991, during which marine SO_4 was initially retained by catchment soils, relative to marine Cl (reducing the estimate of xSO_4), and subsequently released (enhancing the estimate of xSO_4). In this context, the xSO_4 reductions at many UKAWMN sites since the mid-1990s (Figure 5.3) are encouraging, and may well represent the resumption of a long term declining trend. Longer term datasets, described in Chapter 6, provide further evidence that the period of rising xSO_4 during the early 1990s represents the temporary disruption of a long term downward trend, and that this downward trend has had, and will continue to have, a positive impact on surface water acidity. Large forecast emissions reductions under the UNECE multipollutant, multi-effect protocol suggest that these recovery trends should continue in future years, becoming statistically significant at an increasing number of sites.

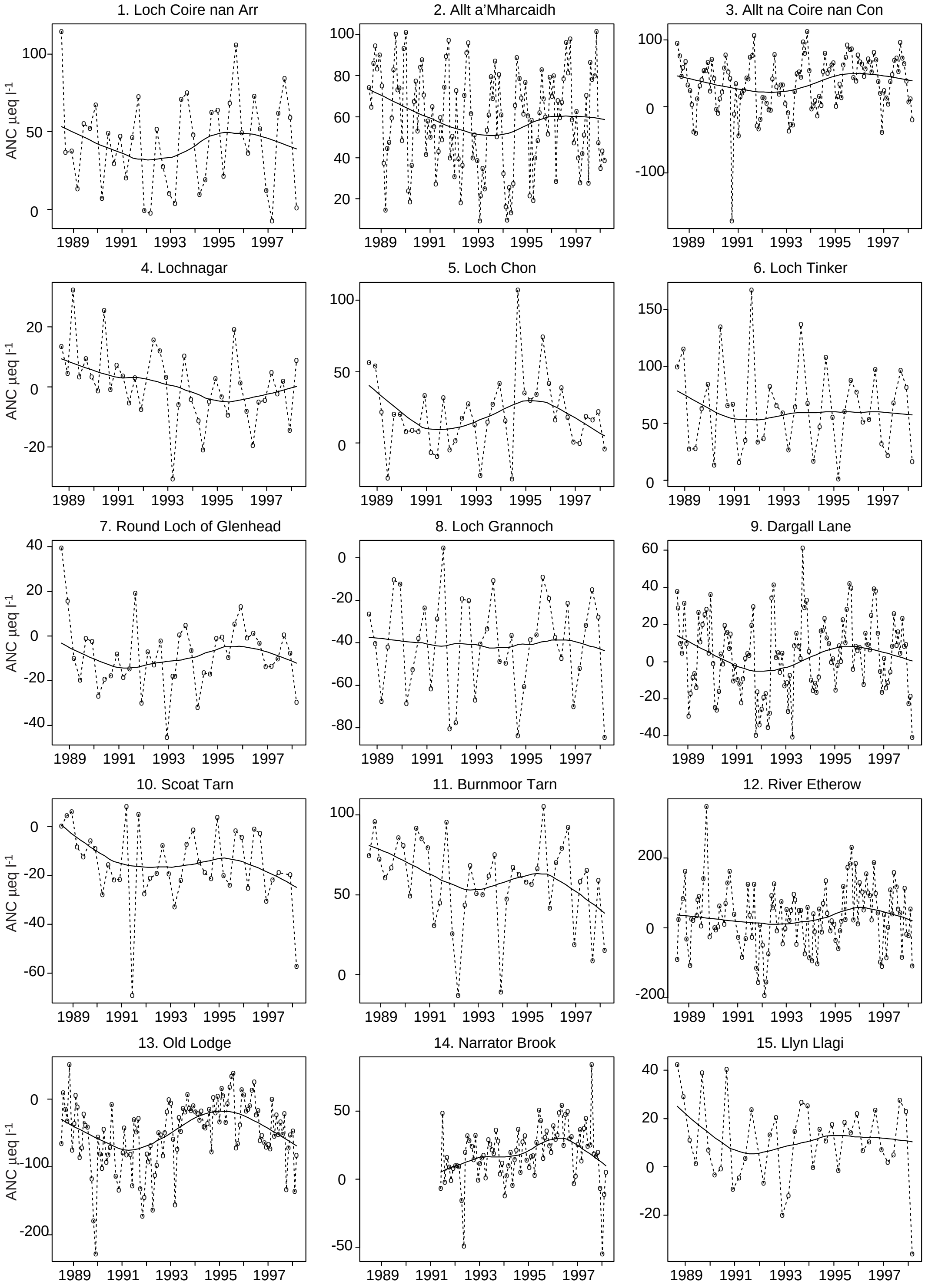
(iii) Variations in ANC

Although trend analysis of ANC was not undertaken, time series (Figure 5.4) show similar variations to those observed for alkalinity. The majority of sites exhibit a degree of cyclicity in ANC over the ten years, many showing ANC minima during 1990-1992, and maxima during 1995-1996. This is believed to be linked to the decadal-scale climatic cycles referred to above, which are discussed in detail in Section 5.3.3. As for alkalinity and pH, few sites show evidence of an overall trend in ANC, perhaps the most compelling being a decline in ANC at Lochnagar, consistent with rising NO_3 and falling pH at this site.

Figure 5.4

Temporal trends in Acid Neutralising Capacity (ANC) (µeq l^{-1}) at UKAWMN sites (1988-1998)

Smoothed line represents LOESS curve (Section 3.1.2)



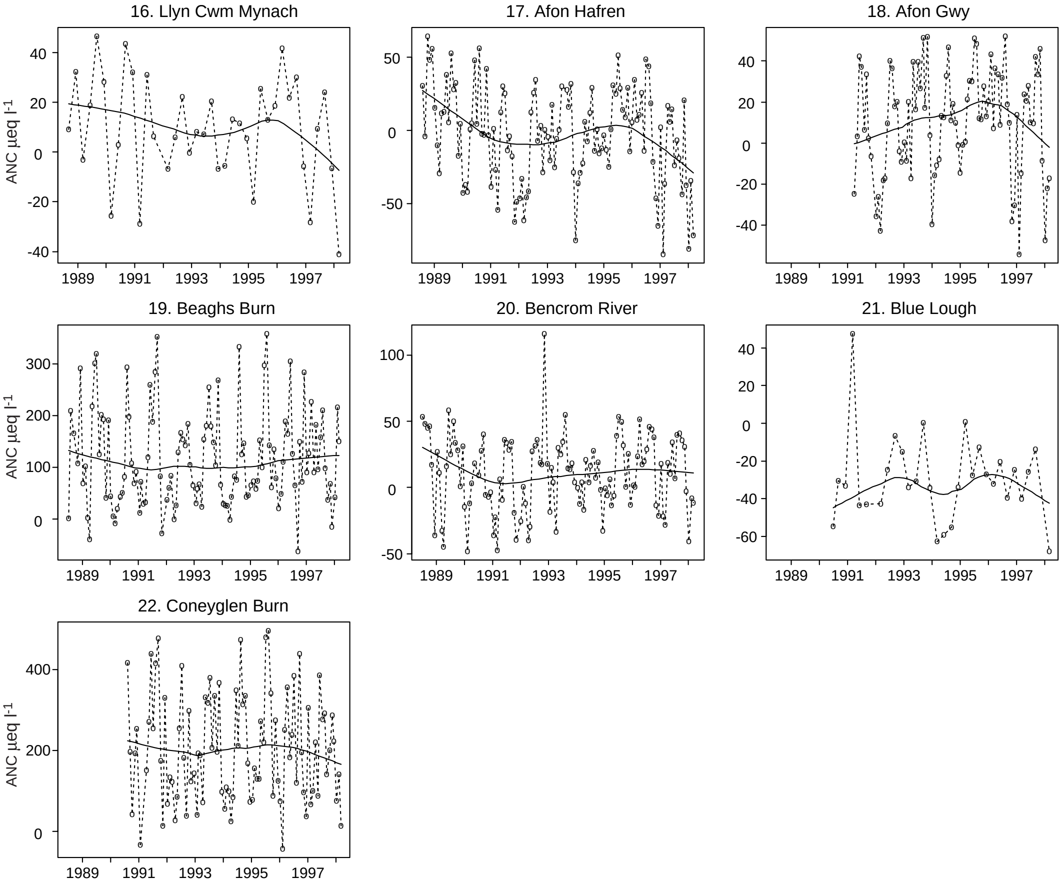


Figure 5.4 (continued)

Temporal trends in Acid Neutralising Capacity (ANC) (µeq l^{-1}) at UKAWMN sites (1988-1998)

5.2.2 Nitrate

Deposition of NO_3 and NH_4 has either remained stable or has risen slightly over the last decade (Chapter 2). Nitrogen saturation theory (Section 5.1.2) suggests that even a constant N input might be expected to lead to an increase in N output, and rising NO_3 trends have indeed been observed at six UKAWMN sites (Table 5.3). A rising trend is also suggested by time series data for Loch Grannoch (Figure 4.8.2e) but here and perhaps at others sites, any long term trend is difficult to detect amid large episodic and seasonal fluctuations. NO_3 is also thought to be affected by inter-annual climate variations; this is discussed in Section 5.4.

Of the six sites with rising NO_3 trends, the most compelling increases are at the River Etherow and Round Loch of Glenhead (Figures 4.12.2e and 4.7.2e), where steady changes over the ten years suggest increasingly severe catchment nitrogen saturation. Following apparent step changes at Lochnagar (in 1993, Figure 4.4.2e) and Loch Chon (in 1996, Figure 4.5.2e) concentrations have so far remained high, and again nitrogen saturation may be the cause. At Old Lodge, the 1991-1998 record is currently too short to confirm that changes have occurred, whilst at the Bencrom River (Figure 4.20.2e) fluctuating concentrations over the monitoring period suggest that climatic factors may be the dominant influence.

Table 5.3

Sites with increasing NO_3

SKT = Seasonal Kendall Test; REG = Linear regression.

	NO_3 (μeq l^{-1})	
Site	**SKT**	**REG**
Lochnagar	*+1.4**	*+1.1**
Loch Chon	*+0.9**	-
Round Loch of Glenhead	*+0.9***	*+0.6**
River Etherow	*+2.1***	*+1.5**
Old Lodge	*+0.7**	-
Bencrom River	*+1.0**	-

** Trend significant at $p < 0.05$; ** trend significant at $p < 0.01$; *** trend significant at $p < 0.001$.*

5.2.3 Dissolved Organic Carbon

At 19 of the 22 sites in the Network, including all those in Scotland and Northern Ireland, rising DOC trends have been observed using one or both methods of trend analysis (Table 5.4). The only sites without observed DOC increases are Narrator Brook, Llyn Llagi and Llyn Cwm Mynach. Given the limited number of trends observed for other determinands, the consistency of the increases identified for DOC is remarkable, suggesting that concentrations may be rising in upland areas throughout most of the UK. At some sites these increases are extremely large; concentrations have doubled or more over the ten years at Loch Coire nan Arr, Allt na Coire nan Con, Dargall Lane, Scoat Tarn and Coneyglen Burn. Rising DOC trends have previously been noted at the Afon Hafren (1983-1993) by Robson & Neal (1996) and at the Afon Cyff and Afon Gwy (1980-1996) by Reynolds *et al*. (1997). Increase in water colour, which is strongly related to DOC concentration, has also been recorded at four Galloway lochs and three Trossachs streams between 1985 and 1995 (Harriman *et al*., 1995a) and in the Pennines between 1979 and 1998 (Naden & McDonald, 1989; Watts *et al*., in review).

The identification of widespread DOC increases at the UKAWMN sites raises three major questions. Firstly, do these trends represent a sustained, long-term increase in surface water DOC concentrations, or are they simply natural fluctuations? Secondly, what is the cause of observed changes? Finally, what, if any, are the biological implications of these changes?

<u>(i) Validity of Trends</u>

Time series data for sites exhibiting DOC trends generally suggest that these trends are ‘genuine’ (Figure 5.5). Unlike many other determinands there are few indications of cyclicity, with the majority of sites exhibiting steady, linear increases over time. This is reflected in the high level of SKT signficance at many sites (Table

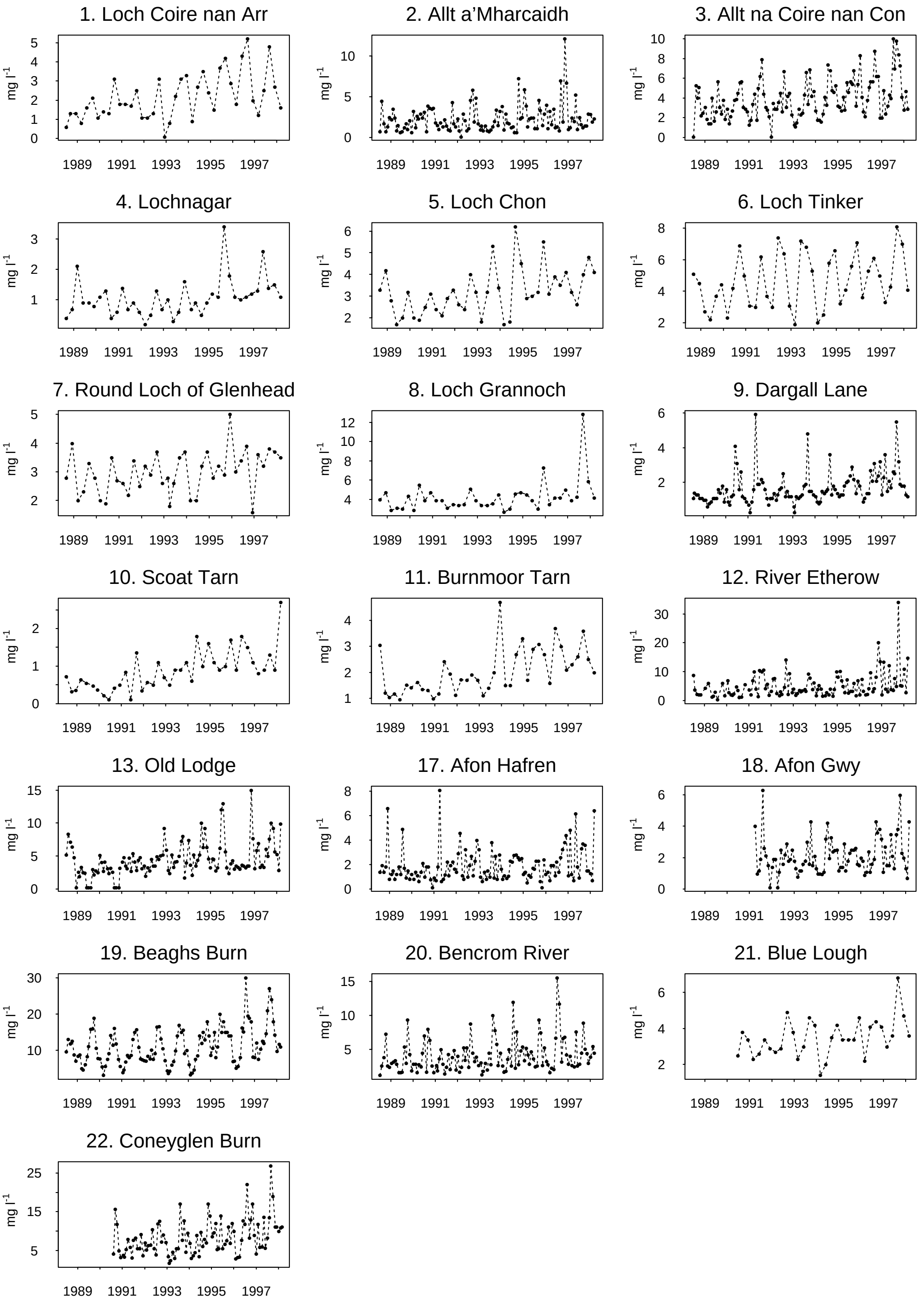


Figure 5.5

DOC at sites with rising trends

5.4) with increases at 12 sites significant at p <0.01. The analyses of Reynolds *et al*. (1997) and Robson & Neal (1996), showing similar increases for earlier time periods at the Gwy and Hafren, also support the conclusion that the changes observed in UKAWMN data form part of a sustained rising trend.

Interestingly, annual measurements of transparency (summer secchi disc depth) and the maximum depth of macrophyte growth (which is inversely correlated with DOC between sites) at UKAWMN lakes have not shown any apparent change over the last decade. This appears to suggest that increased DOC may not have led to an associated rise in colour in lake waters. Since the fraction of coloured compounds within the DOC total has been shown to vary (Molot & Dillon, 1997) it is therefore possible that observed DOC increases could have been in the low molecular-weight colourless forms. However, since colour is known to have increased in Galloway, the Trossachs and the Pennines (Harriman *et al*., 1995a; Watts *et al*., in review) and since there is evidence for an increase in absorbance at 250nm at some sites

Table 5.4

Sites with increasing DOC trends

	DOC				**Non-labile Al**	
Site	**SKT (mg l^{-1})**	**REG (mg l^{-1})**	**1st Year Mean (mg l^{-1})**	**Annual % increase**	**SKT (µg l^{-1})**	**REG (µg l^{-1})**
Loch Coire nan Arr	*+0.25***	*+0.21***	*1.0*	*23%*	*+1.00**	*+1.13***
Allt A'Mharcaidh	-	*+0.11**	*2.2*	*5%*	-	-
Coire nan Con	*+0.28***	*+0.28***	*2.8*	*10%*	*+2.40*	*+0.215*
Lochnagar	-	*+0.08**	*1.1*	*8%*	-	-
Loch Chon	*+0.20***	*+0.16***	*3.4*	*5%*	-	-
Loch Tinker	*+0.18**	-	*4.1*	*5%*	-	-
Round Loch	*+0.13***	*+0.09**	*2.9*	*4%*	*+2.31*	*+1.94***
Loch Grannoch	*+0.13**	-	*3.9*	*3%*	-	-
Dargall Lane	*+0.10***	*+0.11***	*1.1*	*10%*	*+0.86**	-
Scoat Tarn	*+0.10***	*+0.12***	*0.5*	*22%*	-	-
Burnmoor Tarn	*+0.18***	*+0.17***	*1.6*	*11%*	*+0.25**	-
River Etherow	*+0.27**	*+0.48***	*4.2*	*9%*	*+5.00***	*+4.27**
Old Lodge	*+0.28***	*+0.35***	*4.4*	*7%*	-	-
Afon Hafren	*+0.07**	-	*2.1*	*3%*	-	-
Afon Gwy	*+0.10**	-	*2.2*	*5%*	-	-
Beagh's Burn	*+0.60***	*+0.65***	*9.5*	*7%*	-	-
Bencrom River	*+0.14***	*+0.21***	*3.3*	*5%*	-	-
Blue Lough	*+0.19**	*+0.18**	*3.0*	*6%*	-	-
Coneyglen Burn	*+0.78****	*+0.80***	*6.4*	*12%*	*+1.86**	*+2.42**

SKT = Seasonal Kendall Test. REG = Linear regression.
First year mean calculated using data for April 1991-March 1992 at Afon Gwy, Blue Lough and Coneyglen Burn, April 1988-March 1989 at all other sites. Annual percentage increase calculated using mean of SKT and regression trend estimates where both are significant.
** indicates trend significant at $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.*

(Harriman, pers. comm), it is possible that the observations above may reflect measurement limitations. This issue could be addressed in future by partitioning DOC in water samples by molecular weight using ultra-filtration, by measuring absorbance at a number of wave lengths, and or, by increasing the frequency of secchi disc readings.

(ii) Possible Causes of Rising DOC

At this stage, it is difficult to identify a mechanism for observed DOC increases. Krug & Frink (1983) argued that increasing mineral acid inputs to soils would cause a decrease in organic acid leaching, and hence in the DOC concentration of surface waters. This hypothesis was supported by palaeolimnological data showing a decline in DOC concentrations of Norwegian lakes concurrent with acidification during the early twentieth century (Davis *et al.*,1985). Modelling work by Tipping & Hurley (1988) suggested that with reductions in acid deposition, rising soil pH will lead to increased organic matter solubility, and hence to greater DOC in runoff. It is possible therefore that reduced acid deposition at UKAWMN sites over the last decade may be responsible for the rising DOC trends observed. However, this mechanism does not accord well with the geographical distribution of rising trends, as some of the largest increases have been at sites in low deposition areas, notably Loch Coire nan Arr, Allt na Coire nan Con, Beagh’s Burn and Coneyglen Burn (Table 5.4). Since these sites have never been seriously acidified, it is unlikely that changing soil pH could be influencing DOC.

An alternative explanation for the observed trends may be a climatically driven increase in rates of organic matter decomposition. The steady increase in DOC identified for 1983-1993 at the Afon Hafren observed by Robson & Neal (1996) is accompanied by similar increases in Iodide (I) and Bromide (Br). Neal *et al.* (1990) note that both halogens are strongly influenced by microbial processes, with autumn stream maxima associated with peaks in the decomposition and washout of organic material. The rising trends in I and Br observed at the Hafren were therefore considered by Robson & Neal (1996) to indicate a decomposition source for DOC increases. However, interactions between microbial organic matter decomposition and climate are complex. For instance, Christ & David (1996) found higher DOC production in a forest organic horizon with increased moisture content, while Mitchell & McDonald (1992) observed elevated concentrations for extended periods following droughts. Decomposition rates also increase exponentially with rising temperature (Christ & David, 1996).

Data presented by Marsh (1999) indicate an increased frequency of low flow conditions (and hence dryer soils) in southeast Britain during the last decade. No comparable trend has been observed in northwest Britain, and in general it is thought that rainfall patterns may be too spatially variable to account for consistent DOC trends throughout the UK. However mean temperatures show a much tighter spatial correlation, and data from the Central England Temperature Record (Hulme, 1999) indicate that the period 1988-1997 was on average 0.5˚C warmer than the 1961-1990 mean. In addition, the average number of days with mean temperatures above 20˚C during 1988-1997 (7.4 days yr^{-1}) was more than double the long term mean. Given the exponential relationship between decomposition and temperature, this apparent warming trend within the UK may be sufficient to explain the observed DOC increases. The increased number of hot summer days may be particularly significant since most decomposition can be expected to occur at these times.

(iii) Environmental Significance of Rising DOC.

Rising levels of DOC may have significant implications for stream and lake biota. The organic acids, which form part of the DOC, can have a significant negative impact on pH and alkalinity. Increases in organic acidity over the study period may therefore have reduced, or even negated, any recovery in pH and alkalinity resulting from reduced mineral acid anion concentrations. However, DOC has been shown to reduce fish mortality under acidic conditions, both through the complexation of toxic labile Al to non-labile forms and by reducing the toxicity of the remaining labile Al. (Baker *et al.*, 1990;

Roy & Campbell, 1997). Since DOC supply is believed to be the limiting factor in non-labile Al generation (Driscoll *et al.*, 1984), this may explain the rising non-labile Al trends observed at seven sites with rising DOC (Table 5.4). Therefore, in terms of fish sensitivity to acidification, DOC increases may have a beneficial effect on UKAWMN surface waters.

Increases in water colour, although not yet identified at the UKAWMN lakes, will reduce the depth to which photosynthetically active radition penetrates, and as a result could restrict plant growth. High levels of colour are also considered to be a problem for drinking water (e.g. Mitchell & McDonald, 1992). Conversely, an increase in colour may provide aquatic organisms protection from the potentially harmful effects of UV-B radiation (e.g. Schindler *et al.*, 1996) which could be increasing in mid-latitudes as a result of stratospheric ozone depletion (e.g. Bjorn *et al.*, 1998).

■ 5.3 Impact of marine ion cycles on acidity and trend detection

5.3.1 Chloride Variations

Inter-annual variations in marine ion deposition, and subsequent cyclical fluctuations in surface water concentrations of a range of ions, have been examined in detail for eight UKAWMN lakes in the Trossachs, Galloway, the Lake District and north Wales by Evans *et al.* (in press). Figure 5.6 shows Cl time series and LOESS curves for these sites, along with Cl deposition for nearby monitoring sites. In all four regions, a peak in lake concentrations between 1989-1991 can be directly linked to elevated deposition inputs over the same period. An additional period of high Cl concentration at the Trossachs sites during 1993 corresponds to a second deposition peak in this region. Sea-salt deposition is in general highly episodic, with most inputs occurring during winter frontal storms. However, Reynolds & Pomeroy (1988) showed that physical mixing within the catchment damps surface water Cl response. Consequently, although significant seasonality is evident in the time series shown in Figure 5.6, concentrations may remain elevated over sustained periods.

The patterns of surface water Cl variation observed at the sites studied by Evans *et al.* (in press) are mirrored at other west coast sites on the UK mainland. As noted in the site descriptions (Chapter 4), Dargall Lane, the Afon Hafren, Afon Gwy and Narrator Brook show virtually identical patterns of Cl variation to those observed in the Galloway, Lake District and north Wales lakes, with concentration maxima during the early 1990s (Figures 4.9.2f, 4.14.2f, 4.17.2f and 4.18.2f). This suggests that coastal areas ranging from southwest England to southwest Scotland have experienced very similar patterns of sea-salt deposition over the last decade. A period of high Cl concentration at Old Lodge during 1989-1991 (Figure 4.13.2f) suggests that this may also have extended along the English south coast.

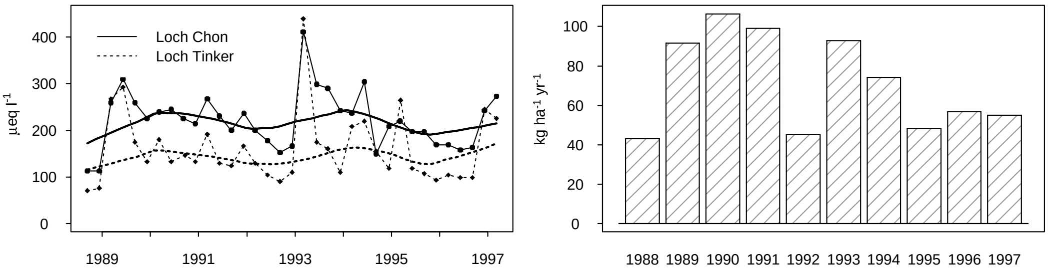
Observed patterns of Cl variation for the Trossachs lochs are matched by those at the coastal sites in northern Scotland, Loch Coire nan Arr and Allt na Coire nan Con, and to some extent also by the inland sites, the Allt a’Mharcaidh and Lochnagar (Figures 4.1.2f-4.4.2f). These sites all exhibited elevated concentrations during 1989-1990 and 1993, indicating that both high deposition periods recorded in the Trossachs affected a wider area of northern Scotland. Cl variations at the Northern Ireland sites (Figures 4.19.2f-4.22.2f) are less consistent, perhaps reflecting their varied positions relative to coastlines, although concentrations appeared generally higher during 1990-1991 and 1995-1996.

5.3.2 Cations and Acidity

While deposited Cl is considered to be conservative within the catchment, accompanying cations have been shown to undergo chemical reactions through the ‘sea-salt effect’ (Wright *et al.*, 1988; Langan, 1989). High soil water concentrations of marine cations, primarily Na and Mg, cause displacement of other cations held on the soil exchange complex, which are then leached to surface waters. Na and Mg are in turn displaced as soil water

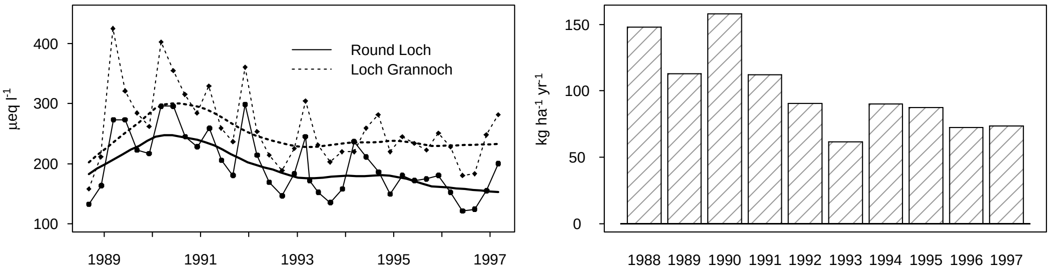
(a) Trossachs

(b) Deposition at Balquidder



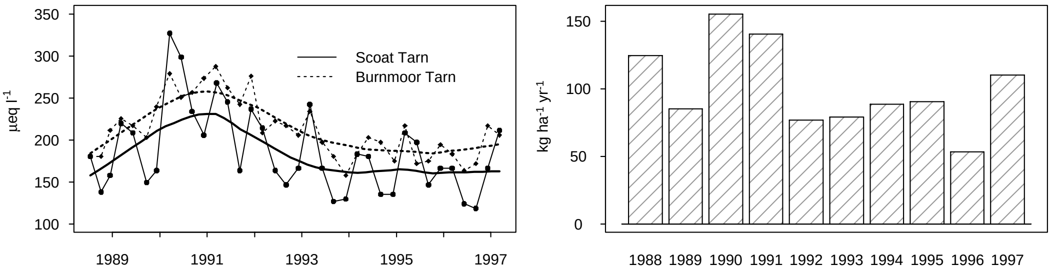
(c) Galloway

(d) Deposition at Loch Dee



(e) Lake District

(f) Deposition at Bannisdale



(g) North Wales

(h) Deposition at Beddgelert

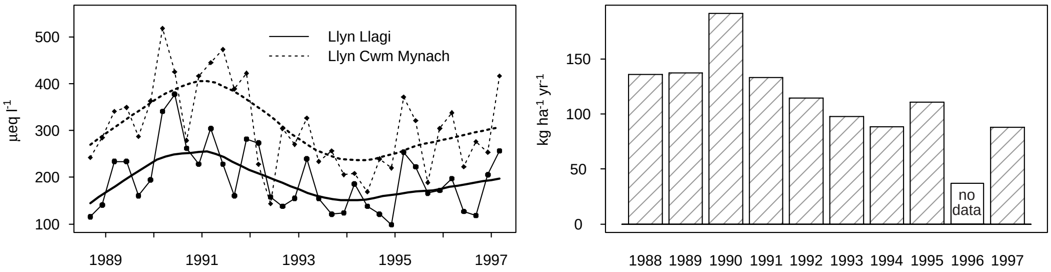


Figure 5.6

Left) Cl time series for four geographical pairs of UKAWMN lakes (µeq l^{-1})
Right) Estimated annual Cl flux measured at local deposition monitoring station (kg ha^{-1} yr^{-1})

concentrations return to pre-event levels, giving no overall change in the long term in either soil or surface water composition. Previous studies have in general considered the sea-salt effect as a transient process, focusing on episodic acidification due to H^+ displacement, but other cations with non-marine sources, notably Ca^{2+} and labile Al, may also be affected. Additionally, the sustained periods of elevated Cl observed at many UKAWMN sites suggest that the effects of soil ion exchange on runoff composition, may persist over much longer timescales than has previously been envisaged.

The influence of sea-salt inputs on surface water chemistry was assessed through linear regression between Cl (as a chemically inert indicator of marine inputs) and a range of potentially affected variables: xNa, xMg, xCa, H^+, labile Al and xSO_4. A negative correlation between the non-marine component of an ion and Cl suggests that this ion is adsorbed in the soil during periods of high sea-salt inputs, a positive correlation that it is displaced. For interpretation, sites were split into three categories based on the suggestion of Harriman *et al.*, (in press) that sites at an intermediate distance from the coast, with

Table 5.5

Slope and significance of regressions between Cl and a range of non-marine variables.

	xNa	**xMg**	**xCa**	**H^+**	**Al_{lab}**	**xSO_4**
‘COASTAL’ SITES						
Loch Coire nan Arr	*-0.22****	-	-	*+0.002****	-	*-0.05****
Allt na Coire nan Con	*-0.28****	*-0.03****	*+0.04****	*+0.01****	*+0.08****	*-0.06****
Beagh’s Burn	*-0.37****	-	-	-	*+0.05****	-
‘INTERMEDIATE’ SITES						
Loch Chon	*-0.27****	*-0.12****	-	*+0.02****	*+0.16****	*-0.06**
Loch Tinker	*-0.25****	*-0.10****	-	*+0.01****	-	*-0.08**
Round Loch of Glenhead	*-0.19****	*-0.07**	-	*+0.02**	*+0.31****	-
Loch Grannoch	*-0.27****	*-0.08****	*+0.05***	-	*+0.89***	-
Dargall Lane	*-0.26****	*-0.02**	*+0.08****	*+0.02****	*+0.23****	*-0.05***
Scoat Tarn	*-0.21****	*-0.04**	*+0.05****	*+0.03**	*+0.93****	*-0.09****
Burnmoor Tarn	*-0.23****	-	*+0.21***	-	-	-
Old Lodge	*-0.24****	-	*+0.13****	-	-	-
Narrator Brook	*-0.49****	*-0.07****	-	*+0.03****	*+0.34****	*-0.12****
Llyn Llagi	*-0.21****	*-0.07****	*+0.07***	*+0.03****	-	*-0.07***
Llyn Cwm Mynach	*-0.19****	*-0.05****	*+0.15****	-	-	*-0.06**
Afon Hafren	*-0.34****	*-0.10****	-	*+0.09****	*+1.24****	-
Afon Gwy	*-0.33****	-	-	*+0.04**	*+0.52***	-
Bencrom River	*-0.26****	-	*+0.10****	-	*+0.29**	-
Blue Lough	*-0.16***	-	-	-	*+0.64**	-
Coneyglen Burn	*-0.38****	-	-	*+0.02***	-	-
‘INLAND’ SITES						
Allt a’Mharcaidh	*-0.04****	*-0.10****	-	*+0.02****	*+0.1**	*-0.04**
Lochnagar	-	-	*+0.11****	-	*+0.6***	-
River Etherow	-	-	*+0.13***	-	-	-

*All variables analysed in µeq l^{-1} except labile Aluminium (Al_{lab}) (µg l^{-1}). *** indicates correlation significant at $p < 0.001$, ** significant at $p < 0.01$, *significant at $p < 0.05$. Correlations with $p > 0.05$ considered non-significant and omitted from table.*

generally moderate marine ion concentrations but receiving occasional large sea-salt inputs, undergo the most severe sea-salt acidification. At sites further inland sea-salt episodes are rare and generally minor, whereas in exposed coastal areas sea-salt deposition is continuously high, leading to proportionally small concentration changes in response to individual events, and therefore minor changes in acidity. Sites were classified on the basis of location and Cl concentrations as follows:

- 'Coastal': Very high Cl deposition. Maximum runoff concentrations > 600 µeq l^{-1} with large peaks during most years.
- 'Intermediate': Moderately high Cl deposition, maximum runoff concentrations commonly in range 350-500 µeq l^{-1}. Large inter-annual variations in deposition leading to cyclical variations in runoff Cl.
- 'Inland': Low Cl deposition, maximum runoff concentrations generally < 300 µeq l^{-1}. Some inter-annual variability but magnitude of changes insufficient to produce major sea-salt episodes.

In practice, the majority of acid-sensitive regions of the UK are in 'intermediate' locations, and this is reflected in the classification of UKAWMN sites. Only Loch Coire nan Arr, Allt na Coire nan Con and Beagh's Burn can be classified as 'coastal', whilst only the Allt a'Mharcaidh, Lochnagar and the River Etherow are 'inland'(high Cl concentrations at the Etherow are probably due to road salt, as noted in Section 4.12). Classifications and results of regression analyses are shown in Table 5.5, and some example time series in Figures 5.8-5.12.

Relationships between Cl and non-marine cations are generally consistent between sites. At all coastal and intermediate sites, xNa exhibits a highly significant inverse correlation with Cl, with slopes ranging from -0.16 to -0.49. These strong correlations indicate that marine Na is consistently retained on exchange sites following large sea-salt inputs. This effectively reduces the calculated xNa of runoff, and frequently results in a value below zero. Significant inverse correlations between xMg and Cl at 11 sites demonstrate an equivalent process for marine Mg. The lower number of sites showing this relationship, and the smaller slopes observed, reflect the smaller amount of Mg in sea-salt relative to Na, and the proportionally greater non-marine Mg sources at some sites. Of the inland sites, the Allt a'Mharcaidh shows a similar inverse correlation for xNa and xMg to more marine-influenced sites, but the slope of -0.04 for xNa is much lower than elsewhere. At Lochnagar and the River Etherow no significant relationship is observed between Cl and either xNa or xMg, confirming that these sites are minimally influenced by sea-salt inputs.

Relationships between Cl and xCa, H^+ and labile Al, where observed, are invariably positive. In addition, at least one of these variables is significantly correlated with Cl at every coastal and intermediate site. Therefore, as would be expected, it appears that the retention of Na and Mg on exchange sites during sea-salt events is always accompanied by the displacement of one or more of Ca, H^+ and labile Al. However, the specific responses of individual catchments vary considerably. At Burnmoor Tarn, Old Lodge and Llyn Cwm Mynach, regression analyses suggest that only Ca is significantly displaced by Na and Mg inputs. At many other sites (e.g. Loch Chon, Round Loch, Narrator Brook, Afon Hafren, Afon Gwy) only the acid cations H^+ and labile Al appear to respond to sea-salts, whereas at Allt na Coire nan Con, Dargall Lane and Scoat Tarn all three cations are correlated with Cl. Therefore, although sea-salt effects operate at all these sites, the impact on surface water acidity may be minor at some and severe at others. The behaviour of individual catchments is not well related to site acidity, with for example both the acidic Old Lodge and circumneutral Burnmoor Tarn dominated by Ca displacement, although Table 5.5 does suggest some regional consistency in the response observed. It seems likely that local factors such as weathering supply and the nature of the exchange complex may determine specific cation response to sea-salt inputs.

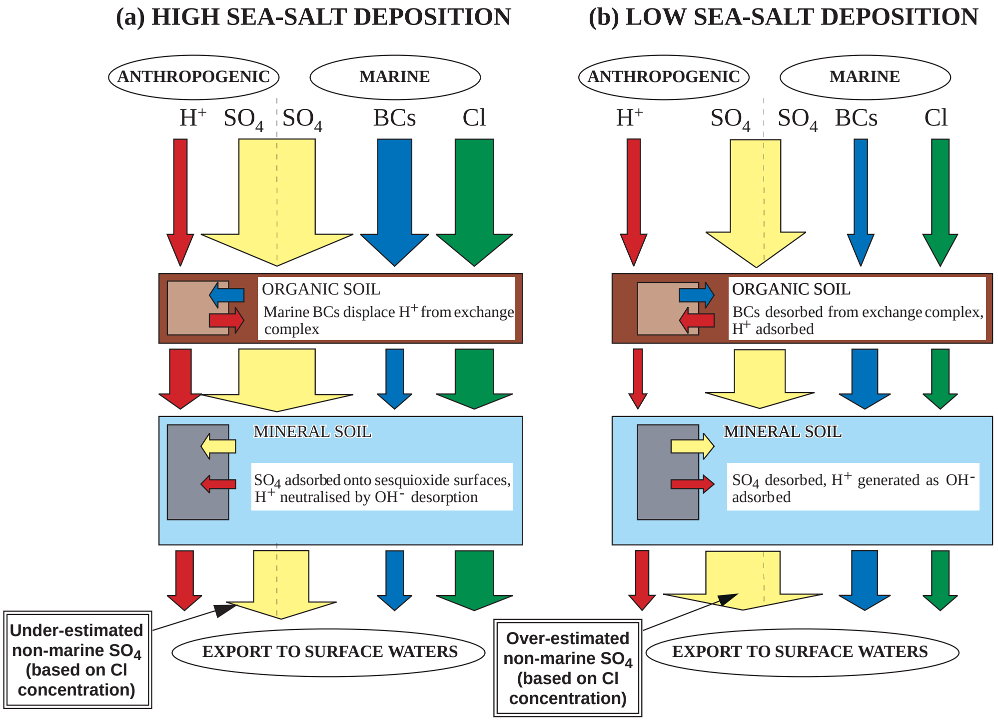
It is important to note that the strength of the relationship between Cl and acidity cannot solely be attributed to marine ion effects. Major storm events, during which most sea-salt is deposited, coincide to some extent with periods of high rainfall, when the contribution of relatively alkaline base-flow to surface waters can be diluted by surface runoff. Further work is therefore required to ascertain the relative influence of these two processes on inter-annual variation in acidity. Finally, it is worth noting that although all three coastal sites do show some displacement of non-marine cations by sea-salts, the slopes associated with the correlations in Table 5.5 are generally lower than at the intermediate sites. This appears to be consistent with the suggestion of Harriman *et al*. (in press) that acidification by sea-salts is less severe at sites experiencing very large and frequent deposition inputs.

5.3.3 Sulphate

Correlations between xSO_4 and Cl, included in Table 5.5, are significant at 10 of the UKAWMN sites. In all cases this relationship is negative, with slopes ranging from -0.04 to -0.12. The existence of a correlation between xSO_4 and Cl is surprising, since marine SO_4 is often considered to pass conservatively through the catchment. However Evans *et al*. (in press) have proposed a mechanism by which the elevated concentrations associated with large sea-salt inputs could cause temporary SO_4 retention. Unlike cation exchange processes, which occur mainly on organic matter in surface horizons, sulphate adsorption takes place on sesquioxides produced by weathering in

Figure 5.7

Hypothetical model of the influence of varying sea-salt deposition on SO_4 adsorbtion/ desorbtion within catchments and on marine/non-marine estimates from surface water samples



BCs = base cations. Arrow widths represent relative concentrations of specific ions as they pass from the atmosphere, through the soil profile and into the surface water. Only the concentration of conservative Cl remains relatively constant along the pathway. The use of fixed marine Cl:SO_4 and Cl:base cation ratios to estimate marine/non-marine fractions, leads to inevitable errors.

mineral soils, notably podzolic B horizons. The two processes are thus separated within the soil profile, and can be considered to operate in sequence as water percolates downwards. As water rich in marine ions passes through the soil, ‘sea-salt’ cation exchange processes occur first, leaving water entering the mineral soil enriched in both marine-derived SO_4 and H^+. Although most soils in the UK are believed to be fully saturated with SO_4 in the long term (Jenkins *et al*., 1997a) adsorption capacity is a function of concentration, and also of acidity, which increases the positive charge of sesquioxide surfaces (Johnson & Cole, 1980; Curtin & Seyers, 1990; Harriman *et al*., 1995b). Therefore, water rich in SO_4 and H^+ passing through the mineral soil during sea-salt events may temporarily increase adsorption capacity, leading to retention of some marine SO_4. Since adsorbed SO_4 is replaced in the soil water by desorbed OH^-, the impact of this will be to partially offset the episodic acidification generated by cation exchange processes. The proposed mechanism is illustrated in Figure 5.7.

A hypothesis of SO_4 retention during sea-salt events is supported by the observed inverse correlations between xSO_4 and Cl, and also by observations of individual episodes. During the large January 1998 sea-salt episode at Narrator Brook, for example (Figure 4.14.2), Cl rose from 250 to 480 $\mu eq\ l^{-1}$ but total SO_4 remained constant. This implies that virtually all incoming marine SO_4 was adsorbed by catchment soils, leading to an observed fall in xSO_4 from 51 to 23 $\mu eq\ l^{-1}$. At the coastal Loch Coire nan Arr and Allt na Coire nan Con, xSO_4 levels have been observed to fall below zero during sea-salt events, and sea-salt episode data presented by Harriman *et al*. (1995b) for a range of Scottish streams show a similar pattern of xSO_4 decrease leading to the peak of a sea-salt episode. Finally, many of the UKAWMN sites exhibit generally opposing long term cyclicity in Cl and xSO_4 concentrations (e.g. Figures 5.8, 5.10, 5.11, 5.12), consistent with the operation of a SO_4 adsorption/desorption mechanism over a prolonged timescale. This is discussed further below.

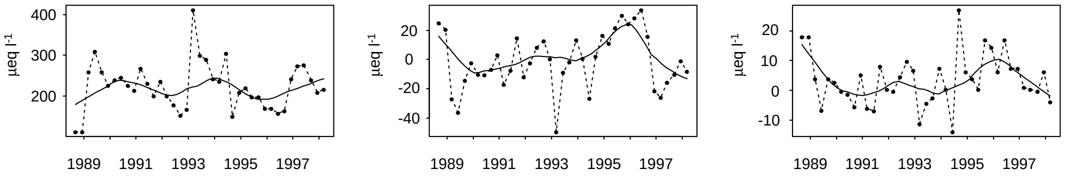
5.3.4 Timescale and significance for trend detection

Although the sea-salt effect is generally considered to operate on an episodic timescale, it has already been noted that Cl concentrations have remained elevated for prolonged periods at many sites, resulting in widely observed, long term cyclicity. Given the relationships established in Section 5.3.2, inter-annual cyclicity would therefore be expected in the non-marine cations, xNa, xMg, H^+ and labile Al. This is certainly the case for xNa, time series which are often virtually the inverse of those for Cl (e.g. Figures 5.8-5.12). For example, xNa values were continuously negative for a year or more during 1989-1990 at Lochs Chon and Grannoch, Round Loch of Glenhead, Llyn Llagi and Llyn Cwm Mynach, but continuously positive for comparable periods during 1996-1997, when Cl was generally low. Cyclical variations in xMg, xCa, H^+ and labile Al are also evident in a large number of time series, including the examples given in Figures 5.8-5.12. It appears therefore that soil water concentrations, and the associated cation exchange equilibria, adjust gradually over time to changes in marine ion deposition. This is consistent with previous observations of strongly damped soil water and runoff Cl variations at Plynlimon (Reynolds & Pomeroy, 1988) but has not previously been identified with regard to sea-salt effects on acidity.

Variations in xSO_4 also show clear cyclicity. This has already been noted in individual site descriptions (Chapter 4), with concentrations at many locations having risen following the 1990 Cl deposition peak until around 1994 (Figure 5.3). The five year analysis of UKAWMN data (Patrick *et al*., 1995) consequently identified rising xSO_4 trends at a number of sites, but Figure 5.3 suggests that since 1994 concentrations at most sites have fallen. Since deposition data for the same areas do not show comparable increases over the first half of the monitoring period (Chapter 2), it seems probable that the observed surface water xSO_4 cyclicity may have been driven by marine ion cycles, and resulting adsorption/desorption. Effectively the ratio between Cl and marine SO_4 in runoff fluctuates as the latter adsorbs and desorbs from

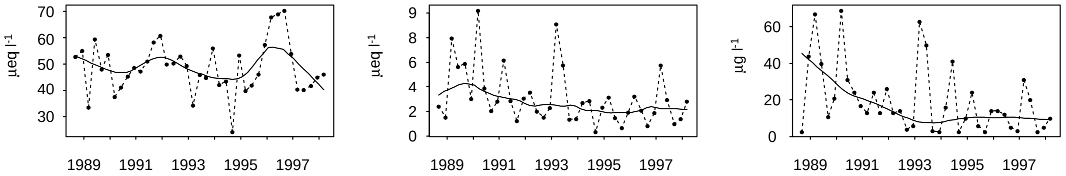
Figure 5.8

Cl and correlated non-marine determinands, Loch Chon


(a) Chloride

(b) Non-marine Sodium

(c) Non-marine Magnesium

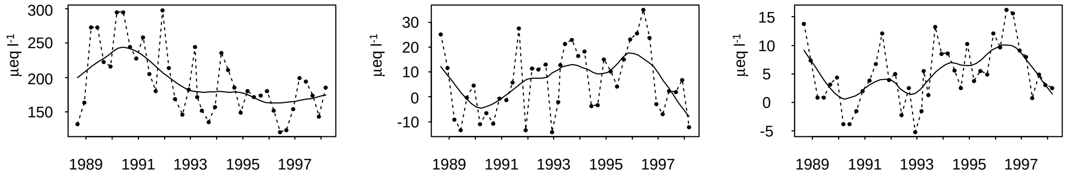

(d) Non-marine Sulphate

(e) Hydrogen Ion

(f) Labile Aluminium

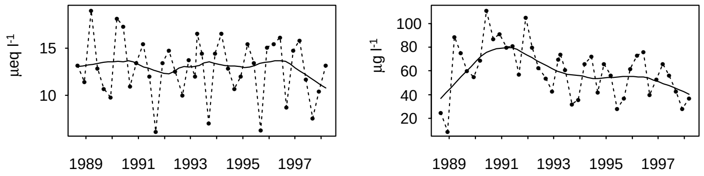
Figure 5.9

Cl and correlated non-marine determinands, Round Loch of Glenhead


(a) Chloride

(b) Non-marine Sodium

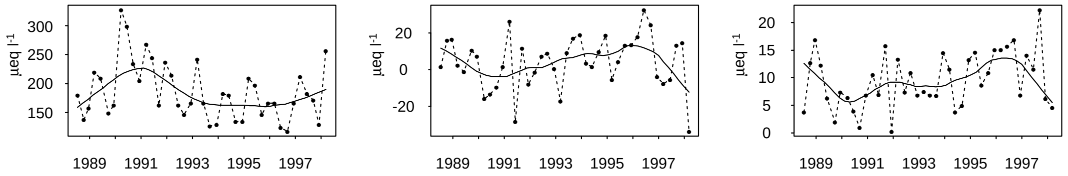
(c) Non-marine Magnesium


(d) Hydrogen Ion

(e) Labile Aluminium

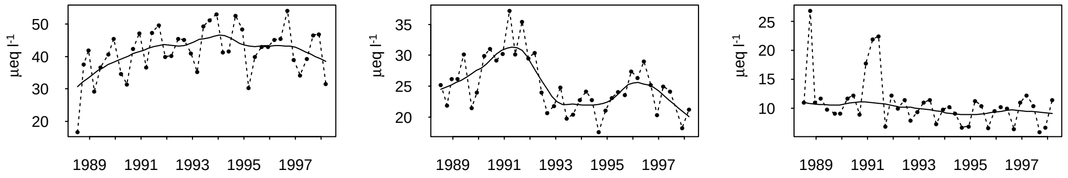
Figure 5.10

Cl and correlated non-marine determinands, Scoat Tarn


(a) Chloride

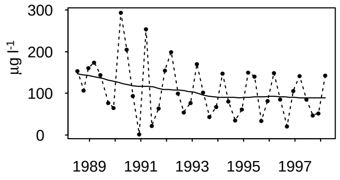
(b) Non-marine Sodium

(c) Non-marine Magnesium


(d) Non-marine Sulphate

(e) Non-marine Calcium

(f) Hydrogen Ion


(g) Labile Aluminium

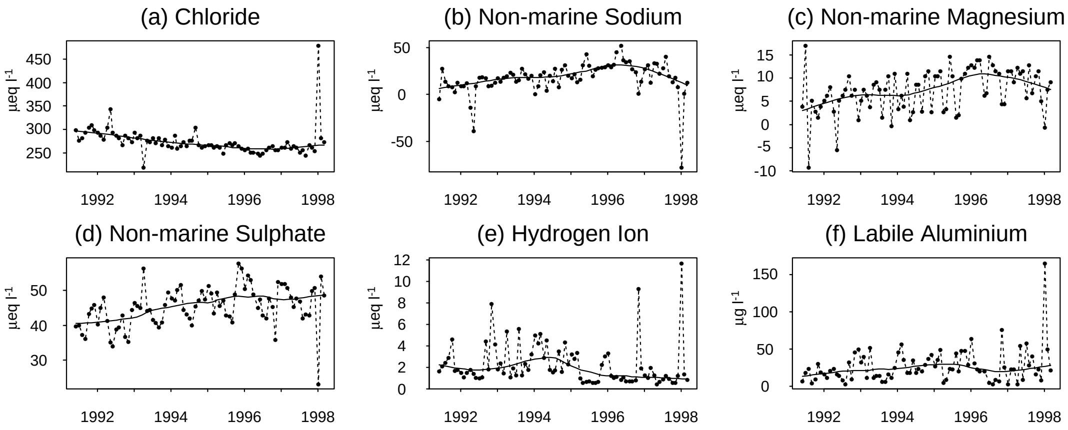


Figure 5.11

Cl and correlated non-marine determinands, Narrator Brook

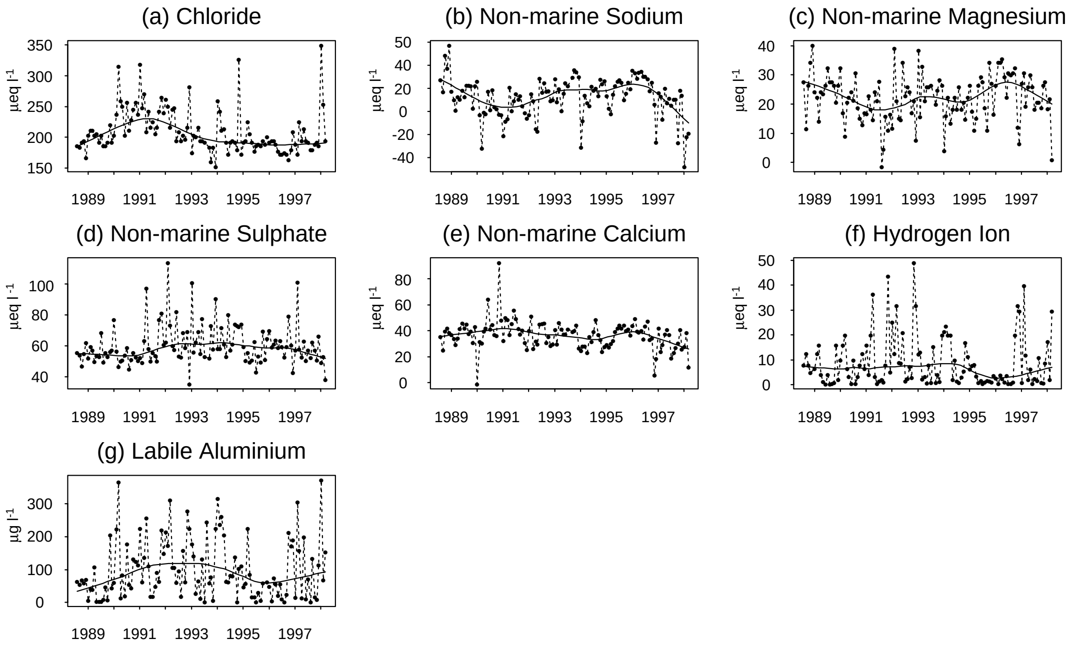


Figure 5.12

Cl and correlated non-marine determinands, Afon Hafren

the soil, leading to an error in the calculation of xSO_4 based on fixed sea-salt ratios (Figure 5.7).

Observations of the UKAWMN dataset suggest, then, that a large number of sites experience long term cyclicity in marine ion deposition, and consequently in surface water levels of chloride, base cations, sulphate, labile Al and acidity. Since this cyclicity appears to operate, in many cases, over a timescale at least as great as the ten years over which monitoring has been carried out, there are two major implications for trend detection.

First, there is the likelihood of identifying spurious trends using monotonic trend detection techniques. Robson & Neal (1996) gave an example in which seasonally varying data superimposed on a single sinusoidal cycle were mis-indentified as a significant trend using SKT. This problem has to a large degree been overcome in the present study through the use of LOESS curves to visually identify cyclicity in time series. However, the frequency with which both SKT and regression detected significant trends in Cl, Na, Mg and Ca, as noted in individual site descriptions, illustrate the need for caution in this respect. Apparent increases in pH and alkalinity at a number of sites were also linked to marine ion cycles rather than long term site recovery.

The second problem for trend analysis is that genuine, anthropogenically driven changes may be obscured by climatically driven fluctuations in marine ion deposition. In effect these can be considered sources of ‘noise’, along with flow and seasonally-related variations, but due to their duration climatic cycles are less easy to isolate without a longer dataset than that currently available. Although relatively few sites in the UKAWMN have exhibited clear xSO_4 decreases or pH/alkalinity increases, it is thought that underlying improvements may have been obscured by climatic factors, and that these may become apparent after further monitoring.

5.3.5 The North Atlantic Oscillation as a controlling mechanism

The North Atlantic Oscillation (NAO) has recently been recognised as an important influence on European climate (e.g. Hurrell, 1995; Rodwell *et al*., 1999). North Atlantic weather systems are dominated by two ‘centres of action’, the Iceland Low and the Azores High, and the NAO Index (NAOI) is quantified as the difference in surface pressure between these two locations. Pressure gradients and inter-annual variability tend to be greatest during winter, leading to the most pronounced weather variations at this time. For the UK, winters characterised by high values for the NAOI, i.e., large pressure gradients, are associated with relatively warm, wet weather, dominated by strong southwesterly or westerly air flows. Occasional negative values represent a reversal of pressure systems, where blocking highs over Scandinavia or the northeastern Atlantic lead to colder winters dominated by northeasterly winds. Storms, and hence sea-salt deposition, tend to be most frequent during high NAO conditions. Conversely, low or negative NAO winters are associated with dry, cold conditions, and low sea-salt deposition. Unusually high winter NAOI values were recorded during the late 1980s and early 1990s, coinciding with the peak in surface water Cl concentrations at the majority of UKAWMN sites. Lower NAOI values in more recent years have coincided with lower observed Cl concentrations, and overall there appears to be a strong correlation between NAOI and Cl (Figure 5.13). The second Cl peak in northern Scotland during 1993 coincided with a brief period of high NAOI, but Lamb Weather Indices (Davies *et al*., 1991) obtained from the Climatic Research Unit, University of East Anglia, show that this was associated primarily with westerly rather than southwesterly airflows. Sites further south on the UK mainland are thought to be partly sheltered from westerly storms by Ireland, and thus did not receive major sea-salt inputs at this time. This interpretation is supported by Cl peaks at the two coastal Northern Ireland sites, Beagh’s Burn and Coneyglen Burn concurrent with those in northern Scotland (Figures 4.19.2f, 4.22.2f).

In recent decades the NAO has shown approximately decadal cyclicity. Although it appears that only one major NAO ‘cycle’ has occurred during the ten years of UKAWMN monitoring, an earlier high NAOI period was

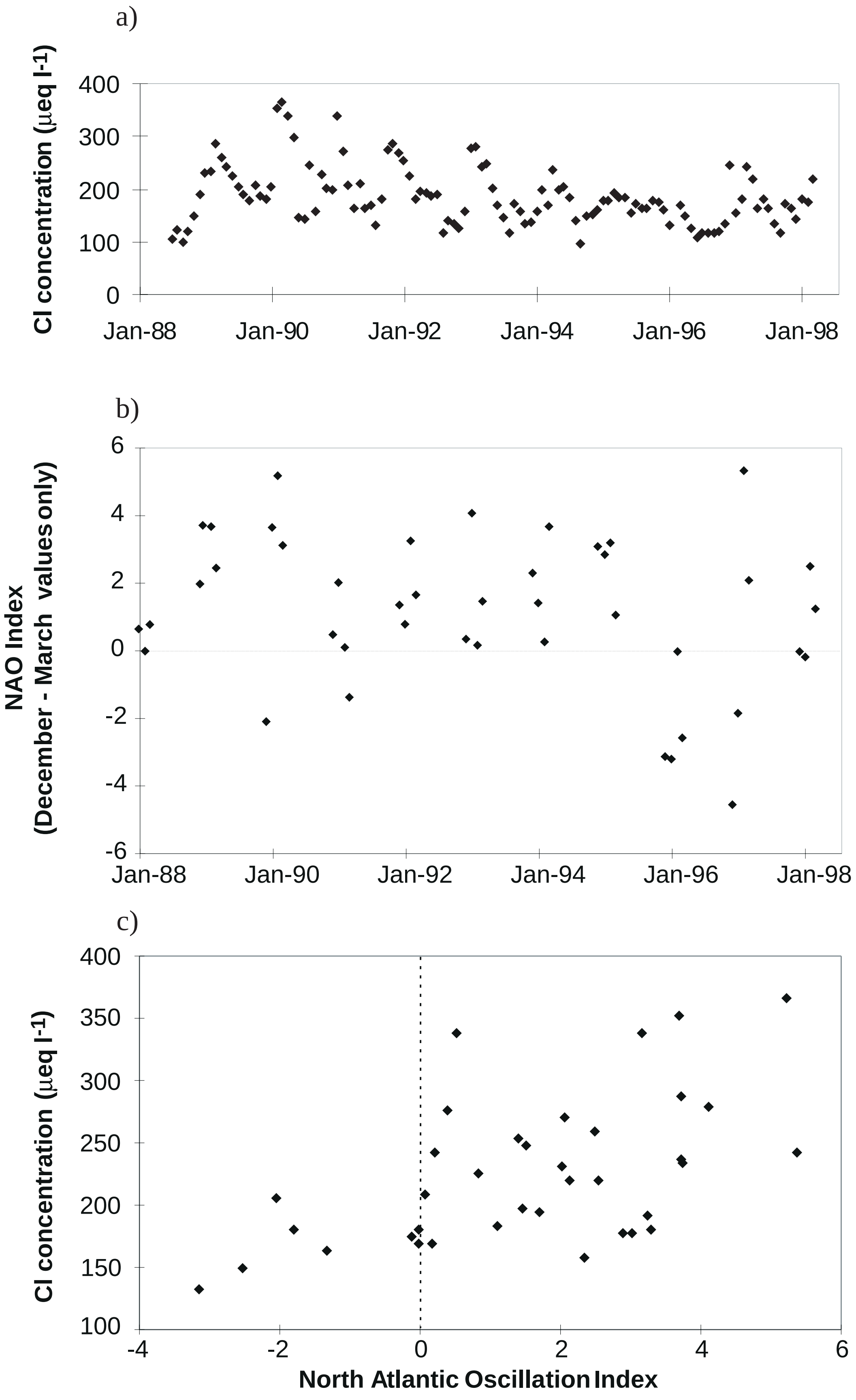


Figure 5.13

a) Chloride concentration time series for Dargall Lane (1988 - 1998) b)Monthly North Atlantic Oscillation Index (NAOI) (December - March only) (1988 - 1998) c) Scatter plot of temporal relationship between Cl concentration at Dargall Lane and NAOI for the previous month. Data are for winter NAOI only (i.e. December - March)

recorded during 1983-1984. In Chapter 6, data are presented for five sites in Scotland and Wales where monitoring extends back to this period, and it appears that this NAOI peak was again accompanied by high Cl concentrations. These data also support an inverse relationship between xSO_4 and Cl over a longer time period.

5.3.6 Summary

Long term cyclicity in a wide range of surface water determinands has been observed at many of the UKAWMN sites, and can be linked to inter-annual variations in sea-salt deposition. It is thought that this variability in deposition is the result of natural climatic fluctuations, probably driven by the North Atlantic Oscillation. Changes in marine ion inputs affect surface water chemistry through the sea-salt effect, whereby marine-derived Na and Mg displace non-marine H+, labile Al and Ca from the soil. In most instances this leads to the transient acidification of runoff, although the relative extent to which individual non-marine cations are displaced appears to vary depending on catchment soil properties. There is also evidence to suggest that adsorbtion of SO_4 is enhanced during periods when sea-salt inputs are high, while desorbtion occurs when inputs are low. This transient soil retention and release of SO_4, in response to climatic variations, has not previously been recognised as an influence on surface water chemistry. The major impacts appear to be that; (a) acid anion concentrations are reduced during high Cl periods, partially offsetting acidification caused by cation exchange processes; and (b) the ratio between marine SO_4 and Cl in runoff varies in time, generating an error in the calculation of non-marine SO_4 based on fixed sea-salt ratios.

Although the sea-salt effect has previously been thought of as an episodic process, the long term cyclicity observed in the UKAWMN data suggest that effects may be sustained over prolonged periods in the UK. The presence of climatically driven cyclicity in determinands such as pH and xSO_4 has important implications for trend detection in coastal regions of the UK and elsewhere, indicating that monitoring periods in excess of ten years are required in order to clearly identify the effects of anthropogenic emission changes on acid-sensitive surface waters.

■ 5.4 Climatic Influences on Nitrate Variations

Spatially, mean NO_3 concentrations in UKAWMN freshwaters show a positive relationship with N deposition (see Section

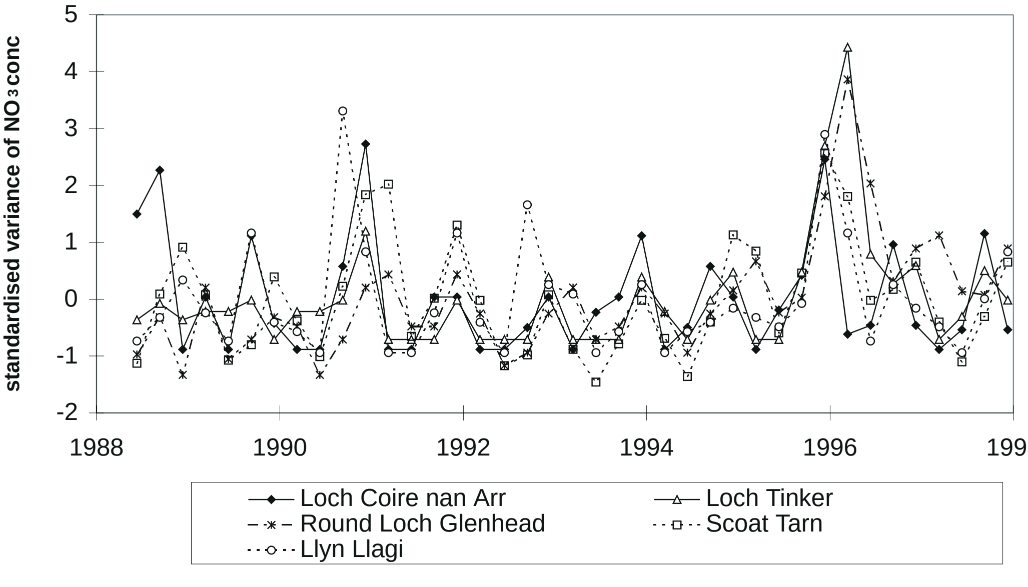


Figure 5.14
Variance in NO_3 concentration (standardised by the site mean) for 5 UKAWMN lakes (1988 -1998)

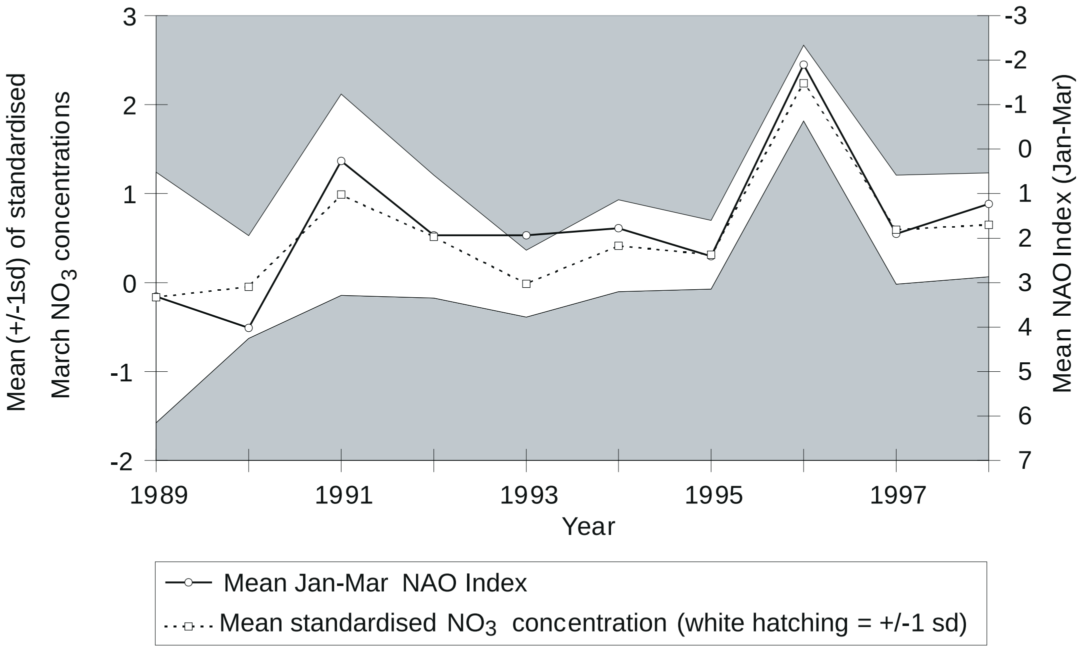


Figure 5.15

The relationship between the mean of standardised March NO_3 concentrations for 9 UKAWMN lakes (+/- 1 standard deviation), and the mean January-March NAO Index, 1989-1998

From: Monteith *et al.* (in press). © John Wiley & Sons Ltd.

5.1.2). However, over the past decade, temporal variation in NO_3 concentration, often strongly correlated between sites, shows little relationship with temporal patterns in N deposition. NO_3 concentrations usually peak in the spring, and since lakes are only sampled quarterly, March samples from lakes tend to represent the annual maximum. Figure 5.14 demonstrates that for most lake sites, NO_3 concentrations were relatively high in the March samples of 1991 and 1996. NO_3 peaks at monthly sampled stream sites usually occur between December and March and again, for several sites, these peaks are relatively elevated in the springs of 1991 and 1996 (Figure 5.2).

Interannual variation in NO_3 concentration has been observed in a number of studies in recent years. Several climatic parameters have been proposed to explain this phenomenon, including summer drought (Reynolds *et al*., 1992), summer temperature (Murdoch *et al.*, 1998) and winter freeze thaw (Mitchell *et al.*, 1996). Given the strong correlation between the NO_3 time series of most UKAWMN lakes, Monteith *et al*. (in press) adopted a meta-analysis approach (ie. reducing NO_3 time series for a group of sites to a single variable) to explore possible relationships between NO_3 concentration and climatic variables. Rainfall time series were rejected as potential explanatory variables, since temporal variation in precipitation has been highly variable across the UK over the past decade. Analysis therefore focused on mean monthly air temperature, taken from the Central England Temperature Record (CET) (Hulme, 1999), which is highly correlated with air temperature records for sites across the UK, and the North Atlantic Oscillation Index (NAOI) (see section 5.3.5) which is increasingly being shown to represent variations in UK climate at the regional scale.

Similarity between UKAWMN lakes in NO_3 time series is demonstrated in Figure 5.14 which compares lake concentrations standardised by the site mean. Atypically, the seasonal NO_3 leaching pattern at Lochnagar changed abruptly in 1993 (section 4.4) and this site was removed from further analysis as a statistical outlier. Blue Lough was also removed due to the relatively short time series available. The mean of the standardised variance of March NO_3 concentration for the remaining nine lake sites was strongly and inversely correlated with the mean January to March NAOI (linear regression: $r^2 = 0.90$ $P < 0.0001$; Spearman Rank correlation: $r^2 = 0.85$ $p<0.001$)(Figure 5.15). The latter correlation demonstrates that this relationship is not simply driven by a chance coincidence of extreme values for concentration and NAOI in two years (1991 and 1996). Winter temperature has been shown to be closely related to winter values for the NAO (Hurrel, 1995) and this relationship appears to link high NO_3 leaching with cold winters. Indeed, mean standardised March NO_3 is also significantly and inversely correlated with mean January to March CET (linear regression: $r^2 = 0.61$ $p<0.01$) and mean December to March CET (linear regression: $r^2 = 0.67$ $p<0.01$).

Similar relationships hold for UKAWMN stream sites although, given the greater between-site temporal variability in NO_3 concentration, a meta-analysis approach was deemed inappropriate. NO_3 time series for monthly sampled stream sites demonstrate how the timing of peak concentration varies between years. For several stream sites the strongest relationships with climatic variables were found between the annual peak NO_3 and mean December to March NAOI.

As an independent test of the NO_3:NAO relationship the authors also analysed the eighteen year record available for the Afon Gwy, which has been monitored as part of the Plynlimon experiment (Reynolds *et al.*, 1997). Again, the relationship between peak winter NO_3 and mean December to March NAOI was highly significant. Although the relationship appears to reflect an effect of low winter temperatures on high NO_3 leaching, the mechanism is as yet unclear. The correlation between on-site measured air temperature and NO_3 concentration in the longer Afon Gwy dataset is relatively weak. However a strong relationship was found between the number of days with grass minimum temperature <=-4° c and peak winter NO_3 concentration. It is possible that for the Gwy catchment, this temperature is associated with a critical threshold for freezing in the upper soil horizons, which could have a biocidal effect on soil microbial biomass, and cause damage to plant roots and changes in soil organic matter. Thawing in spring could then make the resulting lysis products available for mineralisation, while low temperatures and frost damage to plants might restrict terrestrial uptake, hence maximising potential leaching into freshwaters.

Further work is necessary to elucidate the precise nature of the link between NO_3 concentrations and the NAO. However, it would appear that NO_3 leaching from these systems is strongly influenced by a regional to global scale climatic process, and this has to be carefully considered when assessing temporal trends and their likely causes.

■ 5.5 Influence of Forestry on surface water chemistry

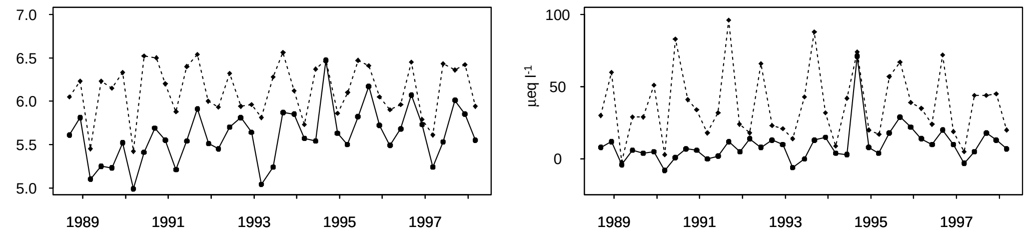
The UKAWMN contains three sets of ‘paired’ forest and moorland catchments. These are Loch Chon and Loch Tinker in the Trossachs (3 km apart), Loch Grannoch and Round Loch of Glenhead in Galloway (14 km), and the Afon Hafren and Afon Gwy in Mid Wales (3 km). Table 5.6 summarises catchment characteristics, and shows that geology and soils are largely similar for each pair. Differences do exist in the lake and catchment sizes of the two Scottish pairs, and in the altitude of the Trossachs pair, which may cause differences in surface water chemistry that are unrelated to forestry. Nevertheless all three pairs are felt to be sufficiently similar that a general assessment of forest impacts on runoff chemistry can be undertaken.

5.5.1 Loch Chon and Loch Tinker

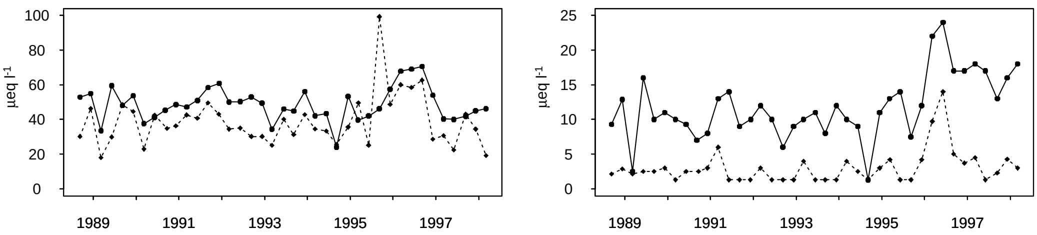
The two Trossachs lochs drain adjacent catchments, with the same underlying geology. However Loch Chon is at lower altitude, has a larger catchment and lake area, and soils have a higher mineral content than at Loch Tinker. Mean chemistry data (Table 5.7) and time series (Figure 5.16) show substantial differences between the two lochs; Loch Chon is consistently more acidic, with higher acid anion and aluminium levels. Ca concentrations are similar, suggesting that differences in catchment base cation supply are not important, although higher DOC levels at Loch Tinker reflect the dominance of organic soils in this catchment. The higher xSO_4, NO_3 and Cl concentrations at Loch Chon are thought to result from enhanced dry and

Figure 5.16

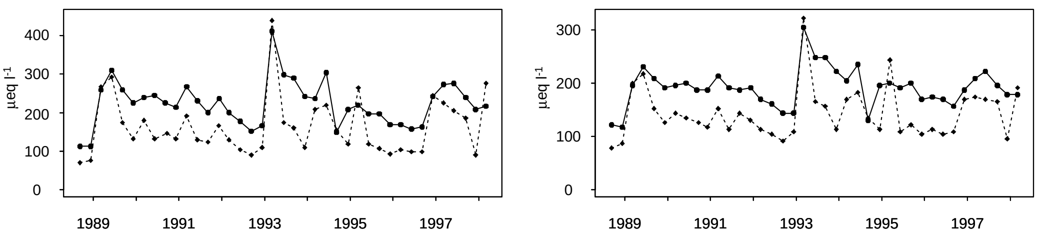
Water chemistry time series for the forested : moorland pair, Loch Chon and Loch Tinker


(a) pH

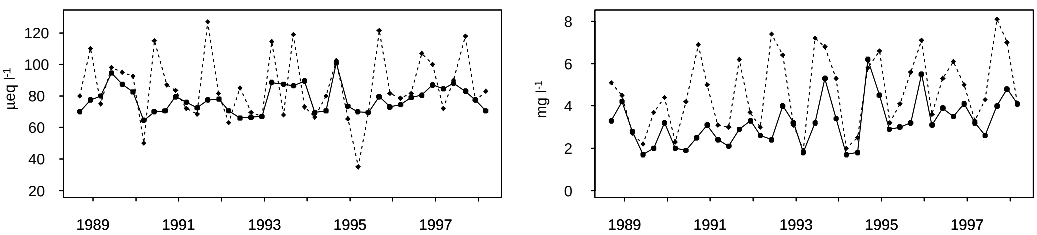
(b) Alkalinity


(c) Non-marine Sulphate

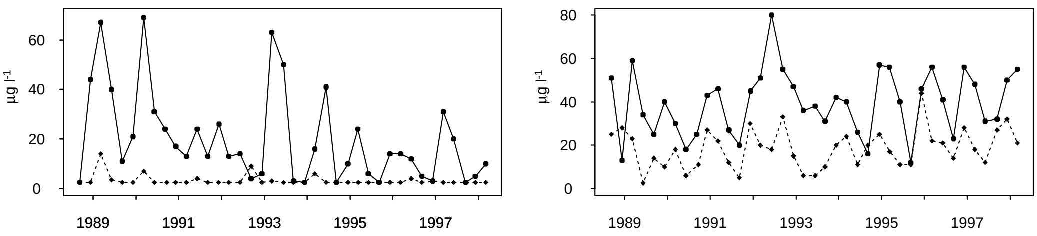
(d) Nitrate


(e) Chloride

(f) Sodium


(g) Calcium

(h) Dissolved Organic Carbon


(i) Labile Aluminium

(j) Non-labile Aluminium

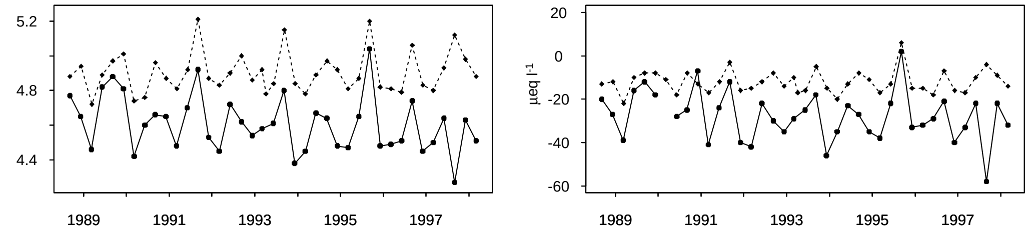
Solid line represents Loch Chon (forested), dashed line Loch Tinker (moorland)

Figure 5.17

Water chemistry time series for the forested : moorland pair, Loch Grannoch and Round Loch of Glenhead

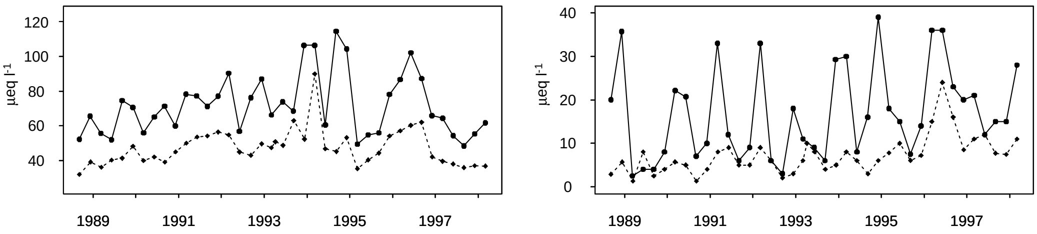
(a) pH

(b) Alkalinity



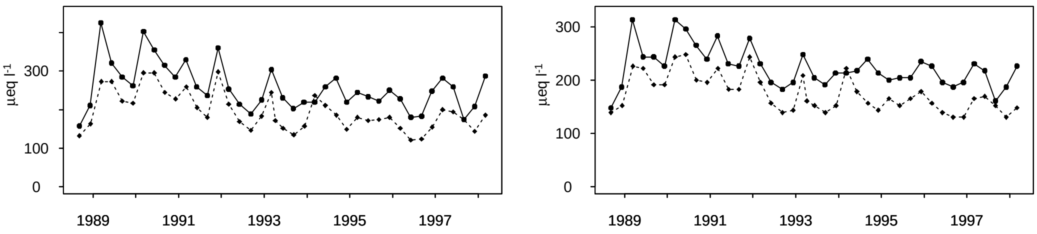
(c) Non-marine Sulphate

(d) Nitrate



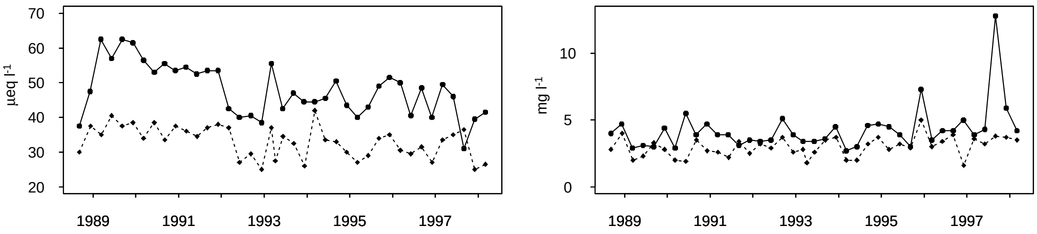
(e) Chloride

(f) Sodium



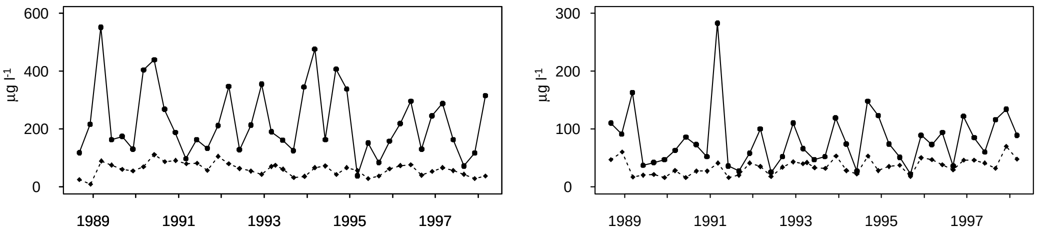
(g) Calcium

(h) Dissolved Organic Carbon



(i) Labile Aluminium

(j) Non-labile Aluminium



Solid line represents Loch Grannoch (forested), dashed line Round Loch of Glenhead (moorland)

Table 5.6

Characteristics of paired forested and moorland catchments

Site	Forest (%)	Geology	Soils	Min. Altitude (m)	Catchment Area (ha)	lake Area (ha)
Loch Chon	*44%*	*Mica schists and grits*	*Peaty gleys, peaty podzols*	*100*	*1570*	*100*
Loch Tinker	*0%*	*Mica schists and grits*	*Peat*	*420*	*112*	*11*
Loch Grannoch	*70%*	*Granite*	*Peat, peaty podzols, peaty gleys*	*210*	*1287*	*114*
Round Loch	*0%*	*Tonalite, granite*	*Peat, peaty podzols*	*295*	*95*	*13*
Afon Hafren	*50%*	*L. Paleozoic sedimentary*	*Peat, stagnopodzols*	*355*	*358*	*-*
Afon Gwy	*0%*	*L. Paleozoic sedimentary*	*Peat, stagnopodzols*	*440*	*210*	*-*

occult deposition of marine and pollutant ions to the forest canopy (Mayer & Ullrich, 1977). Mean NO_3 concentrations in particular are a factor of four times higher than at Loch Tinker, where the majority of samples are below detection limits (Figure 5.16d). NO_3 at Loch Chon only fell below detection limits once during the monitoring period, suggesting that afforestation has caused increased N leaching at this catchment. The combined impact of elevated xSO_4 and NO_3 at Loch Chon has been to cause significant additional acidification, with estimated reductions of 0.5 pH units and 14 µeq l^{-1} of alkalinity (Table 5.7), and a major associated increase in levels of labile Al. These conclusions are supported by a palaeolimnological study by Kreiser *et al.* (1990), which suggests that pH values dropped rapidly at Loch Chon following catchment afforestation in the 1950s, whilst pH at Loch Tinker remained relatively constant over the same period.

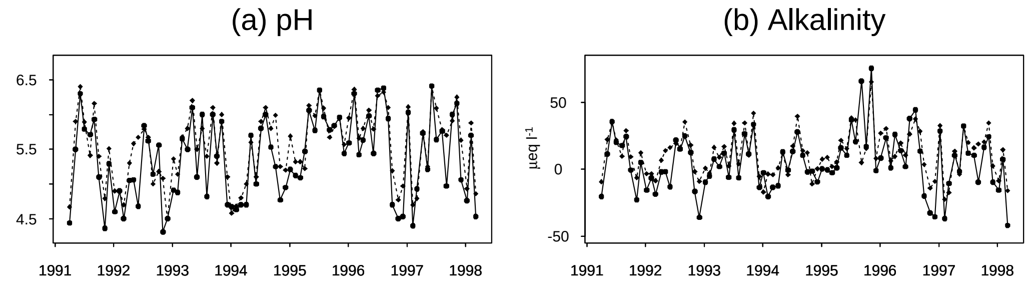
5.5.2 Loch Grannoch and Round Loch of Glenhead

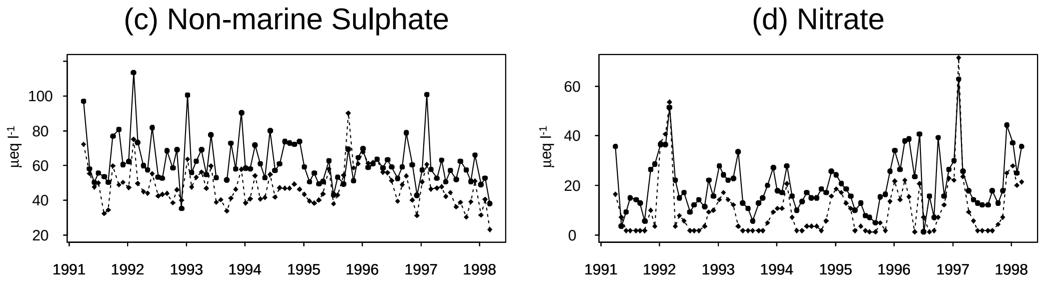
The Galloway lochs are generally comparable in terms of geology, soils and altitude, although Loch Grannoch has a larger lake and catchment area than Round Loch. Chemical differences between the two sites are very similar to those between Lochs Chon and Tinker, with xSO_4, NO_3 and Cl all higher at the forested Loch Grannoch (Table 5.7). Time series (Figure 5.17) indicate that higher xSO_4 and Cl levels are sustained throughout the year, whereas NO_3 concentrations are very similar to those at Round Loch during summer but rise to much higher peaks during winter. This suggests that elevated N inputs to Loch Grannoch are largely retained during the growing season, but washed out during the dormant season. Although both lochs are acidic, the higher pollutant anion concentrations at the forested site have led to consistently lower pH and alkalinity, and much higher labile Al. Higher Ca and Mg at Loch Grannoch may be due to displacement from the soil by incoming H^+, or simply to a greater weathering supply in this catchment.

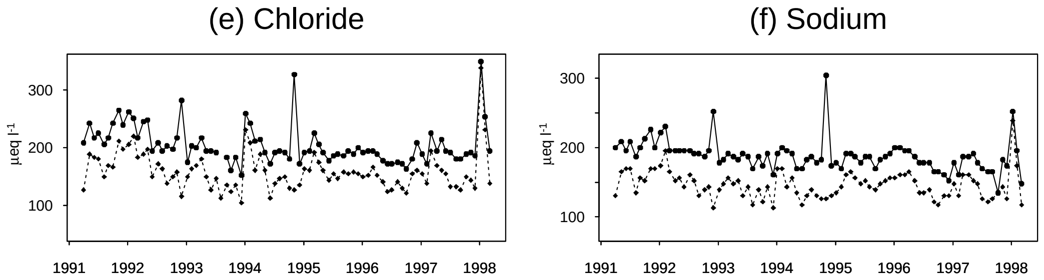
A notable feature of time series data for the Galloway lochs is that, whereas the Round Loch may have shown a slight improvement in pH over the monitoring period, Loch Grannoch appears to have acidified further since 1988.

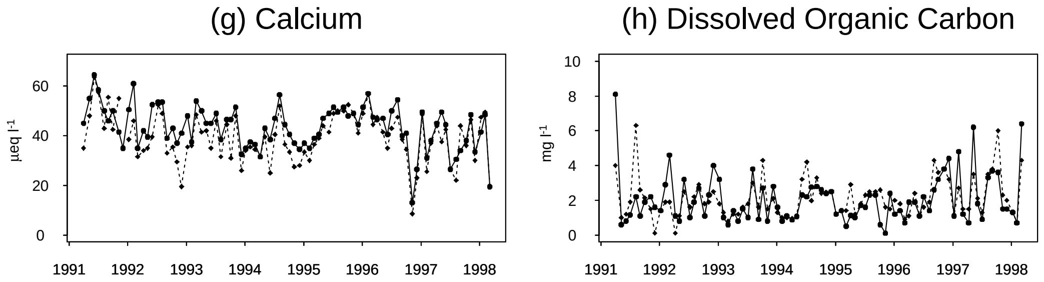
Figure 5.19

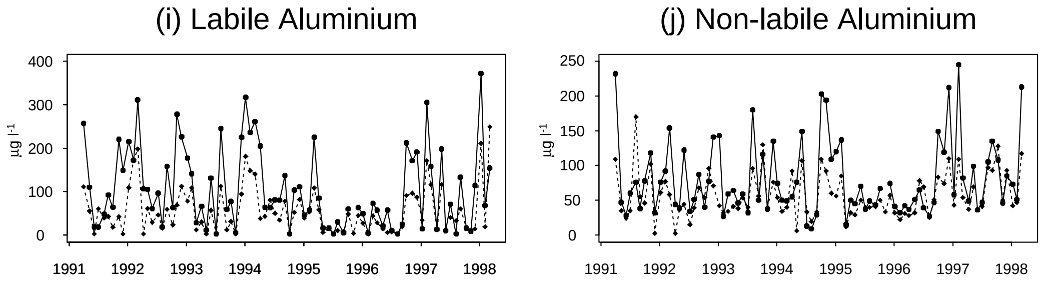
Water chemistry time series for the forested : moorland pair, Afon Hafren and Afon Gwy











Solid line represents Afon Hafren (forested), dashed line Afon Gwy (moorland)

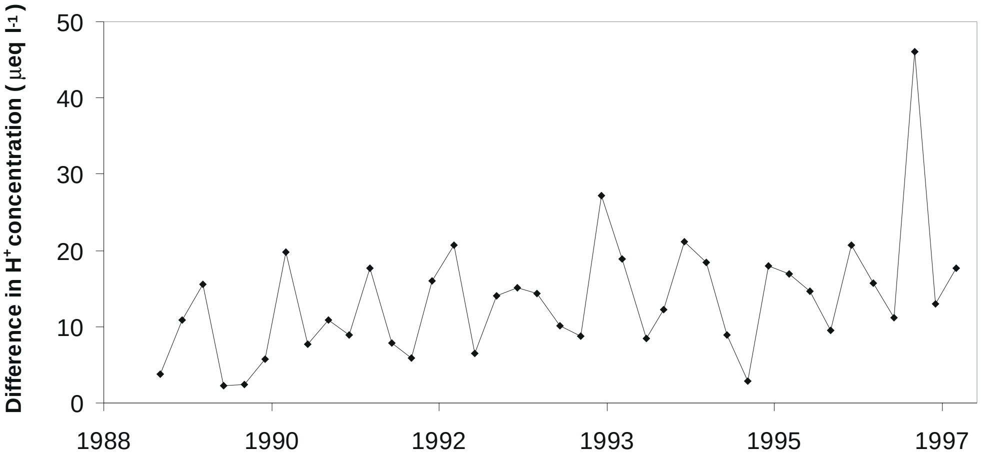


Figure 5.18

Temporal difference between H^+ concentration of Loch Grannoch and Round Loch of Glenhead (1988-1998)

Neither trend was significant in the original trend analysis, but a Seasonal Kendall analysis of the difference in H^+ concentrations between sites shows a highly significant increase, of around 0.8 μeq l^{-1} H^+ per year (Figure 5.18). This supports the earlier suggestion that forestry at Loch Grannoch is causing a continued deterioration in water quality.

5.5.3 Afon Hafren and Afon Gwy

The Hafren and Gwy catchments are very similar in all respects other than land-use, and are therefore well suited to an assessment of forestry impacts. As in the Scottish catchment pairs, concentrations of xSO_4, NO_3 and Cl are higher at the forested Hafren (Table 5.7, Figure 5.19). Differences in NO_3 time series are particularly striking, since concentrations at the Gwy consistently fall below detection limits during summer, whereas those at the Hafren remain continuously elevated (Figure 5.19d). These patterns conform to Stage 1 and Stage 2 N saturation respectively as defined by Stoddard (1994) (Section 5.1.2). Since there are no other major differences between sites, it is probable that the more advanced N saturation stage at the Hafren can be attributed to the effects of afforestation. As would be expected given the higher xSO_4 and NO_3 levels, the Hafren is more acidic, with lower pH and higher labile Al concentrations. However differences between streams, particularly for alkalinity, are less pronounced than in the Galloway or Trossachs lochs. Results for the two Plynlimon streams are consistent with those of a previous study including the Gwy and Hafren by Reynolds *et al.* (1986), which showed that Na, Cl, SO_4, NO_3, Al and H^+ output fluxes were enhanced by forestry.

5.5.4 Summary

The three sets of closely located forest and moorland catchments in the UKAWMN suggest a consistent pattern of water chemistry response to afforestation. In each case, the forested site exhibits higher concentrations of xSO_4, NO_3 and marine ions, lower pH and alkalinity, and higher labile Al. Afforestation has previously been cited as a cause of increased acidification in a range of studies (e.g. Nilsson *et al.*, 1982; Stoner and Gee, 1985; Jenkins *et al.*, 1990), with the main mechanisms thought to be enhanced dry and occult deposition to the forest canopy (Mayer & Ullrich, 1977); base cation uptake from the soil by the growing forest (Miller, 1981); and decreased water yield concentrating pollutants in surface waters (Neal *et al.*, 1986). The importance of uptake appears to be low at the UKAWMN sites, since non-marine base cation concentrations are generally at least as high at forested as at moorland catchments. However, forests in the UKAWMN catchments are generally at or close to maturity and it is probable that uptake was more important in the past. NO_3 uptake is also likely to have been higher in the past when biological requirements were greater (Emmett *et al.*, 1993).

Table 5.7

Mean values of major chemical determinands for paired forested and moorland catchments

SITE	Alkalinity	pH	xSO_4	NO_3	Cl	Ca	Mg	Na	Al_{lab}	Non-labile Al	DOC
Loch Chon (F)	*4.8*	*5.6*	*49*	*12*	*223*	*78*	*51*	*191*	*20*	*40*	*3.2*
Loch Tinker (M)	*18.8*	*6.1*	*39*	*3*	*163*	*85*	*48*	*143*	*3*	*18*	*4.7*
Loch Grannoch(F)	*-13.9*	*4.6*	*72*	*17*	*257*	*48*	*54*	*223*	*225*	*81*	*4.3*
Round Loch (M)	*-6.1*	*4.9*	*47*	*7*	*195*	*33*	*46*	*174*	*60*	*35*	*3.0*
Afon Hafren (F)*	*5.5*	*5.4*	*62*	*21*	*205*	*44*	*65*	*188*	*105*	*80*	*2.0*
Afon Gwy (M)	*5.9*	*5.6*	*48*	*11*	*159*	*40*	*54*	*146*	*56*	*57*	*2.1*

** Means for Afon Hafren based on April 1991 to March 1998 data, corresponding to shorter record at Afon Gwy. (F) = forested; (M) = moorland. All variables in μeq l^{-1} except pH, Al (μg l^{-1}) and DOC (mg l^{-1}).*

Table 5.7 demonstrates that mean xSO_4 concentrations are 26%, 53% and 29% greater at Loch Chon, Loch Grannoch and the Afon Hafren respectively, than their moorland pairs. The equivalent increases in Cl are 37%, 32% and 29%, whilst NO_3 is increased by a factor of between two and four. The disproportionately large increases in NO_3 suggest that enhanced N inputs have increased the degree of N saturation in forested soils, and this is supported by seasonal NO_3 patterns at forested sites characteristic of more advanced saturation stages. It should be noted that since none of the three forested catchments has been planted over more than 70% of its area, an entirely forested catchment would be expected to show even larger increases in acid anion concentrations, and hence greater acidification.

■ 5.6 Summary

- Spatial variations in water chemistry appear generally consistent with deposition; concentrations of xSO_4 are lowest at relatively unimpacted northwestern sites, and highest in more polluted southern and eastern areas. NO_3 variations are similar, ranging from near-zero concentrations at low impacted sites to substantial leaching at some higher deposition sites, indicative of advanced stages of nitrogen saturation.

- Relationships between deposition and surface water chemistry are complicated by a range of catchment-specific factors. A comparison of paired moorland and forest catchments supports the conclusion that afforestation causes increased SO_4 and NO_3 concentrations in runoff, and hence greater acidity. Catchment altitude also appears to be an important influence on N leaching, whilst variation in geological buffering capacity further complicates spatial patterns in pH and alkalinity.

- Temporal trend analysis suggests limited chemical recovery at UKAWMN sites during the last decade. Decreases in xSO_4 were restricted to the River Etherow, Lochnagar and Old Lodge, all in central/eastern locations with relatively high dry deposition inputs. The lack of downward trends elsewhere may result from; (a) smaller S deposition reductions in areas dominated by wet deposition; (b) high short term variability masking relatively small expected decreases; (c) inter-annual xSO_4 fluctuations linked to climate, specifically variations in sea-salt inputs; and (d) possible desorption of sulphur stored in catchment soils. Since the mid-1990s, xSO_4 appears to have declined at a larger number of sites, which may indicate the start of more widespread recovery.

- In accordance with the lack of widespread xSO_4 reductions, few sites exhibit clear recovery in pH and alkalinity. At the three sites with declining xSO_4, NO_3 has increased, and at the Etherow and Old Lodge base cations have decreased. In addition, organic acidity (i.e. DOC) has increased at all three sites. These changes appear so far to have offset any positive impact of xSO_4 reductions. At Lochnagar, NO_3 increases have been sufficient to cause continued loch acidification. At all sites, it appears that chemical recovery will require substantial further reductions in S and N deposition.

- Significant increases in pH and alkalinity were observed at six and four sites respectively, but in the absence of downward trends in acid anion concentrations it is not possible to confidently attribute these changes to deposition reductions at this stage.

- Increases in NO_3 at Lochnagar, Round Loch of Glenhead, Loch Chon and the River Etherow suggest increasing N saturation at these catchments. However, direct links between N deposition and runoff at many sites may be masked by natural episodicity, seasonality and climatically-driven inter-annual cyclicity. It is believed that spring NO_3 maxima in surface waters may be inversely related to winter temperature, with variations driven by the North Atlantic Oscillation.

- Major increases in DOC concentrations have been observed at many sites; significant rising trends have been identified at 19 of the 22 UKAWMN sites, with concentrations at six sites having doubled or more during the last decade. These trends are of particular importance to the UKAWMN, since increases in organic acidity could reduce or even negate any increases in pH or alkalinity resulting from reductions in mineral acidity. At present the cause of these increases cannot be identified with confidence, although one proposed mechanism is the increased microbial decomposition of soil organic matter due to increasing summer temperatures. This mechanism would, under a scenario of increasing global temperatures, be expected to lead to further increases in DOC and colour levels in upland waters. The biological impacts of these changes are likely to be varied, including reduced light penetration due to increased water colour, and reduced fish toxicity under acidic conditions due to organic complexation of aluminium.

- Inter-annual cyclicity in sea-salt deposition appears to be a major cause of chemical variation in the UKAWMN dataset. The majority of sites are close to western or southern coasts, and receive large sea-salt inputs during westerly or southwesterly frontal storms. The frequency of these storms has been shown to vary substantially from year to year, with maxima associated with high winter values of the North Atlantic Oscillation Index. Marine ion concentrations at near-coastal sites have therefore shown highly consistent cyclical variations, with a major peak during the high NAOI 1989-1991 period. Cation exchange processes (the ‘sea-salt’ effect) have led to associated cyclical variations in non-marine cations, including H^+ and labile Al, generating more acidic conditions in high sea-salt years. Periods with high NAO Index are also associated with high rainfall, and this will also increase acidity through cation dilution. It is suggested that a parallel process of marine SO_4 adsorption and desorption may operate, leading to cyclical fluctuations in calculated xSO_4 that are unrelated to variations in pollutant S deposition.

- Climatically-driven cyclicity in important chemical variables, such as xSO_4, NO_3, and pH, has important implications for trend detection. Cyclical variations may either mask underlying, anthropogenically-driven trends, or generate spurious trends. The approximately decadal timescales over which these variations appear to operate imply that monitoring will need to operate over long periods in order to adequately assess the impact of anthropogenic factors on surface water quality.

6

Comparison to Longer Term Datasets

Chris Evans,
Ron Harriman &
Brian Reynolds

Prior to the creation of the UKAWMN in 1988, few upland surface waters in the UK were regularly monitored. However a limited number of good quality datasets, some going back to the late 1970s, do exist for several areas of Scotland and Wales. Some of these sites were subsequently incorporated within the UKAWMN, while others continue to be monitored independently. Together, they provide an invaluable resource both for critically assessing the intrepretation of the UKAWMN data in the preceding chapter, and for placing the chemical changes observed in this ten year dataset into a longer term context. In the following sections, data are presented for five representative sites in central and southwestern Scotland, and in mid-Wales. Analysis of this data has been limited to visual interpretation, and should therefore be considered as a preliminary assessment.

Data for seven determinands (pH, SO_4, xSO_4, NO_3, Cl, Na and Ca) are shown for all sites (Figures 6.3, 6.4 & 6.5), whilst either DOC or a comparable measure (total organic carbon, TOC, or absorbance) are shown depending on data availability. Methods of alkalinity measurement do not appear to have been consistent between sites, and are not included.

6.1 Caorainn Achaidh Burn

The Caorainn Achaidh Burn (Loch Ard: Burn 2) has been monitored since 1979 by the Freshwater Fisheries laboratory (FFl), Pitlochry, as part of the Loch Ard group of streams (Harriman & Morrison, 1982; Harriman *et al*., 1995a). The steep 5 km^2 catchment drains the northern slopes of Ben Lomond in central Scotland, and the sampling point is approximately 3 km west of the Loch Chon UKAWMN site. Land-use is predominantly unimproved moorland, with a small area of deciduous woodland in the lower valley. The stream was sampled once or twice per month prior to 1986, although there were two substantial unsampled periods from January 1982 to March 1983, and from May 1984 to October 1985. From 1986 to the present, samples have been collected on a weekly basis.

The most striking feature of time series for the Caorainn Achaidh Burn (Figure 6.1) is a marked decline in sulphate concentrations, which is consistent with the declining trend reported by Harriman *et al.* (1995a). Between 1979-1982, mean xSO_4 was 115 $\mu eq\ l^{-1}$, but by 1996-1998 this had more than halved, to 53 $\mu eq\ l^{-1}$. Virtually all the decline took place prior to 1989, since when concentrations have remained relatively constant. These patterns of variation are consistent with the near-constant xSO_4 levels observed from 1988-1998 at the nearby Lochs Chon and Tinker, but suggest that large xSO_4 reductions may well have occurred at the two UKAWMN lochs before sampling began. Despite the change in xSO_4 at the Caorainn Achaidh Burn there is little evidence of an increase in pH, possibly due to large, short term episodic variation at this steep, flashy catchment. NO_3 appears to have experienced large inter-annual variations in peak concentrations, perhaps linked to climatic factors (Section 5.4), but there is no indication of an overall rising trend.

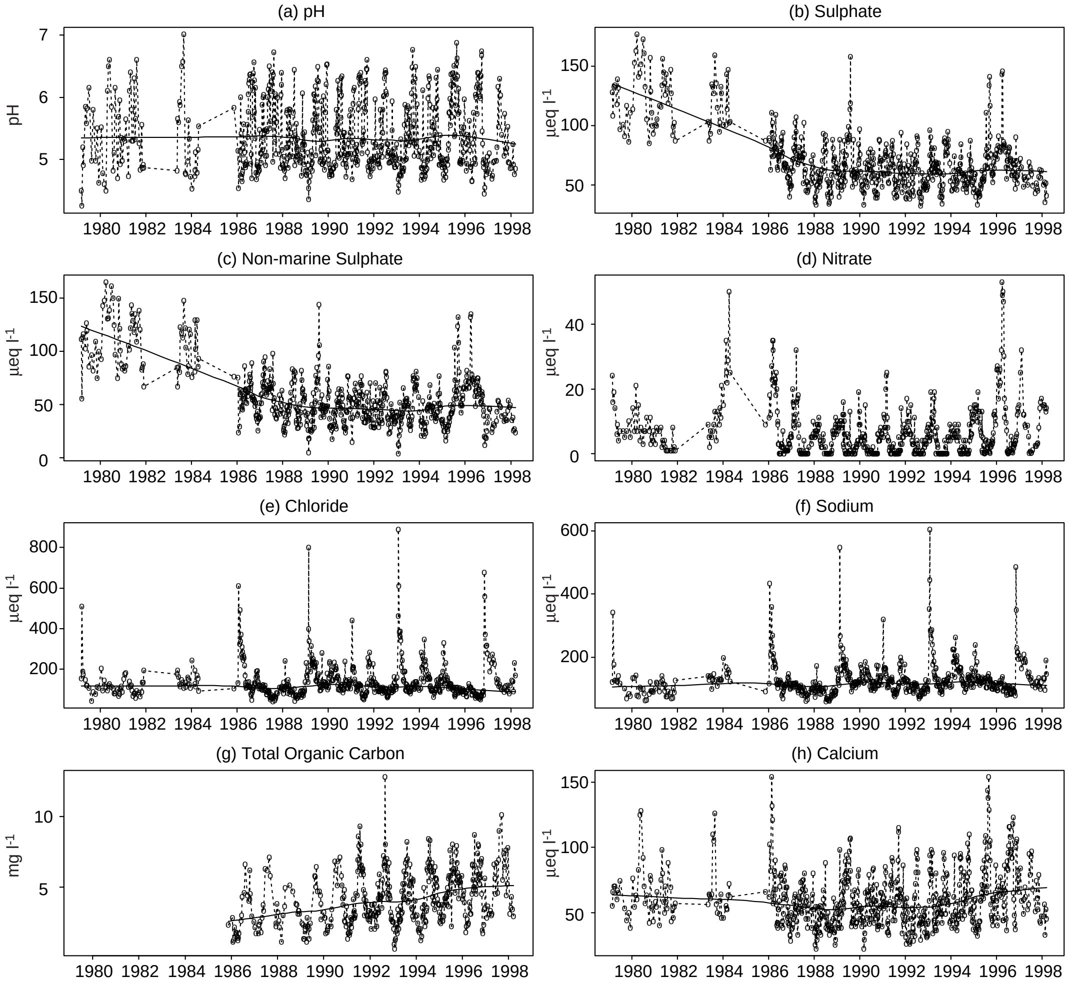
Variations in Cl and Na closely match those at Lochs Chon and Tinker, with peaks in 1989 and 1993, but in general peak concentrations are very much higher, and background concentrations somewhat lower. This variability may again reflect the steep, thin soils of the catchment which (together with the absence of a lake) provide limited storage of water between rain events. Although there appears to be some year-to-year variability in marine ion concentrations, the impact of sea-salt inputs may largely be restricted to episodic timescales, rather than the significant inter-annual cycles observed at the less hydrologically responsive UKAWMN catchments.

Finally, although monitoring of DOC only began during late 1985, there has since been a very

Figure 6.1

Long term trends, Caorainn Achaidh Burn

Smoothed line represents LOESS curve (Section 3.1.2)



marked and approximately linear increase at this site. This is highly consistent with observations at the Trossachs lochs and elswhere in the UKAWMN, suggesting that organic carbon concentrations began rising some time prior to the creation of the UKAWMN, and that changes do not simply reflect a short term fluctuation.

■ 6.2 Round Loch of Glenhead

Round Loch of Glenhead, Galloway, is a peaty moorland site forming part of the UKAWMN (Section 4.7), and has been monitored by FFl since 1979. Prior to 1988 sampling was intermittent, with three samples collected in 1979 and one to three per year from 1984 to 1987. From 1988 onwards, sampling has been maintained at approximately a monthly frequency. (UKAWMN sampling during this time took place quarterly).

Long term data for Round Loch (Figure 6.2) show a major decline in SO_4 concentrations. As at the Caorainn Achaidh Burn, virtually all the decrease appears to have taken place before UKAWMN monitoring began in 1988. However, at Round Loch, this change appears to have been accompanied by a rise in pH levels, indicating overall chemical recovery and this is consistent with palaeoecological evidence from diatom pH reconstruction that some recovery had taken place at the site by the late 1980s (Battarbee *et al.*, 1988). A very clear cycle in Cl and Na, peaking in 1990-1991, matches that observed in the UKAWMN data, and there appears also to have been an earlier peak in 1984. Ca concentrations are moderately correlated with Na

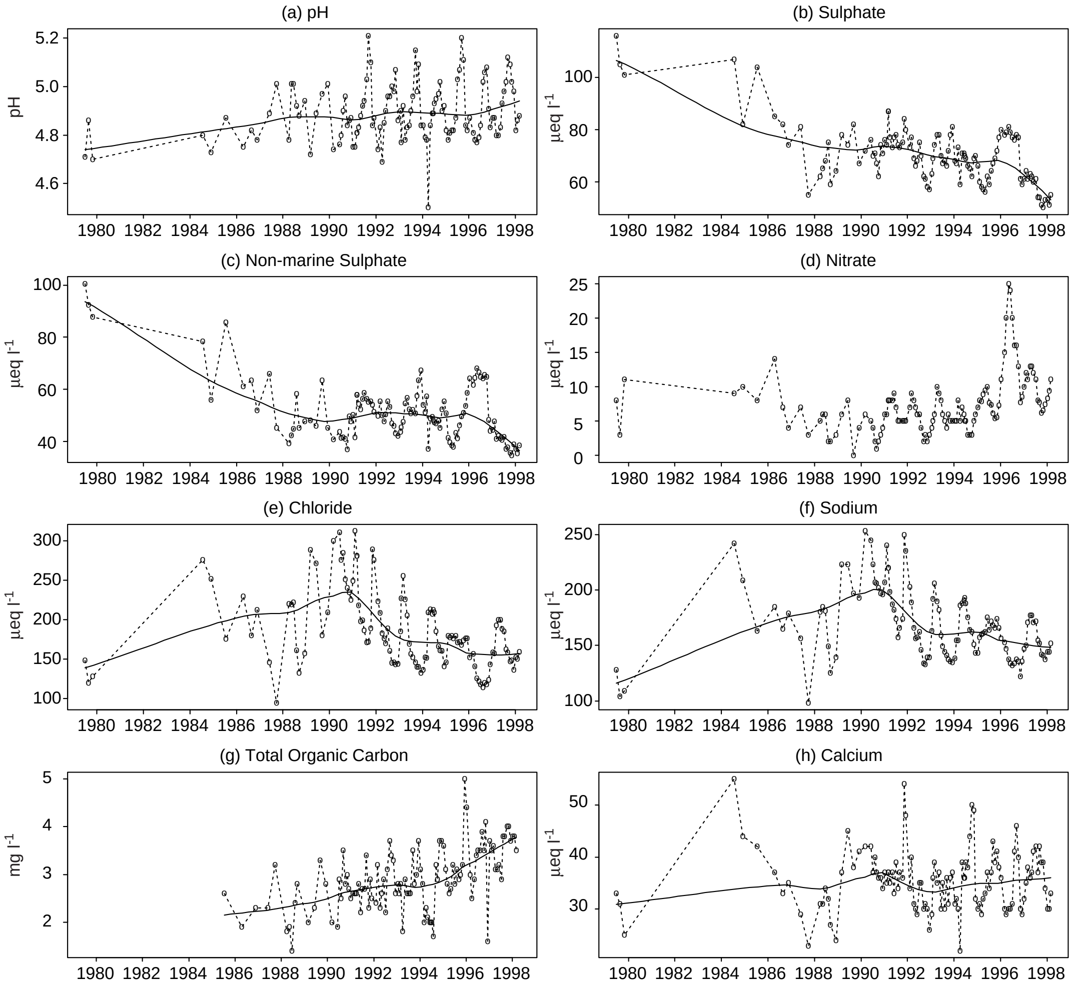


Figure 6.2

Long term trends, Round Loch of Glenhead

Smoothed line represents LOESS curve (Section 3.1.2)

and Cl, and some inverse correlation between xSO_4 and Cl is evident from 1988 onwards.

Monthly data for Round Loch confirm that NO_3 has risen substantially since 1988. However, relatively high concentrations earlier in the record argue that this rise may not be driven by catchment nitrogen saturation, and instead may be linked to climatic fluctuations. The increase in DOC observed in the UKAWMN data is shown to have occurred more or less linearly since sampling began in 1984.

■ 6.3 Dargall Lane

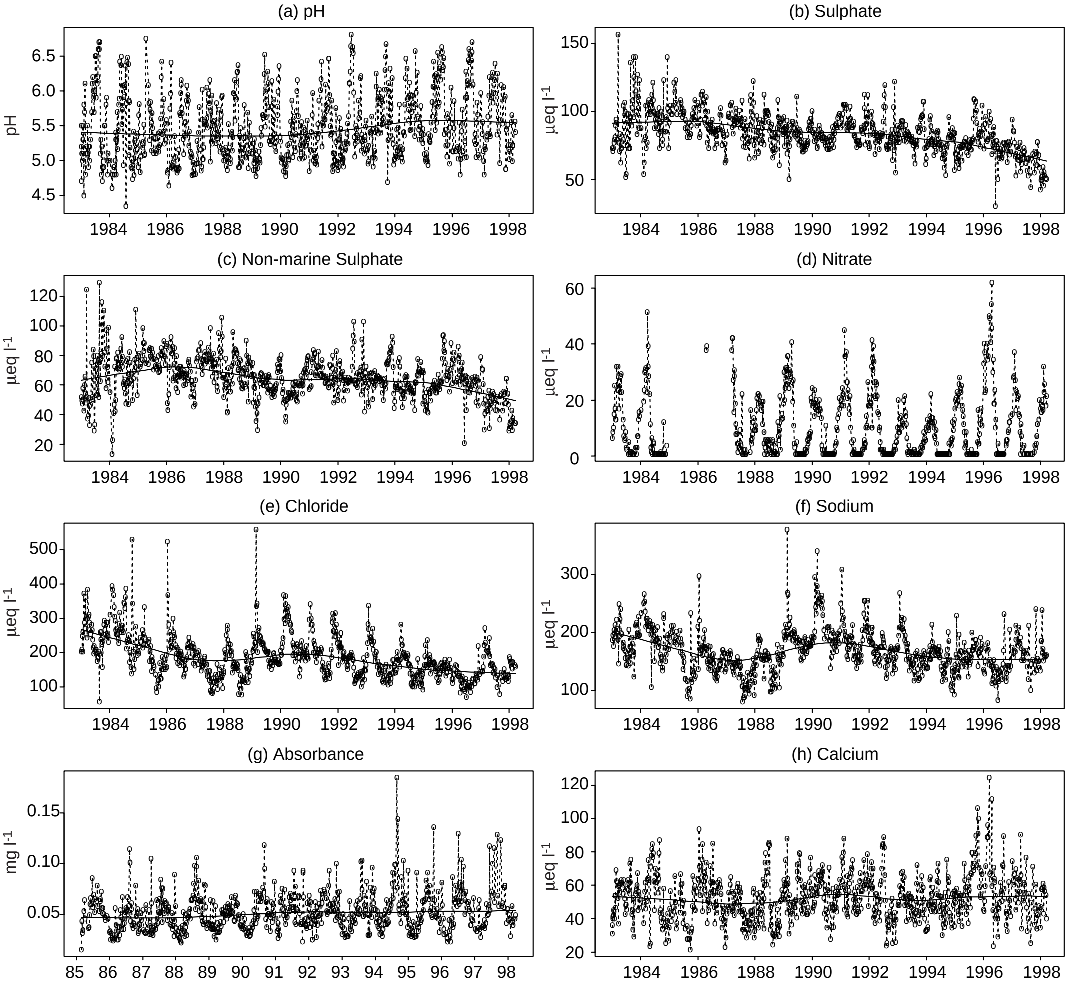
Dargall Lane, a moorland catchment containing a mixture of podzols, peaty gleys and blanket peats, has been monitored since the early 1980s as part of the Loch Dee Project, coordinated by the Solway River Purifaction Board (Lees *et al*., 1989). For this study, stream chemistry data for 1983 to 1998 have been obtained from the Scottish Environmental Protection Agency (SEPA), South West Region. Samples have been collected at weekly intervals throughout this time, and since this monitoring has taken place separately from UKAWMN monitoring at the same site (Section 4.9), this dataset provides an excellent validation, as well as an extention, of the UKAWMN data. An analysis of trends at Dargall Lane and adjacent sites was undertaken by Langan *et al*. (1997), and indicated a reduction in xSO_4, no trend in pH or NO_3, and strong inter-annual cyclicity in sea-salt ions.

Time series (Figure 6.3) support these findings, indicating that SO_4 and xSO_4 have declined at Dargall Lane, although to a somewhat lesser

Figure 6.3

Long term trends, Dargall Lane

Smoothed line represents LOESS curve (Section 3.1.2)



degree than at the preceding sites. There is weak evidence for an increase in stream pH, which may to some extent have been masked by large episode-scale variations. Cyclicity in Cl and Na is clearly evident, indicating that climatically driven fluctuations in sea-salt inputs have a major influence on stream chemistry. The 1990 peak in these ions is consistent with that observed in the UKAWMN data, with an additional peak apparent in 1983-1984. Both Cl peaks correspond to periods of low xSO_4, and in general there is a good inverse correlation between these anions. No overall trends are observed for either NO_3 or Ca, although the latter appears weakly correlated with Na and Cl. An apparent increase in absorbance over the monitoring period is consistent with observations of rising DOC in the UKAWMN data.

■ 6.4 Afon Hafren

The Afon Hafren, in mid-Wales, is a predominantly forested catchment containing a mixture of peaty podzols and peats, and has been monitored as part of the UKAWMN since 1988 (Section 4.17). Additional sampling of this stream has been carried out by the Institute of Hydrology on a weekly basis since 1983. A Seasonal Kendall analysis of data for 1983-1993 was undertaken by Robson & Neal (1996), who identified an increasing trend in DOC, and inversely related fluctuations in Cl and xSO_4. The 1983-1998 data presented here (Figure 6.4) are consistent with these observations, indicating that DOC has continued to rise throughout the 15 years. Very pronounced cyclicity is observed for Cl, Na and xSO_4, with Cl peaks in 1984 and 1990

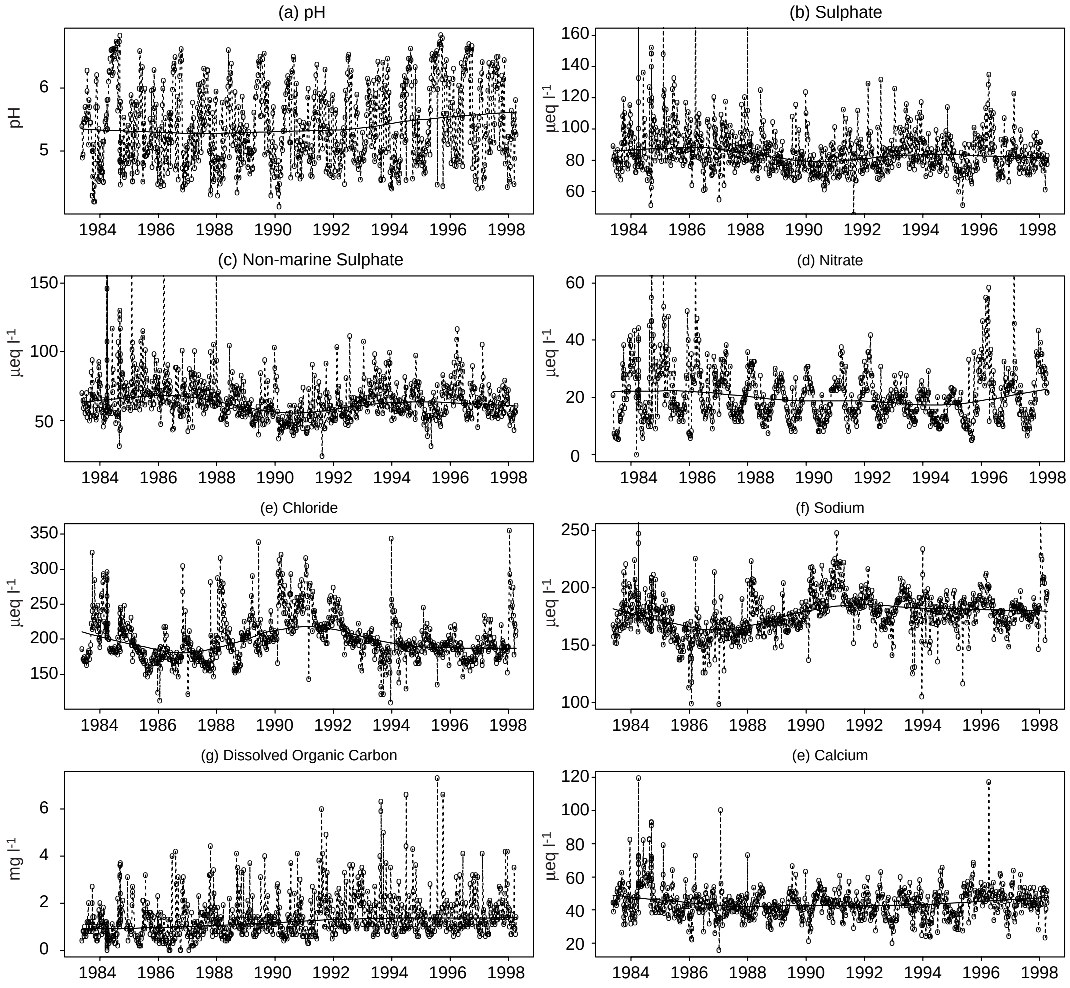


Figure 6.4

Long term trends, Afon Hafren

Smoothed line represents LOESS curve (Section 3.1.2)

corresponding to xSO_4 minima, and also to the Cl peaks observed at Dargall Lane. There is little evidence of an overall decline in xSO_4 at the Hafren, and together with high levels of episodic variation this may account for the lack of detectable recovery in pH. There are also no clear trends in either NO_3 or Ca.

6.5 Afon Gwy

The Afon Gwy, a moorland catchment with peaty podsol and peat soils adjacent to the Hafren, has been monitored by the Institute of Terrestrial Ecology since late 1979. Apart from missing data during 1982, the stream was sampled weekly until 1990, and monthly thereafter. The site became part of the UKAWMN in April 1991 (Section 4.18). A Seasonal Kendall trend analysis was undertaken for the 1980-1996 dataset by Reynolds *et al.*, (1997), who identified a significant decrease in xSO_4, and increases in pH and DOC.

The 1979-1998 data presented here (Figure 6.5) expand only slightly on those analysed by Reynolds *et al.* (1997), and their findings remain applicable. Although sulphate data appear rather noisy in the early part of the record there has clearly been a decrease over the monitoring period, and this has been accompanied by a substantial rise in pH. However, as at other sites, most of the change seems to have occurred during the early to mid 1980s. Pronounced cyclicity in Na and Cl is observed throughout the record, and as at other sites the main peaks appear to have occurred in 1984 and 1990-1991. Large variations in annual peak NO_3 concentrations have also been observed, but there

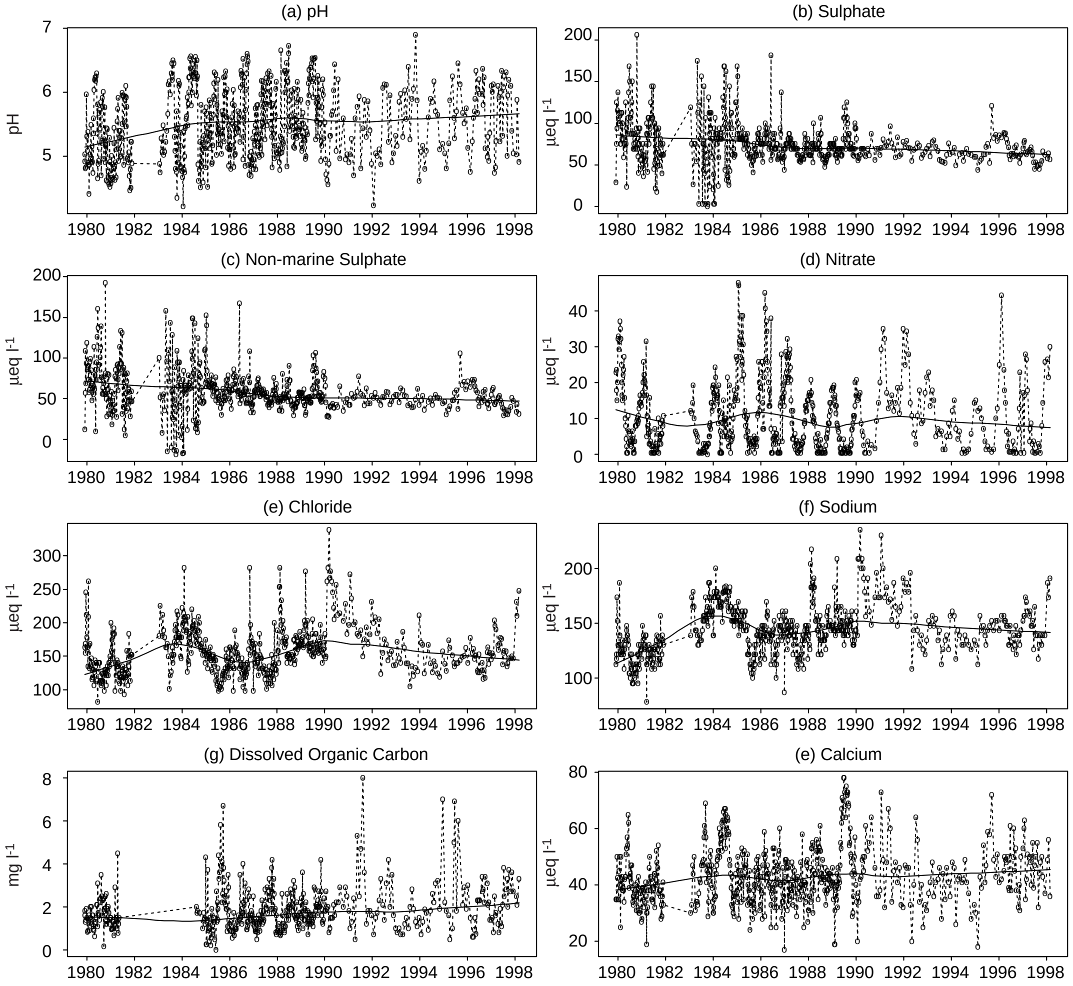


Figure 6.5

Long term trends, Afon Gwy

is no overall trend. DOC concentrations appear to have risen, although as indicated by the UKAWMN trend analysis the magnitude of this change has been relatively small.

6.6 Summary

Based on the five sites considered here, the following general conclusions can be drawn with regard to the interpretation of UKAWMN data in the preceding chapter.

- Where higher frequency datasets exist for UKAWMN sites (Dargall Lane, Round Loch of Glenhead, Afon Hafren and Afon Gwy), these correspond well with UKAWMN data. This suggests that the current UKAWMN sampling frequencies (monthly at rivers, quarterly at lakes) adequately capture overall patterns of long term variation, although an increased frequency would allow a more sensitive detection of trends.
- It appears that the relatively stable xSO_4 concentrations observed during the 1988-1998 period of UKAWMN operation are not necessarily representative of longer term trends. Most of the sites considered here exhibited large xSO_4 reductions during the early to mid-1980s, corresponding to large deposition reductions at this time (RGAR, 1997). At a number of sites, an associated pH increase has been observed. Since the mid-1980s, there has been little further decline in sulphur deposition at these sites (Chapter 2), all of which are in west coast locations, remote from major emission sources. However future reductions in sulphur deposition on a similar

scale to those observed in the early 1980s can be expected to lead to further decreases in surface water xSO_4, and subsequently to increases in pH.

- Climatically driven cyclicity in marine ions is observed in varying degrees at all five sites. The large 1990 peak observed at many UKAWMN sites occurs in all longer term datasets, in addition to which a peak of similar magnitude can be identified for 1983-1984. Like the 1990 peak, this corresponds to a peak in the winter North Atlantic Oscillation and can be attributed to an increased frequency of westerly storms at this time. The presence of this earlier peak implies that levels of climatic and chemical variability observed in the 1988-1998 data are probably typical over the longer term. Additional peaks in marine ions observed at the Caorrainn Achaidh Burn are consistent with those observed at the two Trossachs UKAWMN sites.

- In general, the inverse relationship between marine ion and xSO_4 concentrations suggested by the UKAWMN data is strongly supported. This climatically driven fluctuation in calculated xSO_4 is believed to be driven by short term adsorption and desorption of marine SO_4, which leads to an overestimate and underestimate of the marine SO_4 component respectively (Section 5.3.4) and is effectively superimposed on longer term, deposition driven trends.

- No trends are observed in NO_3, indicating that catchment soils and vegetation continue to immobilise a high proportion of N inputs. It is uncertain whether continued N deposition will ultimately cause increased NO_3 leaching, which might counteract any improvement in runoff acidity resulting from xSO_4 decreases. Large inter-annual variability in NO_3, linked to climatic factors, demonstrate the need for continued high quality long term monitoring if evidence of nitrogen saturation is to be detected against a background of natural fluctuations.

- All five sites exhibit increases in DOC or a comparable determinand, supporting the intrepretation that long term, monotonic increases are occurring at many UKAWMN sites.

7

Biology Discussion

Don Monteith

Introduction

Palaeoecological records and bio-monitoring provide convincing evidence that freshwater acidification has resulted in detrimental change to aquatic biota through the loss of sensitive taxa and a general reduction in diversity (e.g. Battarbee *et al*., 1990; Schindler *et al*., 1989; Rutt *et al*., 1990; Muniz, 1991; Jeffries, 1997). Emissions reduction policy is aimed at reversing the chemical effects of acidification, in order to improve biological status and perhaps even to restore ecosystems to a pre-impacted condition. However, evidence for chemical and biological recovery from acidification, even at the international scale, is still fairly limited and it is far from clear how aquatic biota in acidified upland waters in the UK might respond to improving conditions.

Some of the strongest evidence for a biological response to chemical recovery comes from lakes in the heavily impacted Sudbury area of Ontario, Canada, where marked chemical improvements followed major reductions in local smelter emissions (Gunn & Keller, 1990). Here, acid sensitive species of phytoplankton, zooplankton, and macroinvertebrates have re-invaded or increased in abundance as lake pH has increased (Gunn & Keller, 1990; Nicholls *et al*., 1992; Locke *et al*., 1994; Griffiths & Keller, 1992). Experimental studies have also demonstrated that an increase in pH is usually followed by colonisation of more acid sensitive species. However, time lags are usually observed, and there is some evidence that biota of more acidified systems take longer to respond, while the new community may not resemble the pre-acidified one (Jeffries, 1997).

There is rarely any inventory available to tell us what has been lost from acidified freshwaters. Fossil remains in lake sediments do however provide an excellent record of biological change through time for certain lake biota, and in particular the diatom community. Diatoms and other fossil organisms can also be used to set pre-industrial 'base-lines' which provide hypothetical biological restoration targets. However, there are several groups of freshwater organisms which do not leave strong fossil evidence and stream systems do not possess any sediment record. Historical and palaeoecological evidence alone is therefore insufficient to directly infer how sensitive freshwater ecosystems, as a whole, have been impacted by acidification. Consequently it is also unclear how these systems might respond biologically if and when their environments begin to recover chemically.

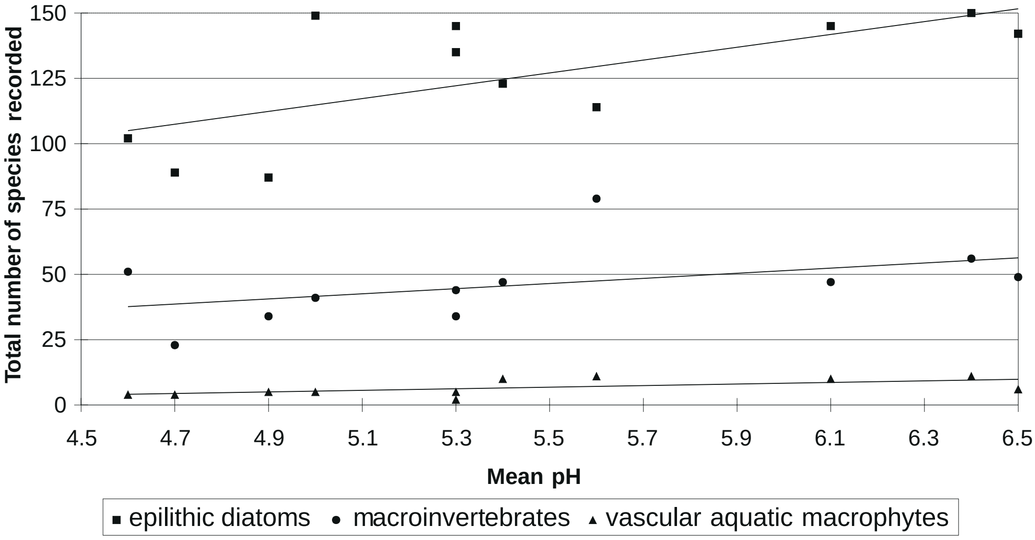
7.1 Spatial acidity-biology relationships

An alternative approach to understanding acidification impacts at the ecosystem level, is to use monitoring data to make biological comparisons of sites across an acidity gradient. Clear spatial correlations have been demonstrated between freshwater fauna and flora and acidity in many studies (e.g. Harriman and Morrison, 1982; Townsend *et al*., 1983; Roberts *et al*., 1985; Flower, 1986; Ormerod *et al*., 1987). In the following Sections (7.1.1-2) we present a descriptive overview of the relationship between monitored biological characteristics and acidity for UKAWMN sites only. It is important to note that although acidified, palaeoecological records demonstrate that some UKAWMN lakes are naturally moderately acid. In addition, the sites differ in many attributes other than acidity such as: other aspects of chemistry, substrate, altitude, and in the case of lakes, size, depth and exposure to wind, and these are also important in determining biological properties. The ecosystems of the less acid sites, therefore, do not necessarily provide good analogues for the pre-industrial condition of the more acid sites. Analysis of integrated physio-chemical and biological datasets for a considerably larger number of sites than those represented by the UKAWMN would be necessary for this issue to be adequately addressed.

Figure 7.1

Relationship between the total number of species recorded (1988 - 1997) for epilithic diatoms, macroinvertebrates and vascular aquatic macrophytes (submerged or floating leaves) and the mean pH of UKAWMN lakes for the same period

Lines for each biological group fitted by linear regression



7.1.1 Biological characteristics of UKAWMN lakes in relation to acidity

Total species numbers for the biological groups monitored at UKAWMN lakes are generally positively correlated with pH (Figure 7.1), and this is consistent with findings from other studies (e.g. Schindler *et al.*, 1989; Stewart & Freedman, 1989; Gunn & Keller, 1990; Jefferies, 1997). These measures of bio-diversity are derived from various methods of survey and analysis and are therefore not directly comparable. Consequently they should not be taken to represent differences in total community diversity between sites. For example, diatoms are sampled from only one habitat, i.e., the epilithon, and at only one time of year. Only 300 individual valves are identified from each microscope slide, and less common taxa may never be recorded even if they were collected within the original sample. Aquatic macrophyte data, on the other hand, should provide a relatively accurate inventory of higher plant species for each site.

The four strongly acid lakes with a ten year mean pH of 5.0 or less (Loch Grannoch, Blue Lough, Round Loch of Glenhead and Scoat Tarn) are generally species-poor. Their submerged vascular flora is mainly restricted to isoetid species which are adapted to low nutrient concentrations and a CO_2-only carbon source, i.e. *Isoetes lacustris* L. (Quillwort), *Lobelia dortmanna* L. (Water Lobelia), *Littorella uniflora* (L.) Asch. (Shoreweed). The Bulbous Rush *Juncus bulbosus* var *fluitans* L. is also abundant at these sites. These four species occur across the entire UKAWMN acidity gradient. The total number of epilithic diatom species counted in samples from Loch Grannoch, Blue Lough and Round Loch of Glenhead is low. Assemblages are dominated by the acidobiontic *Tabellaria quadriseptata* Knudson but are also well represented by *Eunotia*, *Navicula* and *Frustulia* species. Scoat Tarn is an exception, exhibiting a larger number of diatom species (predominantly *Eunotia* spp.), a common feature of other higher altitude oligotrophic lakes (Cameron pers. comm.). With the exception of Loch Grannoch, species representation of macroinvertebrates is also low; the acid tolerant family, the Leptophelbiidae, is the only mayfly representative, and otherwise assemblages are dominated by chironomids and relatively low numbers of acid tolerant beetle, Hemipteran, stonefly and caddisfly species. Loch Grannoch is surprisingly diverse for an acid lake, with several species of acid tolerant mayfly and caddisfly having been recorded. As a large water body, Loch Grannoch is fed by several sub-catchments with varying chemical characteristics. This, in addition to the greater variation in habitat type offered by a larger system, could account for the relatively enhanced site diversity. Trout densities in the outflows of all four lakes are low with those for Blue Lough, Loch Grannoch and Scoat Tarn particularly impoverished.

Llyn Llagi, Llyn Cwm Mynach, Loch Chon and Lochnagar (all with mean pH between 5.0 and 6.0) exhibit a range of biological characteristics. Lochnagar can be considered a statistical outlier, which seems to reflect the extreme altitude of the site (790 m). Here the aquatic macroflora may be restricted by a combination of factors including acidity, low temperatures, low nutrient availability, poor littoral substrate quality, prolonged winter ice cover and high winds. *Isoetes lacustris* and *Juncus bulbosus* var. *fluitans* are the only vascular plants at the site. Loch Chon, Llyn Cwm Mynach and Llyn Llagi all support *Myriophyllum alterniflorum* which is absent from the more acid sites, while the former two have sheltered, silty, littoral zones colonised by water lilies, *Nuphar lutea* (L.) Sm. and *Nymphaea alba* L., and emergent species including *Equisetum fluviatile* L. (Water Horsetail) and *Carex rostrata* Stokes (Bottle Sedge).

The total number of epilithic diatom species recorded for these four sites is intermediate for UKAWMN lakes, with the exception of Lochnagar for which numbers (like the next highest altitude site Scoat Tarn) are relatively high. Macroinvertebrate species richness at Llyn Llagi, Llyn Cwm Mynach and Lochnagar is also intermediate for UKAWMN lakes. These sites are characterised by moderate numbers of mayfly, stonefly, beetle and caddisfly species. Lochnagar is the only UKAWMN lake for which there is no record for Hemipterans. Species richness for Loch Chon is the highest for all UKAWMN lake sites, again possibly reflecting the diversity of habitats and spatial variation in chemistry in this relatively large lake with convoluted shoreline and sheltered bays. The relatively elevated calcium concentration of Loch Chon, compared to most other lakes, is also likely to have a beneficial influence on diversity. Numbers of mayfly and Hemipteran species in particular, greatly exceed those recorded in any other UKAWMN site. The trout populations in the outflows of these sites, all of which have relatively low labile Al concentrations, are generally high, while the density at Llyn Llagi is intermediate. Electro-fishing at Lochnagar is conducted at a distance down-stream of the water chemistry sampling point, and conditions here are likely to be better buffered and therefore less acid, than the reported chemistry for the loch.

The least acid lakes, Burnmoor Tarn, Loch Coire nan Arr and Loch Tinker (all with mean pH of greater than 6.0), exhibit high species richness of aquatic macrophytes, and epilithic diatoms. These sites are the only lakes which contain the acid sensitive charophyte species *Nitella flexilis*, and they also support populations of other relatively acid sensitive species including *Myriophyllum alterniflorum* (Alternate Water-milfoil) and the Bladderwort *Utricularia* sp. L., in addition to the isoetid species named above. The diverse diatom epilithon is dominated by taxa with only slightly acid optima, and particularly *Achnanthes minutissima* Kütz. and *Brachysira vitrea* (Grun.). Samples from Burnmoor Tarn include the normally planktonic *Cyclotella kuetzingiana* var. *minor*, although it is likely that this species is deposited on to the sampled substrate and is not truly epilithic (i.e. growing attached). The macroinvertebrates include numerous mayfly, stonefly, beetle and caddisfly species amongst other groups. The mildly acid conditions are not associated with elevated trout densities. The outflow of Loch Coire nan Arr is the only site to support even a moderate trout density, although it is possible that regulation of flow following the installation of a dam may have had a detrimental effect. It appears that although normally non-acid, occasional highly acid spate events (and associated high labile Al concentrations) (Section 4.11) may be important in limiting the population in the outflow of Burnmoor Tarn, while fish parasites have been identified as a possibly detrimental factor in the outflow of Loch Tinker.

7.1.2 Biological characteristics of UKAWMN streams in relation to acidity

The aquatic macrophyte communities of UKAWMN streams consist almost entirely of bryophytes. However, a general ecological distinction can be made between those relatively diverse sites, which include aquatic mosses, and those populated only by liverworts. Ormerod *et al.* (1987) found a clear relationship between aquatic macroflora and macroinvertebrate composition and acidity in Welsh streams, and similar relationships are apparent here. The identification of links between stream chemistry and the aquatic biota is complicated by the highly flow dependent (i.e. episodic) nature of stream acidity (Section 7.3.1). Sites with acid soils and relatively base-rich sources of groundwater show marked chemical variation, and the use of mean pH to characterise overall conditions is inadequate in representing the potentially limiting factor of acid episodes. The following classification is therefore based on the mean of pH values beneath the lower quartile for each site, in order to represent the more acid conditions experienced.

Those UKAWMN streams with a mean for the lowest 25% of pH values greater than 5.2, i.e., the least acid sites, Allt a'Mharcaidh (5.9), Allt Coire nan Con (5.3), Narrator Brook (5.4) and Coneyglen Burn (5.4), are clearly the most diverse. Their aquatic macrofloras are characterised by mixed communities of mosses and liverworts; truly aquatic (i.e. permanently submerged) mosses are absent from all other stream sites. The moss genus *Hygrohypnum* spp. Lindb. is dominant at three sites, whereas *Rhynchostegium ripariodes* (Hedw.) is the most abundant species at Narrator Brook. The acid sensitive red alga *Lemanaea* sp., has been recorded periodically in both the Allt a'Mharcaidh and Narrator Brook. All four sites have relatively diverse epilithic diatom floras, dominated by *Achnanthes minutissima*, and are often well represented by *Synedra minuscula* Grun., *Fragilaria vaucheriae* (Kütz) and *Gomphonema angustatum* [agg.] (Kütz). Macroinvertebrate species richness is the highest for all streams, with between 40 to 52 species having been recorded over the past decade. Mayfly and caddisfly species are particularly well represented. Total trout density is also higher than for all other streams and the best buffered of these, Allt a'Mharcaidh and Narrator Brook, exhibit significantly higher densities than the two more episodic systems.

Biological characteristics of the remaining seven stream sites are less easily characterised with regard to acidity. The submerged aquatic macroflora is confined to acid tolerant liverwort species, while the most acidic sites are largely monospecific (almost exclusively *Scapania undulata* (L.) Dum. in the River Etherow (< lower quartile mean pH 4.1), Old Lodge (pH 4.4), Beagh's Burn (pH 4.8) and the Afon Hafren (pH 4.8), and almost exclusively *Nardia compressa* (Hook.) in the Bencrom River (pH 4.6)). Dargall Lane, where labile Al concentration is relatively low, supports a moderate trout density, while density at the other sites, all of which have high labile Al concentrations, is very low. The macroinvertebrate assemblages of these sites are all dominated by stoneflies and caddisflies, and there is no obvious within-group relationship between species richness and water chemistry. The total number of epilithic diatoms recorded over the decade is relatively low but varies between sites. Large inter-annual variation in species representation at some sites appears to be primarily dependent on the extent to which variation in flow during summer influences acidity (Section 7.4.1). For example, the River Etherow is characterised by contrasting assemblages in high and low summer rainfall years and consequently the total number of taxa occurring over the last decade is higher than for permanently acid Old Lodge.

7.1.3 UKAWMN trout density and acidity

The trout populations of UKAWMN sites are sampled in streams and lakes outflows, and data are therefore directly comparable. Densities vary from very low (<1 trout per 100 m^2) to high (>20 trout per 100 m^2). The higher densities equate to those found in unpolluted chalk-streams (Beaumont pers. comm.). Most sites have lower densities than those predicted by HABSCORE HQS (Chapter 3, Table 7.1), the main exceptions being sites in northern Scotland, southwest England (Narrator Brook), and northwest Northern Ireland (Coneyglen Burn). These sites also tend to be the least acid deposition impacted

Table 7.1

Relationship between observed trout density and that predicted by HABSCORE HQS for 0+ and >0+ fish over the monitoring period

	0+	>0+
Loch Coire nan Arr	=	-
Allt A'Mharcaidh	+	=
Allt na Coire nan Con	-	-
Lochnagar	=	=
Loch Chon	+	=
Loch Tinker	-	-
Round Loch of Glenhead	-	-
Loch Grannoch	-	-
Dargall Lane	-	-
Scoat Tarn	-	-
Burnmoor Tarn	-	-
River Etherow	-	-
Old Lodge	-	-
Narrator Brook	+	=
Llyn Llagi	-	-
Llyn Cwm Mynach	+	-
Afon Hafren	no data	no data
Afon Gwy	no data	no data
Beagh's Burn	-	-
Bencrom River	-	-
Blue Lough	-	-
Coneyglen Burn	=	-

-: mean density lower than predicted
+: mean density higher than predicted
=: mean density similar to that predicted

on the Network. The data therefore suggest that factors related to acidification may limit the trout population across much of the remainder of the Network.

Mean trout densities for the complete UKAWMN record can be linked to mean water chemistry over the same period (Figure 7.2). Although there is only a weak relationship between density and pH (Figure 7.2a), Figure 7.2b suggests a link between trout density and labile Al concentration, with a roughly exponential decline in the maximum observed densities with increasing concentration. Densities above 10 fish per 100 m^2 are restricted to sites with mean labile Al concentration below 70 µeq l^{-1}. However, factors other than mean labile Al are clearly important, as four of the fourteen sites above this chemical threshold also have poor populations. The effect of labile Al on trout populations has been widely studied and is suspected of being a major cause of fish kills in acid sensitive waters (Kelso *et al.*, 1986; Howells *et al.*, 1990; Rosseland *et al.*, 1990). Trout exposed to Al at low pH have been shown to undergo respiratory stress as a result of damage to gills (Meuller *et al.*, 1991, Wilson *et al.*, 1994). Experimental work at sub-lethal exposures (i.e. 30 µg l^{-1} at pH

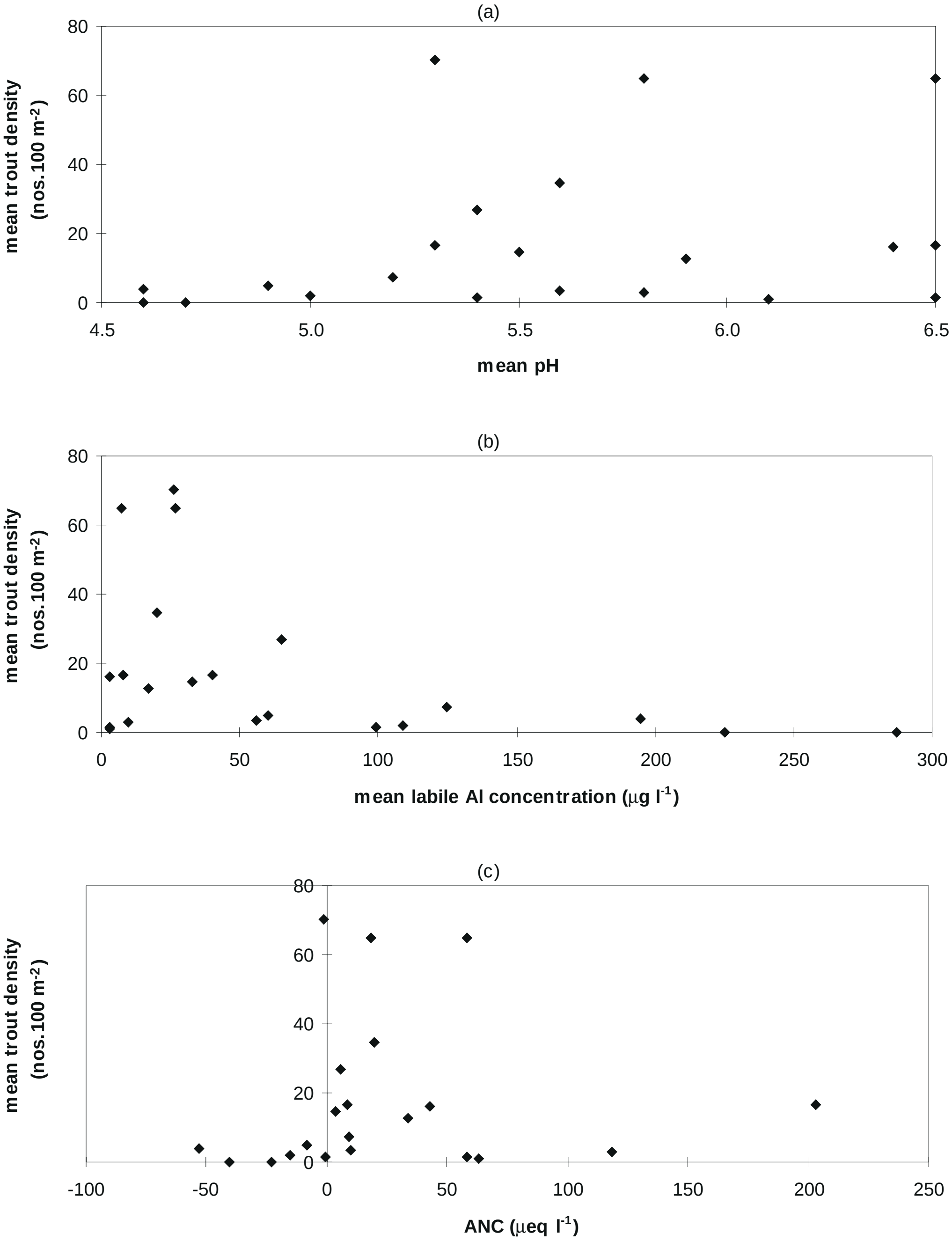


Figure 7.2

Relationship between mean trout density (nos. per 100 m^2) at UKAWMN sites and mean water chemistry 1988-1998 (a) pH, (b) labile aluminium, (c) Acid Neutralising Capacity (ANC)

5.2) has shown depressed feeding rates, lowered red blood cell counts and a reduction in overall swimming activity (Wilson *et al*., 1994, Allin & Wilson, 1999).

Lien *et al* (1993) demonstrated a probabilistic relationship between damage to the trout population in Norwegian freshwaters and Acid Neutralising Capacity (ANC, Section 5.1.1). They proposed an ANC threshold of 20 µeq l^{-1} above which damage was unlikely to occur. UK Critical Loads freshwater maps are based on 0 µeq l^{-1} which, according to the same relationship, provides a 50% probability of damage to trout. The mean of 0 µeq l^{-1} ANC appears to represent a critical limit for UKAWMN trout data, with healthy populations present in several sites where mean ANC is only slightly positive (Figure 7.2c). Only very low densities are found at sites with negative mean ANC, and this is consistent with the findings of Harriman *et al*. (1995c). The only exception to this general rule is at Lochnagar, where mean ANC is fractionally negative but trout density is high. However, it is likely that the water chemistry for the Lochnagar fishing reaches is less acid than the outflow chemistry (see Section 4.4 Fish summary). It should be emphasised that this relationship is based on a 10 year average. Considerable inter-annual variation in ANC occurs at most sites (Figure 5.4), yet long time-series such as this dataset are rarely available for the assessment of long term mean conditions. It would therefore seem that, for sites which are vulnerable to marine influences, and for which only limited chemistry data are available, a 20 μeq l^{-1} ANC limit would provide a more suitable margin of protection.

7.2 Temporal trends in biological data

In the five year interpretative exercise (Patrick *et al*., 1995; Lancaster *et al.*, 1996) statistical time trend analyses were used to detect biological change in UKAWMN data. These methods have been re-employed here (Section 3.2). Biological data have been analysed in isolation from water chemistry data. Strong chemical-biological correlations are not necessarily expected, given the likelihood of non-linear relationships and possible cause-effect time lags. The approaches of linear regression and RDA both test for linear change with time and both over-simplify the anticipated nature of temporal biological recovery. However, for these temporally short datasets, which at most only represent very slight chemical gradients, only small changes in flora or fauna are expected. In addition, results from DCCA (Section 3.2.2) demonstrate that time constrained change in species assemblages is generally low. Linear methods should therefore be the most sensitive to temporal change in the datasets.

The following sections (7.2.1 - 7.2.4) summarise the results of trend analysis for each biological group.

7.2.1 Linear time trends in epilithic diatom communities

Linear trends with time in the epilithic diatom assemblage were identified at nine sites (Table 7.2). Interpretation of how these temporal changes might reflect changes in acidity is assisted by our knowledge of the pH preferences of individual species. The interpretation provided here is based partly on subjective observation of relative species changes and partly on the pH inference technique described below.

pH prediction techniques were developed to reconstruct historical lake pH change from fossil diatom remains in sediment cores. The Weighted Averaging (WA) approach (ter Braak, 1987; Birks *et al.*, 1990), based on the weighted average of the optimal pH of all species in a sample, has been the most widely used in recent years. Reconstructions for UK lakes have mostly been based on a calibration set of surface sediments from 167 lakes from the UK and Scandinavia, developed for the Surface Water Acidification Project (SWAP) (Stevenson, *et al*., 1991). For lake sediments, the WA approach has a root mean square error of prediction of 0.32 pH units. Since this training set is based on sediment diatom assemblages (i.e. mid-lake fossil deposits), it is not generally considered appropriate to apply to epilithic diatom assemblages and may not provide the same degree of precision of prediction. However, the diatom composition of surface sediments of acid lakes is well represented by epilithic taxa and it is clear from the assemblage descriptions in Chapter 4, that the dominant taxa at most sites have SWAP pH optima which are close to the mean site pH. Time series plots of pH inferred from the epilithon samples should therefore at least provide an indication of the temporal direction of pH response in the diatom community. Epilithic diatom inferred pH time series for lakes and streams are presented in Figure 7.3 (a) and (b) respectively.

Of those sites showing linear trends, five are indicative of an increase in pH (Loch Chon, Burnmoor Tarn, Llyn Llagi, Llyn Cym Mynach and Blue Lough), and one is indicative of deterioration (Loch Grannoch), while species shifts at the remaining three sites do not suggest

Table 7.2

Summary of statistically significant linear trends in epilithic diatom and macroinvertebrate communities, and trends identified in acidity, at UKAWMN sites

	Linear trends in epilithic diatoms	*Linear trends in macroinvertebrates*	*trends in alkalinity and pH*
Loch Coire nan Arr			
Allt A'Mharcaidh			
Allt na Coire nan Con		↑	
Lochnagar		↓	*pH↓*
Loch Chon	↑	↑	*pH↑ ALK↑*
Loch Tinker	↔	↔	
Round Loch of Glenhead			
Loch Grannoch	↓	↔	
Dargall Lane			*ALK↑*
Scoat Tarn		↔	*pH↑*
Burnmoor Tarn	↑	↔	
River Etherow			
Old Lodge			
Narrator Brook			*pH↑ ALK↑*
Llyn Llagi	↑	↑	*pH↑*
Llyn Cwm Mynach	↑	↔	
Afon Hafren	↔		
Afon Gwy			*pH↑*
Beagh's Burn			
Bencrom River			
Blue Lough	↑	↔	*pH↑ ALK↑*
Coneyglen Burn	↔	↔	

For biological groups, presence of any symbol represents a significant linear time trend according to RDA and associated restricted permutation test. ↑ = indicative of reduction in acidity; ↓ = indicative of increase acidity; ↔ = not indicative of acidity change according to current understanding of species preferences. For chemistry, presence of symbols represents significant time trend according to Seasonal Kendall Test and or Linear Regression, in alkalinity (ALK) and pH: ↑ = increase; ↓ = decrease.

acidity changes (Loch Tinker, Afon Hafren and Coneyglen Burn).

Species changes at Loch Chon, Llyn Llagi and Blue Lough are consistent with the increases in pH reported for these sites. Furthermore, the changes at Loch Chon and Llyn Llagi are supported by changes in the diatom species assemblages of sediment traps and sediment cores (this is considered in further detail in Section 7.2.5).

Trends indicating amelioration in acidity at Burnmoor Tarn and Llyn Cwm Mynach appear to follow chemical changes which, although statistically non-linear, suggest a recent (i.e. post 1992) increase in pH. At these sites there is less indication of similar temporal change in sediment

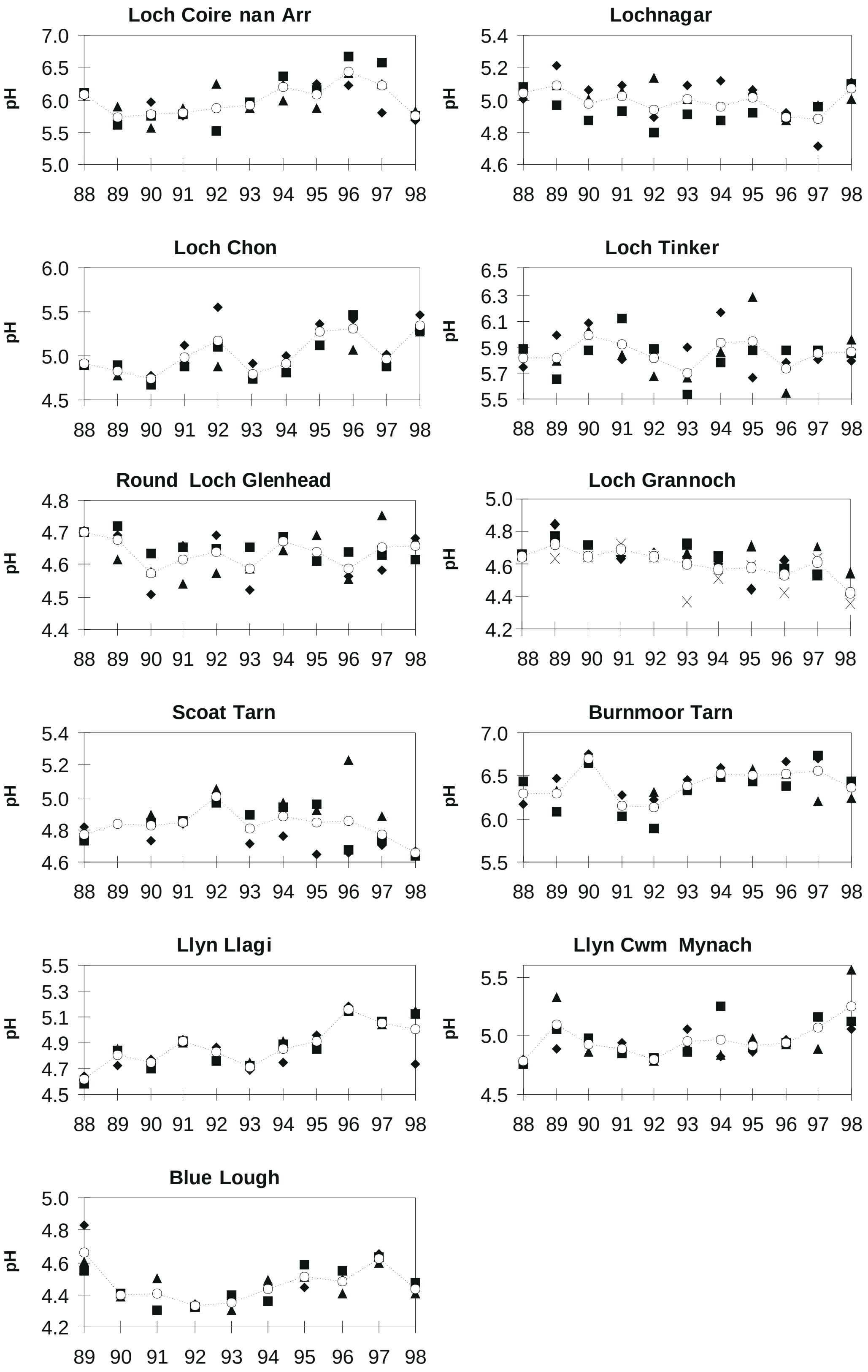


Figure 7.3a

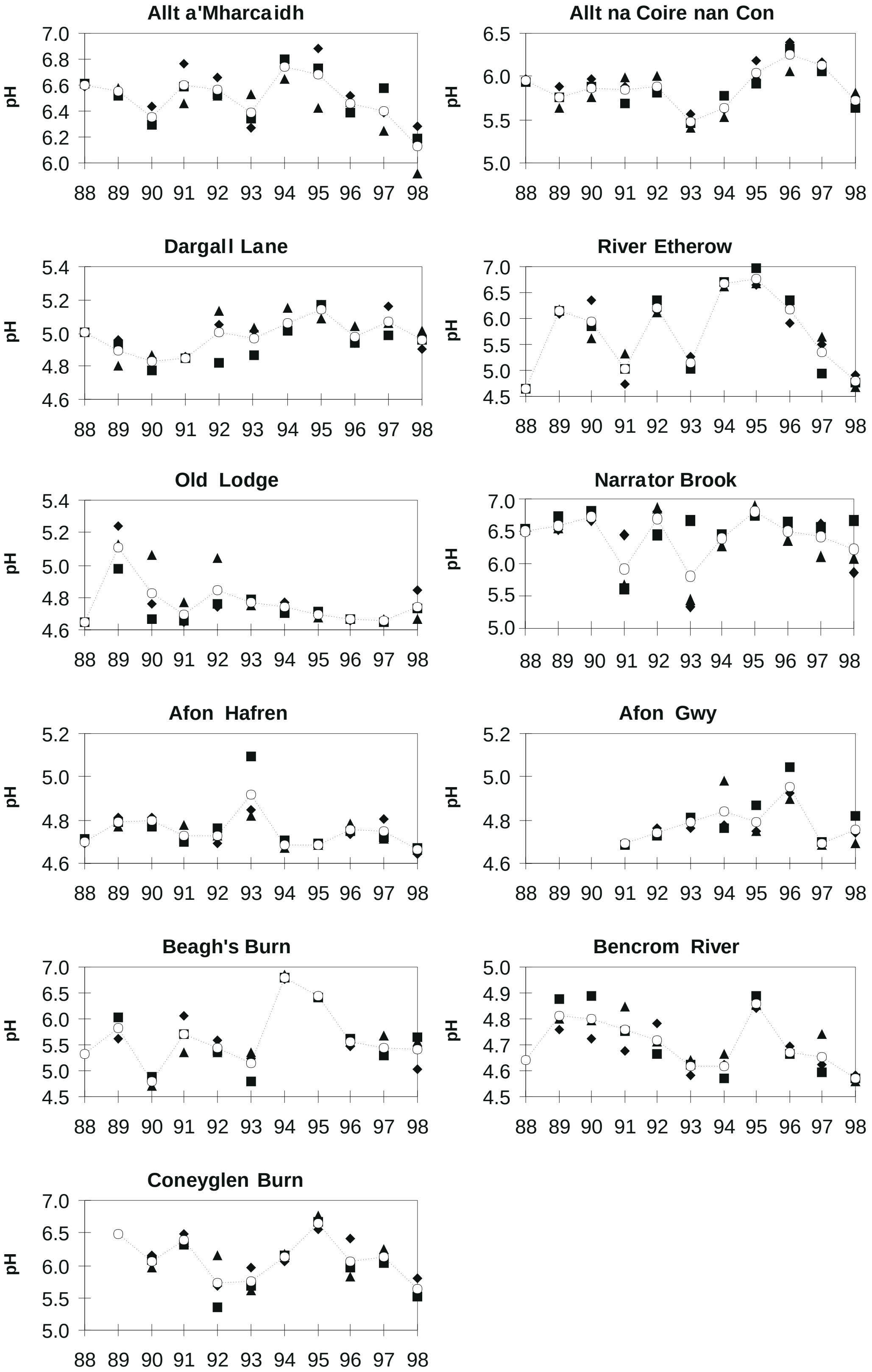
Time series of epilithic diatom inferred pH (all samples) for UKAWMN lake sites (black symbols)

Dotted line indicates variation in annual mean inferred pH (open circle)

Figure 7.3b

Time series of epilithic diatom inferred pH (all samples) for UKAWMN stream sites (black symbols)

Dotted line indicates variation in annual mean inferred pH (open circle)



trap diatom assemblages.

The indication of further acidification in Loch Grannoch is consistent with the LOESS plot for pH (Figure 4.8.2), although no significant trend for pH was found for this site. Likewise, non-linear variation at most other lakes generally appears to reflect their non-linear variation in acidity. Scoat Tarn is the only lake showing linear trends in acidity (improvement), which does not show any clear temporal change in the diatom epilithon. Inter-annual variability in diatom assemblages from stream sites tends to be more marked and is less obviously linked to inter-annual variation in chemistry. However, there is indirect evidence that stream diatoms are primarily influenced by summer acidity. This is considered further in Section 7.4.1.

7.2.2 Linear time trends in macroinvertebrate communities

Eleven sites exhibited statistically significant linear trends in macroinvertebrate data. However, interpretation of these trends is more difficult than for diatom data given the generally wider acidity tolerance of many species and the current lack of information available on species-chemistry relationships for the UK.

Trends at two sites (Loch Chon and Llyn Llagi), are indicative of less acid conditions, while one is indicative of deterioration (Lochnagar) (Table 7.2). As with the epilithic diatoms, the linear trends indicative of improving conditions at Loch Chon and Llyn Llagi (Section 4.5 and 4.15) are consistent with the trends of recovery in water chemistry (however, see Section 7.3), while the trend indicative of deterioration at Lochnagar is consistent with the linear decline identified for pH.

Potential influences on linear change at the remaining eight sites (Allt na Coire nan Con, Loch Tinker, Loch Grannoch, Scoat Tarn, Burnmoor Tarn, Llyn Cym Mynach, Blue Lough and Coneyglen Burn) are less immediately apparent but are considered in more detail in section 7.3.

7.2.3 Linear time trends in trout data

Linear trend analysis was carried out for density and condition factor statistics for the trout population. These data demonstrate considerable inter-annual variability, but few within site time trends have been found, and where they do occur they rarely correspond with changes in water chemistry (see site specific comments in Chapter 4). Fish are highly mobile, relative to other monitored biological groups, and to date it has not been possible to determine to what extent variations in density are driven by mortality and recruitment, as opposed to up- or down-stream migration. Given the large inter-annual variation resulting from the effects of mobility, it is clear that for most sites, the current time series available are of insufficient length for trends to be identified. However, a trend in the density of 0+ trout has been observed at the extremely acid stream, Old Lodge. Here, densities have increased substantially (Figure 4.13.5), and this could represent a general movement of the population upstream from more buffered reaches. The trend is matched by a period of sharply declining labile Al concentration (Figure 4.13.2), accompanied by declining non-marine SO_4 concentration, and may therefore be indicative of biological recovery in response to chemical improvements (Section 4.13). However sea-salt inputs have also reduced over the same period, and further time is therefore required to assess the relative importance of SO_4 decline against climatic influences.

7.2.4 Linear time trends in aquatic macrophyte abundance/cover

Aquatic macrophyte data (consisting of relative abundance measurements for lakes and cover estimates for streams) are the most temporally conservative of all the biological datasets. This is not surprising since: i) aquatic macrophytes tend to be slow growing and perennial, ii) most species have relatively wide tolerance of changes in the chemical and physical environment, and iii) data for lakes is based on a relatively coarse 1-5 scale of relative abundance and this is not particularly sensitive to subtle changes with time. However, spatial studies demonstrate aquatic macrophyte species assemblages do change across broad pH/alkalinity gradients (e.g. Roberts *et al*., 1985; Palmer *et al*., 1992; Allott & Monteith, 1998) and species changes would be expected at UKAWMN sites were substantial improvements in water chemistry to occur.

Temporal trends are apparent at five sites, four of which are streams. At Loch Coire nan Arr there has been a clear reduction in the representation of emergent taxa which almost certainly results from the installation of a dam in 1991 and subsequent water level management. It is unlikely that these species will be able to re-establish around the Loch shoreline unless water level fluctuations cease. Trends at Allt a' Mharcaidh, Allt na Coire nan Con, the River Etherow and the Afon Hafren all appear to result from a reduction in overall cover, rather than any shift in relative species abundance during the interpretative period. Physical scouring during high flow events in the early to middle part of the record, provide the most likely explanation for these changes. Therefore, all linear trends observed in the aquatic macrophyte data most likely result from the effects of physical disturbance, rather than chemical change.

There is no strong evidence for change in aquatic macrophyte composition at those sites showing possible recovery in epilithic diatoms and macroinvertebrates (i.e. Loch Chon and Llyn Llagi). The apparent inertia in species composition at most sites raises the issue of the suitability of aquatic macrophyte monitoring as a tool for detecting biological recovery. However, the relative stability of this group over a period of generally non-directional, or at most very slight, changes in water chemistry can be seen to complement the other more environmentally sensitive but relatively 'noisy' biological datasets. It follows that the appearance, large expansion or disappearance of a species, should these be observed, is likely to be of considerable significance. Furthermore, aquatic macrophytes have a pivotal role in aquatic ecosystems in providing a habitat and food resource. Regular assessment of status therefore provides environmental information which may be important in understanding causes of change in other biological groups.

7.2.5 Supporting evidence for diatom recovery from sediment traps and sediment cores

Evidence for biological recovery from linear trends in epilithic diatom assemblages in Loch Chon and Llyn Llagi is supported by similar floristic trends in sediment trap samples for these sites. Situated in deep water, the contents of these traps should represent the diatom assemblage of the most recently deposited sediment. Comparisons can therefore be made between the historical trend in sediment core diatoms, marking acidification, and the recent annually monitored diatom trend (Figures 7.4 - 7.5).

Sediment core data for Chon11 (taken in 1992) (Patrick *et al*., 1995) shows that the acidification of Loch Chon was marked by a sharp decline in *Achnanthes minutissima* (pH optima 6.3) and *Brachysira vitrea* (pH optima 5.9), and an increase in *Navicula leptostriata* (pH optima 5.1), *Eunotia exigua* (pH optima 5.1) and *Cymbella perpusilla* (pH optima 5.2). Since 1991 the sediment traps show an increase in *B.vitrea* and decreases in *C. perpusilla,* and possibly *E. exigua* and *N.leptostriata*. These changes suggest a small improvement in pH. They also suggest that in its early stages, biological 'recovery' at this site involves a return toward an earlier flora, at least as far as this concerns the dominant taxa. There is no evidence to date of any response in the relatively circumneutral *A. minutissima* and diatom inferred pH (5.2) remains well below that of pre-industrial times (6.3). It should be noted that the change in the diatom inferred pH in epilithon is well correlated, not only with measured March pH, but also negatively with March Cl concentration (Figure 7.8). Floristic changes could therefore primarily represent a response to climatic effects rather than emission reduction induced recovery (Section 7.3).

Evidence of recovery from comparisons of sediment trap and sediment core assemblages is more dramatic and convincing for Llyn Llagi (Figure 7.5). Here, the acidification history involved an early decline in *Achnanthes minutissima* (pH optima 6.3), later decline in *Brachysira vitrea* (pH optima 5.9), temporary dominance by *Eunotia incisa* (pH optima 5.1),

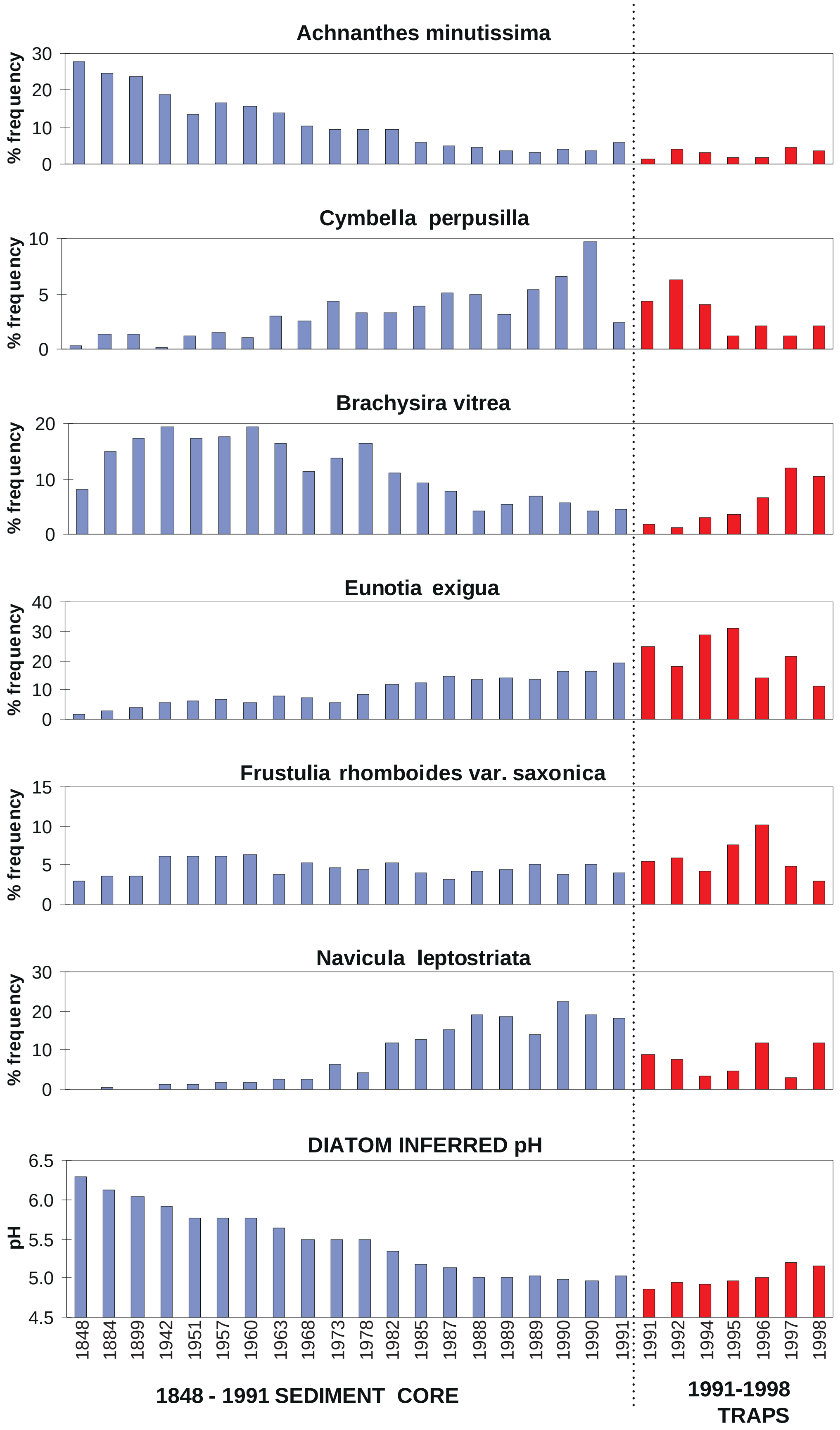
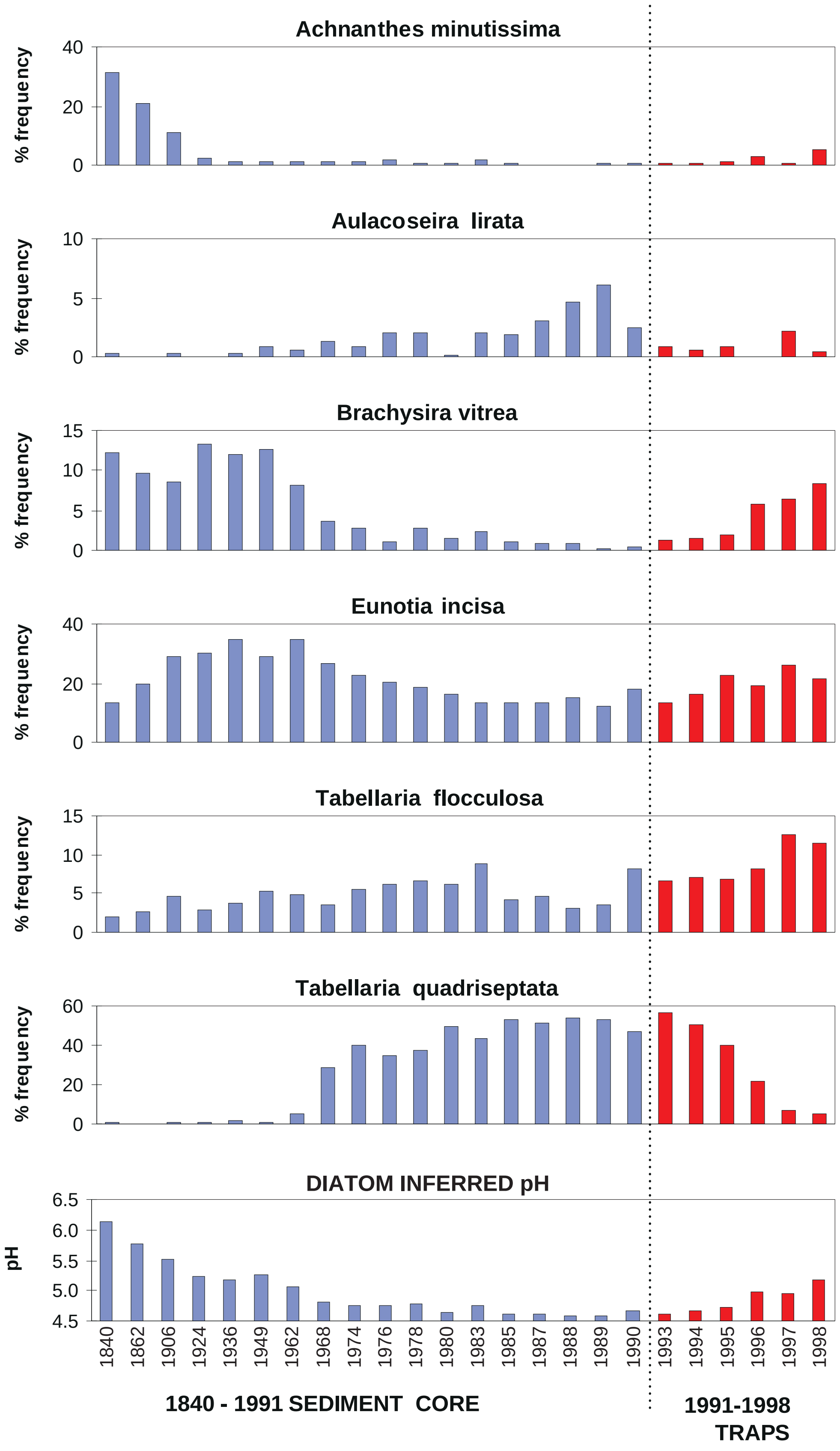


Figure 7.4

Comparison of changes in the representation of dominant diatom taxa in Pb^{210} dated samples from a sediment core sequence (CHON 11) and more recent changes in sediment trap samples from Loch Chon. The bottom graph shows diatom inferred pH (based on weighted averaging) for all samples

Figure 7.5

Comparison of changes in the representation of dominant diatom taxa in Pb^{210} dated samples from a sediment core sequence (LAG 3) and more recent changes in sediment trap samples from Llyn Llagi. The bottom graph shows diatom inferred pH (based on weighted averaging) for all samples



and then displacement of *E. incisa* by *Tabellaria quadriseptata* (pH optima 4.9) which increased to approximately 50% representation. The floristic assemblage of the contents of the first sediment trap, collected in 1993, matched that at the top of the sediment core taken in 1991. However, since 1991 there has been a progressive decline in *T. quadriseptata* and an increase in *E.incisa* and *B.vitrea* in successive sediment trap samples. There is even evidence for a recent small increase in *A.minutissima*. Again, therefore, the diatom flora appears to be reverting to a former state; however, compared to Loch Chon, the rate of change has been far steeper.

There is a taxonomic exception to the general evidence for a return to a previous flora in Llyn Llagi. *Tabellaria flocculosa* appeared to increase slightly over the course of acidification and has continued to increase in sediment trap samples. It is possible that the current abundance of this species will not persist, but it would seem that it has responded to factors other than acidity, e.g. changes in climate, nutrient availability, etc.. This emphasises the possibility that the physio-chemical environment of a theoretically ‘recovered’ lake may differ from its pre-industrial state for reasons other than acidity, and may not therefore have the capacity to support an identical flora and fauna to that which was lost.

Unlike Loch Chon, the observed changes in Llyn Llagi do not appear to correlate with chloride concentration or any other climatically related factor. In short, these changes represent the most convincing evidence of real biological recovery, resulting from an amelioration in pH, observed for the whole Network. There is little evidence for linear change in sediment trap species assemblages for other UKAWMN lakes, although these have not been analysed statistically.

■ 7.3. Further consideration of linear trends in macroinvertebrate and epilithic diatom data

Comparisons between the trend results for water chemistry and biology highlight differences between the two datasets (Table 7.2). Linear trends were found at nine and eleven sites for epilithic diatoms and macroinvertebrates respectively, but temporal trends in acidity related variables were only detected at seven sites. At only two sites, Loch Chon and Llyn Llagi, were linear decreases in acidity mirrored by recovery trends in both epilithic diatoms and macroinvertebrates.

For those sites where chemical improvements have not been observed, biological trends could represent responses to one, or a combination, of the following:

- real recovery in response to chemical changes which have not been detected with the methods of analysis employed (e.g. chemical improvements confined to one time of year);
- lagged recovery, e.g. biological responses to chemical improvements which occurred before the onset of monitoring, as for example suggested in the longer term data sets (Chapter 6);
- responses to other changes in the environment (lagged or immediate), such as changes in climate, or catchment effects such as felling or water level change;
- natural population or ecosystem driven oscillations with a cycle of several years.

It is important that the nature of the trends identified in the biological datasets is adequately understood so that:

i) real biological recovery is recognised if, when and where it occurs;

ii) other trends, which may be indicative of improvement but may not be sustained in the longer term, are not incorrectly attributed to emissions reduction policy; and,

iii) major influences which are not related to chemical recovery may eventually be quantified and statistically ‘removed’, so as to allow more sensitive detection of underlying trends.

Macroinvertebrates

At sites where linear trends have been identified, the inter-annual pattern of variation in assemblages is often very similar. For example, the mean of the annual score of samples on the first axis of PCA (which summarises the component of maximum variation in the species assemblage between samples) tends to be well correlated between those sites which show linear trends but not for most others (see Table 7.3). This suggests that the macroinvertebrate communities of these sites may be influenced by one or more common factor, despite the apparent absence of common trends in water chemistry.

The near west coast location of the sites showing linear trends in macroinvertebrate assemblages may provide a key to understanding the underlying influences (see Figure 7.6). As discussed in Section 5.3.1, sites close to the west coast appear vulnerable to westerly and southwesterly storms, as these influence sea-salt and rainfall enhanced acidity. Since macroinvertebrates are sampled in the spring, and since, for the majority of species captured, the larval stage occurs over the winter-spring period, it is reasonable to hypothesise that the significant time trends in the species assemblages might reflect reductions in winter-spring acidity resulting from the declining influence of these weather conditions over the bulk of the monitoring period.

Water chemistry sampling is inadequate to capture the extent and frequency of acid episodes. Most occur over relatively few days, usually between December and March, but no water samples are collected from lakes between the first week of December and the first week of March. Even monthly samples from streams will not fully represent inter-annual variability in the frequency and intensity of extreme events. In order to test whether winter-spring storminess could explain the observed common variation in the species assemblages we took various monthly combinations of the North Atlantic Oscillation Index (NAOI) (see Section 5.3.5) as surrogate variables for storm activity. These were applied as explanatory variables to the species datasets in Redundancy Analysis (RDA), using the same approach adopted for time-trend analysis (Section 3.2.2).

This analysis showed that the January NAOI can consistently explain a significant proportion of variance in the macroinvertebrate data. Overall the January NAOI is significant for nine sites, all but one of which shows a linear (i.e. time) trend (Table 7.4). Table 7.4 also demonstrates that the correlation coefficients between the mean annual PCA Axis 1 scores, and the January NAOI are high for several sites (i.e. Loch Coire nan Arr, 0.83; Loch Tinker, 0.69; Loch Grannoch, 0.68; and Llyn Cym Mynach 0.80).

Why the weather in the month of January may be of particular importance in influencing inter-annual variability in the macroinvertebrate assemblage is unclear. Westerly storms mostly occur from December to March and are certainly not confined to this one month only. However, chloride concentrations in monthly sampled stream sites often reach their annual peak in samples collected in either January or February, both of which could be influenced by January weather conditions. Furthermore, years in which the January NAOI has been either high or low, have often been characterised by similar extremes in February and March. The January NAOI variable could therefore represent a longer winter-spring period. It is also possible that macroinvertebrate larvae are most vulnerable to acid episodes when at an early stage of development at the beginning of the year.

Perhaps importantly, the January NAOI generally explains a larger proportion of overall variance in sites in mid-west to northwest Scotland, i.e. Loch Chon, Loch Tinker, Allt na Coire nan Con, and Loch Coire nan Arr. At these sites the January NAOI is well correlated with both spring Cl

Table 7.3

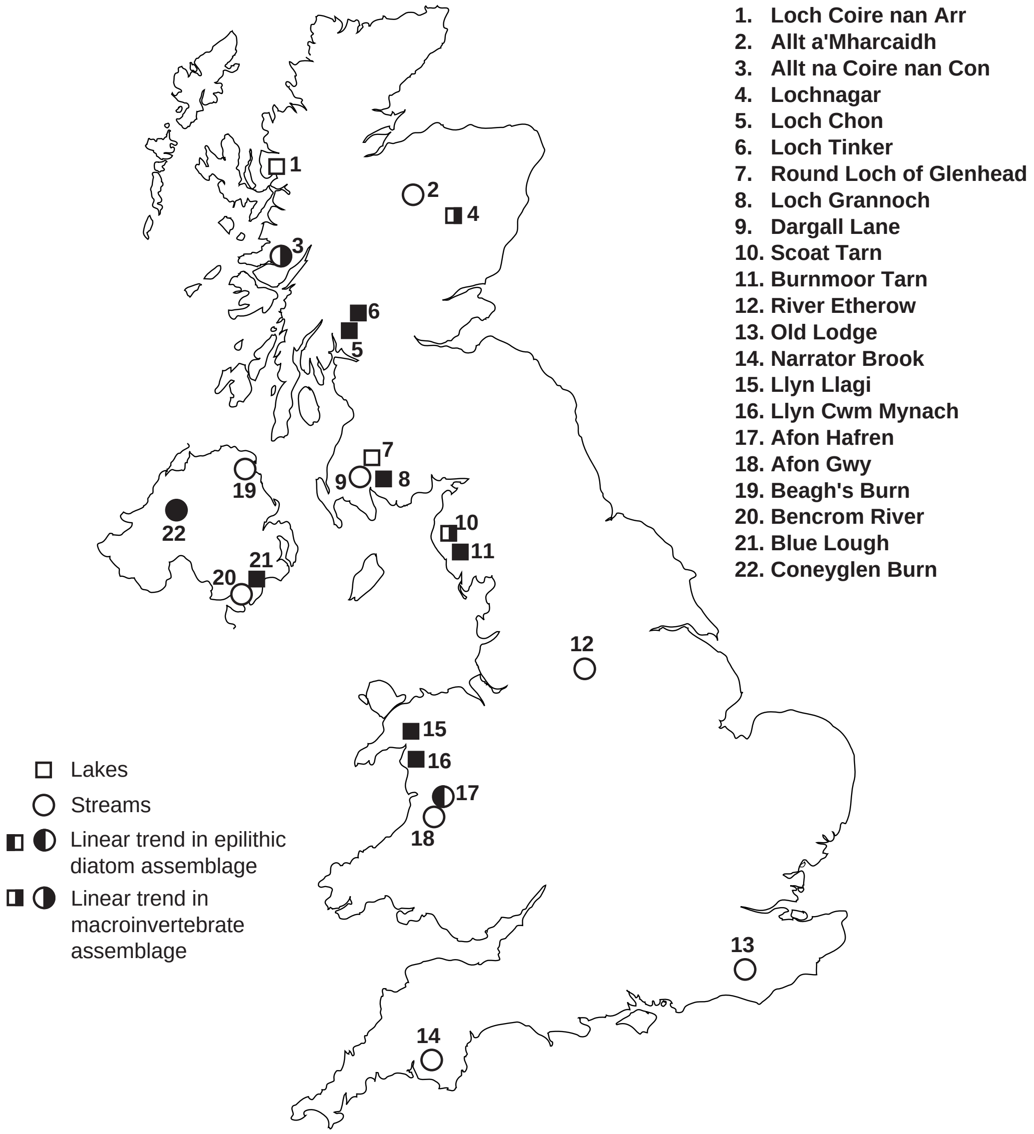
Between-site correlation coefficients (r) for the mean annual score of macroinvertebrate samples on PCA Axis 1

	UKAWMN site number																				
site name and number	3	4	5	6	8	10	11	15	16	21	22	1	2	7	9	12	13	14	17	19	20
Allt na Coire nan Con (3)	1.00	0.44	0.67	0.92	0.90	0.71	0.70	0.62	0.68	0.62	0.79	0.62	0.33	0.17	0.25	0.41	0.38	0.28	0.50	0.67	0.27
Lochnagar (4)	0.44	1.00	0.42	0.39	0.38	0.14	0.70	0.28	0.25	0.27	0.28	0.08	0.24	0.03	0.24	0.19	0.73	0.17	0.48	0.04	0.30
Loch Chon (5)	0.67	0.42	1.00	0.69	0.81	0.77	0.38	0.61	0.84	0.52	0.47	0.77	0.04	0.21	0.50	0.81	0.22	0.01	0.40	0.51	0.10
Loch Tinker (6)	0.92	0.39	0.69	1.00	0.90	0.79	0.76	0.63	0.78	0.67	0.84	0.70	0.37	0.24	0.14	0.40	0.32	0.22	0.39	0.64	0.36
Loch Grannoch (8)	0.90	0.38	0.81	0.90	1.00	0.79	0.59	0.66	0.76	0.68	0.81	0.68	0.13	0.16	0.31	0.50	0.35	0.22	0.31	0.63	0.04
Scoat Tarn (10)	0.71	0.14	0.77	0.79	0.79	1.00	0.51	0.49	0.91	0.41	0.66	0.95	0.36	0.61	0.41	0.69	0.11	0.42	0.00	0.37	0.23
Burnmoor Tarn (11)	0.70	0.70	0.38	0.76	0.59	0.51	1.00	0.44	0.50	0.36	0.68	0.41	0.60	0.30	0.31	0.13	0.74	0.29	0.25	0.14	0.54
Llyn Llagi (15)	0.62	0.28	0.61	0.63	0.66	0.49	0.44	1.00	0.72	0.76	0.22	0.46	0.20	0.03	0.01	0.27	0.40	0.36	0.29	0.32	0.08
Llyn Cwm Mynach (16)	0.68	0.25	0.84	0.78	0.76	0.91	0.50	0.72	1.00	0.63	0.52	0.91	0.19	0.42	0.32	0.67	0.19	0.31	0.19	0.39	0.21
Blue Lough (21)	0.62	0.27	0.52	0.67	0.68	0.41	0.36	0.76	0.63	1.00	0.54	0.38	0.29	0.17	0.04	0.07	0.07	0.07	0.38	0.56	0.01
Coneyglen Burn (22)	0.79	0.28	0.47	0.84	0.81	0.66	0.68	0.22	0.52	0.54	1.00	0.55	0.42	0.16	0.17	0.21	0.13	0.03	0.20	0.63	0.34
Loch Coire nan Arr (1)	0.62	0.08	0.77	0.70	0.68	0.95	0.41	0.46	0.91	0.38	0.55	1.00	0.28	0.52	0.41	0.68	0.02	0.28	0.07	0.36	0.16
Allt a'Mharcaidh (2)	0.33	0.24	0.04	0.37	0.13	0.36	0.60	0.20	0.19	0.29	0.42	0.28	1.00	0.43	0.03	0.19	0.31	0.37	0.00	0.02	0.85
Round Loch Glenhead (7)	0.17	0.03	0.21	0.24	0.16	0.61	0.30	0.03	0.42	0.17	0.16	0.52	0.43	1.00	0.10	0.41	0.03	0.60	0.47	0.32	0.38
Dargall Lane (9)	0.25	0.24	0.50	0.14	0.31	0.41	0.31	0.01	0.32	0.04	0.17	0.41	0.03	0.10	1.00	0.80	0.34	0.08	0.22	0.52	0.13
River Etherow (12)	0.41	0.19	0.81	0.40	0.50	0.69	0.13	0.27	0.67	0.07	0.21	0.68	0.19	0.41	0.80	1.00	0.03	0.17	0.22	0.35	0.08
Old Lodge (13)	0.38	0.73	0.22	0.32	0.35	0.11	0.74	0.40	0.19	0.07	0.13	0.02	0.31	0.03	0.34	0.03	1.00	0.28	0.12	0.17	0.15
Narrator Brook (14)	0.28	0.17	0.01	0.22	0.22	0.42	0.29	0.36	0.31	0.07	0.03	0.28	0.37	0.60	0.08	0.17	0.28	1.00	0.47	0.25	0.21
Afon Hafren (17)	0.50	0.48	0.40	0.39	0.31	0.00	0.25	0.29	0.19	0.38	0.20	0.07	0.00	0.47	0.22	0.22	0.12	0.47	1.00	0.73	0.16
Beaghs Burn (19)	0.67	0.04	0.51	0.64	0.63	0.37	0.14	0.32	0.39	0.56	0.63	0.36	0.02	0.32	0.52	0.35	0.17	0.25	0.73	1.00	0.05
Bencrom River (20)	0.27	0.30	0.10	0.36	0.04	0.23	0.54	0.08	0.21	0.01	0.34	0.16	0.85	0.38	0.13	0.08	0.15	0.21	0.16	0.05	1.00

Sites which have high correlation coefficients will exhibit similar patterns of temporal variation in species composition. The 11 sites shaded are those showing significant linear time-trends according to RDA and associated restricted permutation test. Note that Lochnagar, a non west coast site, and the only site where macroinvertebrate changes appear indicative of deterioration, is relatively poorly correlated with most other sites showing linear trends.

Figure 7.6

UK map showing the location of sites for which linear trends have been identified in epilithic diatom and macroinvertebrate assemblages



concentrations (i.e. March concentrations in lakes and mean January to March concentrations in streams) and January rainfall totals, and as a consequence it is likely to be associated with the frequency and intensity of acid episodes and overall winter-spring acidity for sites in this area (Figure 7.7). For several lakes, macroinvertebrate communities tend to be represented by low numbers of individuals and are dominated by acid tolerant species, such as the mayfly family the Leptophlebiidae, in the early 1990s, while they are relatively diverse, and represented by some acid intolerant taxa in 1996-1997. The former periods correspond with high January NAOI (i.e. stormy conditions), while the NAOI was negative for the latter.

It is interesting to note that the January NAOI is not significant in explaining between-sample variability at Llyn Llagi, for which a time trend has been identified, and where there is convincing evidence of recovery in the diatom community. It is therefore possible that the nature of the temporal trend in macroinvertebrates at this site is different from those observed elsewhere and this increases the possibility that change at this site reflects a longer term response to improving chemistry. However, for the

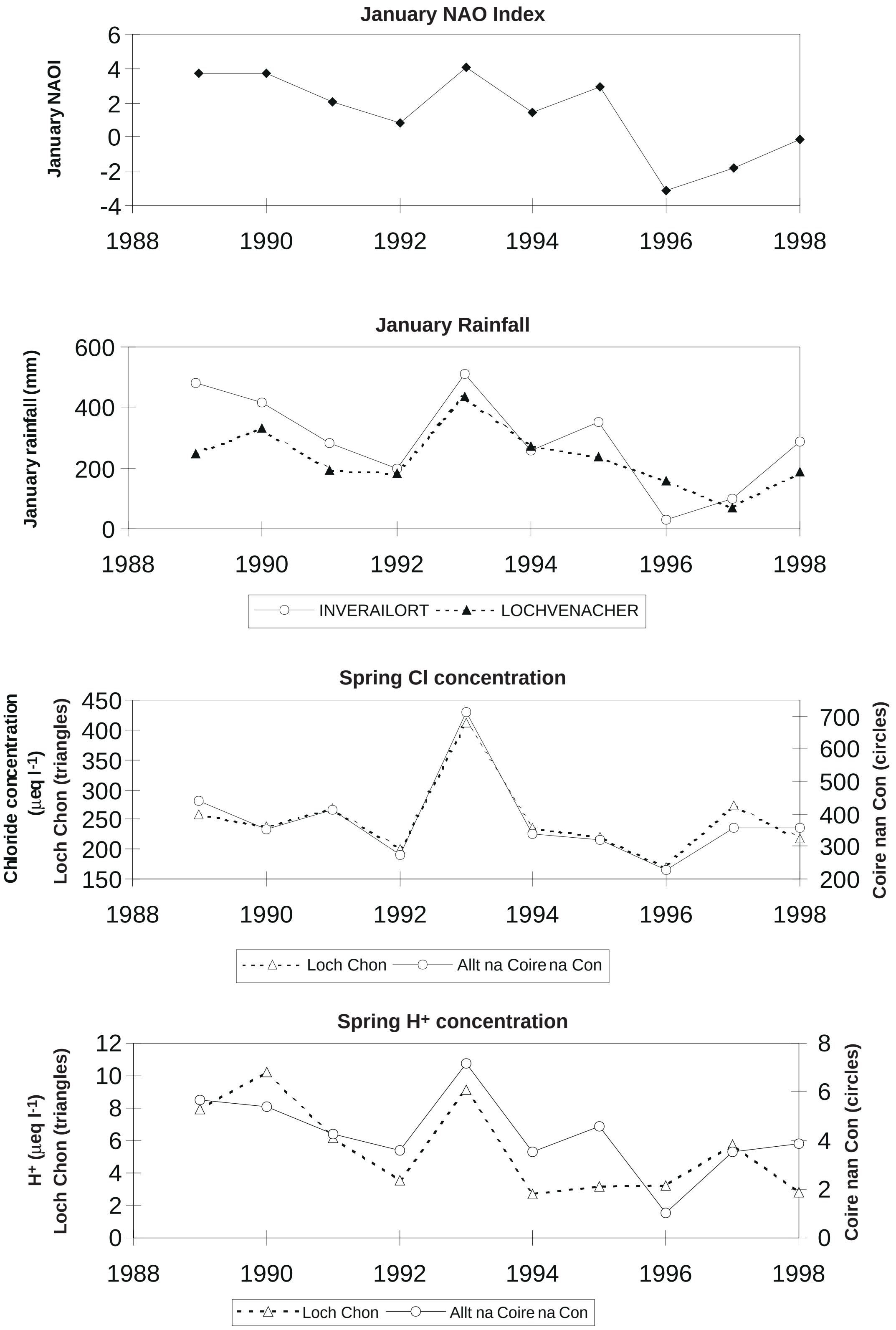


Figure 7.7

Relationship between the January NAO Index, January rainfall, and spring water chemistry for two Scottish sites (mean January to March concentration for Allt na Coire nan Con; March concentration for Loch Chon)

Rainfall data from nearby Meteorological Stations for these sites (Appendix 2)

majority of sites for which linear trends have been identified, it is more likely that changes result primarily from a reduction in winter storm activity. Reductions in intensity and duration of acid episodes provide possible mechanisms. Alternatively, community composition may simply co-vary with acidity. Other effects of inter-annual variations in climate, such as the extent and frequency of water level oscillations, variations in turbulence in the littoral zone or even winter temperatures (winter temperature is positively correlated with the NAO) may also be important. Specific mechanisms are therefore unclear and urgently require further research to ascertain.

These results tentatively suggest that, on an inter-annual scale, macroinvertebrate assemblages may be sensitive to changes in the severity of acid conditions in the winter-spring period. There is evidence from the longer term chemical datasets, described in Chapter 6, that chemical recovery has led to a gradual increase in the pH of the most acid events at some sites. It might therefore be expected that these changes will be tracked by a gradual return of more acid sensitive

Table 7.4

Variance in macroinvertebrate datasets explained by the first axis of PCA (PCA λ_1), and a time trend and the January North Atlantic Oscillation Index (NAOI) when statistically significant. The last column provides the correlation (r) for the relationship between the January NAOI and the mean annual score of samples on the first axis of PCA

site	% variance explained by PCA λ_1	% variance explained by time trend* RDA λ_1	% variance explained by January NAOI* RDA λ_1	correlation coefficient for January NAOI against PCA λ_1
Loch Coire nan Arr	30.6		16.8	0.83
Allt a'Mharcaidh	27.4			0.12
Allt na Coire nan Con	23.6	15.8	10.4	0.52
Lochnagar	26.2	10.4		0.07
Loch Chon	21.4	14.1	10.6	0.59
Loch Tinker	21.1	15.5	11.3	0.69
Round Loch of Glenhead	20.6			0.29
Loch Grannoch	20.6	13.1	10.0	0.68
Dargall Lane	32.8			0.10
Scoat Tarn	19.8	12.0	13.1	0.81
Burnmoor Tarn	23.3	11.6	6.2	0.43
River Etherow	41.4			0.32
Old Lodge	31.1			0.17
Narrator Brook	20.9			0.34
Llyn Llagi	25.0	11.5		0.58
Llyn Cwm Mynach	21.9	12.1	6.9	0.80
Afon Hafren	31.1			0.15
Afon Gwy	27.2			0.16
Beagh's Burn	21.1			0.27
Bencrom River	23.8			0.04
Blue Lough	27.6	14.4		0.50
Coneyglen Burn	28.4	13.9	10.5	0.57

macroinvertebrate taxa. However given the clear importance of inter-annual variability in weather on the chemistry of these sites, it is also likely that the temporal nature of recovery will be far from linear, and more sophisticated statistical techniques may be necessary to more sensitively detect any 'recovery' component within the inter-annual variation.

Epilithic diatoms

Of the nine sites showing temporal trends in epilithic diatom assemblages, only five also show temporal trends in water chemistry (Table 7.2). However, with the exception of the Afon Hafren, all of the sites showing trends in epilithic diatoms also exhibit trends in macroinvertebrates and all have westerly locations (see Figure 7.6). It is therefore possible that climatic controls similar to those proposed above for the freshwater fauna (Section 7.1.1) are important for the diatom flora.

Figure 7.3a demonstrates that for approximately half of UKAWMN lakes, the most acid assemblages occured in the early 1990s (and for several sites 1993) while those in 1996 or 1997 were the least acid. The earlier years were characterised by winters with relatively high winter-spring sea-salt inputs and rainfall, and this may have depressed lake pH well into the growing season. The winter of 1996, on the other hand, was largely free of westerly and south-westerly activity, and most lakes were less acid over this period. Given the west coast location of these lakes, and the temporal patterns in climate discussed above, the trends identified in the epilithon of some sites may therefore again reflect a change in winter-spring storminess over the monitoring period.

The most striking example of how climatic effects may have influenced trends in the epilithic diatom assemblage comes from Loch Chon. For this site the mean annual diatom inferred pH of all samples is exceptionally tightly correlated with measured March chloride concentration and March pH (Figure 7.8). It is therefore possible that the potential recovery discussed earlier for Loch Chon may primarily represent natural variability in response to changes in weather. If this is the case, then the current trend should disappear, once stormy (i.e. high NAOI) winters of the frequency and duration experienced at the onset of monitoring return to the UK.

7.4 Other between-year biological variability

7.4.1 Epilithic diatoms in UKAWMN streams and flow

Site summaries in Chapter 4 indicate that the epilithic diatom assemblages show considerably greater temporal variation in streams than lakes. The most obvious explanation for this is the greater temporal variation in chemistry experienced in most stream systems, resulting from sensitivity to variations in flow.

The acidity response of the stream epilithic flora may again be gauged by analysis of the relative change in diatom inferred pH with time. The application of the SWAP dataset to infer pH from stream epilithon should again be viewed with caution, and particularly since the stream environment is very different from the lake environments on which the method is based. However, it is clear from Figure 7.3b that several stream sites show similar temporal patterns in inferred pH, and these are very different from the trends observed for most lakes.

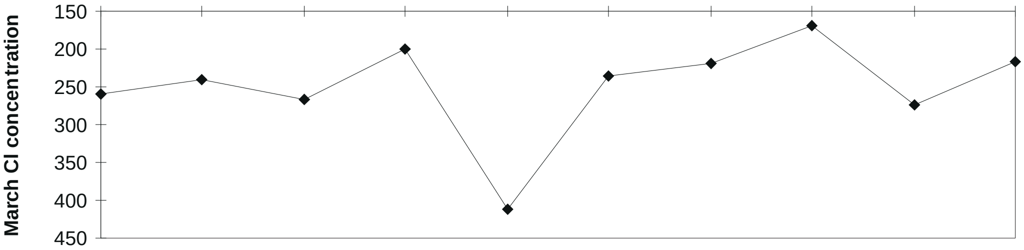
Most UKAWMN stream sites show strong relationships between pH and flow, which results from the changing proportional contributions of various flow paths to the watershed with changing rainfall (Figure 7.9). pH tends to be highest at low flows when the contribution from relatively buffered baseflow is highest. For the majority of stream sites, flow data is only available for the time of sampling, i.e. monthly spot measurements, and it is not possible from this to infer time-integrated flow conditions. We have therefore examined monthly rainfall records for local Meteorological Stations, to see whether flow could explain any of the inter-annual variability observed in diatom inferred pH.

For several sites, negative relationships were apparent between total June-July rainfall and mean annual diatom inferred pH (Figure 7.10).

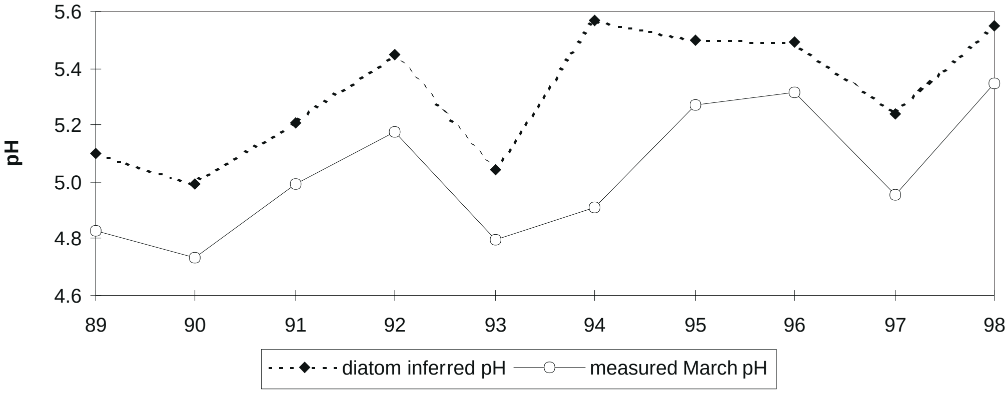
Figure 7.8

Measured chemistry (pH and Cl concentration) of March water samples and mean annual epilithic diatom inferred pH for Loch Chon 1989-1998

(a) March Cl concentration (µeq l^{-1}) (inverted scale)



(b) measured and inferred pH



Given the possible limitations in the application of a lake sediment based transfer function, and other potential errors, such as those associated with the representativity of local Meteorological Station rainfall data for the UKAWMN site, the apparent strength of these relationships is surprising. The only statistically significant linear relationship was for the River Etherow ($r^2 = 0.61$ $p<0.01$); however, the consistently negative regression slopes and relatively high r^2 values (four other sites show r^2 values of more than 0.4) suggest that summer flow may have a dominant influence on inter-annual variability at many sites. It is interesting to note that the weakest rainfall-diatom inferred pH relationships are for Old Lodge and the Afon Hafren, and these sites also show poor relationships between flow and measured pH.

The strength of the Etherow diatom-flow relationship could in part reflect the particularly large gradient in pH which is observed between high and low flows. Inter-annually, the diatom assemblage probably varies more than for any other site on the Network and ranges from a *Eunotia incisa* dominated flora indicative of very low pH, to one dominated by the circumneutral species *Achnanthes minutissima*.

The relationships identified suggest that the assemblages of many sites will represent antecedent flow conditions, perhaps for the previous two months, and it is likely that species representation for most sites will be in a process of continuous change over the spring-summer growing season. The summer sampled (mostly July-August) epilithic diatom assemblages may therefore not be particularly representative of the year-round crop.

The apparent sensitivity of the stream diatom assemblage to fluctuations in flow has obvious

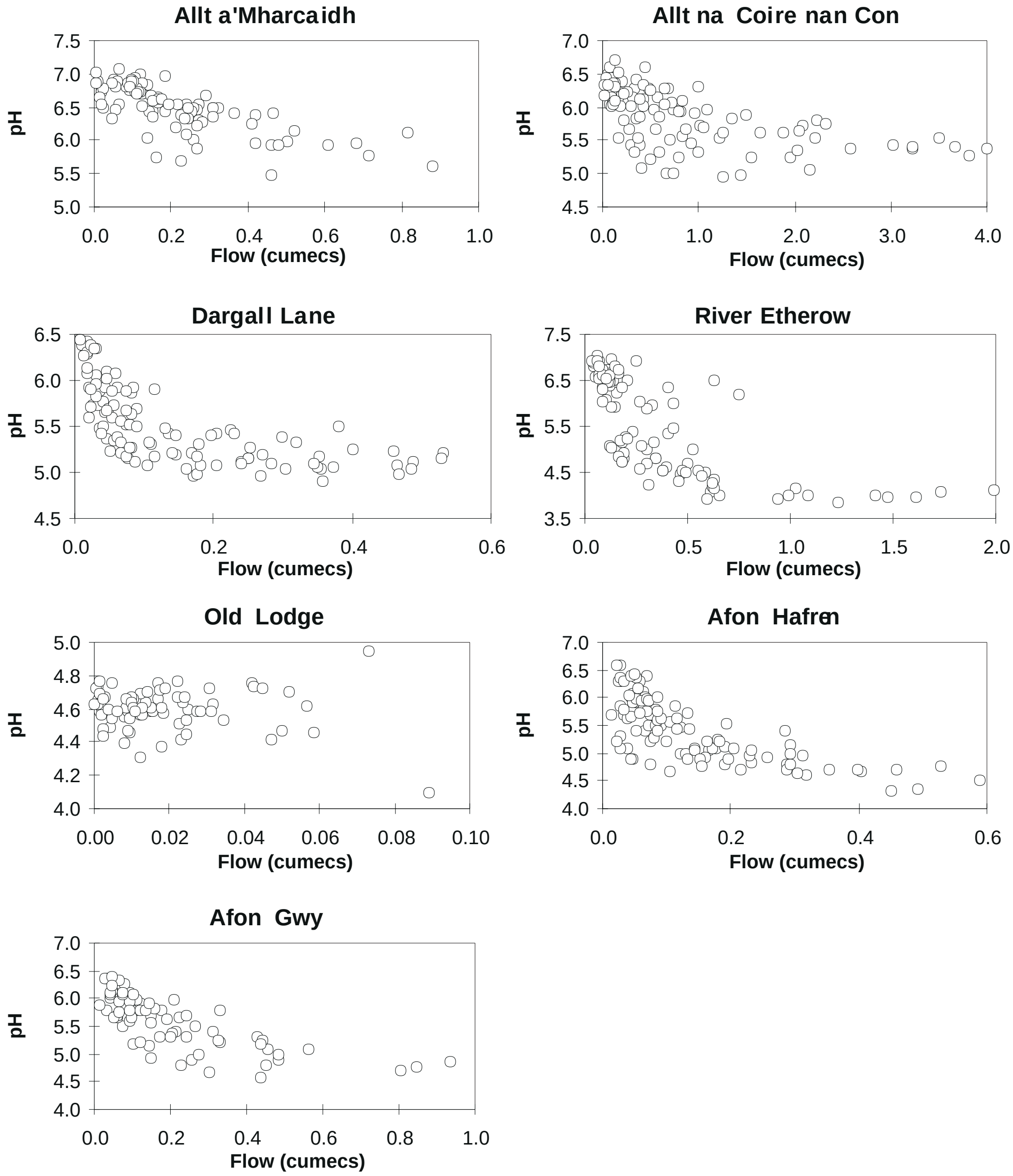


Figure 7.9

The relationship between spot sampled pH and flow for all UKAWMN stream sites for which there are monthly flow measurements

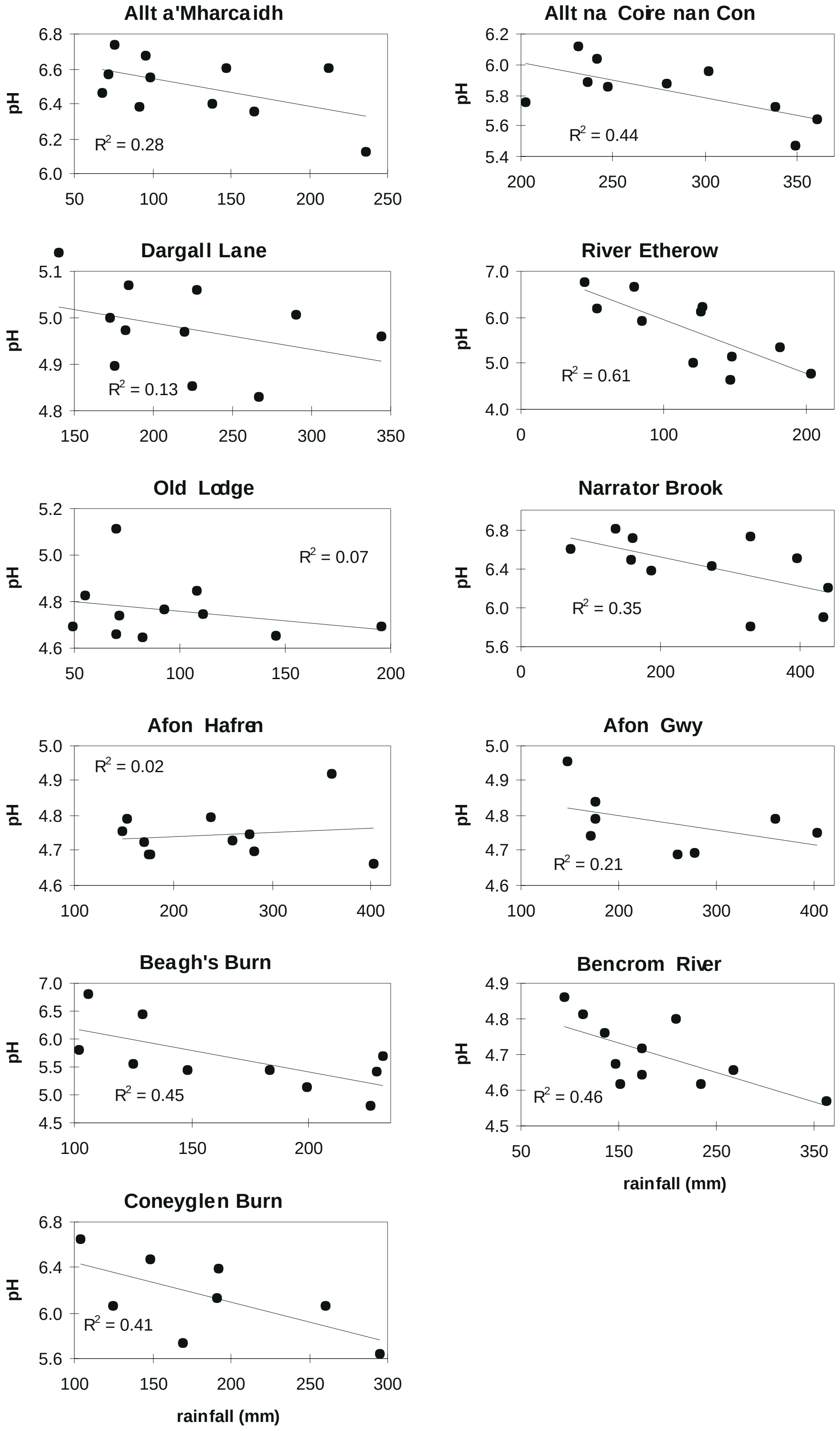
implications for trend detection, in that high inter-annual variability will mask potential recovery signals. It therefore seems likely that identification or statistical validation of epilithic diatom recovery will take considerably longer for streams than lakes. The period required for trend detection could be reduced by increasing the frequency of diatom sampling, perhaps to monthly, over the growing season. Chemical recovery may not involve obvious improvement at low flows, since these are the periods when chemistry is most buffered. With the current sampling regime, it is therefore likely that biological recovery will first become evident in a change through time in the diatom assemblages of high summer rainfall years.

7.4.2 Temporal variation in macroinvertebrate species richness

Spatially there is a general relationship between mean macroinvertebrate species richness and pH for UKAWMN sites (Figure 7.1), and similar links have been identified both spatially and temporally in the scientific literature. The identification of temporal trends in minimum

Figure 7.10

The relationship between mean annual epilithic diatom inferred pH (based on weighted averaging) and total June-July rainfall (mm) (recorded at nearby Meteorological Stations) for UKAWMN stream sites (1988-1998)



species richness (MSR) might therefore provide an indication of the extent of biological recovery. Time series for macroinvertebrate MSR for both lakes and streams are presented in Figures 7.11a and 7.11b, respectively.

Upward trends are apparent in MSR for most UKAWMN streams but no UKAWMN lakes. Loch Chon and Llyn Llagi, both of which show linear trends in the macroinvertebrate species composition which are indicative of biological improvement, provide no indication of a change in MSR with time, and the same is true for most other lakes which show linear trends. Conversely, few trends in species composition have been observed for streams. It therefore appears that temporal variation in species composition and species richness have been largely independent for most sites over the interpretative period.

Temporal patterns in MSR for several stream sites are well correlated (Table 7.5) and correlations appear to be stronger for sites which are geographically close. For example, high correlation coefficients were obtained between Scottish sites, and between these and sites in Northern Ireland. MSR for Old Lodge, which is geographically most remote, is only weakly correlated with that for other sites. The absence of correlations between stream sites and most lake sites (not shown) appears to rule out the possibility that the data represent a change in sampling efficiency over the years.

The most likely explanation for these geographically related, common patterns which are only observed in stream sites, and which do not appear to be directly linked to chemical change, is a change in the winter-spring flow regime. As has been discussed in several other sections of this report, throughout most of the interpretative period there has been a general decline in winter-spring westerly weather activity, and there is evidence from many of the Meteorological Stations close to UKAWMN sites that this was accompanied by a general decline in winter-spring rainfall.

Analysis of local rainfall data provides some indication of negative relationships between rainfall at this time of year and MSR but no common period has been identified for all sites. Negative relationships are apparent between MSR and total January - April rainfall at four sites (Allt na Coire nan Con, Dargall Lane, Old Lodge and Coneyglen Burn) (Figure 7.12), although a linear relationship is only statistically significant at the p=0.01 level for Old Lodge. Interestingly, Old Lodge is one of the few UKAWMN stream sites which shows no evidence for a relationship between flow and acidity (Figure 7.9), and the effect on MSR at this site is therefore more likely to be due to physical, rather than chemical, factors.

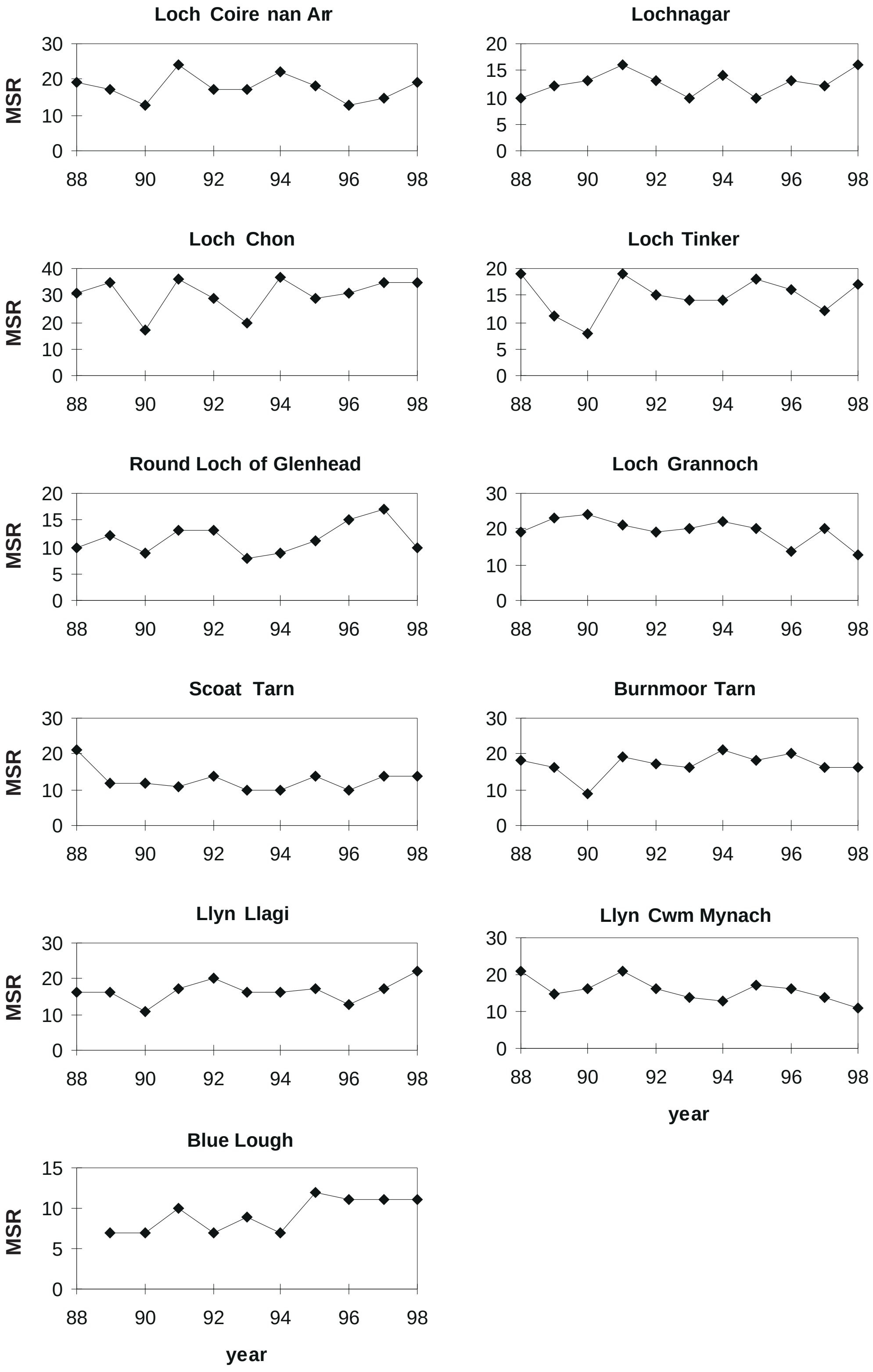
Table 7.5

Between-site relationship (correlation coefficient r) in the temporal variation in macroinvertebrate minimum species richness (10 year stream records only)

				site no.				
	3	*9*	*12*	*13*	*14*	*17*	*19*	*20*
Allt a'Mharcaidh (2)	*0.72*	*0.59*	*0.59*	*0.32*	*0.58*	*0.46*	*0.68*	*0.63*
Allt na Coire nan Con (3)		*0.73*	*0.74*	*0.37*	*0.65*	*0.53*	*0.81*	*0.67*
Dargall Lane (9)			*0.82*	*0.39*	*0.82*	*0.64*	*0.86*	*0.92*
River Etherow (12)				*0.42*	*0.92*	*0.85*	*0.85*	*0.84*
Old Lodge (13)					*0.48*	*0.43*	*0.18*	*0.35*
Narrator Brook (14)						*0.87*	*0.72*	*0.79*
Afon Hafren (17)							*0.68*	*0.68*
Beagh's Burn (19)								*0.88*
Bencrom River (20)								

Figure 7.11a

Time series for macroinvertebrate minimum species richness (MSR) for UKAWMN lakes (1988 - 1998)



Loch Coire nan Arr

Lochnagar

Loch Chon

Loch Tinker

Round Loch of Glenhead

Loch Grannoch

Scoat Tarn

Burnmoor Tarn

Llyn Llagi

Llyn Cwm Mynach

Blue Lough

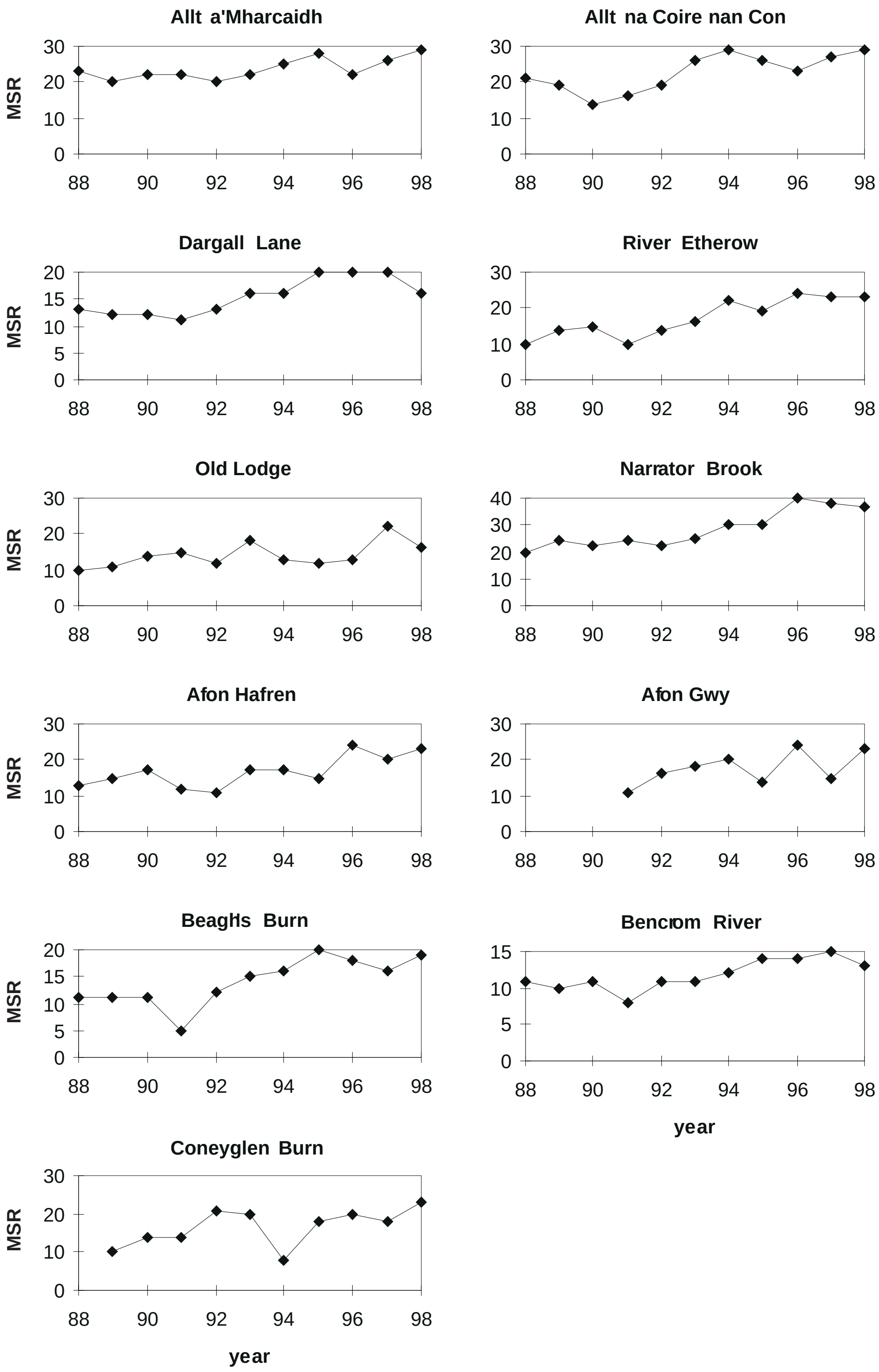


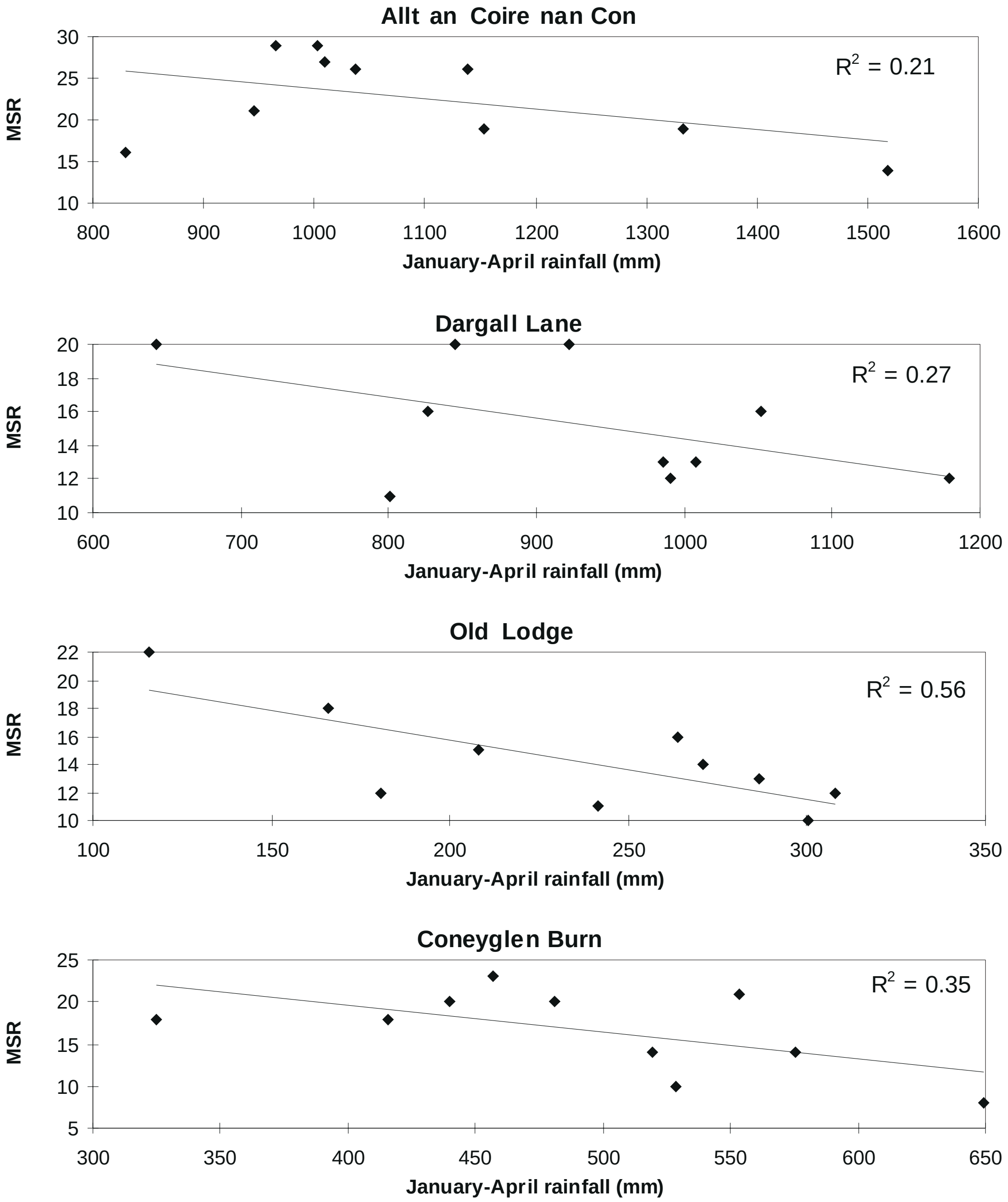
Figure 7.11b

Time series for macroinvertebrate minimum species richness (MSR) for UKAWMN streams (1988 - 1998)

Given the between-site correlations demonstrated in Table 7.5 it seems likely that changes in MSR observed in the majority of streams will reflect the influence of some feature of winter-spring flow, and it is therefore likely that the apparent increases in MSR will not be sustained in the longer term. These findings suggest that, in a monitoring context, macroinvertebrate minimum species richness may be of limited value as an indicator of ecosystem health, at least over the relatively short duration encompassed by this report.

Figure 7.12

Relationship between the annual minimum species richness (MSR) of macroinvertebrate communities in samples from Allt na Coire nan Con, Dargall Lane, Old Lodge and Coneyglen Burn and total January-April rainfall (recorded at nearby Meteorological Stations)



7.5 Summary

- Biological characteristics of UKAWMN lakes and streams reflect site acidity. Generally, the most acid sites have the fewest species and support the lowest trout densities. The least acid sites tend to exhibit relatively high species diversity. However other chemical and physical factors are also likely to be important in determining biological properties. The outflows of the least acid lakes do not have high trout densities.

- For the majority of sites, trout density is lower than that predicted for non-polluted equivalent sites by HABSCORE HQS. Spatially, mean trout density can be linked to mean water chemistry. A roughly exponential decline in density with increasing labile Al concentration is observed, while healthy populations are not found in most sites which have a ten-year mean ANC of less than 0 μeq l^{-1}.

- Temporal trends have been identified in the assemblages of epilithic diatoms and macroinvertebrates at several sites. However, Llyn Llagi and Loch Chon are the only sites exhibiting trends indicative of recovery in both biological groups, which also show significant reductions in acidity.

- Temporal diatom species change in Llyn Llagi is also apparent in sediment trap samples and the trend in the latter is roughly the reverse of that observed in samples toward the top of a sediment core (indicative of acidification) taken from the lake in 1991. The recent changes therefore provide convincing evidence of the early stages of biological recovery, at least at the lowest trophic level, at this site. Similar evidence for ‘reversal’ of the diatom assemblage is apparent at Loch Chon. However here, changes in the epilithic flora can be linked to a reduction in March Cl concentration, and this suggests that the diatom response may be influenced, or even primarily determined, by a reduction in climatically induced acidity over the last decade.

- Of the nine sites with trends identified for epilithic diatoms, trends at five are indicative of an increase in pH, and one is indicative of deterioration. Four of the six sites with trends indicative of a change in acidity show consistent trends in measured pH. Generally for lakes, inter-annual variation in epilithic diatom assemblages can be linked to inter-annual variations in pH.

- Inter-annual variation in epilithic diatom assemblages can be linked to variations in summer rainfall at those stream sites for which there is a strong relationship between flow and pH. This suggests that these assemblages will be particularly dependent on relatively recent antecedent acidity, i.e. for the previous two months.

- Eleven sites exhibit linear trends in the macroinvertebrate assemblage, but trends at only two of these are interpreted as being indicative of recovery, while one is indicative of deterioration. The three sites for which faunal trends are indicative of change in acidity also demonstrate consistent significant trends in pH. Most of the sites where macroinvertebrate trends have been recognised have west coast locations, and the pattern of inter-annual variation in species is very similar between all of these. It is therefore possible that the observed trends reflect a response of the aquatic fauna to a decline in the frequency, duration and intensity of acidic conditions resulting from a reduction in ‘winter westerly’ weather activity. The January North Atlantic Oscillation Index can explain a significant proportion of variation in species assemblages of most sites for which linear trends have been identified.

- Upward trends have been observed in minimum species richness (MSR) of macroinvertebrate samples in most stream sites, and the correlation of temporal variation between sites is strongest for sites which are geographically close. Four sites show a negative relationship between MSR and total January to April rainfall measured at nearby Meteorological Stations. This relationship is strongest at Old Lodge, where there is little evidence of any link between flow and pH, suggesting that physical effects of flow may be more important than chemical effects in this respect.

- Trends in aquatic macrophyte assemblages have been identified at five sites, but all of these most likely result from physical disturbance rather than chemical change.

- Few linear trends were observed in trout population statistics. The relatively high mobility of fish, in comparison to other biological groups, adds to overall sample variability, and for most sites it is likely that even where conditions may be becoming gradually more favourable for fish, several more years of monitoring may be necessary to allow the possible detection of trends. However, in the survey stretch of Old Lodge there has been a striking increase in the density of newly recruited trout during a period of sharply declining labile Al concentration.

8 Summary and Conclusions

Don Monteith &
Chris Evans

8.1 Atmospheric deposition and the impact on UKAWMN sites (1988-1998)

The ultimate aim of emissions reduction policy is to achieve improvements in target environments damaged by the effects of atmospheric deposition. Emission reductions on a national and international level have resulted in a major decline in SO_2 concentration and S deposition in urban and rural areas in central and south England. However, the target environments of concern for the UKAWMN are the acidified freshwaters which are mostly located in more remote parts of the UK. In order to test whether these ecosystems have benefited from implemented policy, a series of functional links, from emissions reduction, through deposition reduction, to the recovery of water chemistry and finally aquatic biota, must be demonstrated. Each link has been discussed in the course of this report, and is summarised below.

Have reductions in anthropogenic emissions led to a reduction in acid deposition in the UK over the past decade?

Undoubtedly yes. Over the period 1986-1997, sulphur emissions reductions of 55% have almost been matched by a 50% reduction in sulphur deposition for the UK as a whole. However, smaller declines in emissions of NO_x are not reflected in deposition trends. In some remote regions NO_3 deposition appears to have increased slightly.

Do we observe reductions in sulphur deposition in the regions with acid sensitive freshwaters?

Nationally, there has been a disproportionate decline in dry, relative to wet, deposition. Substantial reductions in both wet and dry xSO_4 and H^+ concentrations have occurred at sites within 100 km of major emissions sources, and particularly those in the east Midlands and Yorkshire. This has had a major effect in the Pennines area where freshwaters are believed to be some of the most impacted in the entire UK. Sensitive areas at intermediate distances from sources, including mid-Wales and the Lake District have experienced smaller, but still measurable, declines in xSO_4 deposition. However, the majority of UKAWMN sites lie beyond these regions, to the west and north, where rainfall is high and SO_4 deposition is predominantly in wet form. Here, downward xSO_4 trends during the last ten years have been very small and only detectable using regional analysis. The signal at these sites appears to be swamped by noise resulting from climatic variability. Reductions in xSO_4 deposition have therefore occurred in all areas, but rates of reduction are geographically skewed, being virtually undetectable in the more remote regions, including north Wales, and southwest, central and northwest Scotland.

Has deposition reduction led to declines in acid anion concentrations in UKAWMN freshwaters over the last decade and over longer time scales?

Large declines in xSO_4 concentrations have been recorded at Old Lodge (southeast England) and the River Etherow (Pennines). Smaller, but still significant declines in concentration have occured at Lochnagar (northeast Scotland). The effects of small reductions in the deposition flux of SO_4 from non-marine sources at other sites could be masked by noise from inter-annual variability and problems associated with the use of a fixed ratio of SO_4:Cl to correct for sea-salts, since SO_4 is believed to be retained relative to Cl after sea-salt deposition episodes. For the majority of sites therefore, there is little indication of declining xSO_4 concentration over the monitoring period. However, data from longer time series for sites in mid-Wales, and southwest and central Scotland, show that there has been a considerable reduction in xSO_4 concentration from the early 1980s to the present. It is likely that sizeable deposition reductions coincident with a sea-salt correction effect, were responsible for a large decline in xSO_4 concentration at Scottish sites in the mid-1980s.

Although there is spatial correlation between NO_3 deposition fluxes and surface water concentrations, inter-annual variation in NO_3 concentration appear to primarily reflect climatic differences between years.

Have improvements in pH or alkalinity been observed at sites where acid anion concentrations have declined, or elsewhere?

At the River Etherow and Old Lodge, the only sites which have experienced large decreases in xSO_4, there is little evidence of chemical recovery over the interpretative period. The River Etherow exhibits considerable flow-dependent temporal variability in acidity, so detection of an anticipated small overall improvement is particularly difficult here. However, it appears that chemical recovery at both the Etherow and Old Lodge may have been slowed, as a result of base cation declines partly offsetting declines in acid anions. Similar observations of delays in recovery have been made in the United States and Scandinavia, although for the latter it appears that increases in base cation concentrations and alkalinity are now underway. For Lochnagar, the decrease in xSO_4 has been outweighed by an even greater increase in NO_3, and as a result this site has continued to acidify. The longer term datasets available for a limited number of sites provide a more encouraging perspective. Relatively large reductions in xSO_4 observed in the mid-1980s were associated with increases in pH in most cases.

Seven UKAWMN sites do show positive linear trends in pH and/or alkalinity. However, these sites are mostly in areas where deposition reductions have at best been very slight, and most show little evidence for downward trends in total acid anion concentrations. It is therefore possible that most observed trends primarily represent an overall decline in the combined effects of sea-salt deposition and high rainfall, both of which can temporarily enhance acidity. The 1988-1998 period appears at most only to encompass one climatic cycle with regard to these effects. Further years of monitoring are therefore essential before the full extent of their influence can be quantified and statistically removed, so that any underlying deposition related trend may be identified.

Are changes in acidity in UKAWMN sites reflected in aquatic biology?

At two sites, Llyn Llagi and Loch Chon, improvements in pH are matched by linear trends in epilithic diatoms and macroinvertebrates which are indicative of improved conditions. For Llyn Llagi, comparisons between the diatom assemblage of sediment traps (recent) and a sediment core (the past) provide convincing evidence that biological recovery, at least at the lowest trophic level, is underway at this site. This recovery has seen the re-establishment of a similar diatom flora to that lost in the latter stages of acidification. Whether continued improvement might eventually lead to a return to the pre-acidification flora is of course impossible to predict and will only be ascertained by continued monitoring. Similar indications of reversal are evident for Loch Chon, but here it is also possible that the observed trends are at least in part driven by climatic influences.

Inter-annual variation in species assemblages at lake sites which do not show trends, also appears to reflect inter-annual variation in pH. These results are perhaps not surprising given the well established dependence of the diatom flora on pH, but do suggest that this community will respond rapidly, if, when and where real chemical “recovery” occurs.

For the streams, there is strong, although indirect, evidence from rainfall data and flow/pH relationships, that the diatom community reflects mean summer acidity. At sites such as the River Etherow, which undergo large variation in pH depending on the proportional contributions of surface run-off and base-flow, very dramatic improvements in pH at high flow would be necessary for any effect to be observed in the summer diatom samples in the near future. The other primary producer group, the aquatic macrophytes, provide no indication of response to temporal variation in pH.

Linear trends in macroinvertebrate communities, which were identified for 11 sites, (mostly lakes) can also be linked to variation in acidity, although in this case it is unclear whether there is any causal relationship or whether biology and chemistry are simply co-variable. It is likely that these trends reflect a general decline in the intensity and/or duration of acid episodes resulting from the combined effects of enhanced sea-salt deposition and high rainfall over the period of interpretation. If this is the case, and given the evidence from the longer term records of a few sites, that emissions reductions have led to a gradual reduction in severity of spring acidity since the early 1980s, we should expect to see a gradual (although non-linear) improvement in the lake fauna with time. Alternatively however, the lake fauna may primarily be affected by other climatic factors including the frequency and magnitude of lake level oscillations or by inter-annual differences in winter temperature. It is therefore crucial that experimental work is undertaken, in conjunction with continued monitoring, to address these issues.

The apparent sensitivity of the lake macroinvertebrate community to climatic conditions in spring, raises the question as to whether autumn sampling would provide a less “noisy”, and therefore more easily interpretable, record of “recovery” in response to chemical improvements. Similarities in the temporal variation of species richness amongst stream sites, including those which show no relationship between pH and flow, suggest that physical flow conditions are likely to have had a major influence over the monitoring period.

Temporal variation in trout density and condition factor data show less coherence between sites. Assessment of population statistics for fish are complicated by their highly mobile nature. Consequently the relative importance of recruitment, mortality and up- or down-stream migration is very difficult to quantify. Mobility therefore represents another source of noise and lengthens the period of monitoring which is necessary for recovery trends to be identified. There is a suggestion from UKAWMN data that density differences between sites may be related to labile Al concentrations. The most striking within-site relationship identified concerns a significant increase in trout density at Old Lodge which mirrors the reduction in labile Al over the same period. These data suggest that, for sites where healthy populations are already present in better buffered waters downstream, reductions in labile Al might induce rapid upstream migration. To date, temporal relationships between trout density or condition factor and chemistry for most other sites are insignificant.

8.2 Further observations

In addition to answering the primary questions regarding environmental response to the changing acid emission regime, the considerable time series of data collated by the UKAWMN provides new insights into environmental processes in upland freshwater catchments. These are often of direct relevance to the overall aims of the Network, but are also broadening our understanding of the influence of climate variability, and the potential influence of long term climate change on upland freshwaters. The following points summarise the main findings of recent data analysis.

- Increases in NO_3 at Lochnagar, Round Loch of Glenhead, Loch Chon and the River Etherow suggest increasing N saturation of these catchments, although they may also have been influenced by small increases in NO_3 deposition. Concentrations are expected to continue rising unless substantial reductions in deposition are achieved. At other sites, any saturation-related increases that may be occurring are obscured by other sources of variation, including episodicity and seasonality. Inter-annual variations in NO_3 have also been linked to climate; an inverse relationship has been demonstrated between winter temperature and spring NO_3 maxima, and is believed to reflect variations in the North Atlantic Oscillation (NAO).

- Dissolved Organic Carbon (DOC) concentrations have increased strongly in virtually all monitored regions of the UK; highly significant rising DOC trends have been identified at nineteen of the twenty-two UKAWMN sites, with concentrations at six sites having doubled or more during the last decade. The biological impacts of these increases are likely to be varied, including reduced light penetration due to increased water colour which could restrict the depth of plant growth; reduced penetration of potentially damaging UV-B radiation; and reduced toxicity to fish under acidic conditions due to organic complexation of aluminium. It is not currently possible to identify a definite mechanism for DOC increases, or therefore to predict whether they will continue into the future. However, the most the most probable hypothesis is increased microbial decomposition of soil organic matter resulting from increasing summer temperatures. Under a scenario of rising global temperatures, therefore, DOC and colour levels in upland waters may be expected to increase further.

- Inter-annual variability in levels of sea-salt deposition has been identified as a major cause of chemical variation in the UKAWMN dataset. The majority of UKAWMN sites lie within 50 km of western or southern coasts, and receive large sea-salt inputs during westerly or south-westerly frontal storms. The frequency of these storms has been shown to vary substantially from year to year, with maxima associated with high winter values of the NAO Index. Marine ion concentrations at near-coastal sites have consequently shown highly consistent cyclical variations, with a major peak during the high NAOI 1989-1991 period. Cyclical variations have also been observed in non-marine cations, including H^+ and labile Al which are believed to result from cation exchange processes associated with the sea-salt effect. It is proposed that a parallel process of marine SO_4 adsorption and desorption may also operate, leading to cyclical fluctuations in calculated xSO_4 which are unrelated to variations in pollutant S inputs.

- The identification of climatically-driven cyclicity in xSO_4, NO_3, acidity, and other important measures of surface water quality, has major implications for detection of recovery related trends, applicable both to the UKAWMN and to other monitoring programmes. Cyclical variations have the potential either to mask underlying anthropogenically-driven trends, or to generate apparent trends as a result of natural processes. Since these variations appear to operate at approximately decadal timescales, there is clearly a need to monitor over longer time periods in order to fully characterise the impact of anthropogenic factors on surface water quality.

■ 8.3 Assessment of Network Performance

The UKAWMN has been operating for almost 12 years. Over this period it has maintained high standards of sampling and analysis. With very few exceptions chemical and biological sampling has been undertaken with consistent frequency, while minimal personnel changes have helped to ensure that sampling protocols have been maintained through time. Water chemistry laboratories have participated regularly in AQC schemes at both national and international level and have been shown to maintain consistently high standards.

There is little evidence of catchment disturbance at the majority of sites. Problems have arisen at Loch Coire nan Arr, where the installation of a dam and subsequent management of the water level has had adverse biological impacts. At forested sites, considerable clearance and replanting has been instigated at Allt na Coire nan Con, and since the end of the interpretative period, at the Afon Hafren. Forestry at other sites is approaching maturity and felling programmes are expected to be implemented soon. The River Etherow appears to be occasionally influenced by road-salt and survey stretches have also been subject to vandalism. Despite this, the water chemistry record very clearly demonstrates the reduction in xSO_4 and non-marine cations which have resulted from the large decrease in xSO_4 deposition, and the site continues to provide data which are representative for the area.

Sediment traps, which were initially deployed in

1991 with varying levels of success of retrieval in the following year, have now been operating well in all lakes for several years. Trap samples, in conjunction with sediment cores taken at the onset of monitoring, are now providing the most powerful evidence of biological recovery (or inertia) at UKAWMN lakes.

Generally therefore, UKAWMN sites continue to perform well and all are providing high quality data. The extent to which between-site relationships in temporal variation have been used in the analysis for this report underlines the important contribution each site lends to the strength of the whole Network.

8.4 Recommendations

In light of the findings of this report we would recommend:

Continuation of monitoring for the following reasons:

- In common with substantial numbers of other acid-sensitive freshwater catchments in the UK, the majority of UKAWMN sites have clearly acidified, and remain in a damaged state. Most show little evidence of chemical or biological recovery to date and such recovery will only be identified by ongoing monitoring.
- Acid emissions reductions continue to be implemented and deposition of total acidity should continue to decline for the foreseeable future for the UK as a whole. However, the extent to which the impact of future declines on freshwater ecosystems will be observed in the more remote acid sensitive areas is unclear and this can only be verified by further monitoring.
- Deposition of NO_3 may have increased in some remote areas and may continue to do so. Continued monitoring is the only method of assessing the potential impacts.
- Acid pollutants stored in catchment soils are likely to be causing lags in dose-response relationships, while future NO_3 saturation and consequent N breakthrough is possible for some catchments. Lags are also likely between chemical improvements and biological recovery, particularly for organisms further up the food chain. These effects may not be observed for some time yet but will only be verified by monitoring.
- Water chemistry and biology of UKAWMN sites demonstrates marked inter-annual variability, a considerable proportion of which can be attributed to climatic variation. Given the amplitude of “noise” relative to expected rates of recovery, longer time series are necessary to identify underlying trends.
- The UKAWMN has the potential to provide valuable information regarding the impact of possible long term climatic changes on upland freshwater systems. Widespread rising trends in DOC suggest that such changes may already be affecting UKAWMN sites.
- The UKAWMN database represents an unparalleled, high quality and continuous integrated time series for acid-sensitive freshwaters in the UK. As the datasets continue to develop their scientific value continues to increase.
- UKAWMN data are integral to other national (i.e. ECN) and international (i.e. UNECE ICP) monitoring networks.

The UKAWMN would benefit from the following enhancements:

1) Increased frequency of chemical sampling during winter months to better define the extent and intensity of sea-salt and flow driven episodes (ideally to weekly for streams and two weekly for lakes).

2) The inclusion of further biological groups to enhance our understanding of ecosystem level responses. Most importantly, zooplankton samples should be collected at least annually but preferably quarterly. An additional macroinvertebrate survey each Autumn may reveal more stable trends in fauna with time, given the apparent sensitivity of spring samples to climatic variation.

3) More rigorous assessment of transparency by measurement of absorbtion of water samples at multiple wave-lengths. Partitioning of DOC into molecular weight ranges by ultra-filtration, so that the causes of increases (should they continue) be better understood.

4) Continuous measurement of water temperature (including temperature profiles in lakes) using self contained thermistor-dataloggers to enhance our understanding of links between climate and aquatic biology.

5) The collection of additional water, plant and sediment samples for metals analysis, and particularly for Cd, Hg, Pb, Zn and Cu. This would help to address contemporary international directives for this group of transboundary pollutants.

6) The monitoring of an additional site in the locality of Loch Coire nan Arr, which is threatened by water level management, so that this low deposition area will continue to be adequately represented in the future.

7) The monitoring of another close-to-source site, in the east Midlands or southern Pennines, so as to increase representation in areas where S deposition is declining most rapidly.

8) Closer practical links, particularly between the UKAWMN and the UK Acid Deposition Network. Particular areas of collaboration should include investigations into the dose-response relationships for SO_4 and Cl at specific catchments, and other interpretative analysis of temporally coterminous datasets.

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Appendix 1 - Table 1

Linear trend analysis of non-marine SO_4^{2-} in precipitation at UK monitoring sites 1986-1997 (µeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

Site	slope	se	t_val	t_df	t_prob	sigslope
Stoke Ferry	-3.0610	0.6128	4.995	10	0.001	-3.0610
High Muffles	-2.0060	0.6574	3.052	10	0.012	-2.0060
Preston Montford	-0.7790	0.9001	0.865	10	0.407	
Flatford Mills	-3.6040	0.7125	5.057	10	0.000	-3.6040
Thorganby	-2.4080	1.1719	2.055	10	0.067	
Jenny Hurn	-4.7900	0.8817	5.433	10	0.000	-4.7900
Wardlow Hay Cop	-1.4800	0.6322	2.341	10	0.041	-1.4800
Bottesford	-4.8090	0.7266	6.619	10	0.000	-4.8090
Woburn	-3.5150	0.6058	5.802	10	0.000	-3.5150
Compton	-3.2970	0.9557	3.449	10	0.006	-3.2970
Driby	-2.6530	0.7876	3.368	10	0.007	-2.6530
Barcombe Mills	-1.5870	0.4544	3.493	10	0.006	-1.5870
Glen Dye	-0.2300	0.7861	0.293	9	0.776	
Whiteadder	-1.3930	0.5654	2.463	10	0.033	-1.3930
Redesdale	-1.3510	0.6268	2.155	10	0.057	
Bannisdale	-0.3780	0.3305	1.143	10	0.280	
Cow Green Resevoir	-0.7010	0.3539	1.982	10	0.076	
Hillsborough Forest	-1.5070	0.8724	1.727	7	0.128	
Eskdalemuir	-0.4840	0.1258	3.851	10	0.003	-0.4840
Goonhilly	-0.2730	0.4059	0.673	10	0.516	
Yarner Wood	0.0160	0.4124	0.038	10	0.970	
Loch Dee	-0.7710	0.4224	1.826	10	0.098	
Beddgelert	-1.5200	0.8512	1.785	9	0.108	
Tycanol Wood	-0.3910	0.2678	1.461	10	0.175	
Llyn Brianne	-0.3900	0.2183	1.787	10	0.104	
Achanarras	-0.8490	0.3012	2.818	10	0.018	-0.8490
Pumlumon	-0.1390	0.3707	0.376	7	0.718	
Balquhidder	-0.2070	0.4458	0.464	10	0.653	
Lough Navar	-0.0600	0.1405	0.425	10	0.680	
Strathvaich Dam	-0.1900	0.2802	0.679	9	0.514	
River Mharcaidh	-0.6060	0.2779	2.182	10	0.054	
Polloch	-0.5740	0.4342	1.322	5	0.243	

Appendix 1 - Table 2

Linear trend analysis of NO_3^- in precipitation at UK monitoring sites 1986-1997 (µeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

Site	slope	se	t_val	t_df	t_prob	sigslope
Stoke Ferry	-0.8217	0.3990	2.059	10	0.066	
High Muffles	-0.4056	0.3579	1.133	10	0.284	
Preston Montford	0.5035	0.5013	1.004	10	0.339	
Flatford Mills	-0.8636	0.4820	1.792	10	0.103	
Thorganby	-0.5175	0.3317	1.560	10	0.150	
Jenny Hurn	-0.5594	0.3686	1.518	10	0.160	
Wardlow Hay Cop	0.3916	0.3875	1.011	10	0.336	
Bottesford	-0.9965	0.3576	2.786	10	0.019	-0.9965
Woburn	-0.3392	0.4032	0.841	10	0.420	
Compton	-0.7762	0.3956	1.962	10	0.078	
Driby	-0.1259	0.3961	0.318	10	0.757	
Barcombe Mills	-0.2832	0.3716	0.762	10	0.464	
Glen Dye	0.6455	0.4385	1.472	9	0.175	
Whiteadder	-0.1608	0.4001	0.402	10	0.696	
Redesdale	0.1469	0.3202	0.459	10	0.656	
Bannisdale	0.4056	0.1476	2.748	10	0.021	0.4056
Cow Green Resevoir	0.0594	0.1986	0.299	10	0.771	
Hillsborough Forest	0.2333	0.5875	0.397	7	0.703	
Eskdalemuir	0.3042	0.1231	2.470	10	0.033	0.3042
Goonhilly	0.5664	0.3700	1.531	10	0.157	
Yarner Wood	1.0000	0.3642	2.746	10	0.021	1.0000
Loch Dee	0.1643	0.2229	0.737	10	0.478	
Beddgelert	0.2000	0.3260	0.613	9	0.555	
Tycanol Wood	0.3357	0.1772	1.895	10	0.087	
Llyn Brianne	0.4021	0.1177	3.418	10	0.007	0.4021
Achanarras	0.0315	0.2882	0.109	10	0.915	
Pumlumon	0.6333	0.2001	3.165	7	0.016	0.6333
Balquhidder	0.3007	0.3229	0.931	10	0.374	
Lough Navar	0.4755	0.1408	3.378	10	0.007	0.4755
Strathvaich Dam	0.1727	0.1157	1.492	9	0.170	
River Mharcaidh	0.1853	0.1907	0.972	10	0.354	
Polloch	0.0000	0.2020	0.000	5	1.000	

Appendix 1 - Table 3

Linear trend analysis of NH_4^+ in precipitation at UK monitoring sites 1986-1997 (μeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

Site	slope	se	t_val	t_df	t_prob	sigslope
Stoke Ferry	-1.1713	0.7303	1.604	10	0.140	
High Muffles	0.2727	0.6595	0.414	10	0.688	
Preston Montford	-0.2657	0.6729	0.395	10	0.701	
Flatford Mills	-1.3636	0.8771	1.555	9	0.154	
Thorganby	-0.4010	1.8026	0.222	9	0.829	
Jenny Hurn	-0.6294	0.9480	0.664	10	0.522	
Wardlow Hay Cop	0.9790	0.5805	1.686	10	0.123	
Bottesford	-0.5769	0.7649	0.754	10	0.468	
Woburn	-0.3671	0.6914	0.531	10	0.607	
Compton	-0.5245	0.9725	0.539	10	0.601	
Driby	-0.7657	0.7929	0.966	10	0.357	
Barcombe Mills	-1.4441	0.6269	2.303	10	0.044	-1.4441
Glen Dye	0.5091	0.5545	0.918	9	0.383	
Whiteadder	-0.0909	0.4836	0.188	10	0.855	
Redesdale	0.8951	0.6845	1.308	10	0.220	
Bannisdale	0.4790	0.2890	1.657	10	0.128	
Cow Green Resevoir	0.6154	0.2129	2.890	10	0.016	0.6154
Hillsborough Forest	-0.5000	1.1047	0.453	7	0.665	
Eskdalemuir	0.5280	0.2551	2.070	10	0.065	
Goonhilly	0.3986	0.4511	0.884	10	0.398	
Yarner Wood	1.0455	0.5022	2.082	10	0.064	
Loch Dee	-0.3566	0.3938	0.906	10	0.386	
Beddgelert	0.7545	0.4282	1.762	9	0.112	
Tycanol Wood	0.3671	0.2409	1.524	10	0.158	
Llyn Brianne	0.3846	0.1731	2.222	10	0.051	
Achanarras	-1.0000	0.0000		1		
Pumlumon	0.4667	0.3898	1.197	7	0.270	
Balquhidder	0.4441	0.2757	1.610	10	0.138	
Lough Navar	0.5105	0.1505	3.391	10	0.007	0.5105
Strathvaich Dam	0.2000	0.0647	3.091	9	0.013	0.2000
River Mharcaidh	-0.0804	0.1700	0.473	10	0.646	
Polloch	-0.2143	0.2095	1.023	5	0.353	

Appendix 1 - Table 4

Linear trend analysis of non-marine Cl^- in precipitation at UK monitoring sites 1986-1997 (μeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Stoke Ferry	-1.4580	1.2060	1.209	10	0.254	
High Muffles	3.6080	2.2220	1.624	10	0.135	
Preston Montford	-2.3530	3.7460	0.628	10	0.544	
Flatford Mills	-1.3530	1.1320	1.195	10	0.260	
Thorganby	-5.4930	2.3440	2.344	10	0.041	-5.4930
Jenny Hurn	-6.3600	2.1800	2.918	10	0.015	-6.3600
Wardlow Hay Cop	-1.8810	2.9580	0.636	10	0.539	
Bottesford	-4.1430	1.4160	2.926	10	0.015	-4.1430
Woburn	-2.1150	1.4090	1.501	10	0.164	
Compton	-0.6570	2.4100	0.273	10	0.791	
Driby	-0.4200	2.2400	0.187	10	0.855	
Barcombe Mills	-8.4200	6.7950	1.239	10	0.244	
Glen Dye	5.9450	1.2760	4.659	9	0.001	5.9450
Whiteadder	2.4860	1.8950	1.312	10	0.219	
Redesdale	-1.3570	1.8600	0.729	10	0.483	
Bannisdale	0.2800	3.5150	0.080	10	0.938	
Cow Green Resevoir	2.9130	1.1380	2.560	10	0.028	2.9130
Hillsborough Forest	-2.0670	3.4600	0.597	7	0.569	
Eskdalemuir	-0.4620	1.7830	0.259	10	0.801	
Goonhilly	1.3810	8.3020	0.166	10	0.871	
Yarner Wood	-3.1850	4.0650	0.784	10	0.451	
Loch Dee	-2.7620	2.7700	0.997	10	0.342	
Beddgelert	-2.5180	4.0810	0.617	9	0.553	
Tycanol Wood	1.7410	4.4420	0.392	10	0.703	
Llyn Brianne	-0.8150	2.2720	0.359	10	0.727	
Achanarras	-4.0910	3.4150	1.198	10	0.259	
Pumlumon	-4.2000	3.6610	1.147	7	0.289	
Balquhidder	1.6990	3.0560	0.556	10	0.590	
Lough Navar	-12.3460	6.4190	1.923	10	0.083	
Strathvaich Dam	1.0910	3.7700	0.289	9	0.779	
River Mharcaidh	1.5170	2.7680	0.548	10	0.596	
Polloch	-9.6790	7.4570	1.298	5	0.251	

Appendix 1 - Table 5

Trends in precipitation weighted mean concentrations of non-marine SO_4^{2-} for the period 1988-1997 (µeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	0.1500	0.5349	0.280	8	0.786	
Yarner Wood	0.6860	0.3808	1.802	8	0.109	
Barcombe Mills	-1.5840	0.6508	2.434	8	0.041	-1.584
Compton	-1.6660	0.6592	2.527	8	0.035	-1.666
Flatford Mills	-3.2280	0.9429	3.423	8	0.009	-3.228
Woburn	-3.9890	0.8089	4.932	8	0.001	-3.989
Tycanol Wood	-0.3780	0.3937	0.960	8	0.365	
Llyn Brianne	-0.6170	0.2614	2.361	8	0.046	-0.617
Pumlumon	-0.1390	0.3707	0.376	7	0.718	
Stoke Ferry	-3.5950	0.8526	4.217	8	0.003	-3.595
Preston Montford	-1.4290	1.2087	1.183	8	0.271	
Bottesford	-5.4810	0.9871	5.553	8	0.001	-5.481
Beddgelert	0.4150	0.4667	0.889	7	0.404	
Wardlow Hay Cop	-1.8180	0.6797	2.674	8	0.028	-1.818
Driby	-3.8580	0.9418	4.097	8	0.003	-3.858
Jenny Hurn	-5.0340	1.2910	3.899	8	0.005	-5.034
Thorganby	-3.1290	0.7105	4.404	5	0.007	-3.129
High Muffles	-3.0870	0.6997	4.412	8	0.002	-3.087
Bannisdale	-0.7020	0.4454	1.577	8	0.153	
Hillsborough Forest	-1.5070	0.8724	1.727	7	0.128	
Lough Navar	0.0550	0.1816	0.304	8	0.769	
Cow Green Resevoir	-0.9900	0.4823	2.052	8	0.074	
Loch Dee	-0.5890	0.6037	0.975	8	0.358	
Redesdale	-1.2500	0.8740	1.430	8	0.191	
Eskdalemuir	-0.6140	0.1700	3.613	8	0.007	-0.614
Whiteadder	-1.4930	0.8240	1.812	8	0.108	
Balquhidder	0.1170	0.5958	0.197	8	0.849	
Polloch	-0.5740	0.4342	1.322	5	0.243	
Glen Dye	-0.0360	0.9529	0.038	8	0.971	
River Mharcaidh	-0.2040	0.3440	0.592	8	0.570	
Strathvaich Dam	-0.0440	0.3272	0.133	8	0.897	
Achanarras	-0.9220	0.3499	2.635	8	0.030	-0.922

Appendix 1 - Table 6

Trends in precipitation weighted mean concentrations of NH_4^+ for the period 1988-1997 (µeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	0.7091	0.6269	1.131	8	0.291	
Yarner Wood	1.7212	0.5337	3.225	8	0.012	1.7212
Barcombe Mills	-1.6848	0.9064	1.859	8	0.100	
Compton	1.0121	1.1521	0.879	8	0.405	
Flatford Mills	-1.6000	1.0612	1.508	8	0.170	
Woburn	-0.1879	1.0087	0.186	8	0.857	
Tycanol Wood	0.4424	0.3489	1.268	8	0.240	
Llyn Brianne	0.1515	0.2209	0.686	8	0.512	
Pumlumon	0.4667	0.3898	1.197	7	0.270	
Stoke Ferry	-1.6485	1.0359	1.591	8	0.150	
Preston Montford	-0.2545	0.9489	0.268	8	0.795	
Bottesford	-0.8242	1.0776	0.765	8	0.466	
Beddgelert	1.0000	0.6316	1.583	7	0.157	
Wardlow Hay Cop	0.7152	0.8325	0.859	8	0.415	
Driby	-1.4545	1.0892	1.335	8	0.218	
Jenny Hurn	-0.6242	1.3529	0.461	8	0.657	
Thorganby	-0.5765	0.2741	2.103	4	0.103	
High Muffles	-0.4848	0.8695	0.558	8	0.592	
Bannisdale	0.6970	0.3403	2.048	8	0.075	
Hillsborough Forest	-0.5000	1.1047	0.453	7	0.665	
Lough Navar	0.7273	0.1774	4.100	8	0.003	0.7273
Cow Green Resevoir	0.3455	0.2715	1.272	8	0.239	
Loch Dee	-0.0424	0.4022	0.105	8	0.919	
Redesdale	1.3697	0.6500	2.107	8	0.068	
Eskdalemuir	0.5152	0.3538	1.456	8	0.183	
Whiteadder	-0.3636	0.6357	0.572	8	0.583	
Balquhidder	0.7030	0.3798	1.851	8	0.101	
Polloch	-0.2143	0.2095	1.023	5	0.353	
Glen Dye	0.4848	0.6789	0.714	8	0.495	
River Mharcaidh	0.1636	0.1736	0.943	8	0.373	
Strathvaich Dam	0.2424	0.0734	3.305	8	0.011	0.2424
Achanarras	-1.0000			1		

Appendix 1 - Table 7

Trends in precipitation weighted mean concentrations of Cl^- for the period 1988-1997 (μeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	-4.4000	11.6090	0.379	8	0.715	
Yarner Wood	-9.0850	4.9880	1.821	8	0.106	
Barcombe Mills	-7.8550	9.6590	0.813	8	0.440	
Compton	-3.6000	3.0180	1.193	8	0.267	
Flatford Mills	-0.6790	1.4480	0.469	8	0.652	
Woburn	-1.6910	2.0600	0.821	8	0.435	
Tycanol Wood	-3.7940	5.6910	0.667	8	0.524	
Llyn Brianne	-3.5090	2.9130	1.205	8	0.263	
Pumlumon	-4.2000	3.6610	1.147	7	0.289	
Stoke Ferry	-1.5330	1.5880	0.966	8	0.363	
Preston Montford	-5.0060	5.1060	0.980	8	0.356	
Bottesford	-5.0550	1.3650	3.703	8	0.006	-5.055
Beddgelert	-7.7830	4.8810	1.595	7	0.155	
Wardlow Hay Cop	-5.8180	3.7600	1.547	8	0.160	
Driby	-1.1640	2.9320	0.397	8	0.702	
Jenny Hurn	-7.7270	2.5420	3.039	8	0.016	-7.727
Thorganby	-6.3330	1.2620	5.020	5	0.004	-6.333
High Muffles	1.5330	3.0700	0.499	8	0.631	
Bannisdale	-3.7030	4.1650	0.889	8	0.400	
Hillsborough Forest	-2.0670	3.4600	0.597	7	0.569	
Lough Navar	-20.2970	7.0310	2.887	8	0.020	-20.297
Cow Green Resevoir	2.1940	1.1170	1.965	8	0.085	
Loch Dee	-6.5210	2.5470	2.561	8	0.034	-6.521
Redesdale	-1.2670	1.7040	0.743	8	0.479	
Eskdalemuir	-1.7090	1.9350	0.883	8	0.403	
Whiteadder	3.4060	2.0440	1.666	8	0.134	
Balquhidder	2.1450	3.7570	0.571	8	0.584	
Polloch	-9.6790	7.4570	1.298	5	0.251	
Glen Dye	5.3700	1.5090	3.559	8	0.007	5.37
River Mharcaidh	1.6670	3.6380	0.458	8	0.659	
Strathvaich Dam	-2.0180	4.0600	0.497	8	0.632	
Achanarras	-8.4120	3.2970	2.551	8	0.034	-8.412

Appendix 1 - Table 8

Trends in precipitation weighted mean concentrations of H^+ for the period 1988-1997 (μeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	-0.0850	0.4401	0.193	8	0.852	
Yarner Wood	-0.0670	0.2800	0.238	8	0.818	
Barcombe Mills	-0.1150	0.4687	0.246	8	0.812	
Compton	-1.3640	1.1143	1.224	8	0.256	
Flatford Mills	-1.5090	0.5957	2.533	8	0.035	-1.509
Woburn	-2.5760	0.5216	4.938	8	0.001	-2.576
Tycanol Wood	-0.5090	0.3538	1.439	8	0.188	
Llyn Brianne	-0.7880	0.3172	2.484	8	0.038	-0.788
Pumlumon	-0.4000	0.4265	0.938	7	0.380	
Stoke Ferry	-2.1270	0.7332	2.902	8	0.020	-2.127
Preston Montford	-1.2730	1.1042	1.153	8	0.282	
Bottesford	-5.7150	1.5567	3.671	8	0.006	-5.715
Beddgelert	-0.2330	0.3272	0.713	7	0.499	
Wardlow Hay Cop	-2.0850	0.7876	2.647	8	0.029	-2.085
Driby	-2.9210	0.6849	4.265	8	0.003	-2.921
Jenny Hurn	-3.9520	1.5252	2.591	8	0.032	-3.952
Thorganby	-6.9460	1.5459	4.493	5	0.006	-6.946
High Muffles	-3.9880	0.6060	6.580	8	0.000	-3.988
Bannisdale	-1.2000	0.5581	2.150	8	0.064	
Hillsborough Forest	-0.5000	0.5358	0.933	7	0.382	
Lough Navar	-0.4610	0.1911	2.411	8	0.042	-0.461
Cow Green Resevoir	-1.6300	0.7402	2.202	8	0.059	
Loch Dee	-0.5330	0.4195	1.271	8	0.239	
Redesdale	-2.1760	0.7977	2.728	8	0.026	-2.176
Eskdalemuir	-1.3640	0.3682	3.703	8	0.006	-1.364
Whiteadder	-1.7330	0.6331	2.738	8	0.026	-1.733
Balquhidder	-0.1330	0.5253	0.254	8	0.806	
Polloch	-0.6070	0.4670	1.300	5	0.250	
Glen Dye	-0.3090	0.9298	0.332	8	0.748	
River Mharcaidh	-0.5210	0.1825	2.856	8	0.021	-0.521
Strathvaich Dam	-0.5820	0.3395	1.714	8	0.125	
Achanarras	-0.9820	0.3164	3.103	8	0.015	-0.982

Appendix 1 - Table 9

Trends in precipitation weighted mean concentrations of NO_3^- for the period 1988-1997 (µeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	0.9091	0.4629	1.964	8	0.085	
Yarner Wood	1.6364	0.3470	4.715	8	0.002	1.6364
Barcombe Mills	-0.2364	0.5330	0.443	8	0.669	
Compton	-0.3758	0.4747	0.791	8	0.451	
Flatford Mills	-1.3030	0.6453	2.019	8	0.078	
Woburn	-0.4606	0.5889	0.782	8	0.457	
Tycanol Wood	0.4182	0.2452	1.706	8	0.126	
Llyn Brianne	0.3333	0.1639	2.034	8	0.076	
Pumlumon	0.6333	0.2001	3.165	7	0.016	0.6333
Stoke Ferry	-1.0000	0.5715	1.750	8	0.118	
Preston Montford	0.4000	0.6889	0.581	8	0.577	
Bottesford	-1.3758	0.4842	2.841	8	0.022	-1.3758
Beddgelert	0.8667	0.3327	2.605	7	0.035	0.8667
Wardlow Hay Cop	0.2970	0.4887	0.608	8	0.560	
Driby	-0.7091	0.4745	1.494	8	0.173	
Jenny Hurn	-0.6303	0.5269	1.196	8	0.266	
Thorganby	-0.9516	0.4100	2.321	5	0.068	
High Muffles	-0.8364	0.4436	1.885	8	0.096	
Bannisdale	0.4727	0.2044	2.313	8	0.049	0.4727
Hillsborough Forest	0.2333	0.5875	0.397	7	0.703	
Lough Navar	0.5818	0.1988	2.927	8	0.019	0.5818
Cow Green Resevoir	-0.1394	0.2677	0.521	8	0.617	
Loch Dee	0.2424	0.2953	0.821	8	0.435	
Redesdale	0.1818	0.4143	0.439	8	0.672	
Eskdalemuir	0.2788	0.1651	1.689	8	0.130	
Whiteadder	-0.3697	0.5603	0.660	8	0.528	
Balquhidder	0.6182	0.3815	1.620	8	0.144	
Polloch	0.0000	0.2020	0.000	5	1.000	
Glen Dye	0.7091	0.5352	1.325	8	0.222	
River Mharcaidh	0.3697	0.2559	1.445	8	0.187	
Strathvaich Dam	0.3212	0.0952	3.372	8	0.010	0.3212
Achanarras	-0.2970	0.3239	0.917	8	0.386	

Appendix 1 - Table 10

Trends in precipitation weighted mean concentrations of Na^+ for the period 1988-1997 (µeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	-2.8480	9.6820	0.294	8	0.776	
Yarner Wood	-7.2730	4.1450	1.755	8	0.117	
Barcombe Mills	-5.3270	8.1390	0.655	8	0.531	
Compton	-1.9640	2.6260	0.748	8	0.476	
Flatford Mills	0.2360	1.2480	0.189	8	0.855	
Woburn	-0.4970	1.7580	0.283	8	0.785	
Tycanol Wood	-2.9090	4.9720	0.585	8	0.575	
Llyn Brianne	-2.3450	2.4610	0.953	8	0.368	
Pumlumon	-3.1500	3.1120	1.012	7	0.345	
Stoke Ferry	-0.7330	1.4010	0.523	8	0.615	
Preston Montford	-3.3450	4.3490	0.769	8	0.464	
Bottesford	-1.9450	1.2190	1.596	8	0.149	
Beddgelert	-6.6000	4.0090	1.646	7	0.144	
Wardlow Hay Cop	-3.2610	3.2530	1.002	8	0.346	
Driby	0.5760	2.3810	0.242	8	0.815	
Jenny Hurn	-3.6790	2.0710	1.776	8	0.114	
Thorganby	-1.1170	0.8700	1.283	5	0.256	
High Muffles	4.1150	2.4600	1.673	8	0.133	
Bannisdale	-2.0970	3.6100	0.581	8	0.577	
Hillsborough Forest	-1.4670	3.0070	0.488	7	0.641	
Lough Navar	-15.2420	5.4690	2.787	8	0.024	-15.242
Cow Green Resevoir	2.2240	0.9070	2.454	8	0.040	2.224
Loch Dee	-5.0610	2.0690	2.446	8	0.040	-5.061
Redesdale	-0.2610	1.4480	0.180	8	0.862	
Eskdalemuir	0.9390	2.8660	0.328	8	0.751	
Whiteadder	3.6970	1.8310	2.019	8	0.078	
Balquhidder	2.2300	3.2100	0.695	8	0.507	
Polloch	-8.3570	6.4650	1.293	5	0.253	
Glen Dye	4.9270	1.2500	3.941	8	0.004	4.927
River Mharcaidh	1.6360	3.3640	0.486	8	0.640	
Strathvaich Dam	-0.9520	3.9200	0.243	8	0.814	
Achanarras	-6.5880	3.0060	2.191	8	0.060	

Appendix 1 - Table 11

Trends in precipitation weighted mean concentrations of marine SO_4^{2+} for the period 1988-1997 (μeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

Site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	-0.3864	1.1577	0.334	8	0.747	
Yarner Wood	-0.8982	0.5133	1.750	8	0.118	
Barcombe Mills	-0.6036	1.0097	0.598	8	0.566	
Compton	-0.1824	0.3155	0.578	8	0.579	
Flatford Mills	0.0764	0.1488	0.513	8	0.622	
Woburn	-0.0955	0.2117	0.451	8	0.664	
Tycanol Wood	-0.3858	0.5893	0.655	8	0.531	
Llyn Brianne	-0.2615	0.3256	0.803	8	0.445	
Pumlumon	-0.2440	0.3823	0.638	7	0.544	
Stoke Ferry	-0.0773	0.1718	0.450	8	0.665	
Preston Montford	-0.3645	0.4965	0.734	8	0.484	
Bottesford	-0.1979	0.1399	1.415	8	0.195	
Beddgelert	-0.7313	0.4685	1.561	7	0.162	
Wardlow Hay Cop	-0.3582	0.3988	0.898	8	0.395	
Driby	0.0888	0.2905	0.306	8	0.768	
Jenny Hurn	-0.4388	0.2476	1.772	8	0.114	
Thorganby	-0.2642	0.1783	1.482	8	0.177	
High Muffles	0.4630	0.2946	1.572	8	0.155	
Bannisdale	-0.2612	0.4517	0.578	8	0.579	
Hillsborough Forest	-0.1100	0.3551	0.310	7	0.766	
Lough Navar	-0.8309	0.5661	1.468	8	0.180	
Cow Green Resevoir	0.2503	0.1138	2.200	8	0.059	
Loch Dee	-0.5021	0.2311	2.173	8	0.062	
Redesdale	0.0318	0.1860	0.171	8	0.868	
Eskdalemuir	-0.1252	0.2369	0.528	8	0.612	
Whiteadder	0.3355	0.2357	1.423	8	0.192	
Balquhidder	0.2524	0.3821	0.661	8	0.527	
Polloch	-0.9618	0.8001	1.202	5	0.283	
Glen Dye	0.5448	0.1650	3.302	8	0.011	0.5448
River Mharcaidh	0.1915	0.3457	0.554	8	0.595	
Strathvaich Dam	-0.0655	0.4273	0.153	8	0.882	
Achanarras	-0.8297	0.3678	2.256	8	0.054	

Appendix 1 - Table 12

Trends in precipitation weighted mean concentrations of Total SO_4^{2+} for the period 1988-1997 (μeq1^{-1} yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	sigslope
Goonhilly	-0.2360	1.3474	0.175	8	0.865	
Yarner Wood	-0.2120	0.4559	0.465	8	0.654	
Barcombe Mills	-2.1880	1.0612	2.062	8	0.073	
Compton	-1.8480	0.6571	2.813	8	0.023	-1.848
Flatford Mills	-3.1520	1.0335	3.049	8	0.016	-3.152
Woburn	-4.0850	0.8840	4.621	8	0.002	-4.085
Tycanol Wood	-0.7640	0.6879	1.110	8	0.299	
Llyn Brianne	-0.8790	0.4306	2.041	8	0.076	
Pumlumon	-0.3830	0.2894	1.324	7	0.227	
Stoke Ferry	-3.6730	0.9782	3.754	8	0.006	-3.673
Preston Montford	-1.7940	1.2686	1.414	8	0.195	
Bottesford	-5.6790	1.0000	5.679	8	0.000	-5.679
Beddgelert	-0.3170	0.5060	0.626	7	0.551	
Wardlow Hay Cop	-2.1760	0.8595	2.531	8	0.035	-2.176
Driby	-3.7700	1.1174	3.374	8	0.010	-3.77
Jenny Hurn	-5.4730	1.4021	3.903	8	0.005	-5.473
Thorganby	-3.2720	0.7629	4.289	5	0.008	-3.272
High Muffles	-2.6240	0.8366	3.137	8	0.014	-2.624
Bannisdale	-0.9640	0.3820	2.523	8	0.036	-0.964
Hillsborough Forest	-1.6170	0.9118	1.773	7	0.120	
Lough Navar	-0.7760	0.5279	1.469	8	0.180	
Cow Green Resevoir	-0.7390	0.4419	1.673	8	0.133	
Loch Dee	-1.0910	0.5870	1.858	8	0.100	
Redesdale	-1.2180	0.9423	1.293	8	0.232	
Eskdalemuir	-0.7390	0.3087	2.395	8	0.044	-0.739
Whiteadder	-1.1580	0.9075	1.276	8	0.238	
Balquhidder	0.3700	0.7644	0.484	8	0.642	
Polloch	-1.5360	0.8353	1.839	5	0.125	
Glen Dye	0.5090	1.0247	0.497	8	0.633	
River Mharcaidh	-0.0120	0.4824	0.025	8	0.981	
Strathvaich Dam	-0.1090	0.4239	0.257	8	0.803	
Achanarras	-1.7520	0.5363	3.266	8	0.011	-1.752

Appendix 1 - Table 13

Trends in rainfall for the period 1988-1997 (mm yr^{-1}). Significant trends are listed in the final column.

site	slope	se	t_val	t_df	t_prob	Sigslope
Goonhilly	5.5500	12.4600	0.446	8	0.668	
Yarner Wood	5.8500	14.3700	0.408	8	0.694	
Barcombe Mills	8.9200	9.7000	0.919	8	0.385	
Compton	5.1800	12.2700	0.422	8	0.684	
Flatford Mills	-14.2500	9.6300	1.480	8	0.177	
Woburn	-13.0000	12.1900	1.066	8	0.317	
Tycanol Wood	2.5200	13.1400	0.192	8	0.853	
Llyn Brianne	-22.1900	15.2400	1.456	8	0.184	
Pumlumon	-37.5700	35.9600	1.045	7	0.331	
Stoke Ferry	-4.7600	11.2000	0.425	8	0.682	
Preston Montford	-7.8700	7.3800	1.065	8	0.318	
Bottesford	-4.0500	13.7400	0.295	8	0.775	
Beddgelert	-61.2500	51.5600	1.188	6	0.280	
Wardlow Hay Cop	-4.0500	16.8100	0.241	8	0.815	
Driby	-4.5400	12.2400	0.371	8	0.720	
Jenny Hurn	0.0700	8.6600	0.008	8	0.994	
Thorganby	-6.0300	8.3100	0.726	5	0.501	
High Muffles	1.0800	13.0900	0.083	8	0.936	
Bannisdale	-45.7800	30.4900	1.502	8	0.172	
Hillsborough Forest	-0.1000	13.7100	0.007	7	0.994	
Lough Navar	-2.3000	23.0000	0.100	8	0.923	
Cow Green Resevoir	3.5200	17.2900	0.203	8	0.844	
Loch Dee	-71.2800	30.5600	2.332	8	0.048	-71.28
Redesdale	-31.6500	9.5900	3.300	8	0.011	-31.65
Eskdalemuir	-0.7000	19.4400	0.036	8	0.972	
Whiteadder	-20.2700	11.4100	1.777	8	0.114	
Balquhidder	-74.1300	28.8800	2.567	8	0.033	-74.13
Polloch	-75.7500	36.9300	2.051	5	0.096	
Glen Dye	0.1800	18.6800	0.009	8	0.993	
River Mharcaidh	-24.8600	11.7200	2.121	8	0.067	
Strathvaich Dam	-38.4100	23.7400	1.618	8	0.144	
Achanarras	-13.4200	10.2500	1.309	8	0.227	

Appendix 2

Location of nearby Meteorological Stations, rainfall data from which were applied in analysis in Chapter 7. Data supplied by the UK Meteorological Office.

UKAWMN SITE	METEOROLOGICAL STATION	
	name	grid ref.
1. Loch Coire nan Arr	Plockton	NG 802332
2. Allt a'Mharcaidh	Aviemore	NH 896143
3. Allt na Coire nan Con	Inverailort	NM 764816
4. Lochnagar	Balmoral	NO 260946
5. Loch Chon	Loch Venacher	NN 598063
6. Loch Tinker	Loch Venacher	NN 598063
7. Round Loch of Glenhead	Clatteringshaws	NX 554780
8. Loch Grannoch	Clatteringshaws	NX 554780
9. Dargall Lane	Clatteringshaws	NX 554780
10. Scoat Tarn	Eskmeals	SD 085931
11. Burnmoor Tarn	Eskmeals	SD 085931
12. River Etherow	Emley Moor	SE 222130
13. Old Lodge	Edenbridge	TQ 492472
14. Narrator Brook	Princetown	SX 583740
15. Llyn Llagi	Nantmor	SH 603462
16. Llyn Cwm Mynach	Arthog, Fegla Fach Farm	SH 640153
17. Afon Hafren	Cymystwyth	SN 773749
18. Afon Gwy	Cymystwyth	SN 773749
19. Beagh's Burn	Ballypatrick Forest	ID 176386
20. Bencrom River	Silent Valley	IJ 305216
21. Blue Lough	Silent Valley	IJ 305216
22. Coneyglen Burn	Lough Fea	IH 764865

Appendix 3

Participating organisations.

Project coordination:	ENSIS / Environmental Change Research Centre (ECRC), University College London (UCL)
Chemistry database management:	Centre for Ecology and Hydrology (CEH), Wallingford
Biology database management:	ENSIS / ECRC
Central chemistry analyses:	CEH, Wallingford
Local chemistry analyses:	• Freshwater Fisheries Laboratory, Pitlochry, Perths. • Environment Agency, Llanelli
Chemistry AQC:	Water Research Centre (WRc), Medmenham
Continuous stream monitoring:	• TES Ltd, Preston • Scottish Environmental Protection Agency (SEPA) • CEH, Wallingford
Macroinvertebrate analyses:	School of Biological Sciences, QMW
Macrophyte analyses:	ENSIS / ECRC, UCL
Epilithic diatom analyses:	ENSIS / ECRC, UCL
Fishery coordination:	Institute of Freshwater Ecology, Wareham
Fish analyses:	• Freshwater Fisheries Laboratory, Pitlochry, Perths. • Institute of Freshwater Ecology, Windermere • School of Biological Sciences, QMW • Poly Enterprises Ltd.(PEP), Plymouth • Environment Agency, Llanelli & Caernarvon • Department of Agriculture, Northern Ireland
Sediment trap carbonaceous particle and diatom analyses:	ENSIS / ECRC, UCL