THE UNITED KINGDOM ACID WATERS MONITORING NETWORK

ASSESSMENT OF THE FIRST 18 YEARS OF DATA

DATA SUMMARY ANNEX ACCOMPANYING RESEARCH PROJECT FINAL REPORT

Report to the Department for Environment, Food and Rural Affairs
(Contract EPG 1/3/160)

2007

Editors

D. T. Monteith
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ENSIS Ltd, Environmental Change Research Centre, UCL.

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1. INTRODUCTION

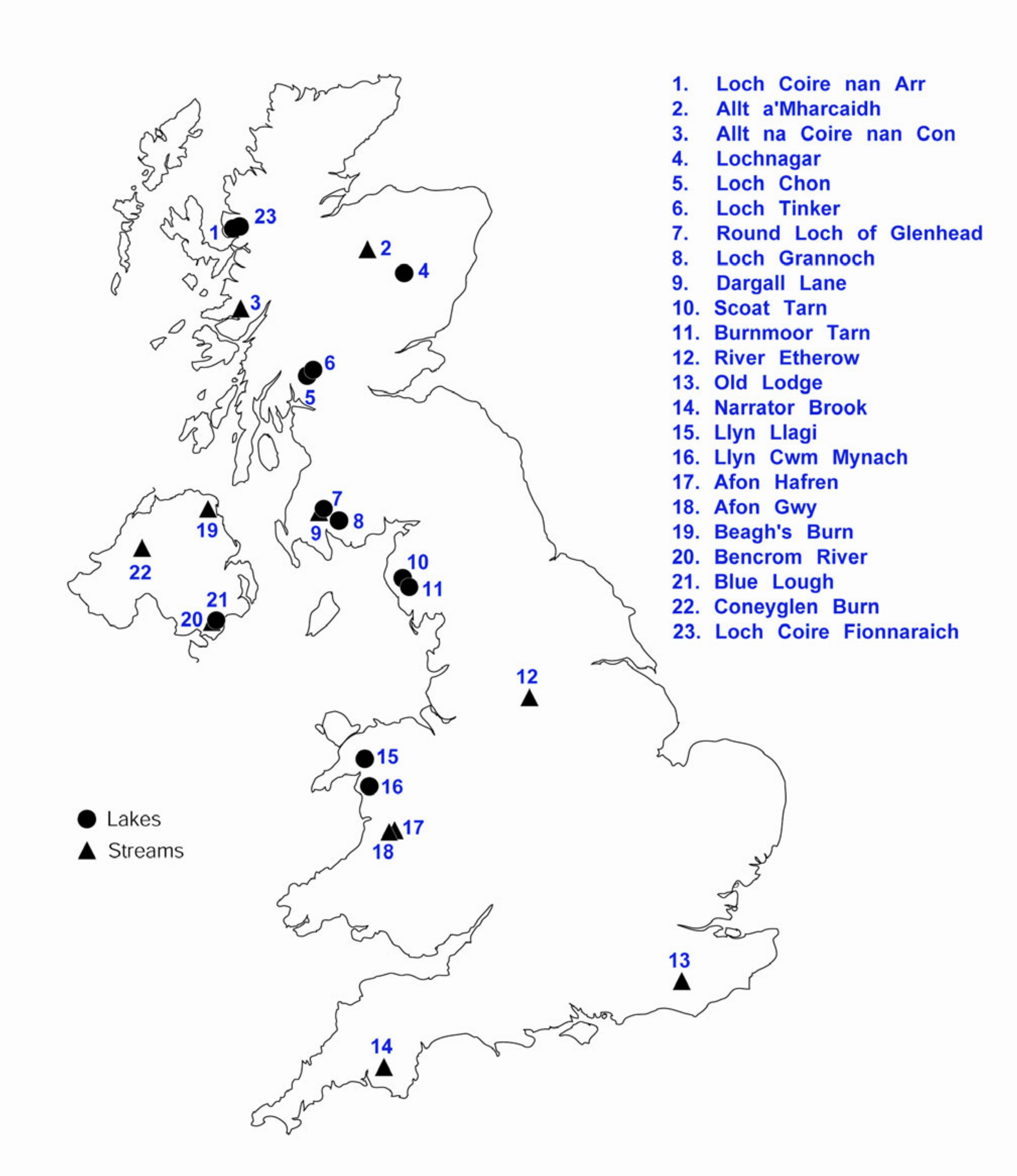
The DEFRA funded UK Acid Waters Monitoring Network (AWMN) is an integrated long-term freshwater monitoring network concerned with assessing the impact of acidic emissions control policy on the ecology of acid-sensitive ecosystems. Currently in its 20th year of operation, this report annex supports the official report to DEFRA marking the termination of contract EPG 1/3/160 and presents and reviews data collated up to March 2006 (water chemistry) or September 2006 (aquatic biology).

Detailed analysis and interpretation of results have been reported to DEFRA every five years (Patrick et al., 1995; Monteith and Evans 2000; Monteith 2005) and the latter two reports are available via the AWMN web page (www.ukawmn.ucl.ac.uk). The next report in this series is scheduled for 2008. This annex provides an update on a site specific basis accompanied by key observations regarding regional trends.

The AWMN is possibly unique internationally for the longevity of its truly integrated (i.e. chemical and biological) high quality freshwater time series. It comprises 22 acid-sensitive lakes and streams (see Figure 1.1) which are sampled for water chemistry quarterly and monthly respectively, and annually for a range of biota, including epilithic and sediment trap diatoms, macroinvertebrates and salmonids. Aquatic macrophytes in lakes are sampled bi-annually. In addition, spherical carbonaceous particles (SCPs), derived from high temperature fossil fuel combustion, and the concentrations of heavy metals in lake sediment are assessed annually, as are heavy metals in catchment mosses, while lake water temperature is now monitored continuously. More detailed monitoring of mercury deposition and lake and catchment concentrations of this and other heavy metals is conducted at one montane AWMN site, Lochnagar.

In the following sections we present time series data, tabulated summary data and an appraisal of trends on a site by site basis. This is followed by a Network-wide summary of findings in the final chapter.

Figure 1.1 Location of UKAWMN Sites



2. METHODS

2.1 Water Chemistry

Sampling and analytical methodologies conform to those outlined by Patrick *et al.* (1991) while the approach to Analytical Quality Control is provided by Patrick *et al.* (1995). AWMN laboratories participate in an AQC programme operated by the Water Research Centre, Medmenham, and results are provided to the AWMN in annual internal reports that are available on request. The programme has found a high standard of accuracy for all the major deteminands analysed in this report.

All chemical data entered on the central water chemistry database at CEH Wallingford are screened to remove erroneous values prior to analysis. Charge balance errors are determined by the ratio of (the sum of base cations minus the sum of acid anions minus alkalinity) to (the sum of base cations plus the sum of acid anions plus alkalinity) expressed as a percentage, where all ions are in $\mu eq\ l^{-1}$. Charges of aluminium and organic anion species are not included and the charge balance is therefore approximate; however in general the error should be close to zero. In rare circumstances where errors are greater than 10% data are rechecked and if any one value for a determinand lies beyond the range of all other values for the site, the sample is discarded. Data are also screened on the basis of the relationship between alkalinity and pH. These data are closely related through carbonate equilibria and should plot on a sigma curve. Exceptions to this general rule are sites with very high concentrations of dissolved organic carbon (DOC).

Wider problems were identified for unstable determinand data at the River Etherow and Old Lodge during the first three years of monitoring. At the time, unstable determinand monitoring was undertaken at local laboratories, but from April 1991 analysis was transferred to what is now the FRS Freshwater Laboratory, Pitlochry. The first three years of data for alkalinity at both sites and pH and nitrate at Old Lodge have been discarded.

Trend statistics presented in Chapter 3 are based on a modified version of the Seasonal Kendall Test, a non-parametric procedure for detecting monotonic changes over time (see Monteith and Evans, 2000) for further details. Trend slopes are determined using the method of Sen (1968).

2.2 Aquatic Biology

The AWMN monitors several biological parameters, providing a range of perspectives on the biological composition and functioning of these ecosystems. These biological components are summarised in Table 2.1. Wider descriptions and sampling methodologies are available from the AWMN web page www.ukawmn.ucl.ac.uk.

Table 2.1 A summary of AWMN biological measurements

Biological Group	Annual Measurement	Representation
Epilithic diatoms	% abundance of taxa in samples from 3-4 locations (stone scrapes)	Relative abundance of epilithic taxa occurring across the site
Sediment trap diatoms Lakes only	% abundance of taxa in sediment trap sample (trap sub-sample)	Relative abundance of the remains of all diatom species contributing to the lake sediment
Aquatic macrophytes – lakes	0-5 classification of abundance, based on several methods (see below)	Relative abundance of all species occurring within the lake
Aquatic macrophytes –streams	% cover of species in 10 consecutive 5 m stretches	Absolute cover of all species across a specified 50 m stretch
Macroinvertebrates	Absolute abundance of taxa in samples from 5 littoral locations (kick sampling)	Relative abundance of littoral taxa occurring across the site
Salmonids (brown trout & Atlantic salmon)	Numbers of fish, and their length and weight, from each age class per unit area of stream (or lake outflow), (electro-fishing)	Density and condition of each age class in the population inhabiting the 150 m sampling stretch

Assessment of aquatic macrophyte populations in lakes is complicated by the spatial heterogeneity of species distribution. Observations confined to relative cover of specific substrate types may not be sensitive to changes at the whole-site level. The aquatic macrophyte survey methods for lakes are therefore designed to detect change using a variety of techniques, including:

1) Mapping distributions of dominant taxa and precise locations of rare taxa during a shoreline walk;
2) Repeatable depth transects from the shoreline to beyond the photic zone using a boat and Ekman grab;
3) Repeatable open-water transects using a grapnel pulled behind a boat and retrieved at defined points. This provides greater spatial coverage of the lake basin and the detection of rarer and unattached plants.

Time trend assessments of epilithic diatom and macroinvertebrate data, provided in Chapter 4, are based on multivariate methods. All multivariate statistical analysis were performed using the programme CANOCO 4.5 (ter Braak, 1998). Epilithic diatom and macroinvertebrate data were first subjected to Detrended Canonical Correspondence Analysis (DCCA), with “sample year” used as a single explanatory variable, in order to determine the time-constrained species gradient lengths. This method provides a measure of species "turnover", in units of standard deviation; a gradient length of 4 or more would imply a complete change in species representation over the monitoring period. The results also indicate whether subsequent time-trend analysis should be based on a linear model (where species show monotonic change) or a unimodal model (where species abundances rise and then fall over the duration of monitoring). In nearly all cases, gradients lengths were less than 3.0 and the linear methods of Principal Components Analysis (PCA) and Redundancy Analysis (RDA) (ter Braak, 1998) were therefore selected.

The degree of linear change in epilithic diatom and macroinvertebrate datasets was examined using RDA, based on inter-species correlations. First, sample year was coded as a series of "dummy" variables, each relating to a specific year. With this approach, samples which are taken in the year corresponding to the dummy variable name, say "1995", score 1 while all other samples score 0. RDA of species data using all sample years as environmental variables indicates how much of the total between-sample variance can be explained by differences between years. (This is represented in CANOCO as the "Sum of Constrained Eigenvalues"). As the sum of all Eigenvalues is unity, subtracting this value from 1 provides the between- sample variance which occurs within years, i.e. between replicate samples.

Second, the year of sampling was used as the single explanatory variable. Here, the first, and only, constrained axis of RDA (λ_1RDA) represents the proportion of the total between-sample variance which can be explained by a linear change in time. This was the only application of RDA to the aquatic macrophyte data which has no within-year replicate component. Monte-Carlo permutations (999 permutations) were used to determine the statistical significance of a time trend in the species data.

3. SITE SUMMARY FORMAT

The chemical, biological and water temperature data (lakes only) are presented in Chapter 4 on a site-by-site basis as follows:

Subsection 1:
Description and assessment of trends and current status of water chemistry and biology.

Figure 1:
Time series plots of key spot sampled chemical determinands for individual samples. The normal number of observations per year is 4 for lakes and 12 for streams. Plots include a LOESS smoother (red line).

Table 1:
Table of water chemistry summary data, including mean, max, min and standard deviation for five yearly periods (and the three year period from April 2003 to March 2006).

Figure 2:
Plots of the percentage abundance of all eplithic diatom species that reach more than 2% abundance in any one sample. Data are presented for all samples.

Figure 3:
Aquatic macrophyte plots. For lakes relative species abundance determined on a five point scale (comparable to the DAFOR scoring system, 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 estimated for 5m sections of a 50m survey stretch and each 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 50m stretches.

Figure 4:
Plots of the percentage abundance of all macroinvertebrate taxa that reach more than 1% abundance in any one sample. Data are presented for each of five one minute kick samples taken from stream riffle or lake littoral locations.

Table 2:
Trend statistics for epilithic diatoms and macroinvertebrate data. Redundancy analysis is applied to determine the amount of variance in the percentage species data that can be explained by a single explanatory variable (sample year). The restricted permutation test provides the most robust statistic (by taking into account potential autocorrelation) that a linear trend could not occur by chance.

Figure 5:
Salmonids. Summary bar plots of mean density of brown trout and Atlantic salmon,

if present, in three 50m reaches (number of individuals caught per 100m^2 survey area) for each year of the monitoring period. (0+ = new recruits, >0+ = all fish over one year of age).

Figure 6:

For lake sites only. Plots of diatom species composition from annually retrieved sediment traps. Species occurring at less than 1% abundance in all years are omitted.

Figure 7:

For lakes only. Time series plots of water temperature monitored by thermistor loggers in a deep water location in the epilimnion (circa 1.5 metres depth) and deep water (circa 1.0 metre from the bottom).

4. SITE SUMMARIES

4.1 Loch Coire nan Arr

4.1.1 Water Chemistry Summary

Loch Coire nan Arr is situated at an altitude of 125 m in northwest Scotland and drains a moorland catchment underlain by Torridonian Sandstone. Non-marine SO_4 concentration (xSO_4) was low at the onset of monitoring; the mean 1988-1993 of 12.6 µeq l^{-1} is significantly lower than 2003-2006 mean concentrations for all other sites on the network. This reflects the low level of xSO_4 deposition in the region and the site represents an effective deposition "control" for the Network. Over the first five years Loch Coire nan Arr had an average pH and alkalinity of of 6.4 and 35.5. µeq l^{-1} respectively, and exhibited very low (mostly below detection) concentrations of labile aluminium. There was no indication from palaeoecological diatom analysis that Loch Coire nan Arr had been acidified by anthropogenic pollutants.

Despite the low deposition regime, Loch Coire nan Arr has experienced a fall in xSO_4 concentration of approximately 50% over the monitoring period. Most of the reduction in xSO_4 occurred after 1996 and the pattern of decline is similar to most other sites on the Network.

Nitrate (NO_3) concentrations normally fall below the limits of detection in at least one, and as many as three, seasons of the year and there is no evidence of any change with time.

Chloride (Cl) concentrations show substantial short term variation but no long term trend. Peak concentrations frequently rise above 400 µeq l^{-1}, reflecting frequent inputs of seasalt owing to the site's close proximity to the sea (2 km to the south and 10 km to the west).

Dissolved organic carbon (DOC) concentrations have doubled approximately over the monitoring period, and preliminary time series analysis suggests that this change can be at least partly explained by reductions in SO_4 deposition over the period (see Section 5.4.5).

Ion balance ANC shows pronounced short term variability, mainly driven by variation in seasalt inputs, but no long term trend. The effect of the small reduction in xSO_4 is therefore masked by the large variability in marine ions.

pH and alkalinity provide no indication of long term trends.

Loch Coire nan Arr has provided a source of fresh water for a fish farm based at Kishorn for many years. Over the past ten years the level of the loch has been raised repeatedly in order to ensure supply at times of low rainfall. By 2005 the loch was being subjected to unnatural water level oscillations amounting to several metres. This has had a major impact on all aspects of the biology and for the past four years the AWMN have operated a nearby site, Loch Coire Fionnaraich, with a view to the replacing Loch Coire nan Arr as the control site for the Network. Despite water level oscillation, and the subsequent loss of biological habitats, there is little evidence that this change in hydrological management has had a marked effect on water chemistry. Short and long term variation in DOC, for example, show very similar patterns to that in the nearest AWMN site Allt na Coire nan Con (Site 3).

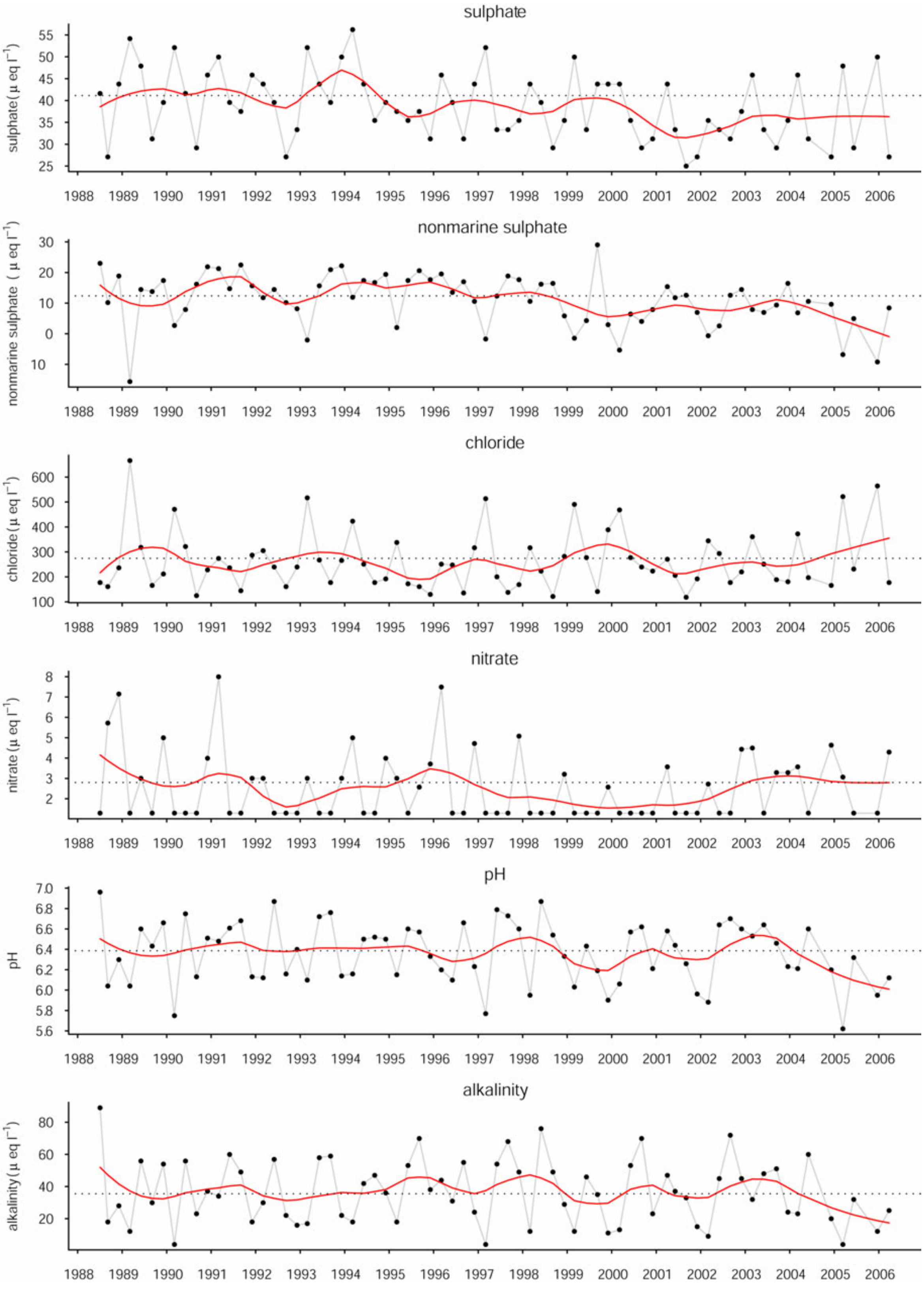
4.1.2 Biology Summary

At the onset of monitoring Loch Coire nan Arr contained diverse plant and invertebrate assemblages, while the outflow supported a substantial brown trout and Atlantic salmon population. Disruption of water levels has resulted in a loss of all emergent macrophytes, a substantial reduction in the density of macroinvertebrates, the loss of *Pisidium* sp., and some caddis and beetle species, and a large decline in the density of salmonids in the outflow. It is not possible to comment on the possible effect of a slight reduction in xSO_4 concentration on the lake biota for these reasons.

4.1.3 Conclusions

Loch Coire nan Arr has been the low deposition “control” lake for the AWMN since its inception. Despite, hydrological interference the chemistry data demonstrate that concentrations of xSO_4 have halved over the monitoring period, and the current concentration of 5 μeq l^{-1} might be considered a realistic “background” concentration for UK freshwaters. Variation in lake acidity is dominated by hydrological variation and seasalt inputs and there are no detectable changes attributable to the small decline in xSO_4. There is little evidence for an impact of hydrological management on lake chemistry, but the lake biota have been affected to the degree that monitoring has now ceased at this site. Future monitoring for the region will focus on the nearby Loch Coire Fionnaraich which exhibits similar chemical and biological characteristics.

Figure 4.1.1 Water Chemistry Summary Plots: Loch Coire nan Arr



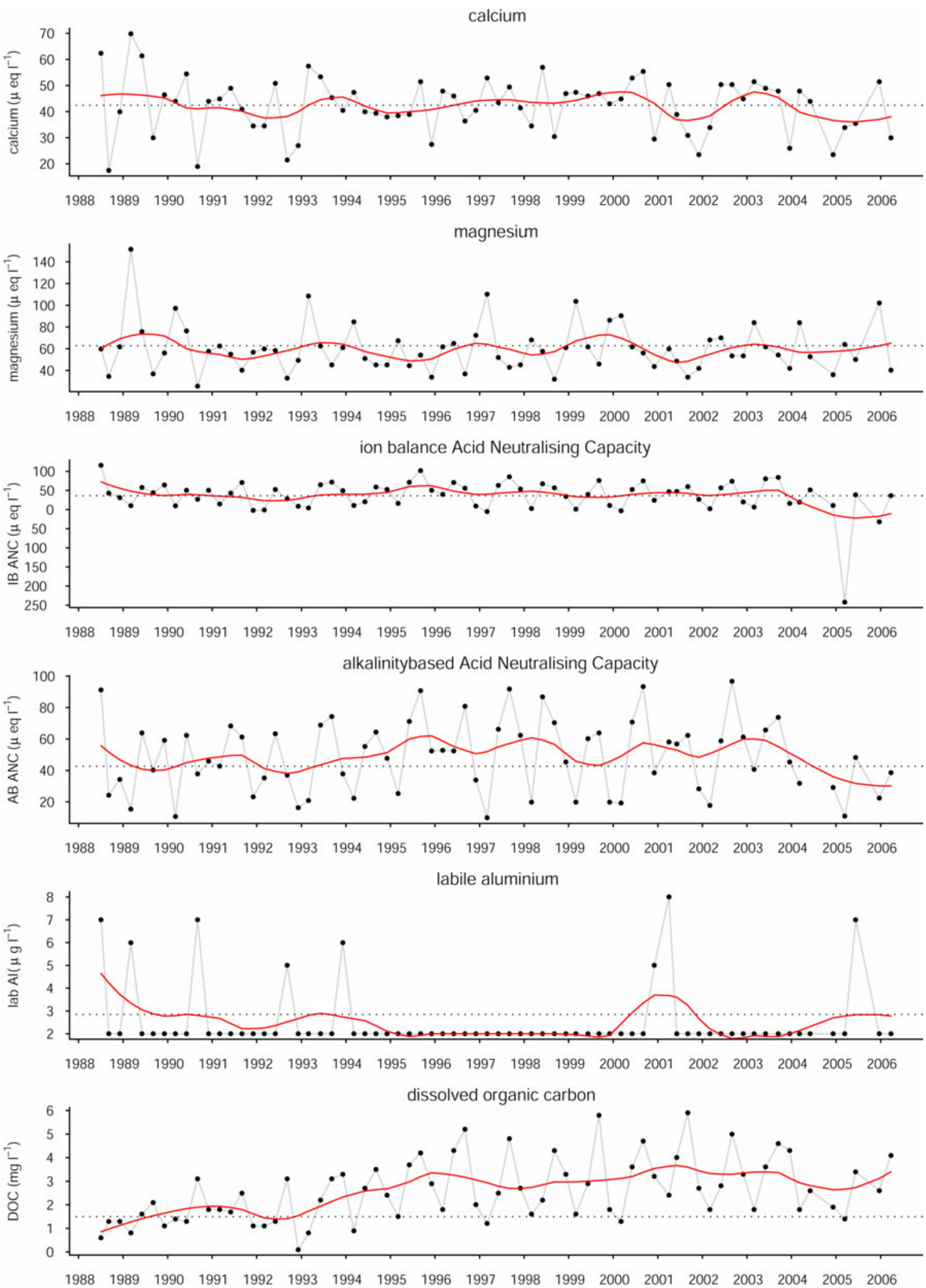

calcium
calcium (µ eq l⁻¹)
magnesium
magnesium (µ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (µ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l⁻¹)
labile aluminium
lab Al(µ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.1.1 Water Chemistry Summary Data and Trend Statistics: Loch Coire nan Arr

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab. Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Jul 1988 - Mar 1993	mean	12.6	2.8	274.3	6.39	35.5	36.2	42.7	40.8	42.4	62.8	239.7	9.5	12.6	2.9	1.5
	st. dev	9.2	2.1	136.4	0.32	21.3	29.3	21.5	16.0	14.8	29.1	89.6	3.5	8.6	1.8	0.8
	min	-15.1	1.3	124.1	5.75	4.0	-2.6	10.8	21.0	17.5	25.5	130.5	2.6	2.0	2.0	0.1
	max	23.2	8.0	665.8	6.96	89.0	115.7	91.2	85.0	69.9	151.4	495.9	15.1	40.0	7.0	3.1
Apr 1993 - Mar 1998	mean	15.2	2.6	242.2	6.40	40.1	47.3	54.0	37.8	42.6	57.5	224.7	7.7	18.1	2.2	2.8
	st. dev	6.1	1.8	100.6	0.30	19.0	29.4	23.4	10.6	6.6	18.0	63.4	2.5	7.5	0.9	1.2
	min	-1.3	1.3	129.8	5.77	4.0	-5.3	9.8	24.0	27.4	33.7	143.6	2.6	8.0	2.0	0.9
	max	22.4	7.5	513.4	6.79	70.0	102.1	91.8	70.0	53.4	110.2	387.2	14.1	36.0	6.0	5.2
Apr 1998 - Mar 2003	mean	8.7	1.9	265.7	6.37	37.6	38.8	53.4	40.3	43.7	60.7	230.3	8.1	15.7	2.5	3.2
	st. dev	7.7	1.1	103.8	0.29	20.5	26.4	24.4	11.5	9.5	18.9	66.9	2.3	9.2	1.5	1.4
	min	-5.0	1.3	118.5	5.88	9.0	-2.8	17.8	23.0	23.5	32.1	134.9	3.8	2.0	2.0	1.3
	max	29.1	4.5	490.9	6.87	76.0	76.0	96.8	62.0	56.9	103.6	378.5	13.3	38.0	8.0	5.9
Apr 2003 - Mar 2006	mean	5.7	2.7	285.2	6.13	29.9	6.4	40.7	42.8	38.9	58.7	224.5	7.9	14.2	2.5	3.0
	st. dev	7.9	1.3	148.7	0.29	17.9	93.7	20.1	17.8	10.4	20.6	81.8	2.5	6.5	1.6	1.1
	min	-9.2	1.3	166.4	5.62	4.0	-241.9	10.9	28.0	23.5	36.2	143.6	5.9	5.0	2.0	1.4
	max	16.5	4.6	564.2	6.64	60.0	84.2	73.8	75.0	51.4	102.0	417.6	12.3	22.0	7.0	4.6
Seasonal-Kendall statistics	Sen-slope	-0.543	-0.016	-0.118	-0.008	-0.438	-0.710	0.098		-0.273	-0.240				0.000	0.138
	P- val	**0.008**	0.553	0.737	0.139	0.204	0.754	0.855		0.390	0.470				0.188	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.1.2 Epilithic Diatom Percentage Abundance Summary: Loch Coire nan Arr

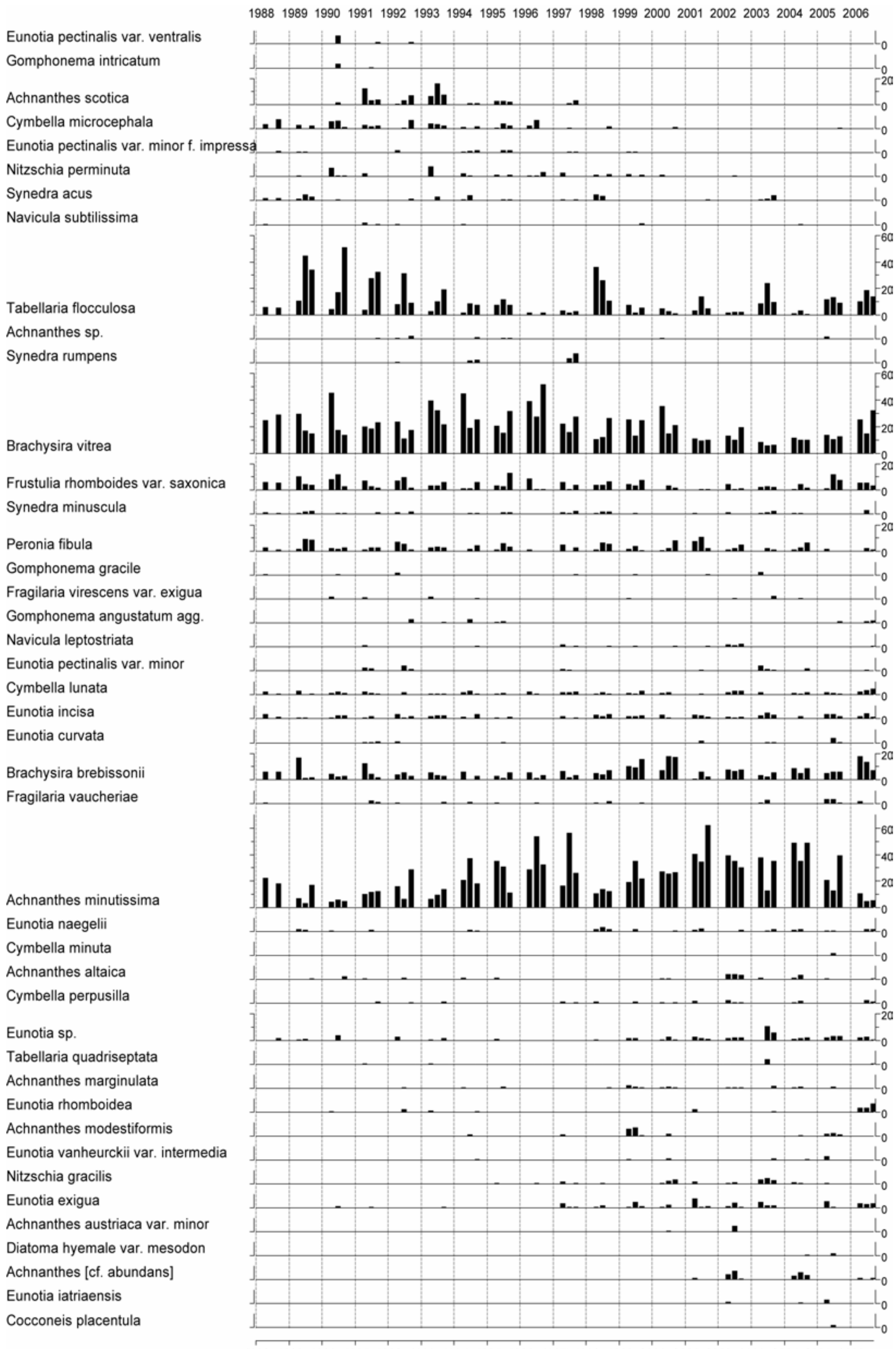
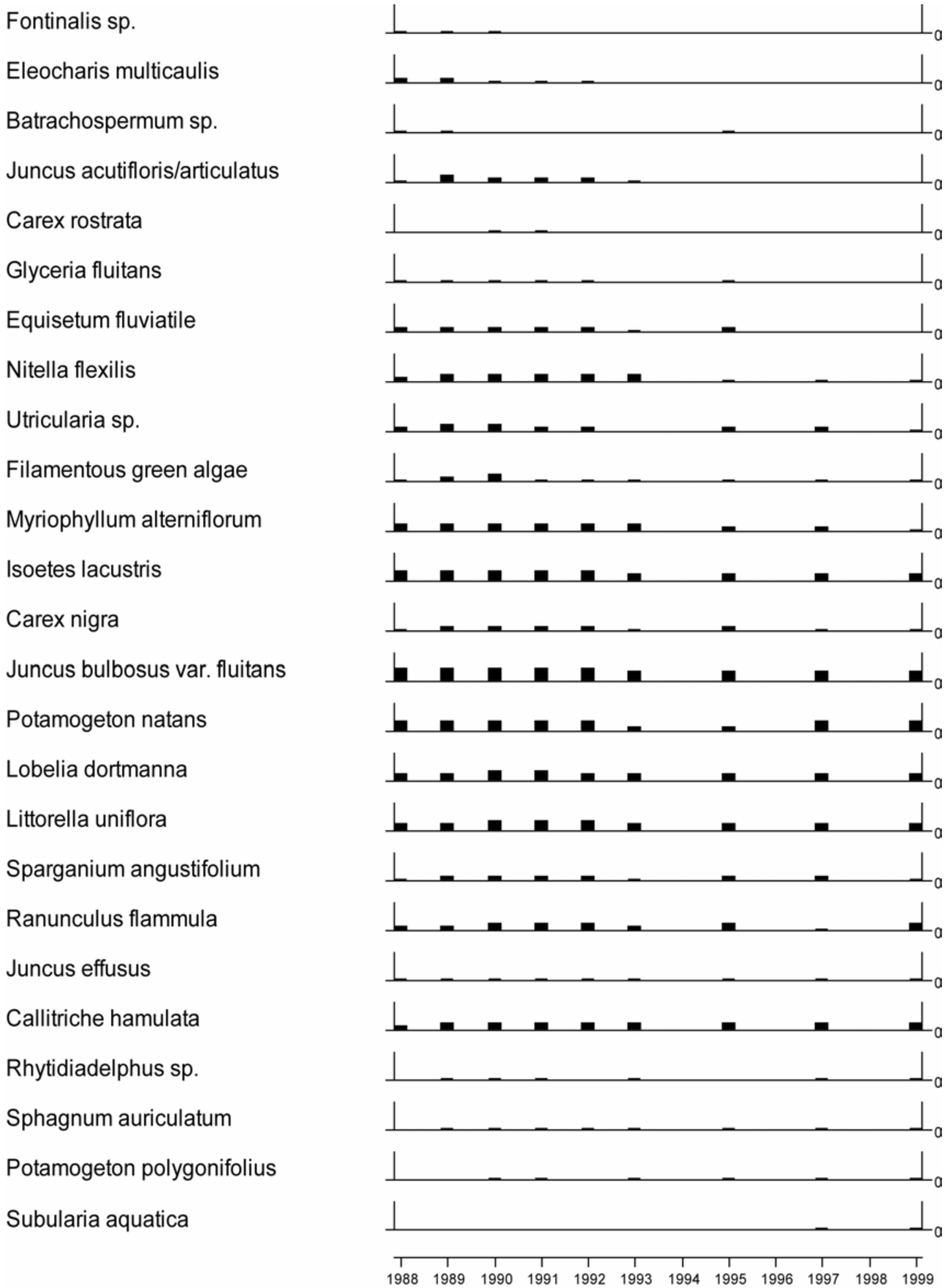


Figure 4.1.3 Aquatic Macrophyte Species Scores (1-5): Loch Coire nan Arr



Aquatic macrophytes no longer surveyed after 1999.

Figure 4.1.4 Macroinvertebrate Percentage Abundance Summary: Loch Coire nan Arr

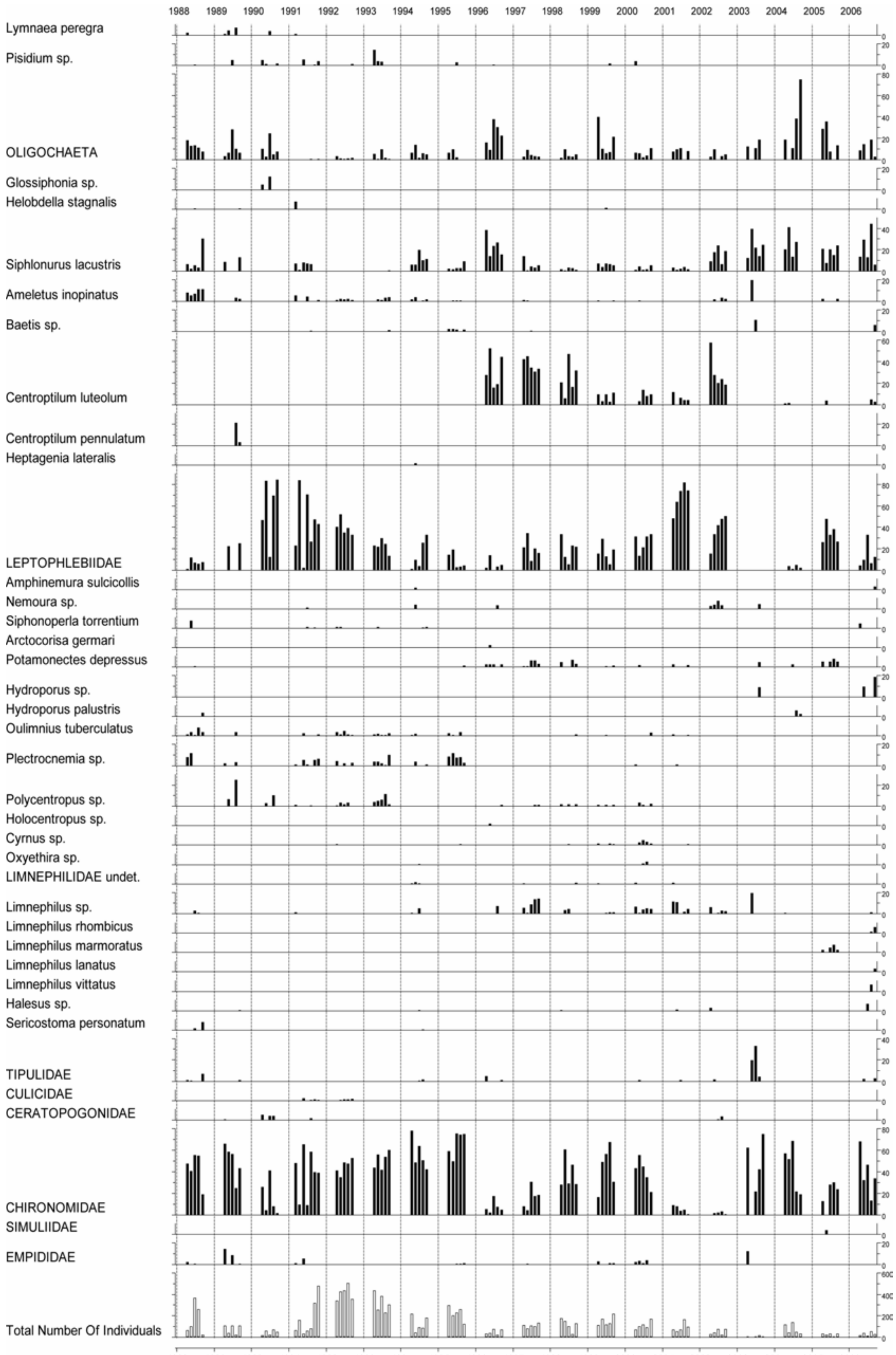
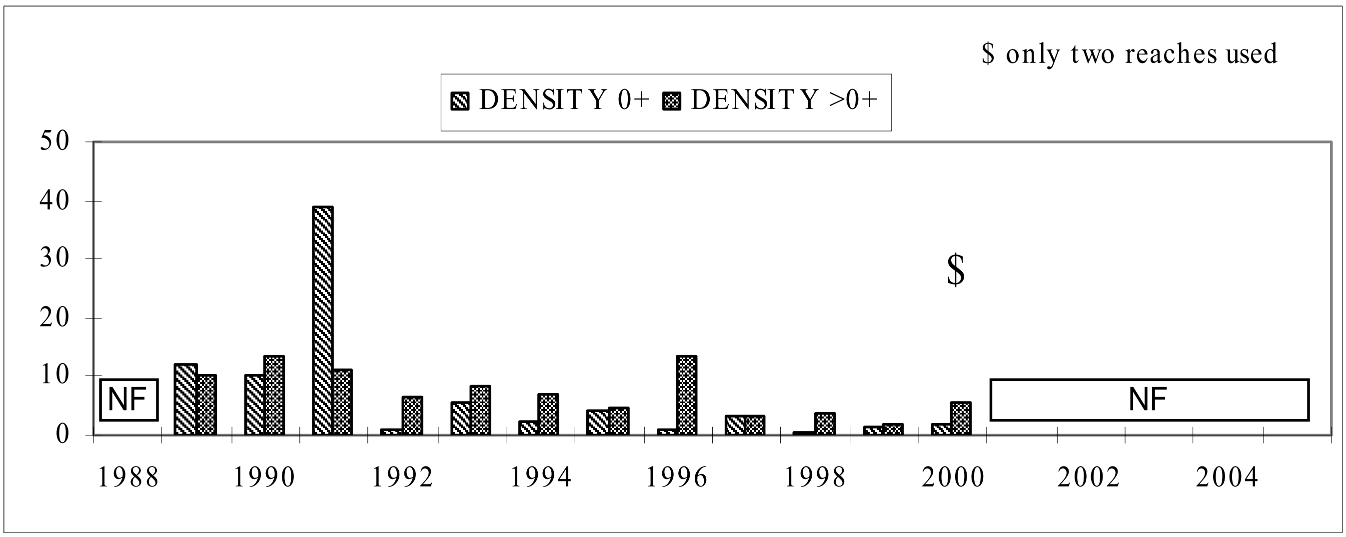


Table 4.1.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Loch Coire nan Arr

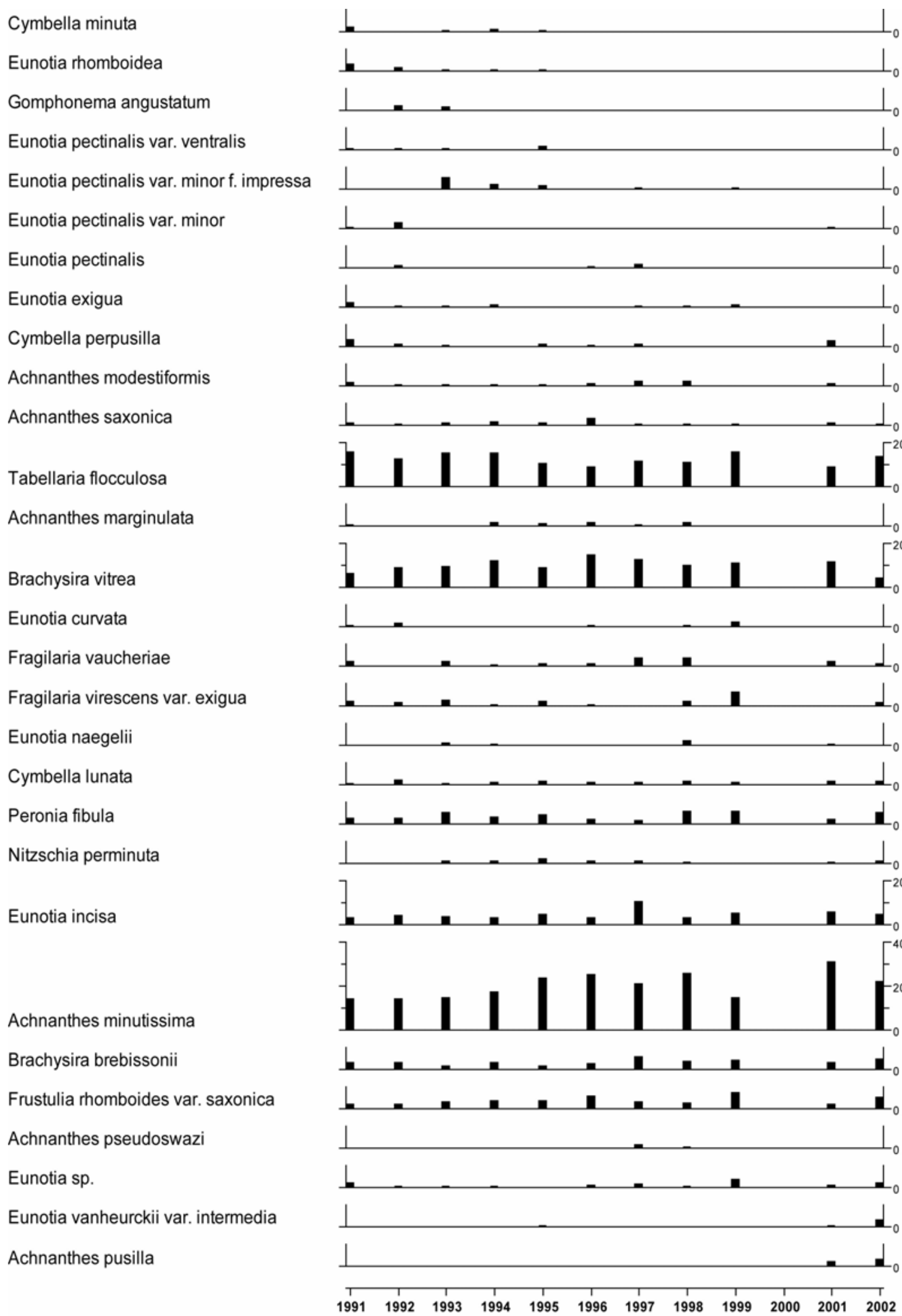
	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1294.33	163	41.9	58.1	0.11	0.64	0.001	0.050
Invertebrates	3263.32	62	37.9	62.1	0.08	0.27	0.001	0.221

Figure 4.1.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Loch Coire nan Arr



NF = Not fished

Figure 4.1.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Loch Coire nan Arr



Sediment trap samples no longer collected after 2002.

4.2 Allt a'Mharcaidh

4.2.1 Water chemistry Summary

The Allt a'Mharcaidh is a fast flowing montane stream draining a granitic catchment in the Scottish Cairngorms. At the onset of monitoring xSO_4 concentrations were relatively low (1988-1993 mean = 33.1 µeq l^{-1}), while mean Ca (42.3 µeq l^{-1}), pH (6.45), alkalinity (42.3 µeq l^{-1}), and labile aluminium concentrations generally below the limit of detection, were indicative of a sensitive but only mildly acidified system.

Over the course of monitoring xSO_4 concentration has declined less than any other site on the Network (with the exception of Narrator Brook – site 14), with a 2003-2006 mean of 29.4 µeq l^{-1}. This is approximately six times higher than for Loch Coire nan Arr, 110 km to the northwest, for the same period.

Nitrate concentrations are normally below the limit of detection and show no long term trend.

Chloride concentrations are low relative to all other sites on the Network, with the exception of Lochnagar, reflecting the site's distance from the coast. Short term variation is also more muted than at most other sites and levels rarely rises above 150 µeq l^{-1}. The stream is therefore protected from the effect of seasalt episodes that drive large acid pulses in sites to the west.

Dissolved organic carbon concentrations have increased only gradually relative to most other sites, possibly since the decline in SO_4 deposition has only been slight and there has been little change in seasalt deposition (see Section 5.4.5).

Despite the fact that xSO_4 trends have been small, and there is little indication of any change in ion-balance ANC, there has been a gradual increase in five yearly pH minima from 5.12 to 5.86, and in minimum alkalinity from -2.0 to 16 µeq l^{-1}, reflecting a decline in the acidity of hydrologically driven acid episodes. Similarly, there has been a tendency for an increasing number of samples to register undetectably low levels of labile aluminium concentration. These changes might be expected to increase survival chances of acid-sensitive aquatic organisms during spates.

4.2.2 Biology Summary

Despite the very gradual decline in the acidity of Allt a'Mharcaidh the composition of the epilithic diatom flora has changed significantly. Curiously, however, this has involved a very slight increase in trace abundances of the acid tolerant species *Eunotia incisa* (SWAP pH optima = 5.1) and the loss of *Hannaea arcus* (SWAP pH optima = 6.0). It is possible that this trend reflects a tendency toward wetter summers and, therefore, more acidic conditions at the time of sampling in recent year. Overall, however, the amount of floristic change is slight relative to most other AWMN sites.

The aquatic macrophyte flora of Allt a'Mharcaidh has been dominated by the acid-sensitive aquatic moss, *Hygrohypnum ochraceum* since the onset of monitoring. While there has been no loss or gain in species, overall macrophyte cover of the stream bed has increased, mainly as a result of an increase in the moss *Fontinalis antipyretica*, and the acid tolerant liverwort *Scapania undulata*. The ephemeral and acid-sensitive red alga *Lemanaea* sp. has been detected more frequently in recent years and also shows evidence for increased cover.

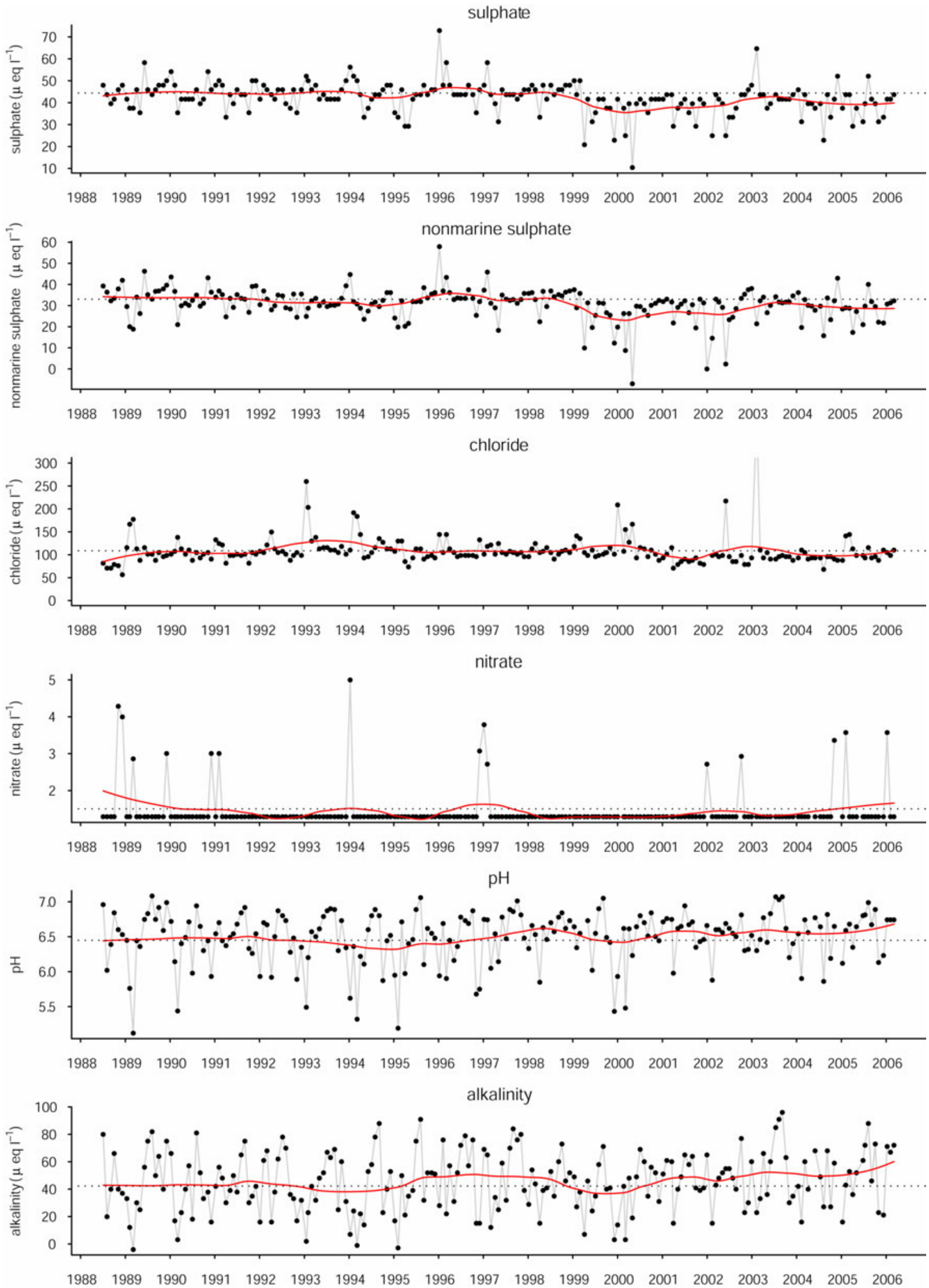
The diverse macroinvertebrate assemblage has been dominated by the acid-sensitive Mayfly genus, *Baetis* sp. and the stonefly *Leuctra inermis* throughout the monitoring period. There is substantial year-to-year variability in relative abundances, but several sensitive taxa have been present in most samples in every year of sampling. The only hint of proportional change is provided by the apparent establishment of the beetle *Elmis aenea*; Dangles *et al.* (2004) identified this species as one of few in stream systems that show a preference for circumneutral as opposed to naturally acid (i.e. high DOC) streams. This suggests particularly acute acid sensitivity and its recent expansion is therefore consistent with an improvement in a water quality. There is some evidence for an increase in macroinvertebrate species richness although numbers of taxa vary markedly from year to year.

Salmonids are represented by both brown trout and Atlantic salmon. Brown trout densities are high relative to most other sites on the Network and do not provide any indication of acid stress.

4.2.3 Conclusions

Allt a'Mharcaidh was one of the least acidified sites on the Network when monitoring began and can be considered to be close to a non-acidified "control". However, despite one of the lowest xSO_4 concentrations at the onset of monitoring, this site appears to have benefited less than most from emission reductions and levels are now close to the AWMN average. It is therefore not surprising that there is only a slight indication of an improvement in acidity (reflected mostly in a reduction in the number of samples with detectable levels of labile aluminium) and minor biological change. While the biological changes are mostly consistent with a reduction in acidity, the slight increase in the abundance of the acid tolerant diatom *Eunotia incisa* is puzzling and warrants further investigation.

Figure 4.2.1 Water Chemistry Summary Plots: Allt a'Mharcaidh



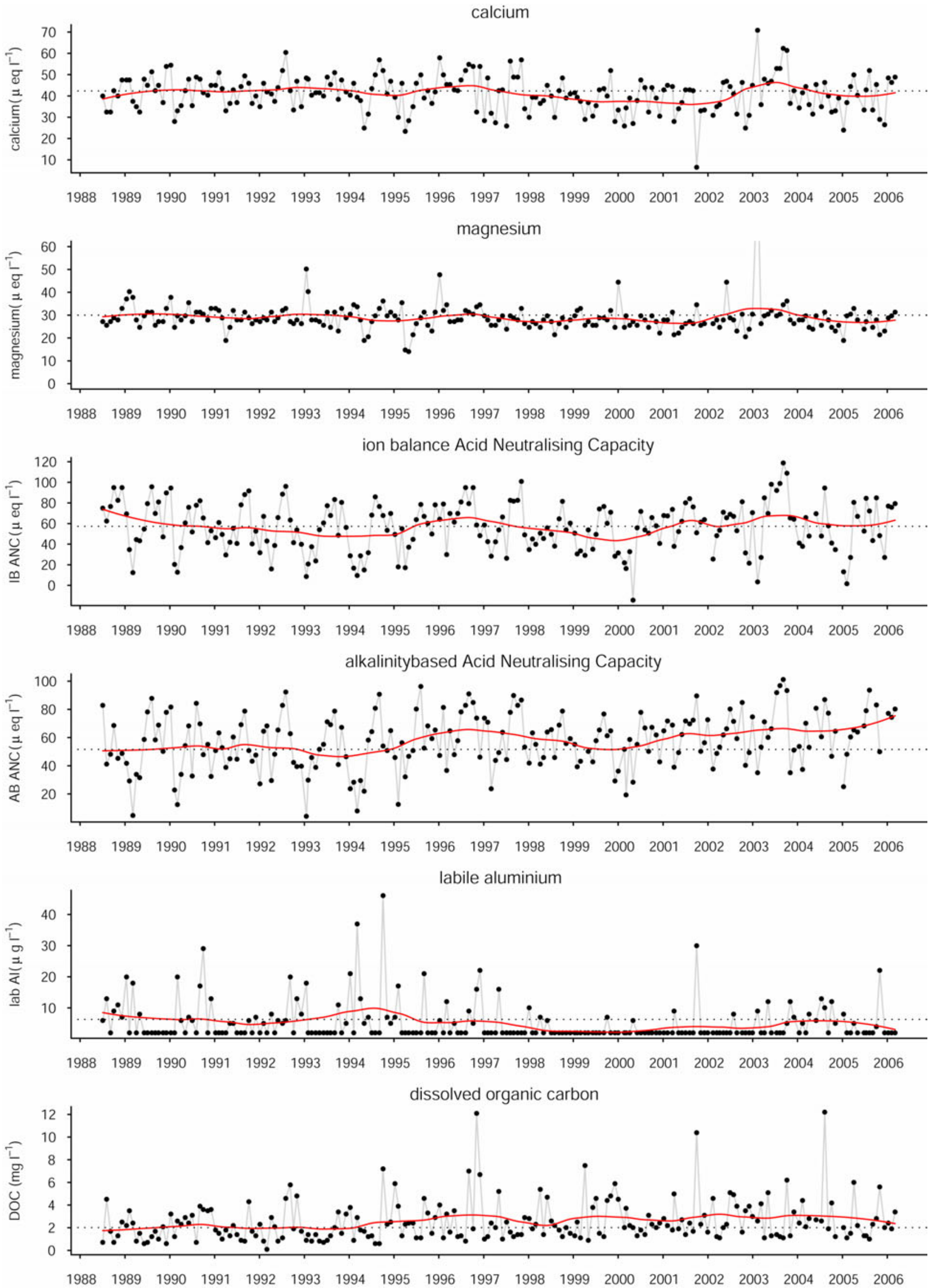

calcium
calcium(µ eq l⁻¹)
magnesium
magnesium(µ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (µ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l⁻¹)
labile aluminium
lab Al(µ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.2.1 Water Chemistry Summary Data and Trend Statistics: Allt a'Mharcaidh

Determinand / **period**		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Jul 1988 - Mar 1993	mean	33.1	1.5	108.6	6.45	42.3	57.3	51.6	23.5	42.3	30.0	132.7	6.7	35.4	6.3	2.0
	st. dev	5.6	0.7	32.0	0.40	21.9	24.1	20.4	3.6	6.7	4.8	18.3	2.3	27.8	6.2	1.3
	min	19.0	1.3	56.4	5.12	-4.0	8.6	4.1	17.0	27.9	18.9	91.4	2.6	2.0	2.0	0.1
	max	46.3	4.3	259.5	7.08	82.0	95.9	92.3	38.0	60.4	50.2	213.2	14.6	114.0	29.0	5.8
Apr 1993 - Mar 1998	mean	32.8	1.4	112.0	6.45	46.2	56.4	57.9	24.4	42.4	28.6	137.4	6.0	35.8	6.3	2.5
	st. dev	6.2	0.6	20.5	0.42	23.8	22.6	20.6	3.4	8.7	5.1	16.5	2.1	36.9	8.6	2.0
	min	18.3	1.3	73.3	5.19	-3.0	9.4	7.9	14.0	23.5	14.0	91.4	2.6	2.0	2.0	0.6
	max	57.9	5.0	191.8	7.06	91.0	100.8	96.3	32.0	57.9	47.7	174.0	13.6	166.0	46.0	12.1
Apr 1998 - Mar 2003	mean	27.8	1.3	111.2	6.51	43.0	51.6	57.3	22.0	38.1	28.7	131.0	5.6	30.3	3.1	2.9
	st. dev	8.8	0.3	48.0	0.32	17.6	20.5	14.9	2.7	8.7	9.5	31.9	0.9	24.5	4.0	1.7
	min	-6.9	1.3	70.5	5.43	3.0	-14.3	19.4	12.0	6.5	20.6	82.7	3.8	2.0	2.0	0.9
	max	38.2	2.9	411.9	7.05	77.0	84.1	89.7	28.0	70.9	93.0	308.9	8.4	109.0	30.0	10.4
Apr 1993 - Mar 2006	mean	29.4	1.5	98.8	6.47	53.3	63.9	67.7	23.6	41.9	28.0	127.2	5.5	32.4	5.1	2.8
	st. dev	5.7	0.6	14.0	0.51	22.0	27.3	18.8	2.5	9.0	3.7	15.8	0.8	37.6	4.7	2.2
	min	15.8	1.3	67.7	5.86	16.0	1.5	25.1	18.0	24.0	18.9	91.4	3.8	2.0	2.0	1.0
	max	42.9	3.6	143.9	7.07	96.0	118.7	101.3	30.0	62.4	36.2	156.6	6.9	175.0	22.0	12.2
Seasonal-Kendall statistics	Sen-slope	-0.354	0.000	-0.188	0.009	0.450	-0.206	0.935		-0.200	-0.111				-0.196	0.060
	P- val	**0.005**	0.342	0.143	0.253	0.092	0.793	**0.002**		0.335	0.058				0.129	**0.008**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.2.2 Epilithic Diatom Percentage Abundance Summary: Allt a'Mharcaidh

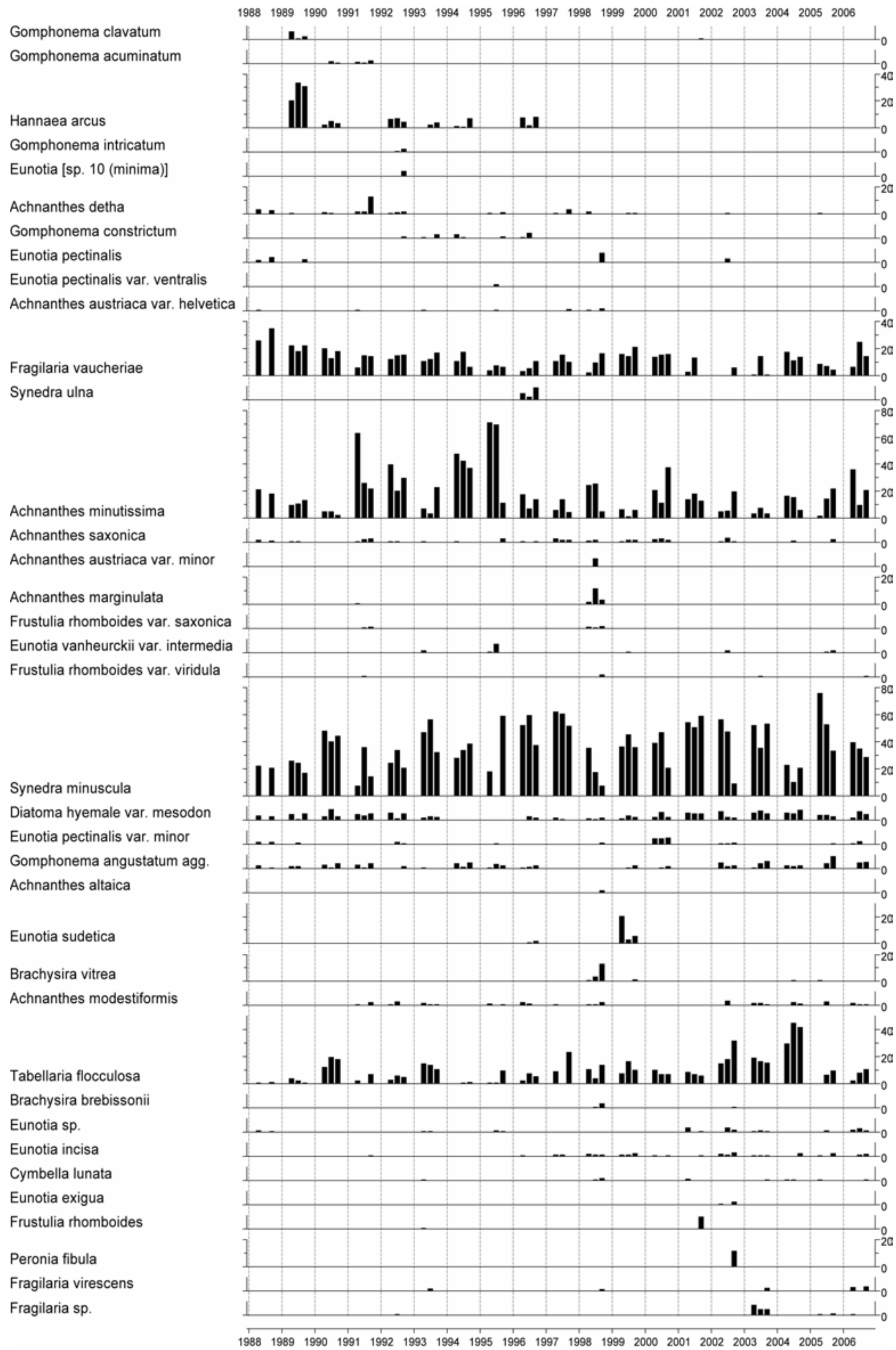
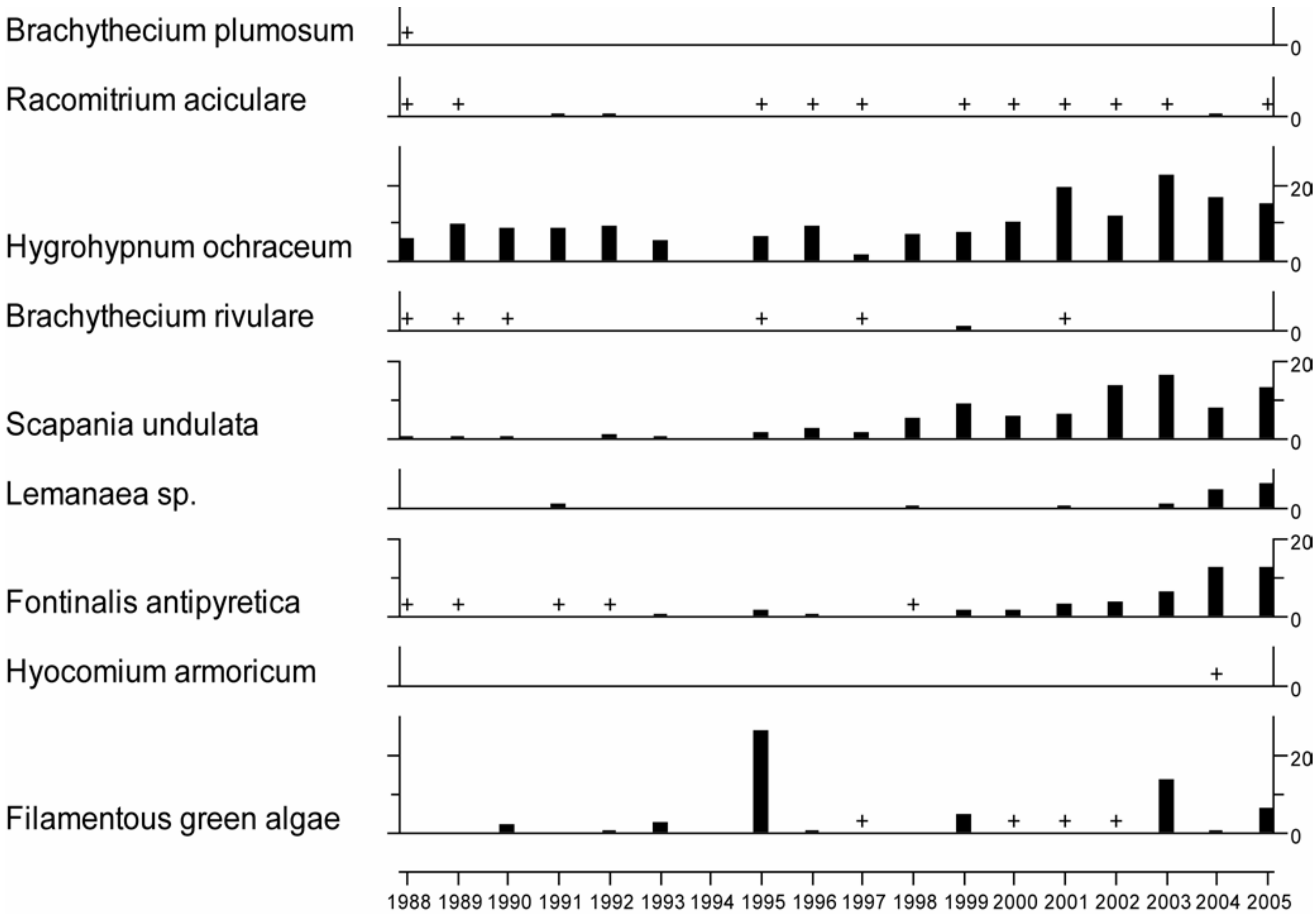


Figure 4.2.3 Aquatic Macrophyte Percentage Species Cover: Allt a'Mharcaidh



+ Represents <0.25% abundance

Figure 4.2.4 Macroinvertebrate Percentage Abundance Summary: Allt a'Mharcaidh

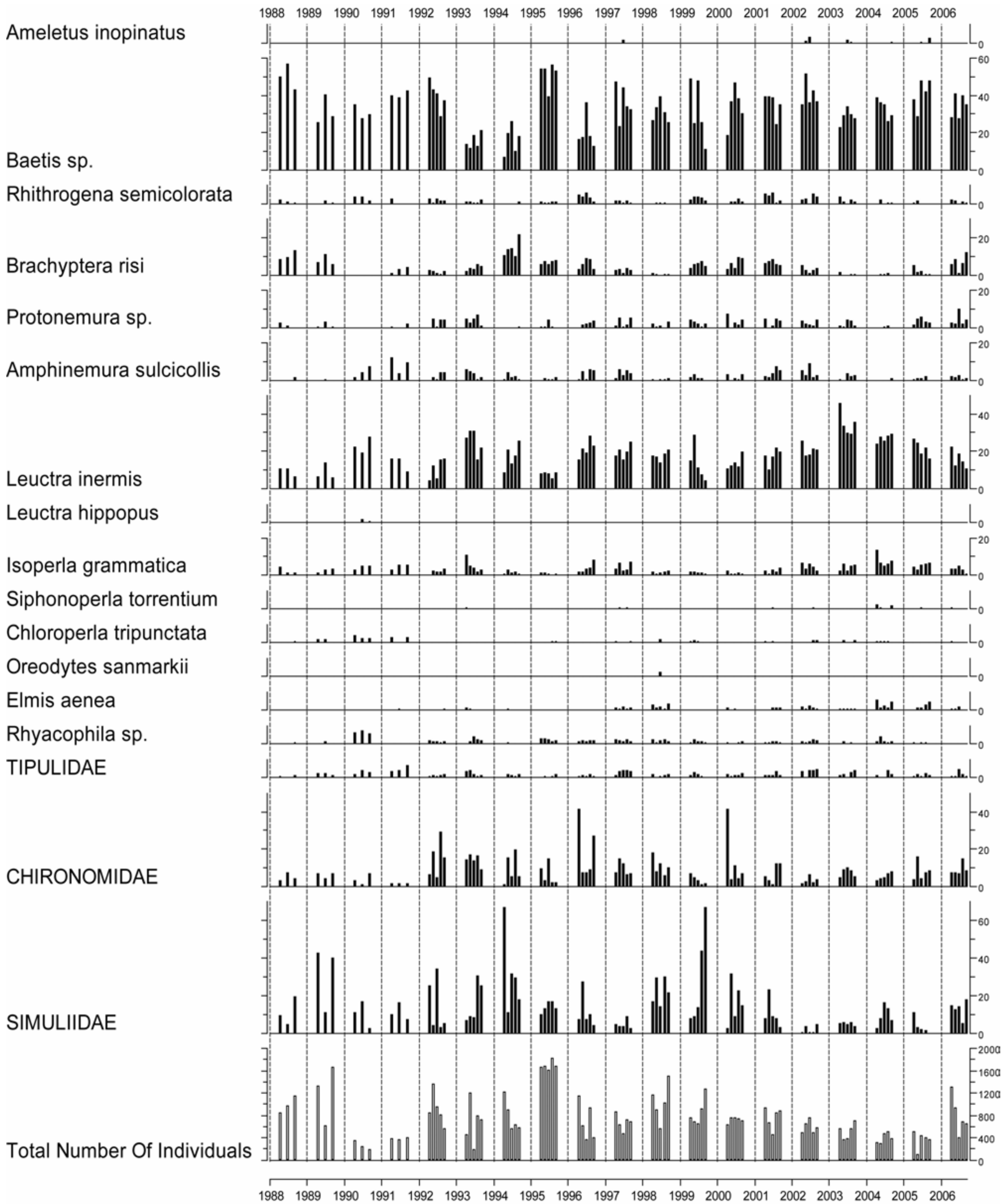


Table 4.2.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Allt a'Mharcaidh

	Total Sum Of Squares	**Number of Taxa**	**Variance Explained Within Year**	**Variance Explained Between Years**	**Linear Trend (λ_1RDA)**	**λ_1RDA /λ_2RDA**	**P unrestricted**	**P restricted**
Epilithic Diatoms	1208.90	102	34.2	65.8	0.10	0.47	0.001	0.015
Invertebrates	893.30	45	44	56	0.07	0.24	0.001	0.080

Figure 4.2.5 Summary of Mean Salmon Density (total numbers $100m^{-2}$): Allt a'Mharcaidh

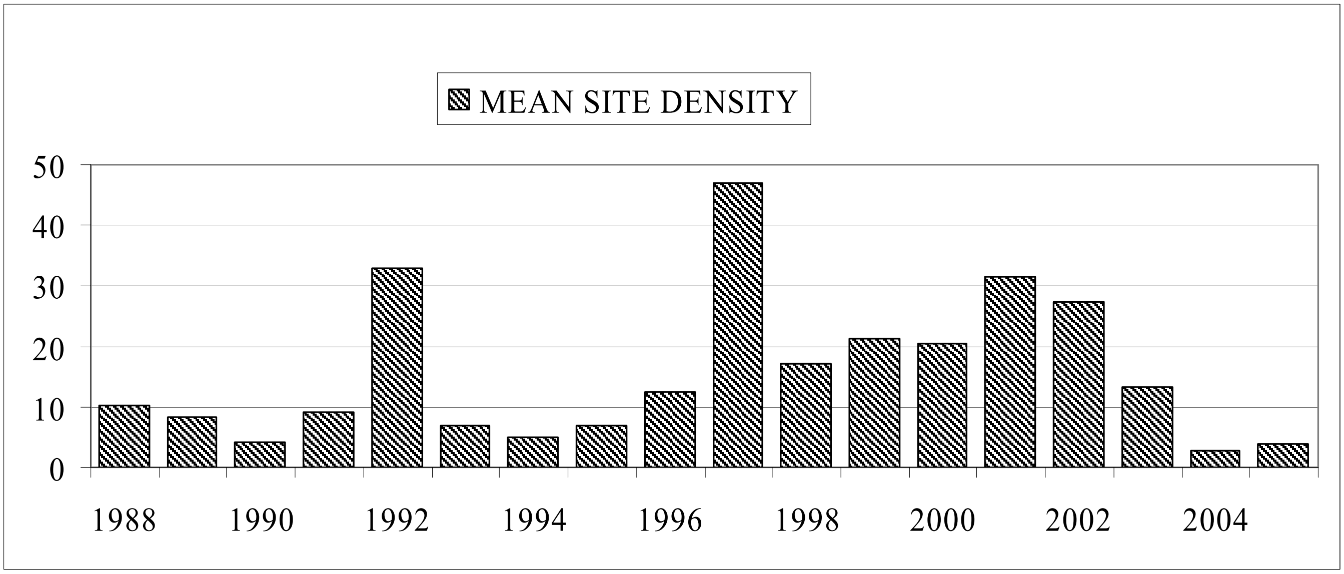
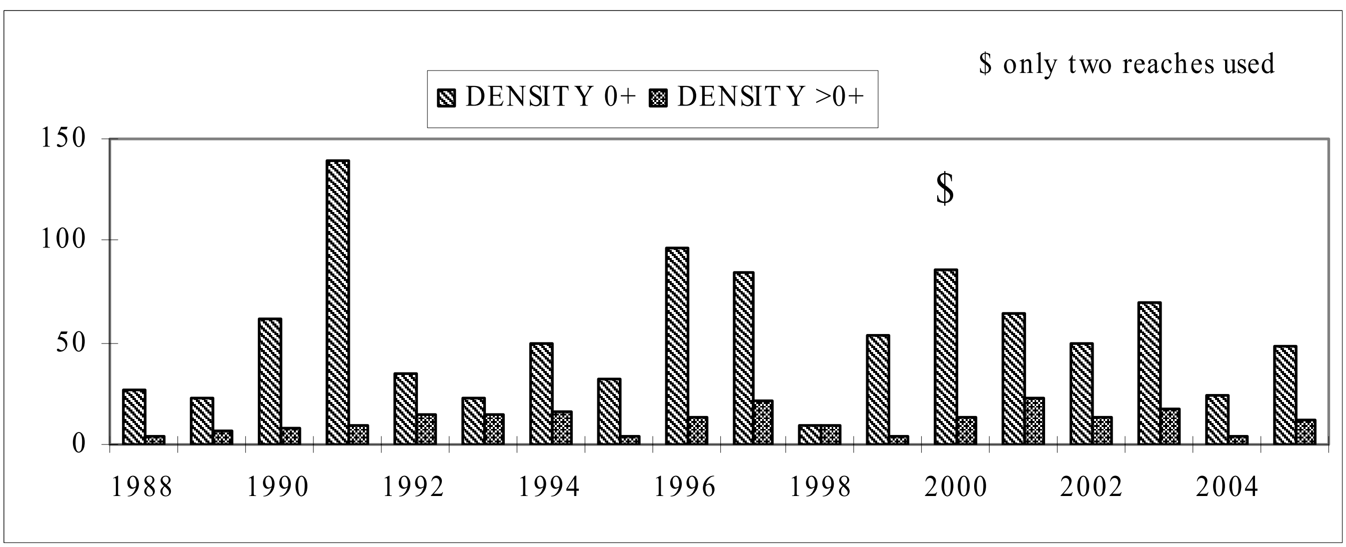


Figure 4.2.6 Summary of Mean Trout Density (numbers $100m^{-2}$): Allt a'Mharcaidh



4.3 Allt na Coire nan Con

4.3.1 Water Chemistry Summary

The Allt na Coire nan Con is a fast flowing montane stream, draining an afforested catchment underlain by a schist/gneiss geology. Over the course of monitoring there has been substantial felling of conifers and replanting of mixed woodland within the catchment. The mean 1988-1993 xSO_4 concentration of 28.4 $\mu eq\ l^{-1}$ was one of the lowest on the Network, reflecting the geographical (low deposition) location. Despite relatively low rates of S deposition, however, water chemistry was indicative of vulnerability to acid episodes. Mean pH and alkalinity were 5.81 and 20.5 $\mu eq\ l^{-1}$ respectively but fell as low as 5.0 and -7.0 $\mu eq\ l^{-1}$ respectively during seasalt driven episodes. The mean labile aluminium concentration of 21.7 $\mu g\ l^{-1}$ was relatively low for the AWMN but levels rose to potentially toxic levels during episodes.

Over the course of monitoring xSO_4 concentrations have fallen by about 30% and remain one of the lowest on the Network. In common with most other sites the clearest decline in xSO_4 occurred between 1996 and 1999 since when there has been no clear trend. However, xSO_4 estimates are complicated by the large variation in seasalt inputs and apparent non-conservative behaviour of sulphate in this catchment which leads to large short term variability. The mean 2003-2006 xSO_4 concentration of 20 $\mu eq\ l^{-1}$ is approximately 3 times higher than that for Loch Coire nan Arr, 73 km to the north. Part of this difference is likely to be due to enhanced pollutant interception by the forest canopy; precipitation weighted xSO_4 concentrations for the local wet deposition site, Polloch, had fallen to 6 $\mu eq\ l^{-1}$ by 2005, the lowest concentration for any wet deposition site in the UK (Vincent and Laurence, 2007).

Nitrate concentrations have remained low throughout the period and have recently lost the seasonal pattern evident over the first ten years of monitoring. This might reflect the effects of felling and replanting in recent years disturbing the cycling of nitrogen within the soil. The majority of samples collected since 2000 have concentrations below the limit of detection.

Concentrations of chloride regularly exceed 500 $\mu eq\ l^{-1}$ during seasalt episodes illustrating the proximity of this site to the coast. Unlike stations further to the south there is no long term trend in the concentration of this anion.

Dissolved organic carbon concentrations show large seasonal variability and have almost doubled over the last 18 years. Most of the change in concentrations occurred between 1996 and 1999 and preliminary time series analysis suggests that the trend can be explained largely by reductions in SO_4 deposition (see Section 5.4.5).

Ion balance ANC is dominated by fluctuations in seasalt and shows no long term trend. Similarly there is no trend in pH or alkalinity. Minimum pH has remained at around 5.0 throughout the period and minimum alkalinity has varied between periods from -7 to -11 $\mu eq\ l^{-1}$. Corresponding labile aluminium maxima, however, have fallen. However, seasalt events are still capable of pushing concentrations considerably over 25 $\mu g\ l^{-1}$, deemed to represent a lower level for potential biological toxicity by Rosseland *et al*. (1990). Given long term climate change forecasts for increased storminess in the northwest Atlantic it is possible that these events will continue and perhaps become more frequent and severe in the future.

4.3.2 Biology Summary

The epilithic diatom community of Allt na Coire nan Con has changed significantly and substantially since the onset of monitoring. Given the minimal evidence for chemical improvement these changes are surprising. The data show a switch from a dominance of *Achnanthes saxonica* in the first half of the record to *Tabellaria flocculosa* and, to a lesser extent, *Eunotia incisa* in more recent years. These changes are consistent with the increase in DOC, according to the relative DOC optima of the taxa in the SWAP dataset, but as the latter is based on lake data this observation must be treated with caution. Further analysis of the data are required to better understand the underlying causes of change.

In common with the diatoms, the aquatic macrophyte characteristics of the survey stretch have also changed substantially over the monitoring period. In the first four years of monitoring the acid-sensitive moss *Hygrohypnum ochraceum* was common, forming substantial areas of cover in some permanently submerged parts of the survey stretch. However, since 1992 the submerged flora has been reduced to a few sparse patches of this moss and the acid-tolerant liverwort, *Scapania undulata*. Although the main change has been the loss in cover of a sensitive species, it seems most likely that these changes result primarily from changing hydrological characteristics of the system. The felling programme commenced around the time of the observed changes and it is feasible that this had a significant impact on flow rates and episodic events particularly, as a result of the reduced retention of precipitation by the forest. An increase in flow energy during spates could have resulted in an increase in the scouring of the stream bed and attached bryophytes.

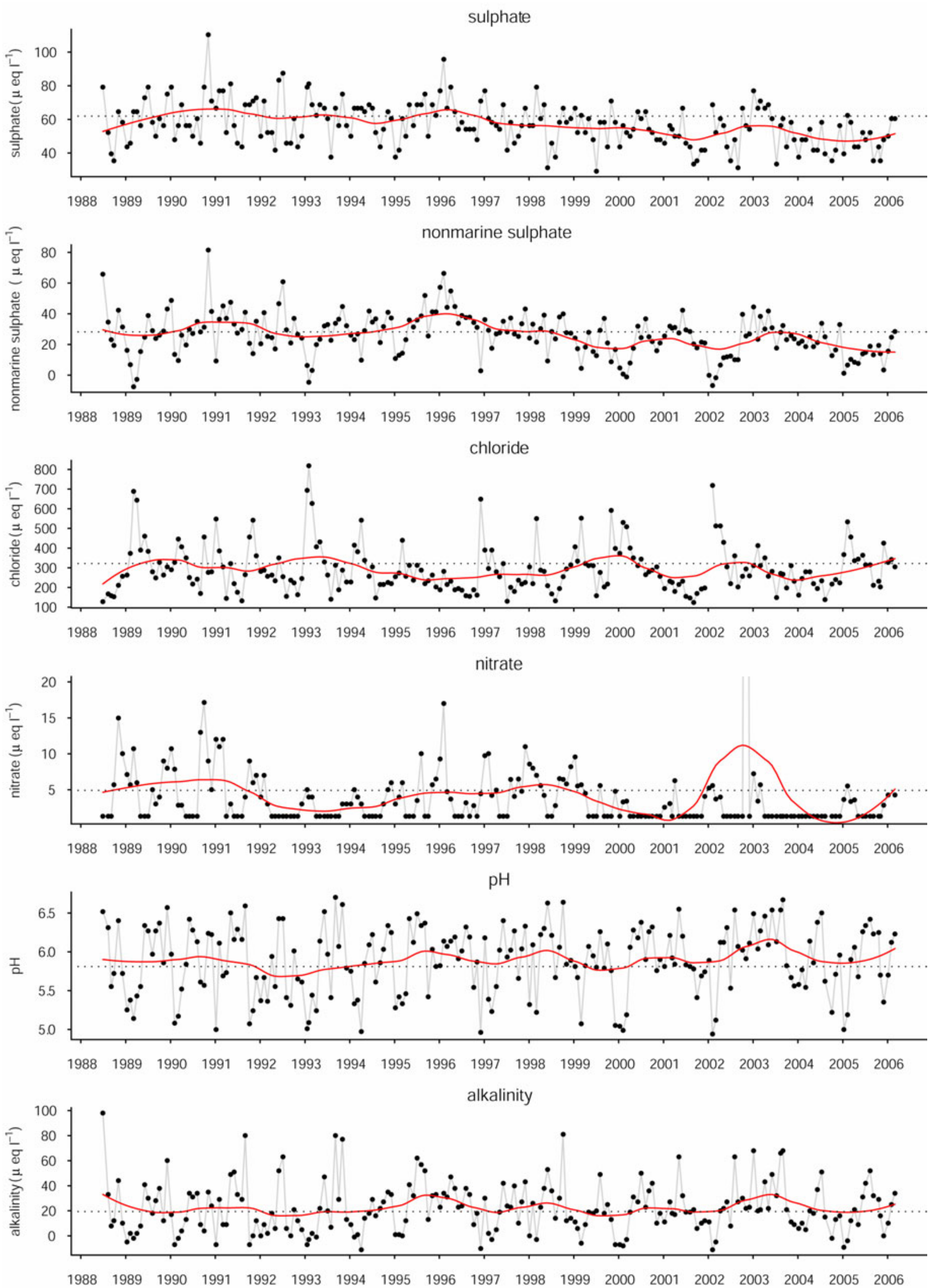
In comparison to the aquatic plant data the macroinvertebrate community shows less evidence of major change over the period. Overall however, the community has changed significantly with time. The main changes are increases in the proportion of the acid-sensitive mayfly, *Heptagenia lateralis*, and the acid-sensitive stonefly *Siphonoperla torrentium*. Kowalik and Ormerod (2006), in their investigation into the importance of acid episodes found that *H. lateralis* only occurred in “circumneutral” streams and not those subject to periodic acid events. Its establishment since 1992 is consistent with a decline in peak labile aluminium concentrations at around this time. Clearly, however, it is able to withstand continued and severe depressions in pH and significant pulses of labile aluminium.

The Allt na Coire nan Con supports both Atlantic salmon and brown trout. Densities of the former show no clear long term trend, but brown trout density has declined in both 0+ and >0+ groups. The fall in brown trout number is inconsistent with the overall reduction in the acidity of the burn.

4.3.3 Conclusion

Allt nan Coire nan Con is a relatively well buffered, but episodically acidic, stream that has received relatively low levels of xSO_4 deposition since monitoring commenced. Despite this however, the 30% decline in concentration over the monitoring period has lead to a significant reduction in peak concentrations of labile aluminium, and this could explain the gradual establishment of some acid-sensitive macroinvertebrate species in recent years. Other biological signals, however, are not consistent with chemical recovery and could rather result from adverse effects on hydrology from forestry practices. Elevated levels of labile aluminium during seasalt episodes could still be exerting negative effects on the macroinvertebrate community and, unless xSO_4 levels are further reduced, this could worsen under a climate change scenario of more frequent and more intense seasalt deposition events (see Section 5.4.3).

Figure 4.3.1 Water Chemistry Summary Plots: Allt na Coire nan Con



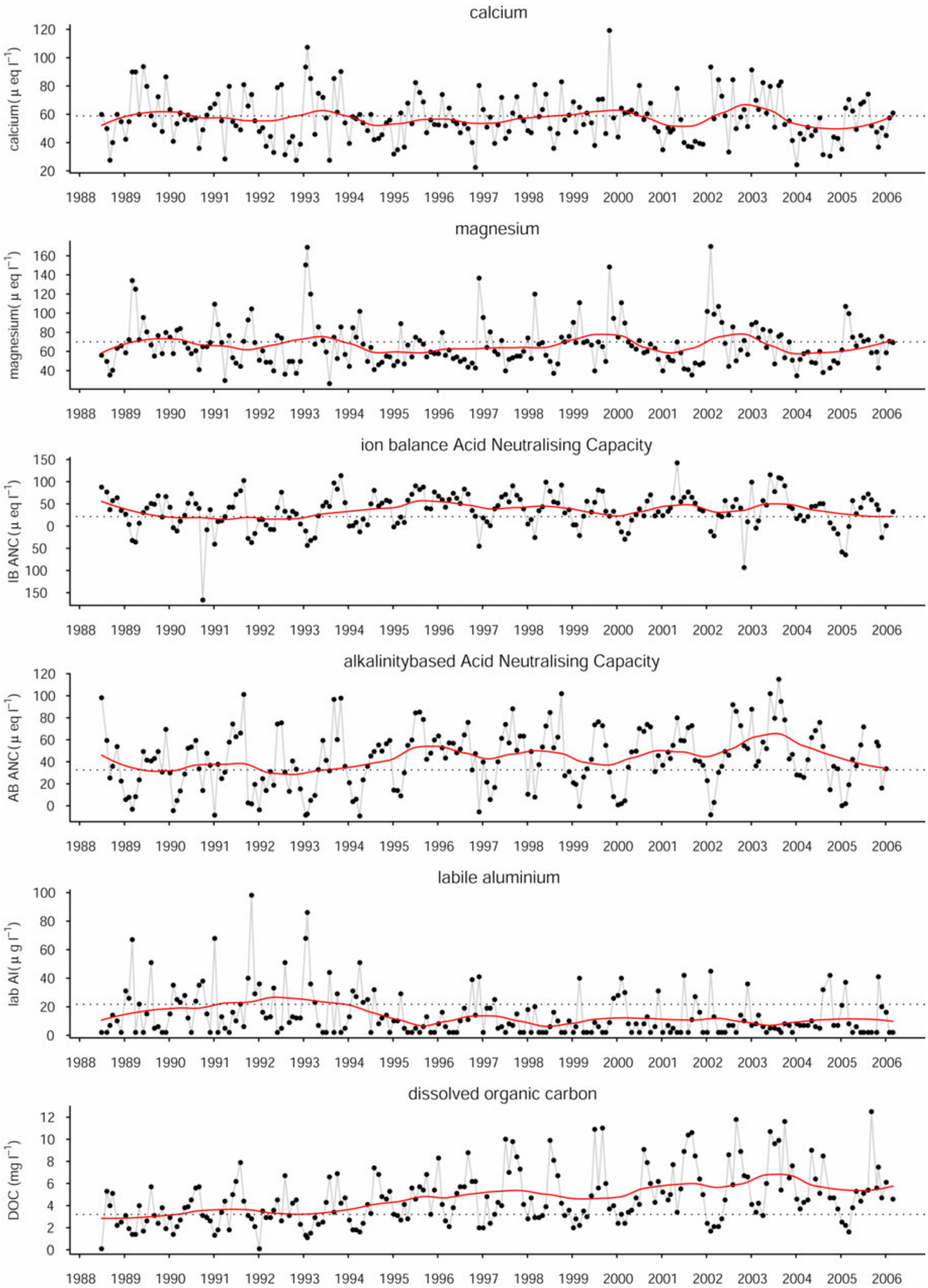

calcium
calcium(μ eq l⁻¹)
magnesium
magnesium(μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al(μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.3.1 Water Chemistry Summary Data and Trend Statistics: Allt na Coire nan Con

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	CB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Jun 1988 - Mar 1993	mean	28.4	4.9	321.9	5.81	20.5	21.3	32.5	48.7	58.9	70.0	272.1	9.1	64.9	21.7	3.2
	st. dev	16.3	4.1	153.0	0.47	22.7	43.6	26.4	17.4	18.6	28.1	91.3	3.4	29.4	22.0	1.6
	min	-7.0	1.3	126.9	5.00	-7.0	-166.4	-8.7	20.0	27.4	29.6	152.3	2.6	12.0	2.0	0.1
	max	81.6	17.1	818.1	6.59	98.0	103.1	101.3	108.0	107.3	168.6	569.9	15.6	129.0	98.0	7.9
Apr 1993 - Mar 1998	mean	32.4	3.9	272.7	5.89	24.4	42.7	44.6	44.0	55.8	62.9	253.0	8.5	66.4	12.8	4.6
	st. dev	11.4	3.2	103.3	0.43	19.6	34.1	25.3	11.6	14.1	19.1	63.2	3.2	26.9	12.2	2.1
	min	3.3	1.3	129.8	4.96	-11.0	-45.1	-9.5	26.0	22.5	26.3	156.6	2.6	15.0	2.0	1.6
	max	66.4	17.0	648.8	6.70	80.0	113.4	97.8	77.0	90.3	136.6	443.7	18.4	131.0	51.0	10.0
Apr 1998 - Mar 2003	mean	22.0	5.3	301.6	5.92	21.9	35.5	47.1	47.0	58.9	69.6	260.2	7.6	61.1	10.5	5.3
	st. dev	11.9	18.2	123.1	0.41	18.8	37.2	25.5	14.2	16.5	25.2	72.7	3.5	27.0	11.9	2.7
	min	-6.1	1.3	124.1	4.94	-11.0	-93.7	-8.4	25.0	33.4	35.4	147.9	2.8	15.0	2.0	1.7
	max	44.8	142.9	719.4	6.64	81.0	142.3	101.8	93.0	119.3	169.5	504.6	27.6	128.0	45.0	11.8
Apr 2003 - Mar 2006	mean	20.0	1.8	280.7	5.74	23.1	36.0	49.2	44.9	54.1	63.0	243.4	7.0	64.6	9.8	5.9
	st. dev	9.2	1.1	85.9	0.68	19.0	42.1	27.8	10.8	15.2	16.3	54.9	2.3	29.2	11.4	2.7
	min	1.1	1.3	138.2	5.00	-9.0	-64.7	-0.1	27.0	24.5	34.5	152.3	3.1	8.0	2.0	1.6
	max	41.8	5.5	533.2	6.67	68.0	115.6	115.1	78.0	82.8	106.9	356.7	13.3	139.0	42.0	12.5
Seasonal-Kendall statistics	Sen-slope	-0.688	-0.109	0.558	0.004	-0.083	-0.220	0.379		0.091	0.251				-0.606	0.159
	P- val	**0.039**	**0.023**	0.737	0.208	0.355	0.509	**0.012**		0.500	0.724				**0.020**	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.3.2 Epilithic Diatom Percentage Abundance Summary: Allt na Coire nan Con

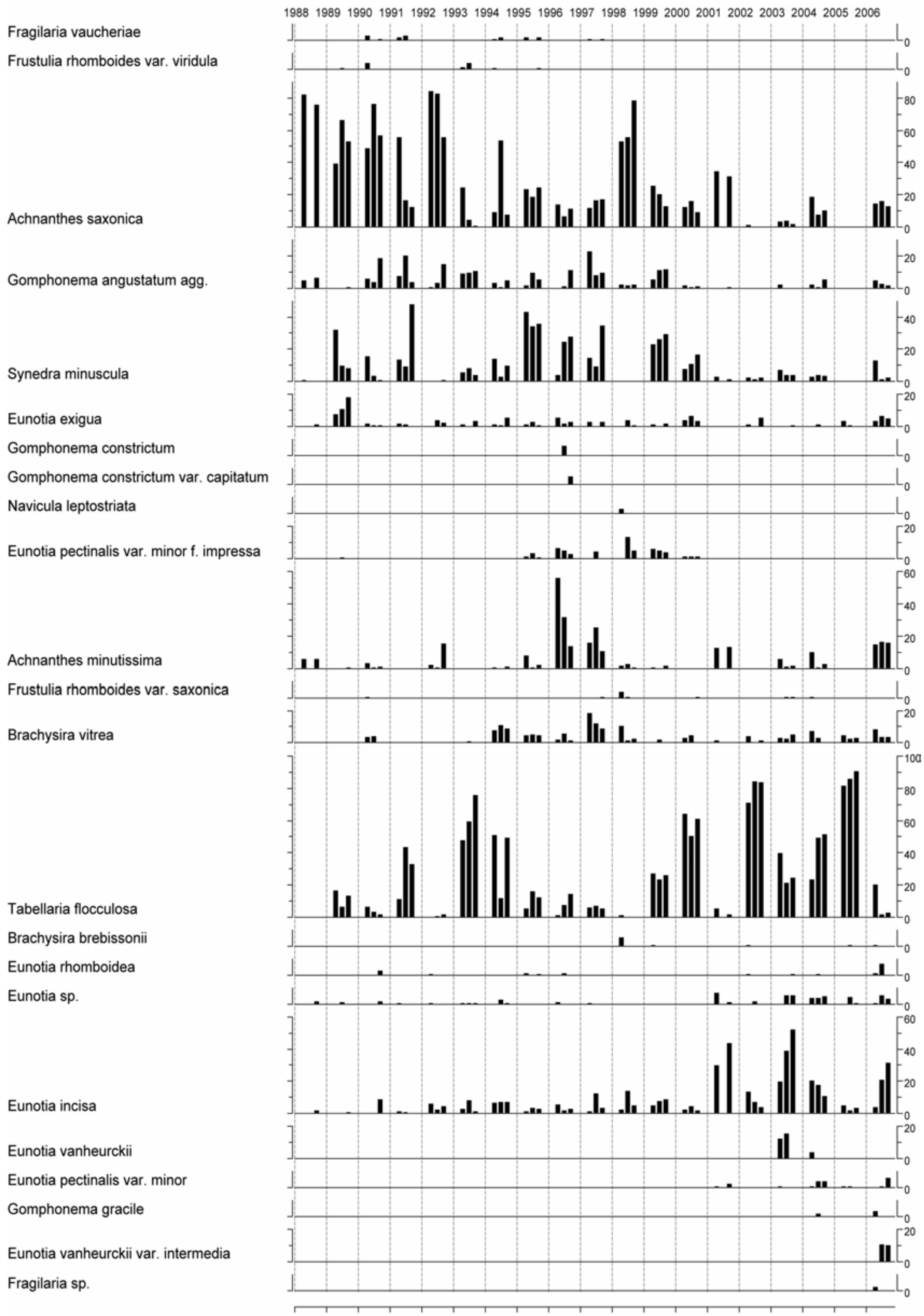
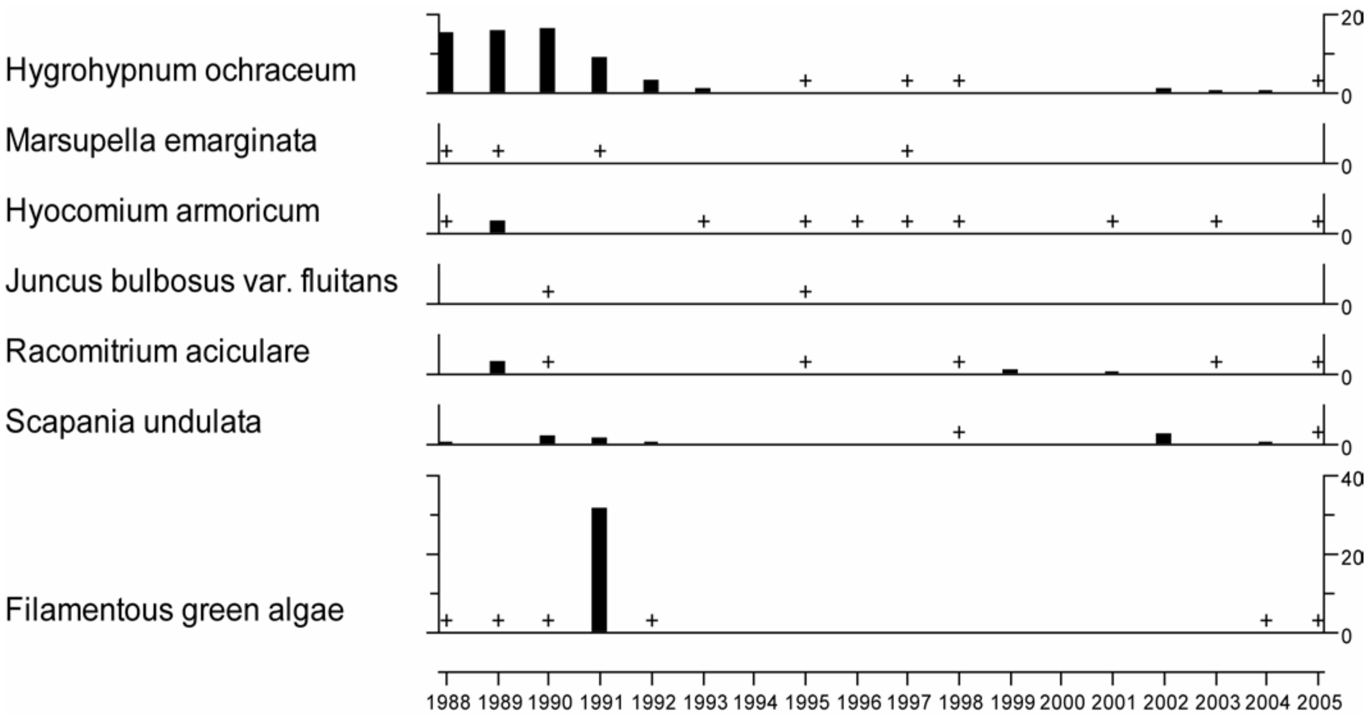


Figure 4.3.3 Aquatic Macrophyte Percentage Species Cover



+ Represents <0.25% abundance

Figure 4.3.4 Macroinvertebrate Percentage Abundance Summary: Allt na Coire nan Con

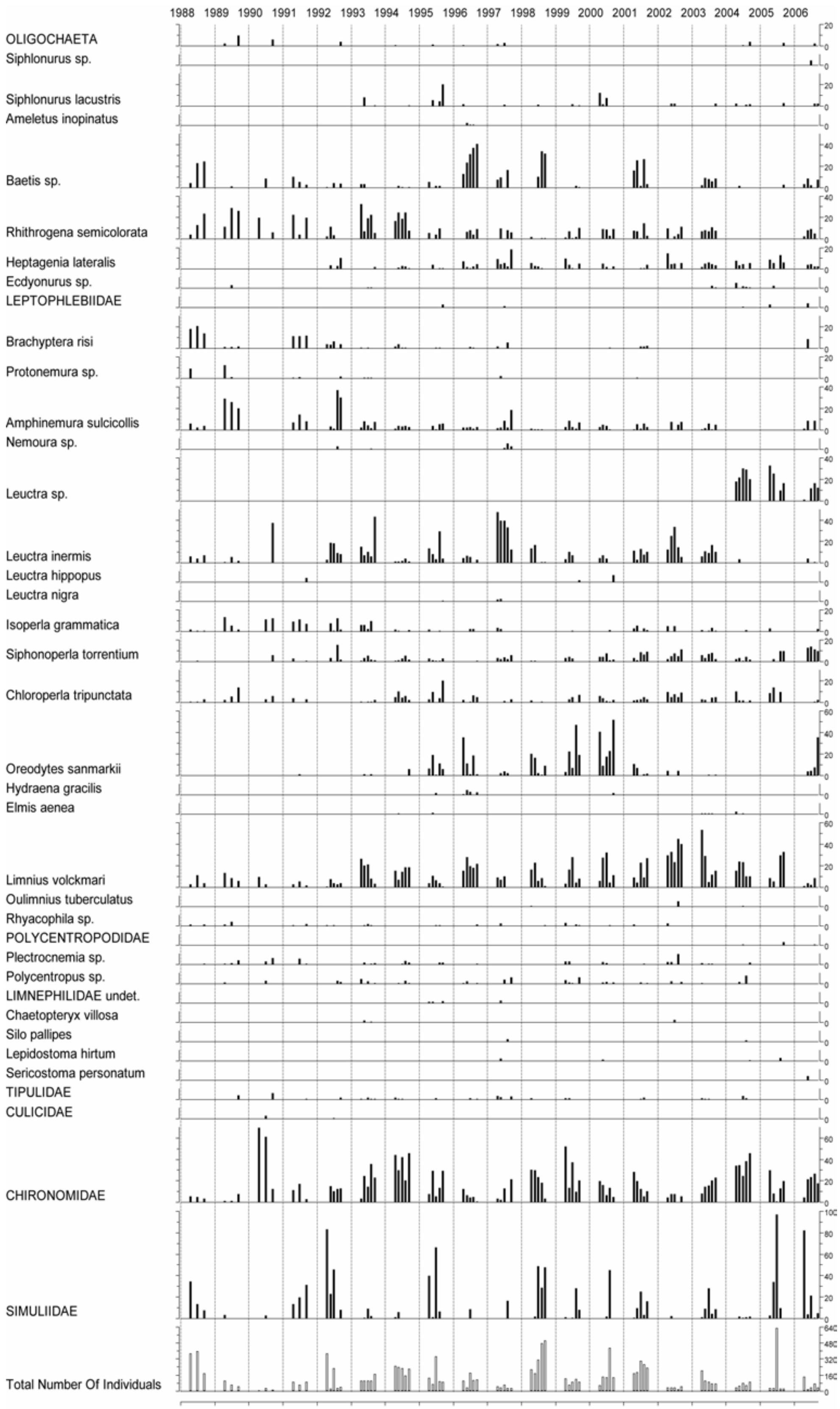


Table 4.3.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Allt na Coire nan Con

	Total Sum Of Squares	**Number of Taxa**	**Variance Explained Within Year**	**Variance Explained Between Years**	**Linear Trend (λ_1RDA)**	**λ_1RDA /λ_2RDA**	**P unrestricted**	**P restricted**
Epilithic Diatoms	1801.70	74	20.1	79.9	0.19	0.57	0.001	0.015
Invertebrates	3530.72	52	46.4	53.6	0.09	0.40	0.001	0.009

Figure 4.3.5 Summary of Mean Salmon Density (total numbers 100m^{-2}): Allt na Coire nan Con

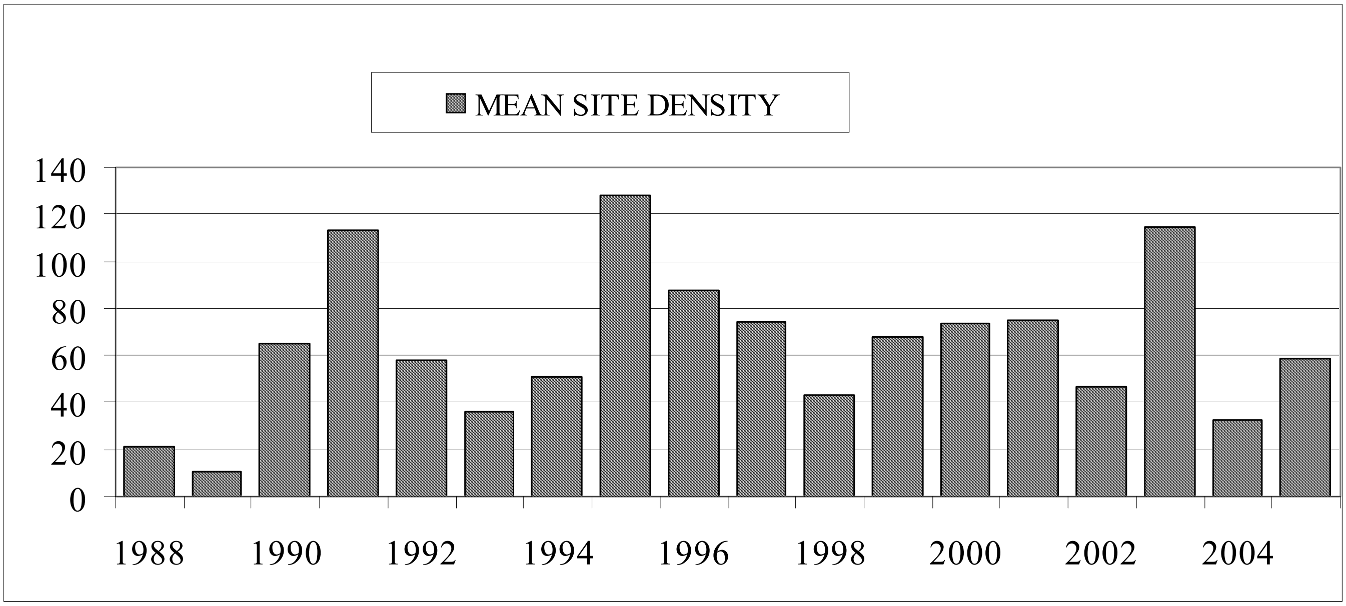
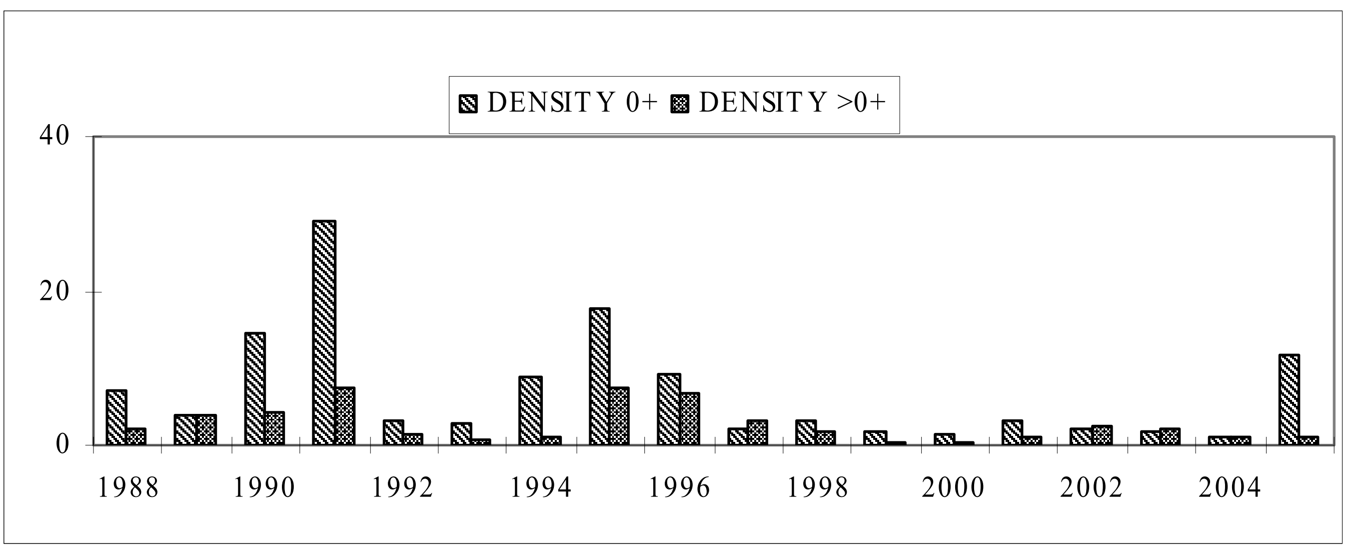


Figure 4.3.6 Summary of Mean Trout Density (numbers 100m^{-2}): Allt na Coire nan Con



4.4 Lochnagar

4.4.1 Water chemistry Summary

Lochnagar is a deep corrie loch lying at 790 m on granite in the Scottish Grampian mountains. It is the only lake on the Network to freeze over each winter. Over the first five years of monitoring (1988-1993) the mean xSO_4 concentration of 51.5 μeq l^{-1} was intermediate for the wider Network. Nitrate (mean = 10.8 μeq l^{-1}) made relatively little contribution to total acidity and in three samples in the first five years was below the limit of detection. The relatively low chloride concentration reflected the limited influence of seasalt compared to AWMN sites closer to the west coast. The loch was clearly acidified, with a mean pH of 5.40 and mean alkalinity of 0.90 μeq l^{-1}, but labile aluminium concentrations were relatively low (mean = 17.9 μg l^{-1}) and with the exception of one extreme sample in 1993, measurements did not exceed 40.0 μg l^{-1} during the rest of the first period.

The xSO_4 time series for Lochnagar is unusual for AWMN sites in showing a relatively linear decline throughout most of the monitoring period; concentrations declined by circa 1 μeq l^{-1} yr^{-1} and by 2003-2006 mean concentration was 35.6 μeq l^{-1}. However, recovery in acidity has not been linear as a result of a step increase in nitrate in 1993. Between 1993-1998 nitrate represented over 30% of total acidity, and in this second period mean pH fell to 5.27, mean ANC become fractionally negative while mean labile aluminium rose to 32.2. μg l^{-1}. The driver of this step change in NO_3 is still unclear, but it is possible that the low levels in the first period resulted from unusually warm winters and a greater retention of N by soil biota.

Since 1993 NO_3 concentrations have remained elevated but have not shown any further increase. As a result of the linear decline on xSO_4 therefore, pH and alkalinity began to climb at around this time and labile aluminium concentrations fell concomitantly. However it is not until the most recent (2003-2006) period that these measures of acidity have fallen consistently below their averages for the first five years. Mean pH for 2003-2006 was 5.52, while mean labile aluminium concentration had declined to 10.5 μg l^{-1}.

The DOC concentration of Lochnagar water has been lower than any other site on the Network, explaining its high transparency (secchi depths of over 10 m are often recorded in summer). However, in common with many other sites on the Network, concentrations have increased substantially. The sharp increase around 1994-1995 coincides with the first clear drop in SO_4 concentration and is therefore consistent with the hypothesis of a controlling effect of acid deposition on organic matter solubility.

4.4.2 Biology Summary

The epilithic diatom assemblage of Lochnagar shows clear inter-annual variability and a significant linear trend. The assemblage has been dominated throughout by *Achnanthes marginulata*, *Tabellaria flocculosa* and *Eunotia incisa*, none of which show any obvious long term change in relative abundance. However, the proportion of *Aulacoseira distans* var. *nivalis* (SWAP pH optima = 5.0) has increased progressively, while *Peronia fibula* (SWAP pH optima = 5.3) and *Eunotia naegelii* (SWAP pH optima = 5.0) have declined, albeit from initial low levels.

The sediment trap assemblage of the loch also shows clear changes over time. *A. distans* var. *nivalis* again shows a clear increase in relative abundance, but in this case the reciprocal response has been in *Achnanthes marginulata* (SWAP pH optima = 5.2).

Palaeoecological work has shown previously that *Achnanthes marginulata* increased in relative abundance in the sediments as the loch acidified over the course of the 20th century; and over the monitoring period it was most abundant in the epilithon and in sediment trap material in the early 1990s, at the time of the increase in NO_3 and acidity. Its decline is therefore consistent with early stages of recovery. However, sediment cores also show an increase in relative abundance of *A. distans* var. *nivalis* during the acidification process, so the reasons for the continued expansion of this acid-loving species remain unclear. Overall, therefore, the sediment data suggest that the diatom flora of Lochnagar is evolving into a community that is new for the site rather than returning along the trajectory followed during acidification.

Lochnagar is characterised by a small number of aquatic macrophyte species and is dominated by *Isoetes lacustris* and *Juncus bulbosus* var. *fluitans*. Both species have increased in abundance. Despite an increase in DOC and associated slight reduction in transparency, *I. lacustris* has expanded it depth range (in early years it was confined to depths of little more than 1 m but is now common down to 3 m in some parts of the loch). *J. bulbosus* var. *fluitans* only occurred in very limited stands at the outset but now occupies substantial areas, particularly down the eastern side of the loch. Reasons for this expansion in respective distributions remain unclear, but might be linked to reductions in the duration of ice cover in recent years and the effect this might have on the seasonal light climate.

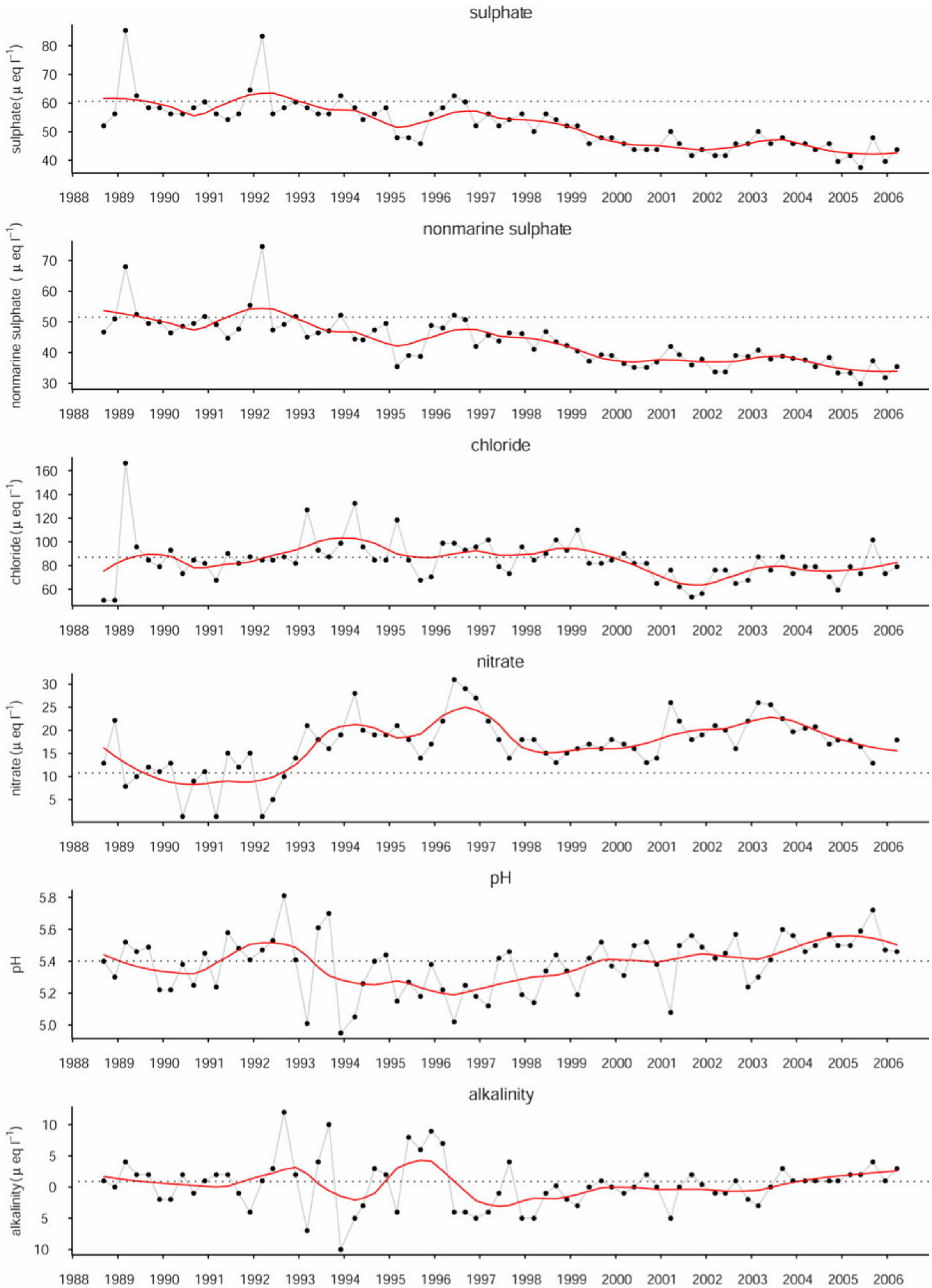
The macroinvertebrate assemblage shows particularly marked inter-annual variability. The acid-sensitive stonefly species, *Capnia* sp., dominated the community in some years but was absent or at very low levels in others. This species was least common at the onset of monitoring and in the period following the increase in NO_3 and acidity from 1993 to 1997. There was no obvious decline in the total number of individuals caught over this most acidic period, during which chironomid larvae comprised most of the assemblage.

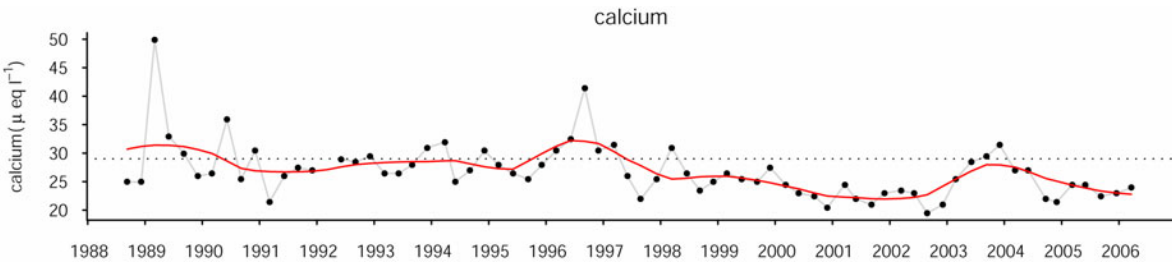
The electrofishing location on the Lochnagar outflow is situated over 2 km downstream the nearest suitable habitat to the loch for electrofishing. The water chemistry of outflow samples may not therefore provide an accurate guide to the acidity levels experienced by the fish in these reaches. Densities of brown trout are generally relatively high and show no significant trend, although in recent years the density of juvenile fish has been lower than that recorded in the early 1990s.

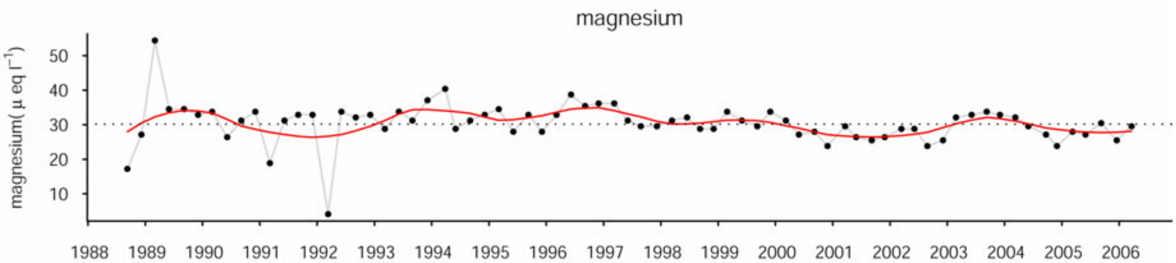
4.4.3 Conclusion

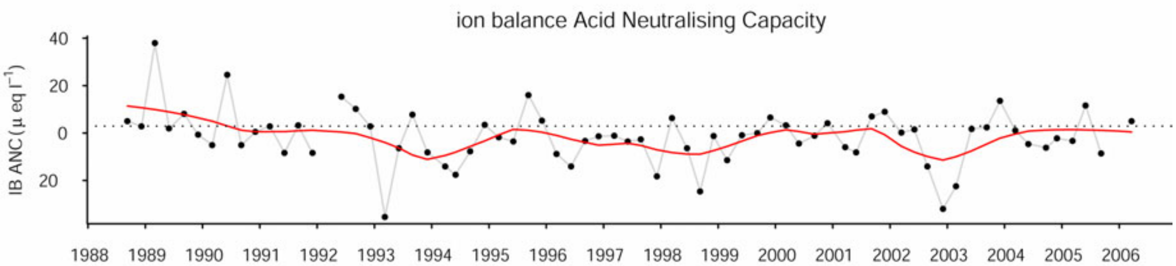
Lochnagar has experienced moderate but gradually declining levels of xSO_4 over most of the monitoring period. However, NO_3 concentrations rose substantially in the early 1990s, resulting in a temporary increase in the overall acid load. In contrast to most sites on the Network therefore, the loch was most acidic in the early to mid-1990s, and this was evident in both peaks in the abundance of the acidophilous diatom *Achnanthes marginulata*, and troughs in the representation of the acid-sensitive stonefly, *Capnia* sp.. While NO_3 concentrations have remained elevated, the continued decline in xSO_4 has finally resulted in acidity levels in the last three years falling below the levels recorded at the outset of monitoring. The diatom species balance of Lochnagar, as indicated by the sediment trap data, points to the development of a new community that cannot be explained by a reversal in acidity alone. The progressive expansion of range of the dominant aquatic macrophyte species cannot be linked to changes in water chemistry, but may reflect a gradual decline in the period of winter ice cover and associated change in light climate.

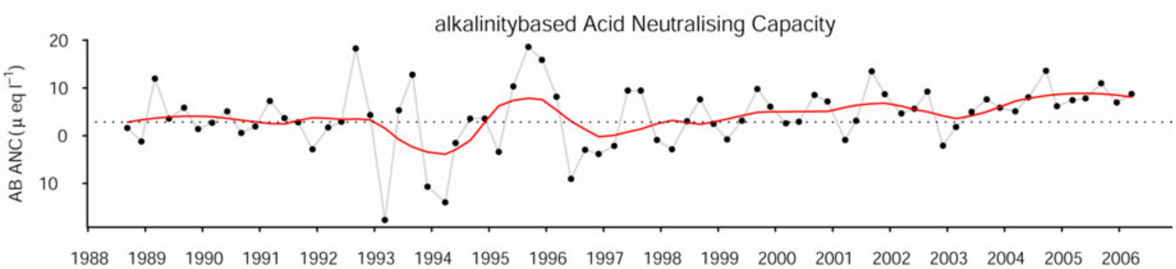
Figure 4.4.1 Water Chemistry Summary Plots:Lochnagar

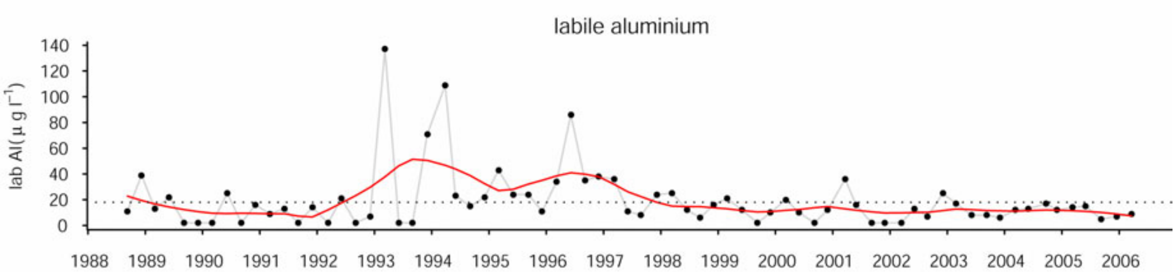



calcium
calcium(µ eq l⁻¹)
50 45 40 35 30 25 20
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006


magnesium
magnesium(µ eq l⁻¹)
50 40 30 20 10
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006


ion balance Acid Neutralising Capacity
IB ANC (µ eq l⁻¹)
40 20 0 20
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006


alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l⁻¹)
20 10 0 10
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006


labile aluminium
lab Al(µ g l⁻¹)
140 120 100 80 60 40 20 0
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

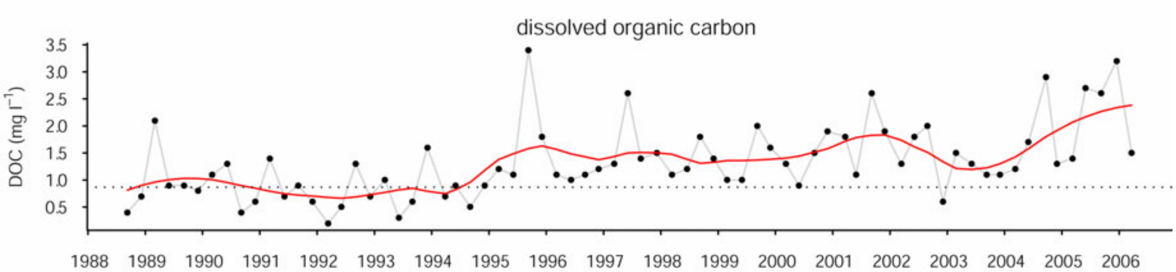

dissolved organic carbon
DOC (mg l⁻¹)
3.5 3.0 2.5 2.0 1.5 1.0 0.5
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.4.1 Water Chemistry Summary Data and Trend Statistics: Lochnagar

Determinand		xSO$_4^{2-}$	NO$_3^-$	Cl$^-$	pH	alk	IB-ANC	CB-ANC	cond	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	sol. Al	lab._Al	DOC
period		µeq l^{-1}	µeq l^{-1}	µeq l^{-1}		µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µS cm^{-1}	µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µg l^{-1}	µg l^{-1}	mg l^{-1}
Sep 1988 - Mar 1993	mean	51.5	10.8	87.0	5.40	0.9	2.9	2.8	20.5	29.0	30.2	92.3	7.5	32.0	17.9	0.9
	st. dev	7.5	5.8	25.1	0.17	3.9	14.9	6.8	6.0	6.2	9.7	21.9	3.9	30.3	30.5	0.4
	min	44.7	1.3	50.8	5.01	-7.0	-35.4	-17.7	4.0	21.5	4.1	69.6	2.6	2.0	2.0	0.2
	max	74.5	22.1	166.4	5.81	12.0	37.9	18.3	35.0	49.9	54.3	174.0	19.4	147.0	137.0	2.1
Apr 1993 - Mar 1998	mean	45.5	20.4	92.0	5.27	0.2	-3.7	2.3	23.1	28.9	33.0	95.5	6.4	51.0	32.2	1.3
	st. dev	4.5	4.8	15.3	0.19	5.8	8.8	8.9	2.8	4.1	3.5	11.2	2.2	30.8	27.6	0.7
	min	35.6	14.0	67.7	4.95	-10.0	-18.4	-14.0	20.0	22.0	28.0	82.7	2.6	6.0	2.0	0.3
	max	52.2	31.0	132.6	5.70	10.0	16.0	18.6	29.0	41.4	40.3	126.2	12.5	125.0	109.0	3.4
Apr 1998 - Mar 2003	mean	38.7	18.0	79.1	5.40	-0.8	-5.1	4.8	19.9	23.6	28.7	81.8	4.9	27.4	12.2	1.5
	st. dev	3.4	3.8	14.6	0.13	2.0	11.0	4.0	2.8	2.2	3.0	11.5	1.2	10.4	8.9	0.5
	min	33.7	13.0	53.6	5.08	-5.0	-32.0	-2.1	17.0	19.5	23.9	52.2	3.8	10.0	2.0	0.6
	max	46.8	26.0	110.0	5.57	2.0	8.9	13.5	29.0	27.4	33.7	100.1	9.5	54.0	36.0	2.6
Apr 2003 - Mar 2006	mean	35.6	19.0	77.6	5.52	1.7	0.9	7.8	19.6	25.4	29.4	81.6	4.6	20.3	10.5	1.8
	st. dev	2.9	3.4	10.1	0.27	1.2	7.0	2.5	0.9	3.2	3.2	7.9	0.7	7.9	3.8	0.8
	min	29.8	12.9	59.2	5.41	0.0	-8.6	5.0	18.0	21.5	23.9	65.3	3.6	8.0	5.0	1.1
	max	38.7	25.6	101.6	5.72	4.0	13.5	13.6	21.0	31.4	33.7	95.7	5.6	32.0	17.0	3.2
Seasonal-Kendall statistics	Sen-slope	-1.066	0.348	-1.058	0.010	0.014	-0.238	0.400		-0.356	-0.206				-0.583	0.061
	P- val	**<0.001**	0.085	0.065	**0.022**	0.478	0.866	**0.005**		**0.013**	**0.020**				0.213	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.4.2 Epilithic Diatom Percentage Abundance Summary: Lochnagar

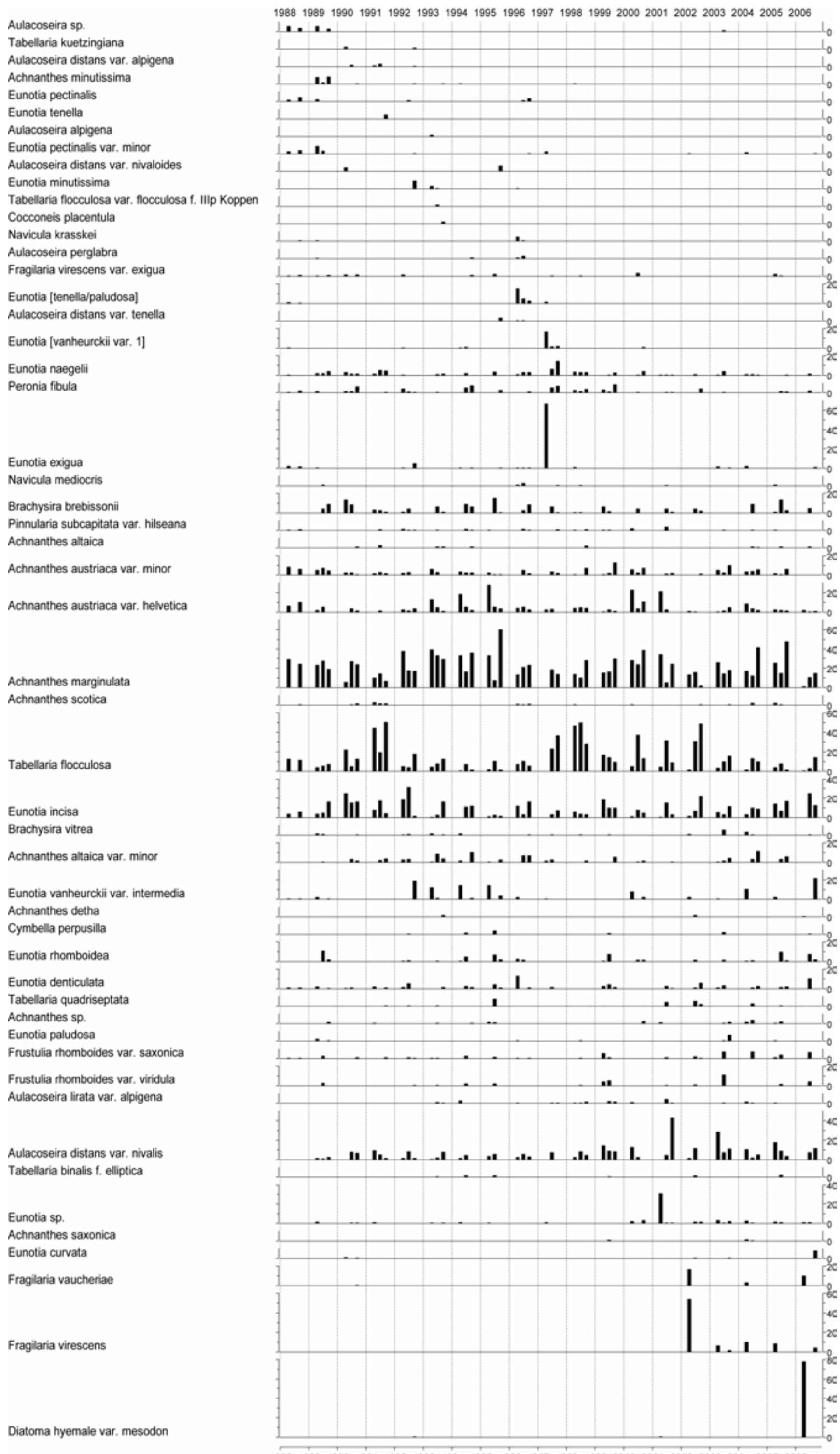


Figure 4.4.3 Aquatic Macrophyte Species Scores (1-5): Lochnagar

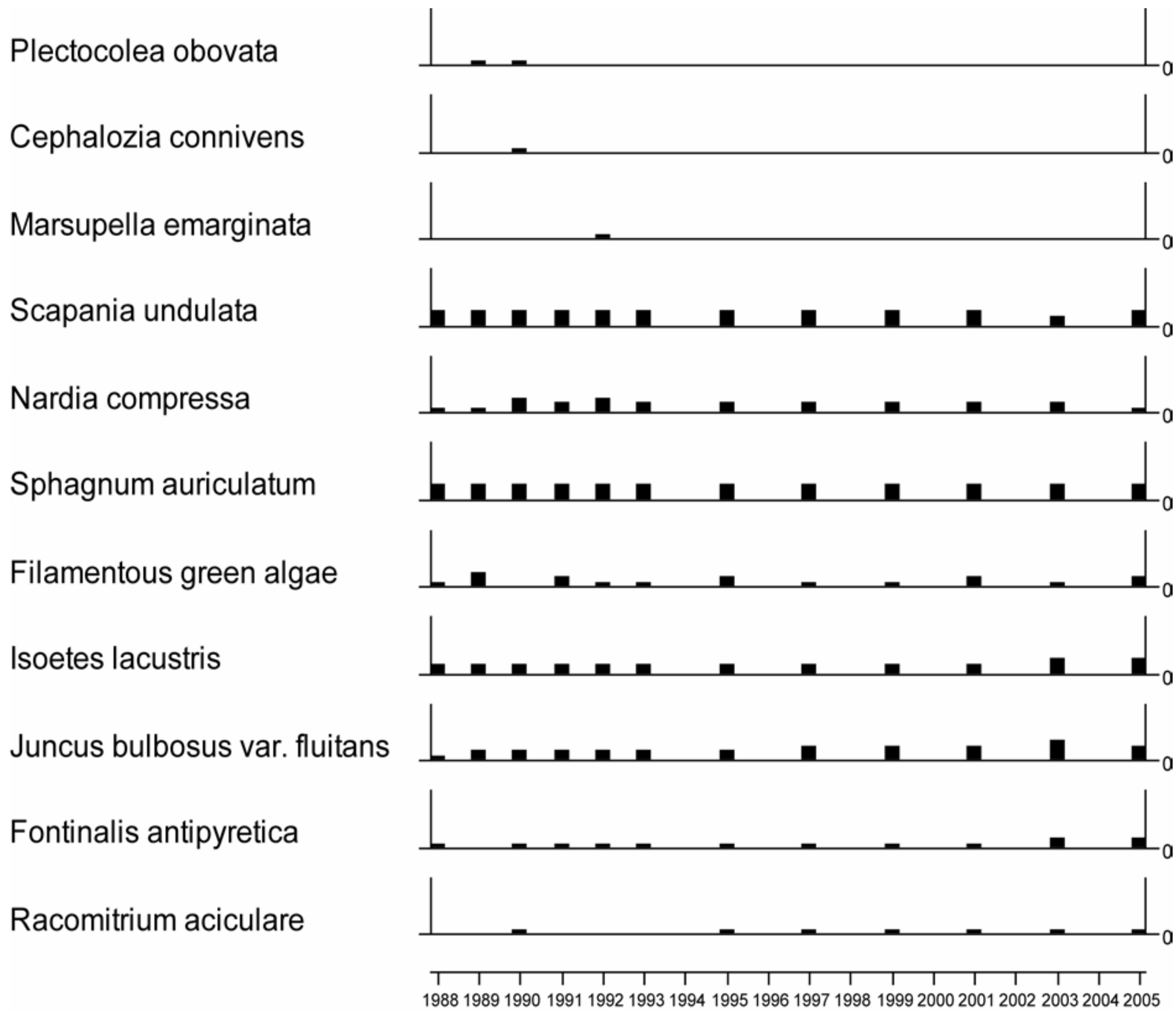


Figure 4.4.4 Macroinvertebrate Percentage Abundance Summary: Lochnagar

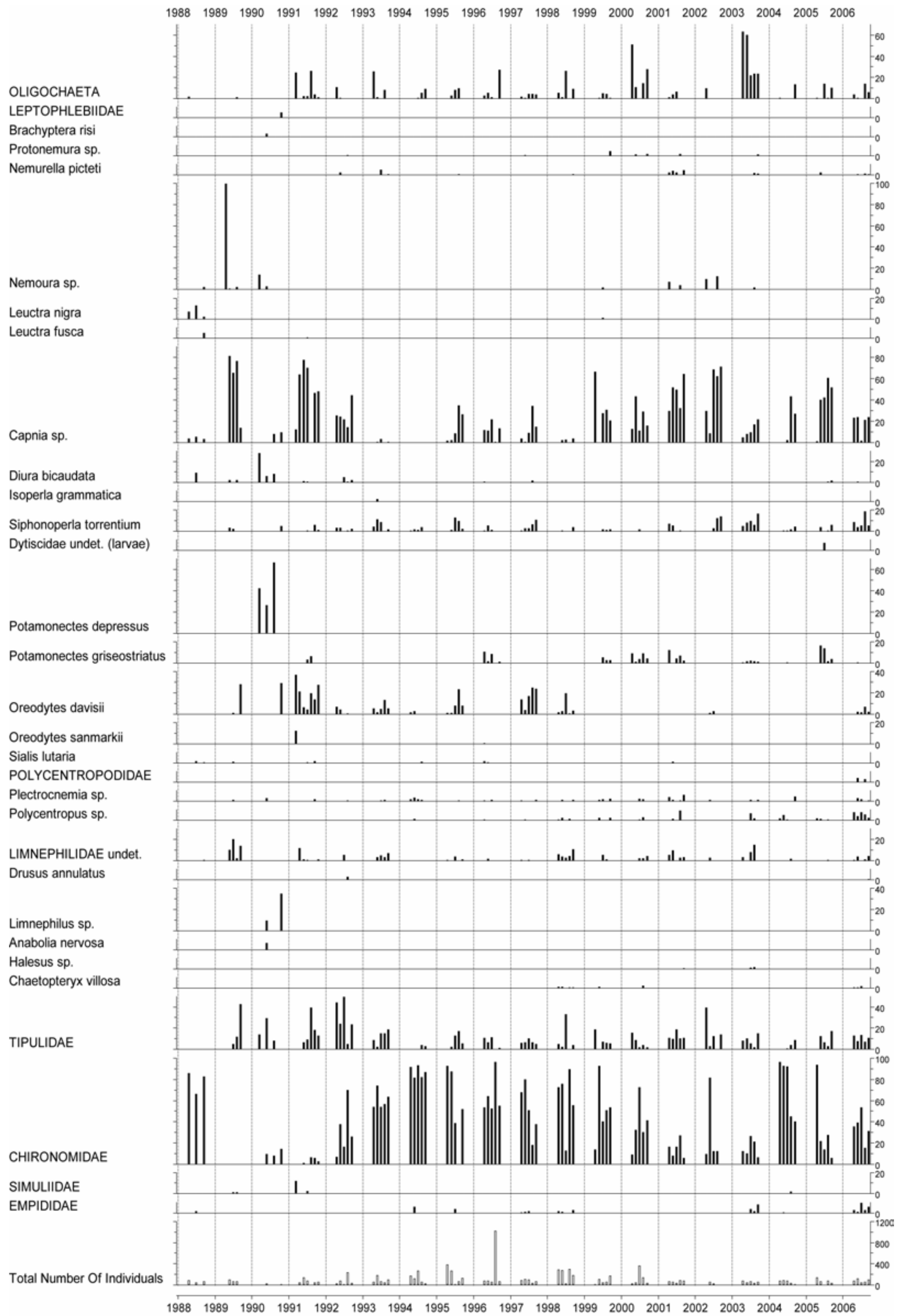
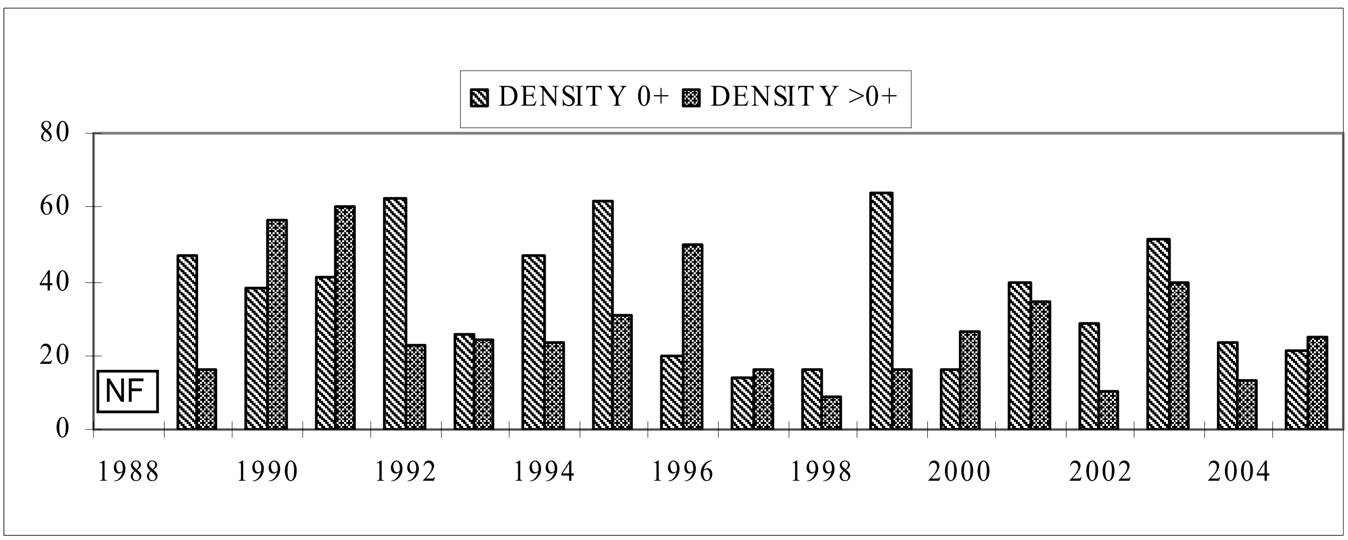


Table 4.4.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Lochnagar

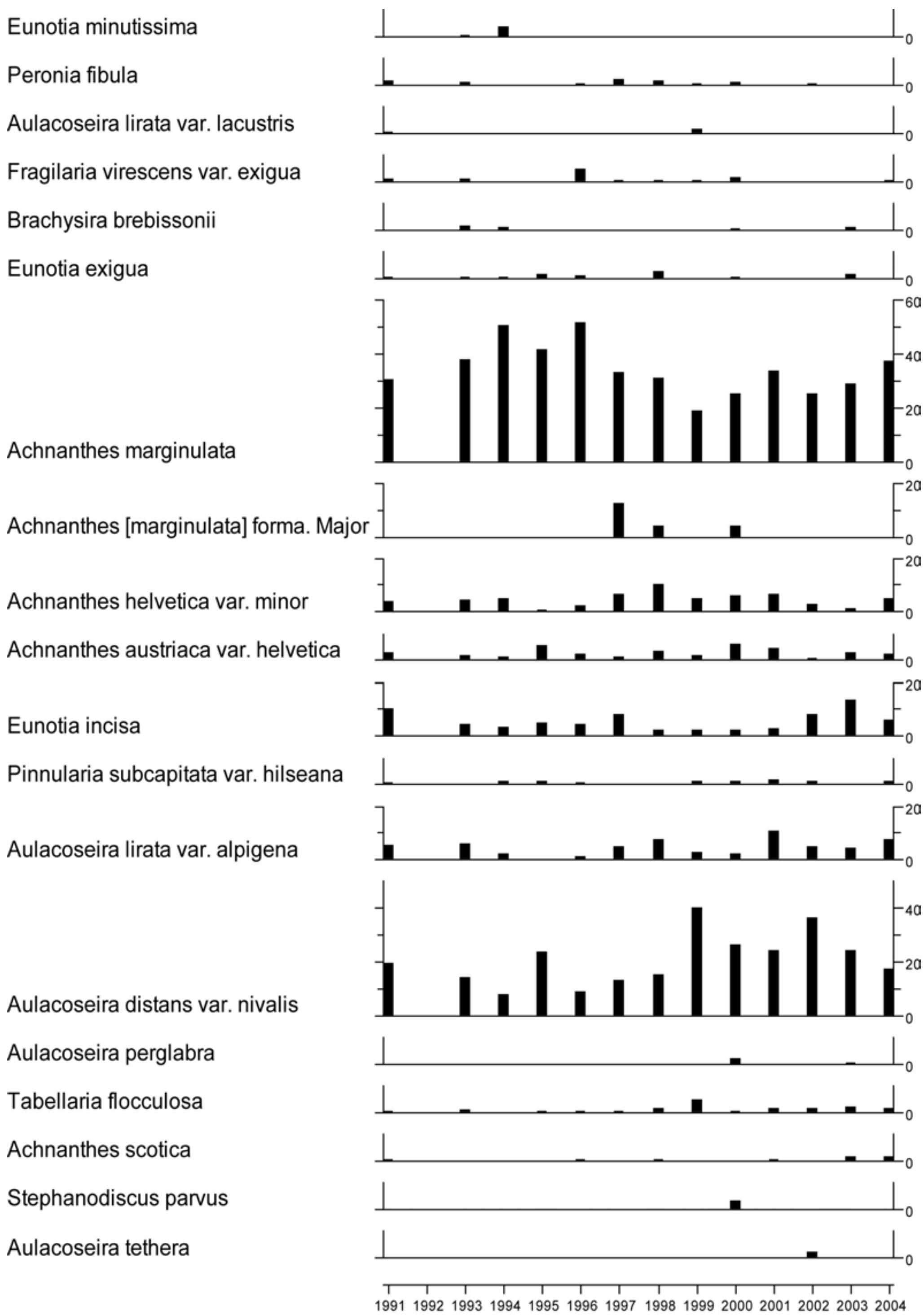
	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1766.81	158	57.1	42.9	0.04	2.37	0.004	0.023
Invertebrates	3546.50	40	52.3	47.6	0.05	0.13	0.001	0.349

Figure 4.4.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Lochnagar



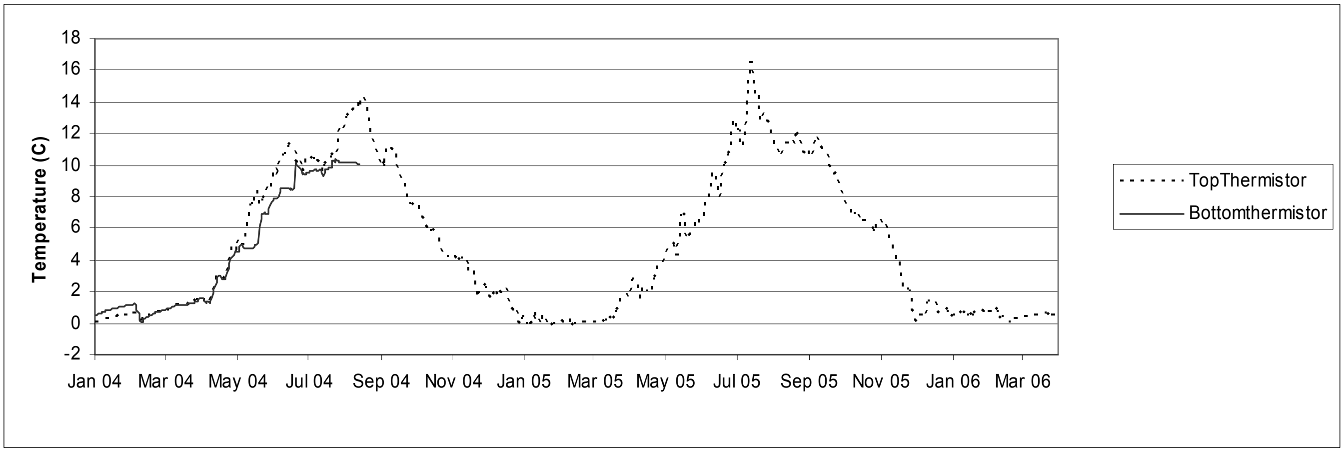
NF = Not fished

Figure 4.4.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Lochnagar



Sediment traps not recovered in 2005

Figure 4.4.7 Thermistor Data: Lochnagar



4.5 Loch Chon

4.5.1 Water Chemistry Summary

Loch Chon is a relatively large, low altitude, acidified lake close to Aberfoyle in the Scottish Trossachs. Approximately half of the catchment is used for commercial forestry, and in the last five years there has been some felling and re-planting. Water temperature records show that Loch Chon is unique among AWMN lakes in being monomictic (i.e. it is permanently stratified from late spring to early autumn) and the lack of mixing over the summer could reduce the residence time for deposited contaminants over this time of year. At the onset of monitoring, mean pH was less than 5.5 and labile aluminium concentrations regularly exceeded 25 $\mu g\ l^{-1}$, a level at which toxicological effects on fish become more likely (Rosseland et al., 1990).

Over the course of monitoring the reduction in xSO_4 concentration has been relatively modest (i.e. circa 25%) but estimates are complicated by large oscillations in seasalt inputs which has led to large short term variability. The clearest decline in xSO_4 occurred between 1996 and 1999 since when there has been no clear trend. At 35.5 $\mu eq\ l^{-1}$ the 2003-2006 mean concentration is one third higher than the xSO_4 concentration of the neighbouring but non-forested Loch Tinker (Site 6), and approximately seven times that of Loch Coire nan Arr (Site 1) in northwest Scotland.

Unusually, NO_3 concentrations have increased significantly, almost doubling between 1988-1993 and 2003-2006. Currently, equivalent NO_3 concentrations are approximately half those of xSO_4, but the relative influence of the NO_3 as an acidifying agent is increasing as the latter continues to decline. The temporal pattern in NO_3 is similar to that for the Round Loch of Glenhead (Site 7), and this tends to rule out forest management as a possible driver.

In contrast to sites further to the southwest, chloride concentrations show frequent peaks associated with seasalt deposition events, and less indication of a long term trend.

Dissolved organic carbon concentrations have almost doubled, and preliminary time series analysis suggests the change can be explained mostly by reductions in SO_4 and consistently low levels of chloride since 2001 (see Section 5.4.5).

Ion balance ANC has increased progressively, from a mean of 8.7 to 42.6 $\mu eq\ l^{-1}$ (1988-1993 to 2003-2006). This large increase, relative to the decline in the combined concentrations of xSO_4 and NO_3, is due largely to the very low inputs of seasalt over the 03-06 period.

pH has climbed progressively over most of the monitoring period from a mean of 5.5 to 6.0 (1988-1993 to 2003-2006). Labile aluminium levels have fallen substantially and are now frequently below the limit of detection. Alkalinity has also increased markedly, with the last negative value recorded in 1997. The 2003-2006 mean of 25.3 $\mu eq\ l^{-1}$ is 20 $\mu eq\ l^{-1}$ higher than the mean for 1988-1993.

4.5.2 Biology Summary

The epilithic diatom community of Loch Chon shows clear and statistically significant change over the monitoring period. The assemblage has shifted from one dominated by *Navicula leptostriata* (SWAP pH optima = 5.1), to one dominated by *Tabellaria flocculosa* and *Brachysira vitrea* (SWAP pH optima = 5.4 and 5.9 respectively). Prior to 1991 *B. vitrea* never reached abundances of more than 5%, but in 2006 this species comprised over half of the assemblage in two of the three samples. Importantly, with respect to recovery trends, Loch Chon has also seen a progressive increase in the classic acid-sensitive species *Achnanthes minutissima* which, while occurring at trace levels throughout, has comprised more than 10% of the assemblage of individual samples in 2004 and 2006. The abundance of *Eunotia incisa* (SWAP pH optima = 5.1) has declined progressively throughout the period. These taxonomic shifts are also reflected in the sediment trap material, in which the acidobiontic (and acidification indicator) *Tabellaria quadriseptata* (SWAP pH optima = 4.9) has not been detected since 1997.

Aquatic macrophyte composition has remained relatively constant, but the sensitive angiosperm *Subularia aquatica*, not detected before 1995, has since been recorded in several locations in all years. Likewise, the charophyte *Chara virgata* was found for the first time in 1999 and recorded in the same location every year of monitoring since.

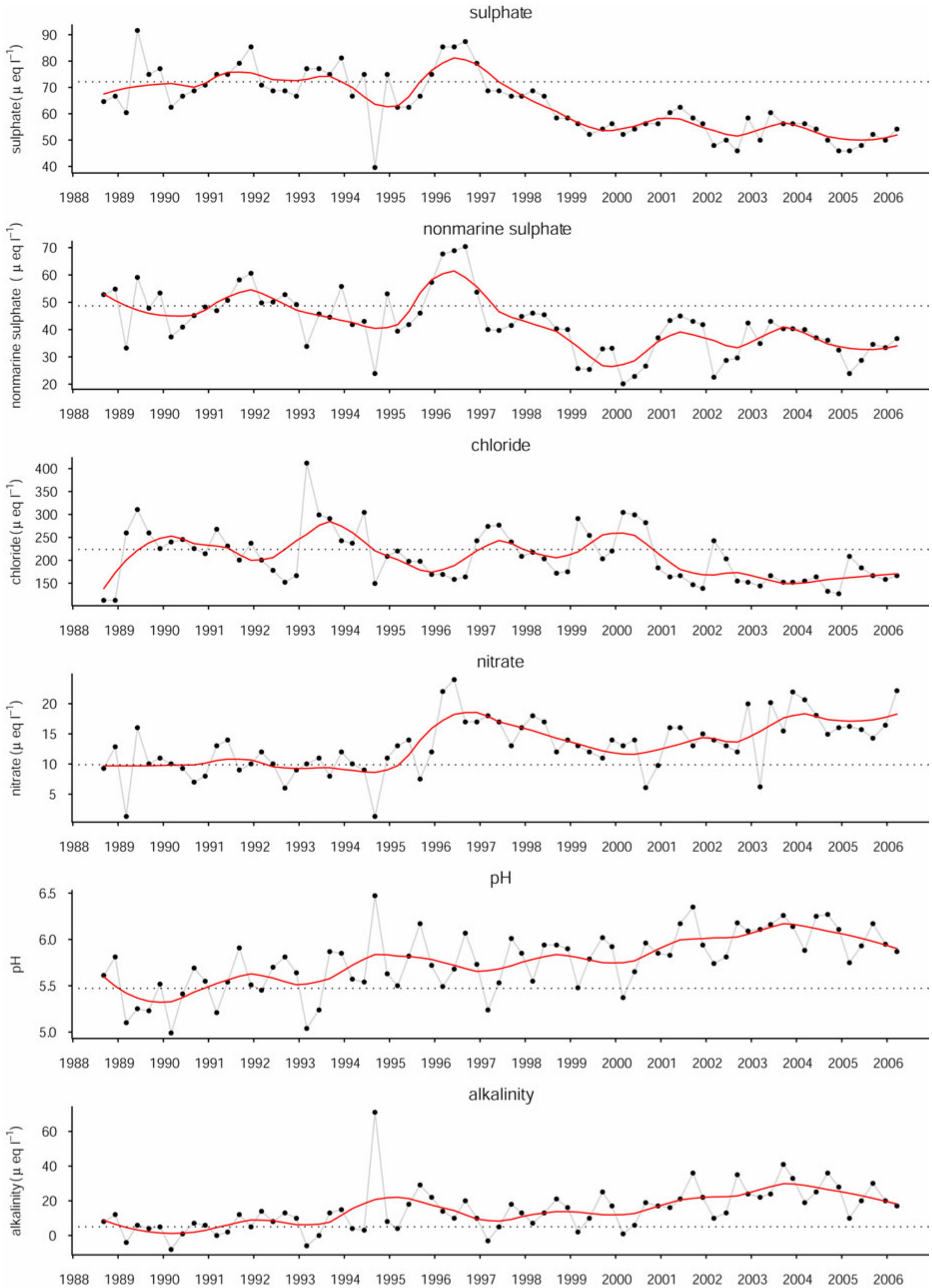
The diverse macroinvertebrate assemblage shows a significant linear trend over the monitoring period. There has been a decline in the relative abundance of the acid tolerant omnivorous corixid *Hespercorixa sahlbergi* and the predatory corixid *Callicorixa praeusta* and an increase in acid-sensitive predatory caddis species *Cyrnus* sp., the gatherer/collector/grazer elmid beetle *Ouliminius tuberculatus*, and the acid-sensitive gather/collector Mayfly *Caenis luctuosa*.

Brown trout have occurred at relatively high densities (compared to most other sites on network) in the Loch Chon outflow burn throughout the monitoring period. There is no clear indication of a long term trend in either 0+ or >0+ age groups.

4.5.3 Conclusions

Loch Chon has undergone a relatively small decline in xSO_4 which has been partly offset by an increase in NO_3. However, the net effect of these changes and relatively low seasalt inputs since 2001 have resulted in a substantial increase in pH and alkalinity and a marked reduction in labile aluminium concentration. Diatoms, aquatic macrophytes and macroinvertebrates all show changes that are consistent with recovery responses to declining acidity. There is no indication of an improvement in the brown trout population in the loch outflow. The recent rise in NO_3 concentration gives cause for concern and requires further investigation, although SO_4 remains the dominant anthropogenic acid anion. Concentrations of xSO_4 remain seven times higher than those for the cleanest site in the Network (Loch Coire nan Arr).

Figure 4.5.1 Water Chemistry Summary Plots: Loch Chon



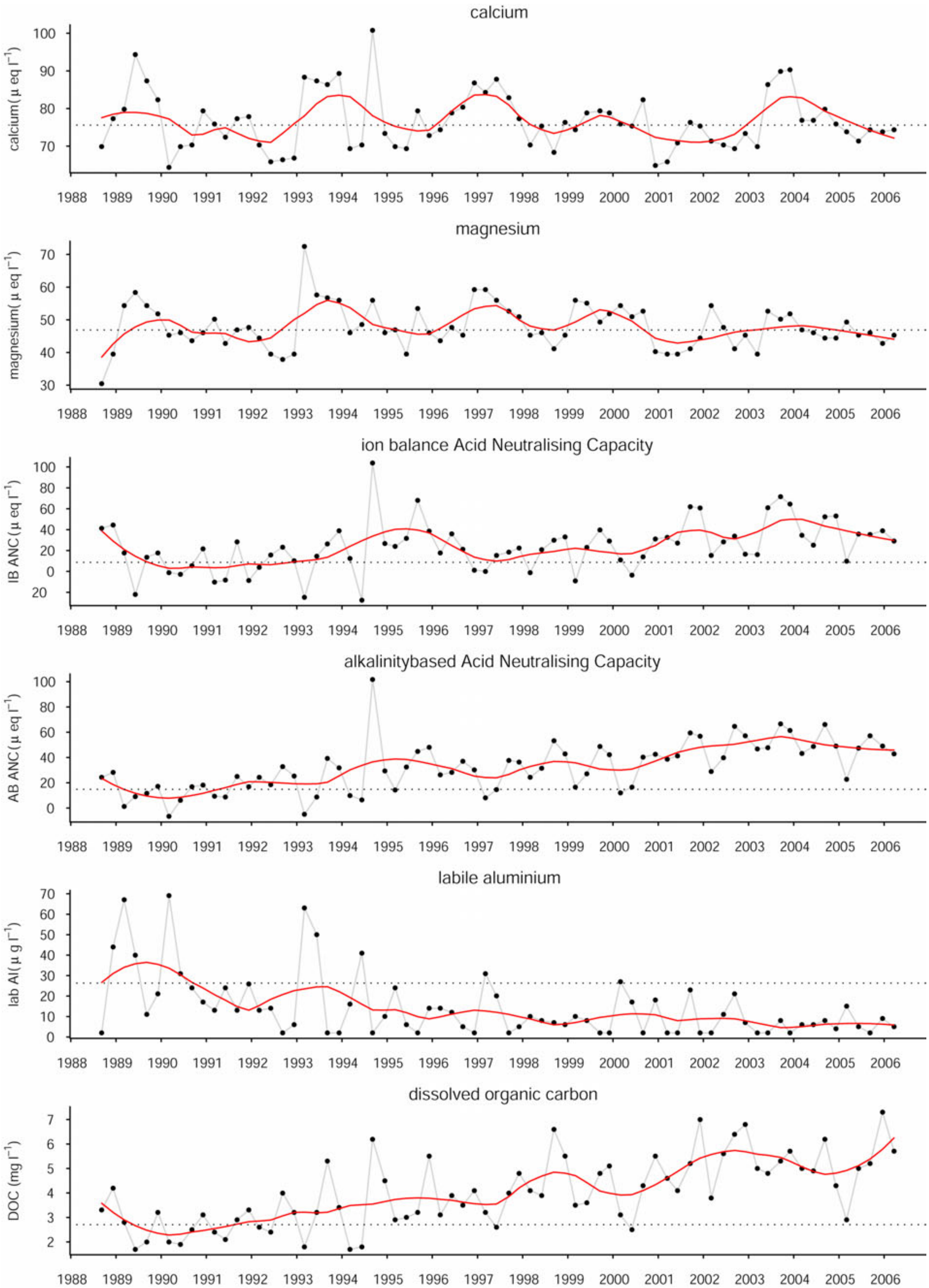

calcium
calcium (μ eq l⁻¹)
magnesium
magnesium (μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al (μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.5.1 Water Chemistry Summary Data and Trend Statistics: Loch Chon

Determinand / period		xSO$_4^{2-}$ µeq l^{-1}	NO$_3^-$ µeq l^{-1}	Cl$^-$ µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na$^+$ µeq l^{-1}	K$^+$ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Sep 1988 - Mar 1993	mean	48.8	9.9	223.7	5.47	5.3	8.7	14.8	38.4	75.6	46.9	186.4	5.6	65.5	26.3	2.7
	st. dev	7.8	3.2	68.6	0.27	6.4	19.2	10.9	8.0	8.3	9.1	41.6	2.7	23.7	21.1	0.7
	min	33.4	1.3	112.8	4.99	-8.0	-24.8	-6.7	23.0	64.4	30.4	117.5	2.6	33.0	2.0	1.7
	max	60.7	16.0	411.9	5.91	14.0	44.5	32.8	61.0	94.3	72.4	304.5	12.5	126.0	69.0	4.2
Apr 1993 - Mar 1998	mean	48.4	13.5	223.3	5.73	14.8	24.4	30.5	40.5	79.6	50.6	195.8	7.0	53.4	13.5	3.7
	st. dev	11.4	5.3	48.3	0.30	15.6	26.8	21.0	5.5	8.6	5.9	29.9	2.1	20.2	13.7	1.2
	min	24.0	1.3	149.5	5.24	-3.0	-27.4	6.5	31.0	69.4	39.5	130.5	2.6	14.0	2.0	1.7
	max	70.4	24.0	304.7	6.47	71.0	103.8	101.8	50.0	100.8	59.2	248.0	12.0	88.0	50.0	6.2
Apr 1998 - Mar 2003	mean	34.2	13.1	204.9	5.90	17.3	25.5	40.4	36.5	73.6	46.8	172.3	6.4	48.5	9.0	4.8
	st. dev	8.3	3.3	55.5	0.23	9.2	17.3	14.7	4.8	4.7	5.9	36.2	0.7	17.1	8.0	1.3
	min	20.4	6.1	138.2	5.37	1.0	-9.2	12.0	28.0	64.9	39.5	100.1	5.1	18.0	2.0	2.5
	max	45.5	20.0	304.7	6.35	36.0	61.9	64.7	47.0	82.3	55.9	243.6	7.7	84.0	27.0	7.0
Apr 2003 - Mar 2006	mean	35.5	17.7	161.0	6.03	25.3	42.6	50.2	33.8	78.6	47.1	139.6	8.4	48.9	6.0	5.2
	st. dev	5.4	2.8	21.4	0.40	8.8	18.1	11.9	2.1	6.5	3.2	14.2	0.7	11.5	3.7	1.1
	min	23.9	14.3	126.9	5.75	10.0	9.8	22.8	29.0	71.4	42.8	113.1	7.7	30.0	2.0	2.9
	max	43.0	22.1	208.8	6.27	41.0	71.5	66.6	37.0	90.3	52.6	161.0	9.5	69.0	15.0	7.3
Seasonal-Kendall statistics	Sen-slope	-1.078	0.482	-4.055	0.035	1.042	1.354	2.111		-0.100	-0.103				-1.175	0.179
	P- val	**0.003**	**0.006**	**0.049**	**<0.001**	**<0.001**	**0.008**	**<0.001**		0.814	0.419				**0.001**	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.5.2 Epilithic Diatom Percentage Abundance Summary: Loch Chon

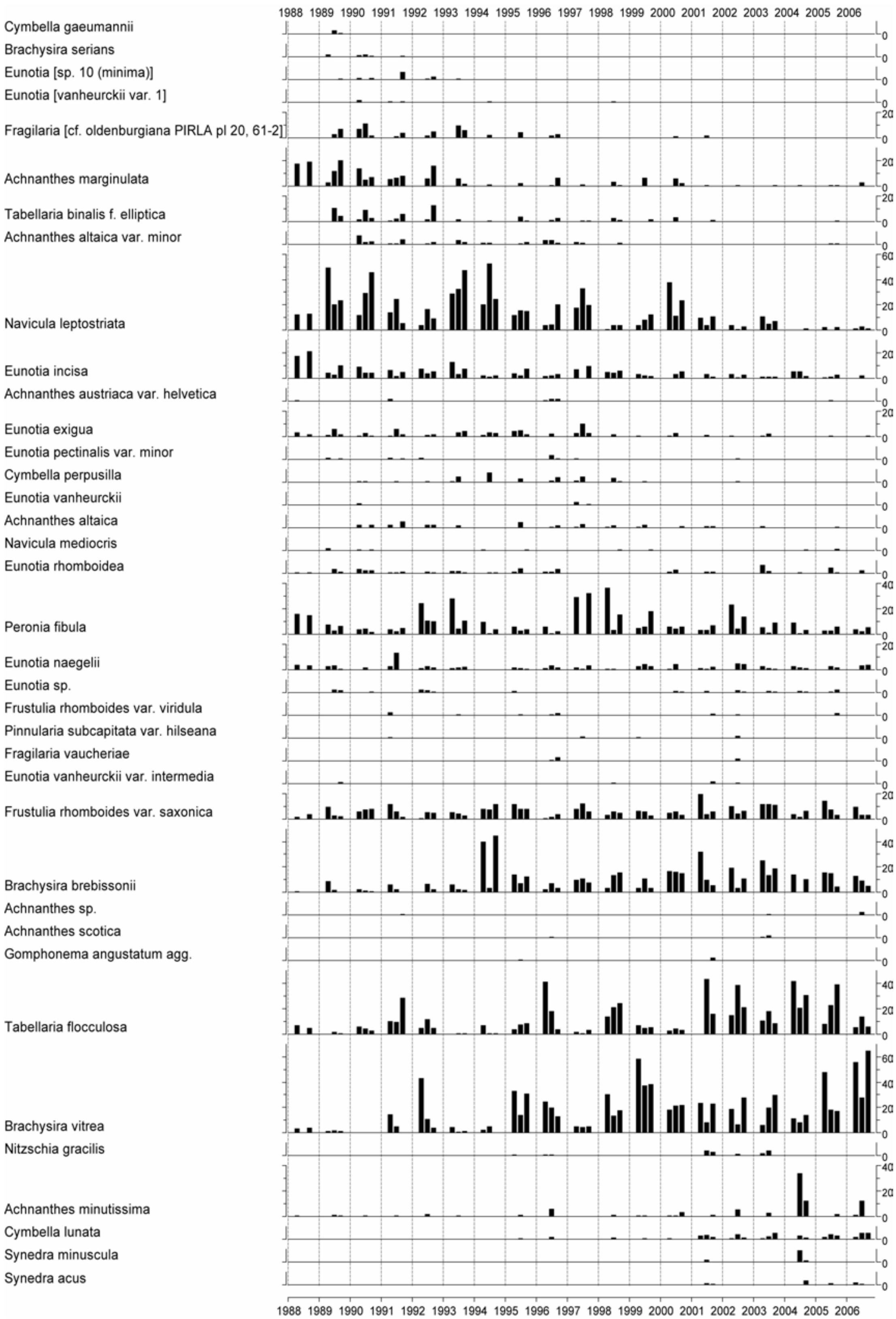


Figure 4.5.3 Aquatic Macrophyte Species Scores (1-5): Loch Chon

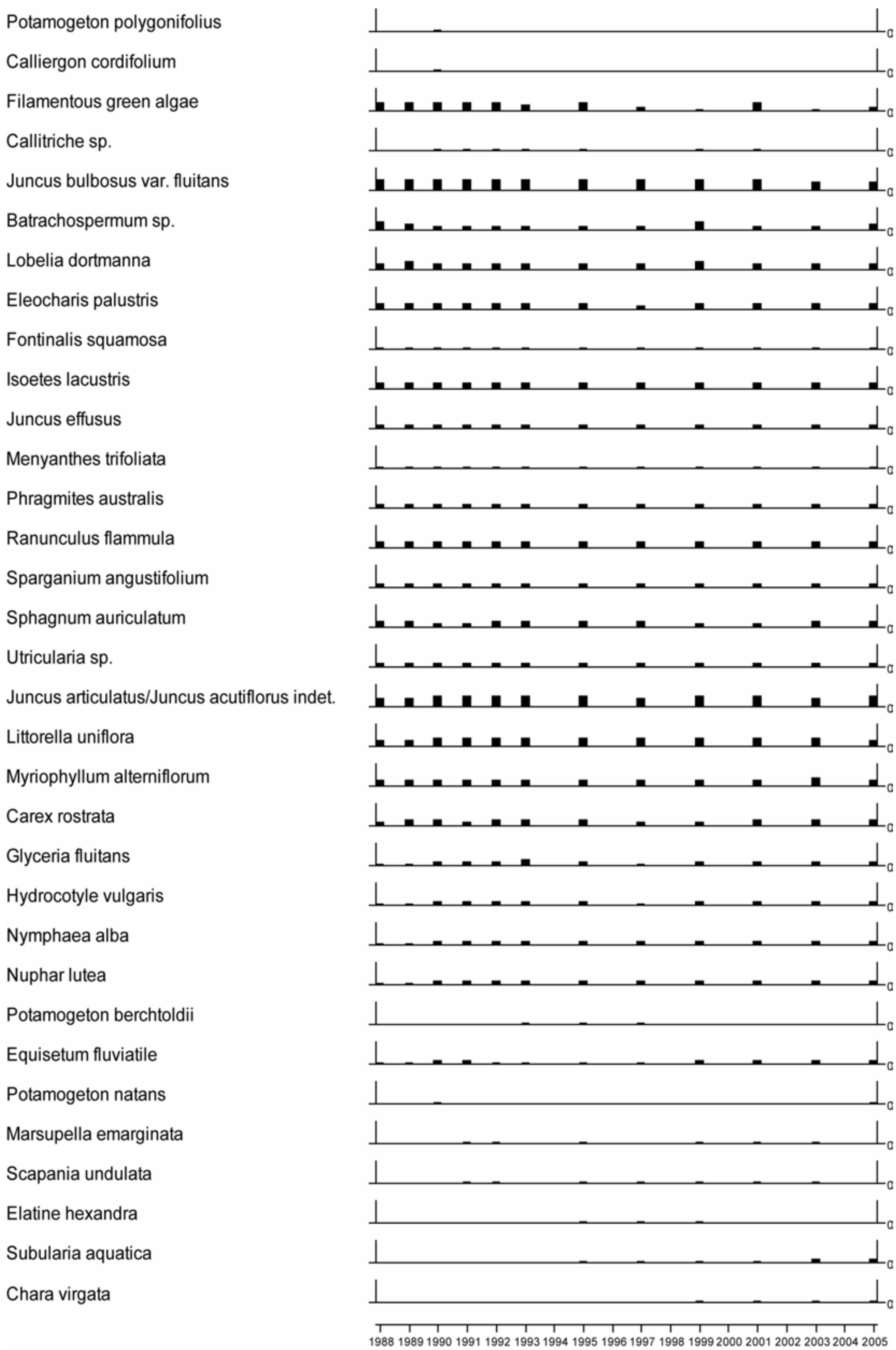


Figure 4.5.4 Macroinvertebrate Percentage Abundance Summary: Loch Chon

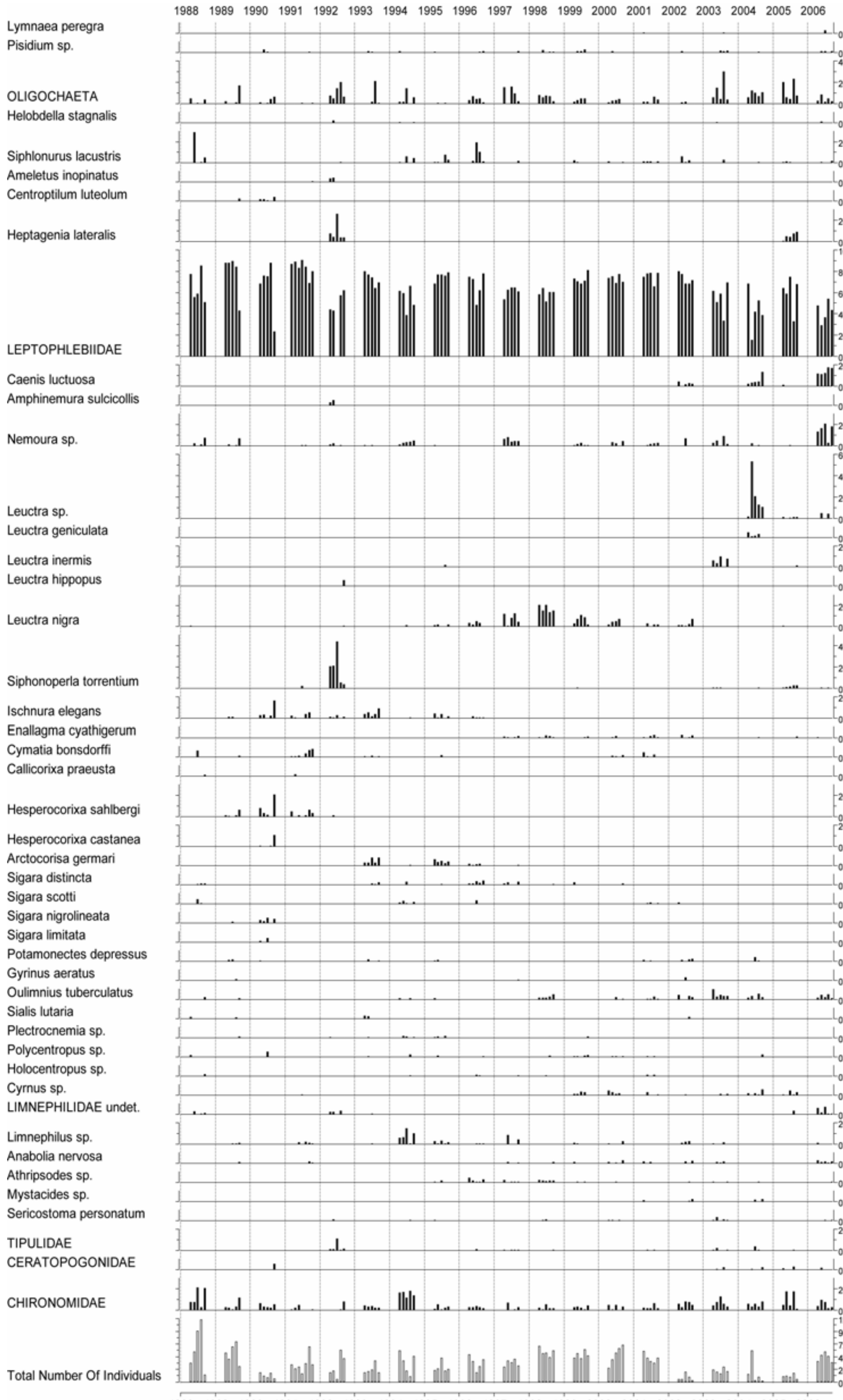
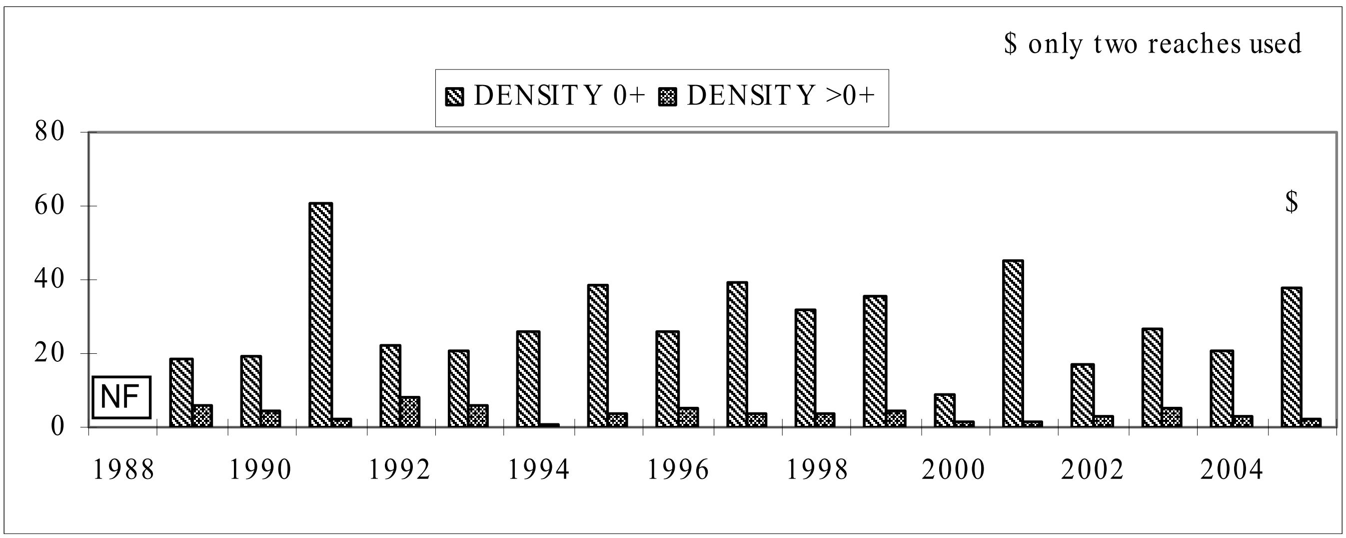


Table 4.5.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Loch Chon

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1623.46	121	39.6	60.4	0.23	1.54	0.001	0.015
Invertebrates	2117.13	90	37.7	62.3	0.09	0.49	0.001	0.001

Figure 4.5.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Loch Chon



NF = Not fished

Figure 4.5.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Loch Chon

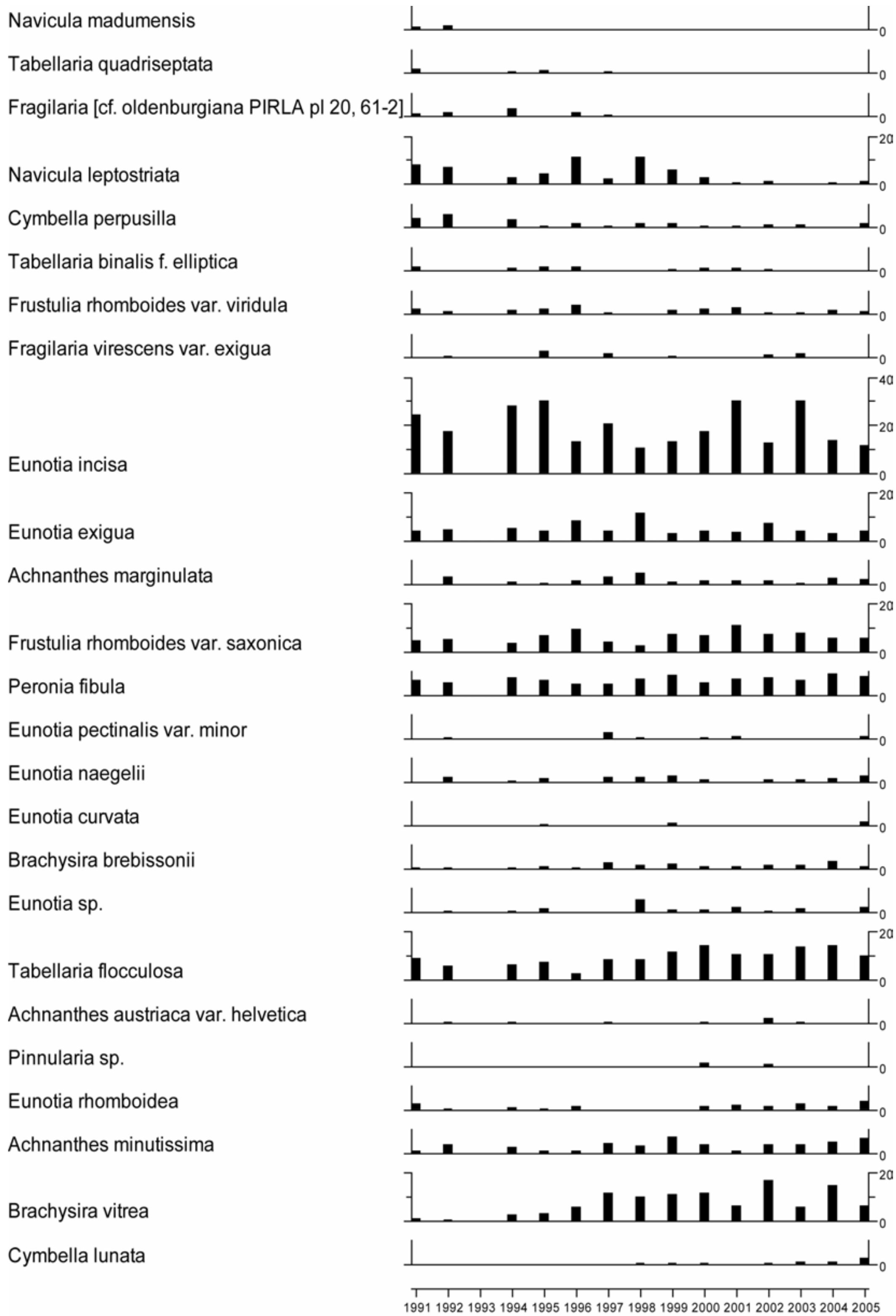
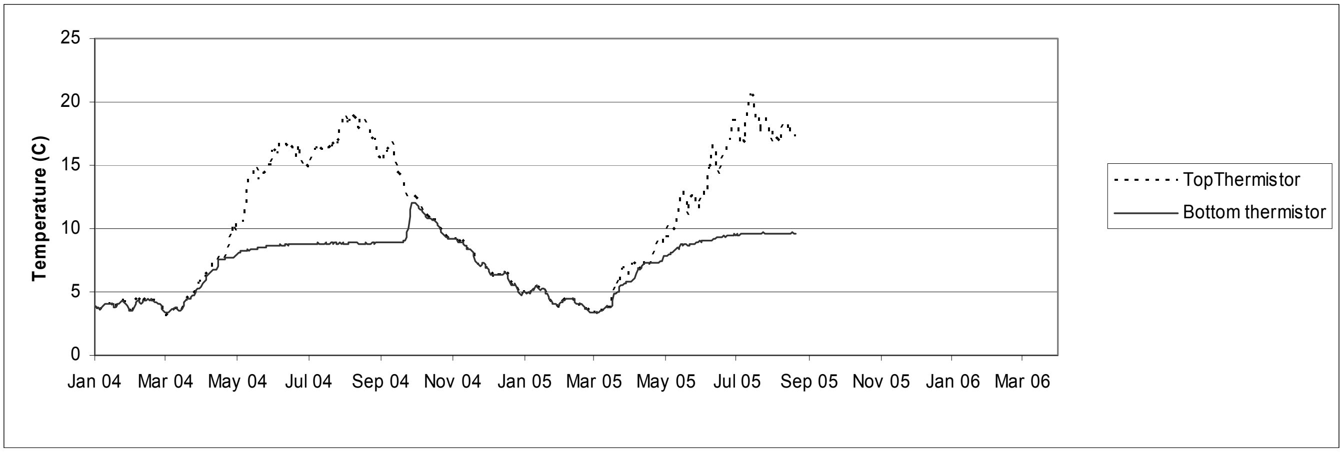


Figure 4.5.7 Thermistor Data: Loch Chon



Thermistors not recovered in 2006

4.6 Loch Tinker

4.6.1 Water Chemistry Summary

Loch Tinker is a moorland site situated 4 km to the east of Loch Chon (Site 5) and at 320 m higher elevation. Palaeoecological analysis of sediment cores from Loch Tinker provides ambiguous evidence with respect to the extent to which this site has acidified; however base cation concentrations are higher than Loch Chon despite acid anion levels being lower, indicating this site is less sensitive to acid deposition.

At the onset of monitoring (i.e. 1988-1993) mean pH was 6.10 and mean alkalinity 35 $\mu eq\ l^{-1}$. Labile aluminium rarely rose above the limit of detection.

Over the course of monitoring xSO_4 concentration has fallen by circa 25% with most of the reduction occurring since 1996. However, the mean concentration between 2003-2006 remained at 26.6 $\mu eq\ l^{-1}$, approximately four times that for Loch Coire nan Arr in northwest Scotland.

In common with Loch Chon and the Round Loch of Glenhead (Site 7) there is some indication for a slight increase in NO_3 concentration since 1996 although there is no significant trend and NO_3 remains only one tenth the concentration of xSO_4 in terms of equivalence. Like the Round Loch of Glenhead, there is also evidence for a change in the seasonality of NO_3 leaching, with a change from almost year round retention (i.e. undetectably low concentrations) to frequently detectable (albeit low) levels.

Also in common with Loch Chon, chloride concentrations vary substantially but do not show the overall downward trend that characterises AWMN sites further to the south.

Dissolved organic carbon concentrations have increased by around 50%, and preliminary time series analysis suggests the most of the change can be explained by reductions in SO_4 and consistently low chloride concentrations since 2001.

Ion balance ANC has increased slightly, i.e. at a similar rate to which xSO_4 has declined. Base cation concentrations show a small reduction (e.g. magnesium concentrations have fallen by about 5 $\mu eq\ l^{-1}$). pH and alkalinity show strong inter-seasonal variability over a gradual long-term increase suggesting that the site was slightly acidified at the onset of monitoring.

4.6.2 Biology Summary

The epilithic diatom community shows statistically significant linear change over the monitoring period although the variance explained by time is small, suggesting a relatively modest shift in species composition. The most important changes have been gradual increases in the classic acid-sensitive species *Achnanthes minutissima* (SWAP pH optima = 6.3) and *Cymbella microcephala* (SWAP pH optima = 6.3) and a decline in the relative abundance of *Fragilaria vaucheriae* (SWAP pH optima = 6.3) from low to undetectable levels. The increase in *A. minutissima* is also evident in the sediment trap data, that also shows an increase in *Brachysira. vitrea* (SWAP pH optima = 5.9) and a concomitant decline in *Fragilaria virescens* var. *exigua* (SWAP pH optima = 5.7).

Aquatic macrophyte composition has remained similar throughout. However the acid-sensitive species *Subularia aquatica* was not detected until 1995 since when it has been found in most years and in increasing abundance. Similarly the acid-sensitive charophyte *Nitella flexilis* var. *flexilis*, although found in the first year of monitoring, was not detected for several years but has become constant since 1999, while *Chara virgata* was found for the first time in 2005.

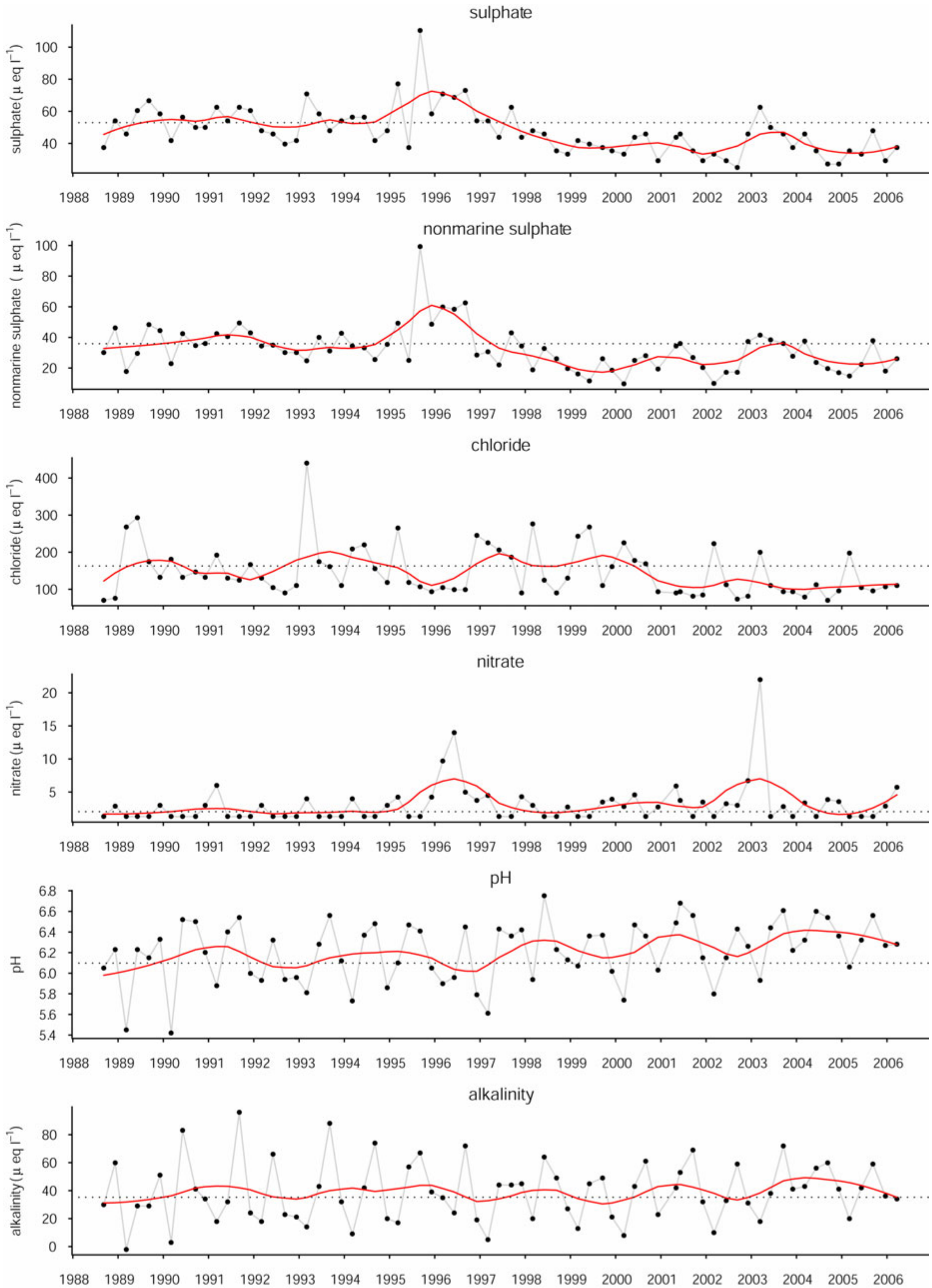
The macroinvertebrate assemblage shows no significant linear trend and remains dominated by Chironomidae. However, the herbivorous/detritivorous caddis *Mystacides* sp. was recorded for the first time in 1995 and has been collected in almost every kick sample since. This species shows one of the strongest trends in the dramatically improving Llyn Llagi (Site 15) so its appearance and subsequent persistence is consistent with a recovery response. Another caddis species absent prior to 1994 but now common is *Oxyethira* sp., which shows varied feeding behaviour.

Brown trout have occurred at very low densities in the loch outflow burn throughout most of the monitoring period. However, the density of new recruits has increased slightly since 2004. Prior to this there was some indication of disease in the population and it is not possible to determine the likelihood that chemical improvement has had any impact.

4.6.3 Conclusions

Loch Tinker is a relatively well buffered lake which nevertheless shows a small improvement in pH and alkalinity in response to a small decline in xSO_4. Diatoms, aquatic macrophyte and macroinvertebrate communities all exhibit changes consistent with a response to a small reduction in acidity. The apparent shift from almost year-round catchment retention of nitrate to frequent seasonal leaching (albeit in low concentrations) gives cause for concern and requires further investigation. Concentrations of xSO_4 remain approximately five times higher than those for the cleanest site in the Network (Loch Coire nan Arr).

Figure 4.6.1 Water Chemistry Summary Plots: Loch Tinker



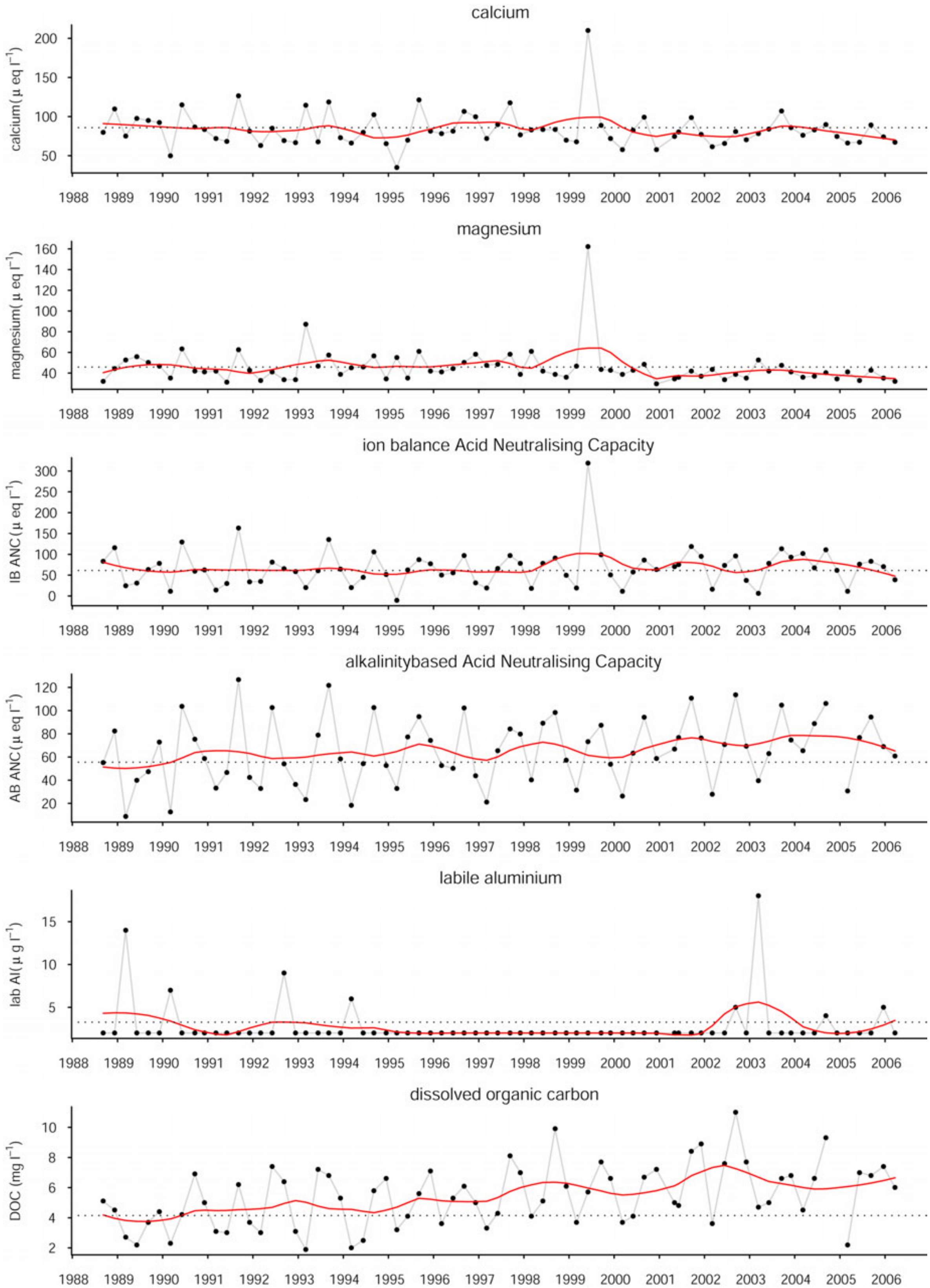

calcium
calcium(μ eq l⁻¹)
magnesium
magnesium(μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC(μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC(μ eq l⁻¹)
labile aluminium
lab Al(μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.6.1 Water Chemistry Summary Data and trend Statistics, Loch Tinker

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		µeq l^{-1}	µeq l^{-1}	µeq l^{-1}		µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µS cm^{-1}	µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µg l^{-1}	µg l^{-1}	mg l^{-1}
Sep 1988 - Mar 1993	mean	36.0	2.0	162.9	6.10	35.3	61.1	55.5	31.0	85.8	45.8	140.1	7.2	19.5	3.3	4.1
	st. dev	8.9	1.3	88.3	0.32	25.7	41.1	31.7	9.6	20.1	14.0	56.1	4.5	10.4	3.2	1.6
	min	17.9	1.3	70.5	5.42	-2.0	11.2	8.6	21.0	49.9	31.3	78.3	2.6	5.0	2.0	1.9
	max	49.6	6.0	440.1	6.54	96.0	163.1	126.8	62.0	126.7	87.2	321.9	18.2	42.0	14.0	7.4
Apr 1993 - Mar 1998	mean	41.2	3.6	163.2	6.16	39.8	60.7	65.3	31.7	84.3	48.4	145.3	7.7	21.0	2.2	5.2
	st. dev	18.5	3.2	62.3	0.29	22.8	34.9	27.9	5.5	21.5	8.6	39.0	3.5	9.3	0.9	1.7
	min	19.1	1.3	90.3	5.61	5.0	-10.3	18.3	23.0	34.9	34.5	95.7	2.6	7.0	2.0	2.0
	max	99.2	14.0	276.5	6.56	88.0	135.2	121.8	42.0	121.3	60.9	243.6	14.6	45.0	6.0	8.1
Apr 1998 - Mar 2003	mean	23.8	3.9	141.6	6.25	37.5	75.7	69.2	27.2	83.0	46.3	124.4	6.1	22.7	3.0	6.4
	st. dev	9.2	4.6	62.0	0.28	18.7	65.5	25.6	4.4	32.1	27.8	44.3	1.2	13.4	3.6	2.1
	min	9.8	1.3	73.3	5.74	8.0	6.1	26.3	21.0	57.9	29.6	60.9	3.8	2.0	2.0	3.6
	max	41.6	22.0	268.0	6.75	69.0	318.9	113.4	35.0	210.1	162.1	248.0	7.9	70.0	18.0	11.0
Apr 2003 - Mar 2006	mean	26.6	2.5	105.8	6.35	45.2	75.5	75.8	25.8	80.4	38.6	96.8	5.7	15.4	2.4	6.2
	st. dev	8.8	1.4	31.6	6.74	14.1	29.5	22.0	3.1	12.0	4.6	15.4	1.4	5.9	1.0	1.8
	min	14.7	1.3	70.5	6.06	20.0	11.0	30.8	21.0	66.4	32.1	74.0	4.3	6.0	2.0	2.2
	max	38.5	5.7	197.5	6.61	72.0	113.3	106.1	33.0	107.3	47.7	130.5	8.9	25.0	5.0	9.3
Seasonal-Kendall statistics	Sen-slope	-0.794	0.112	-2.733	0.011	0.000	-0.098	0.602		-0.918	-0.585				0.000	0.148
	P- val	**0.015**	0.093	**0.037**	**0.009**	0.149	0.226	**0.019**		0.299	**0.038**				0.929	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.6.2 Epilithic Diatom Percentage Abundance Summary: Loch Tinker

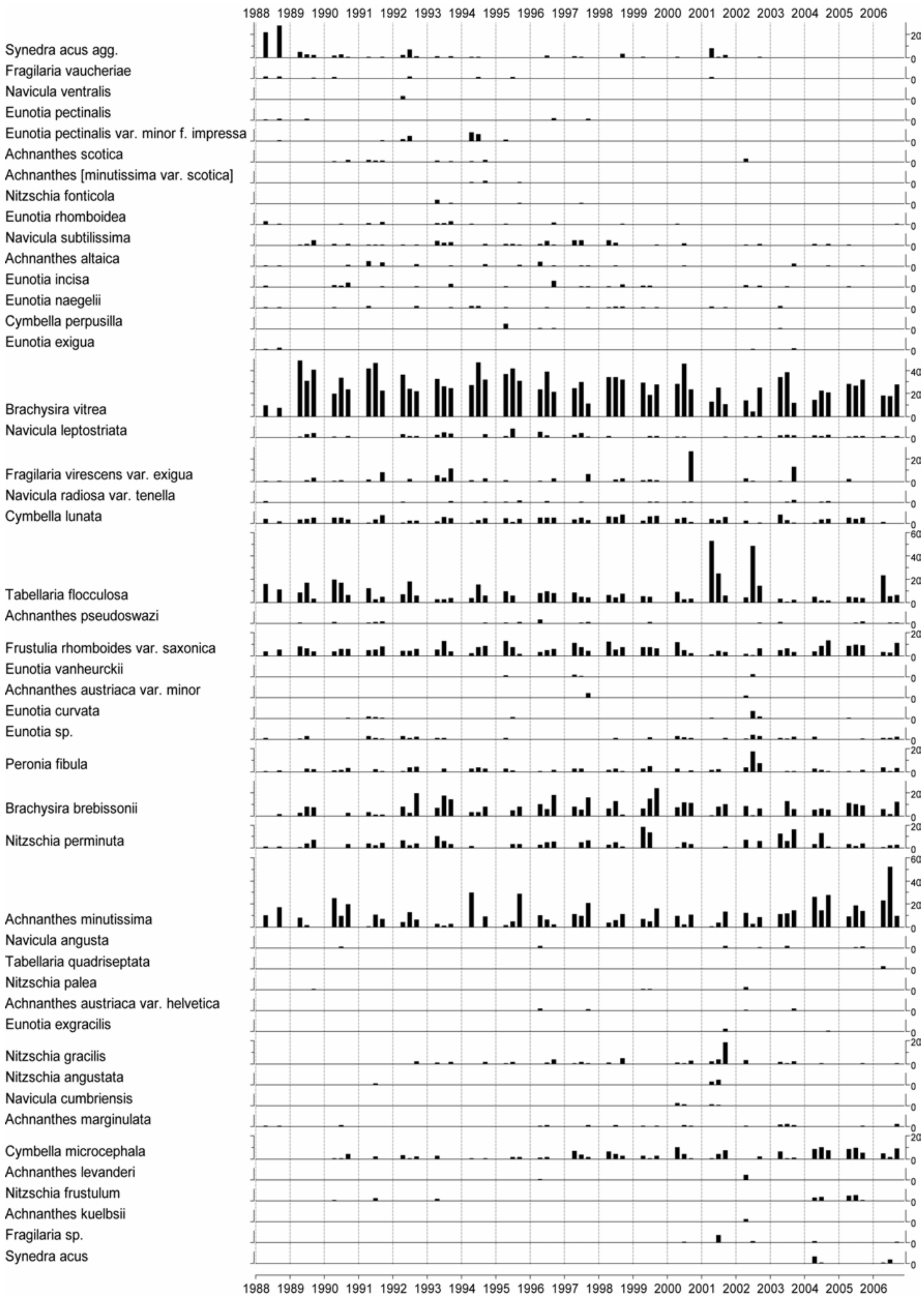


Figure 4.6.3 Aquatic Macrophyte Species Scores (1-5): Loch Tinker

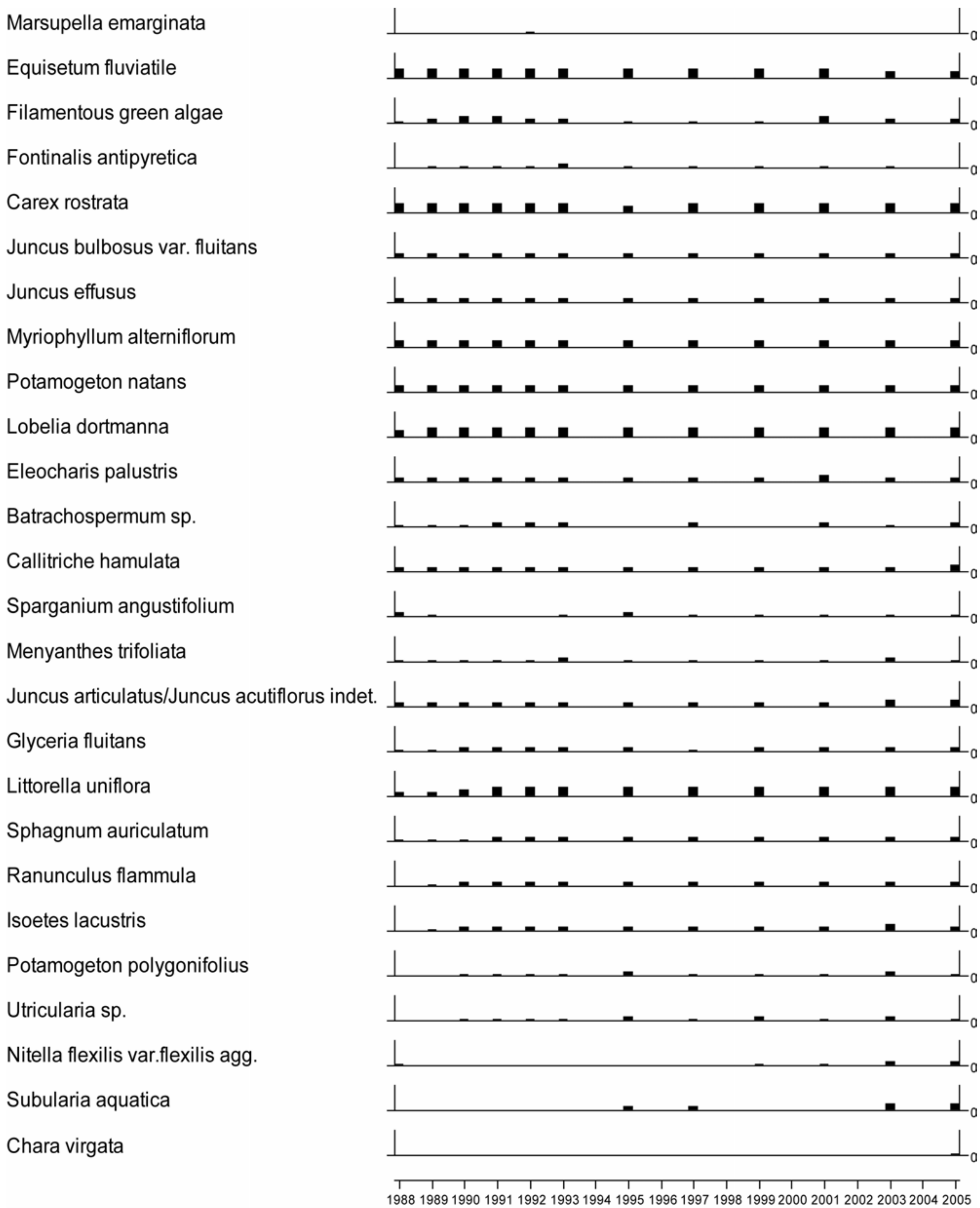
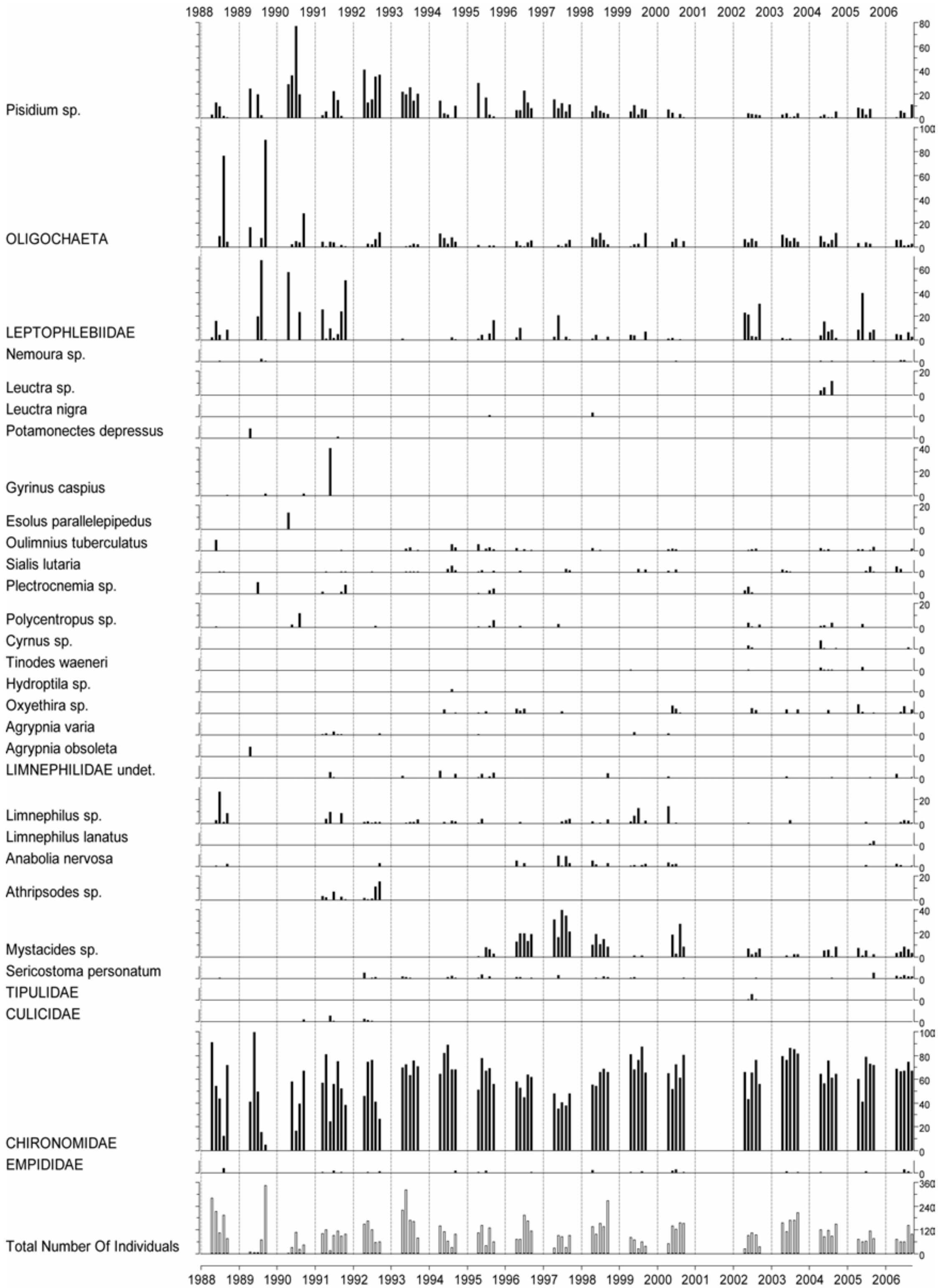


Figure 4.6.4 Macroinvertebrate Percentage Abundance Summary: Loch Tinker

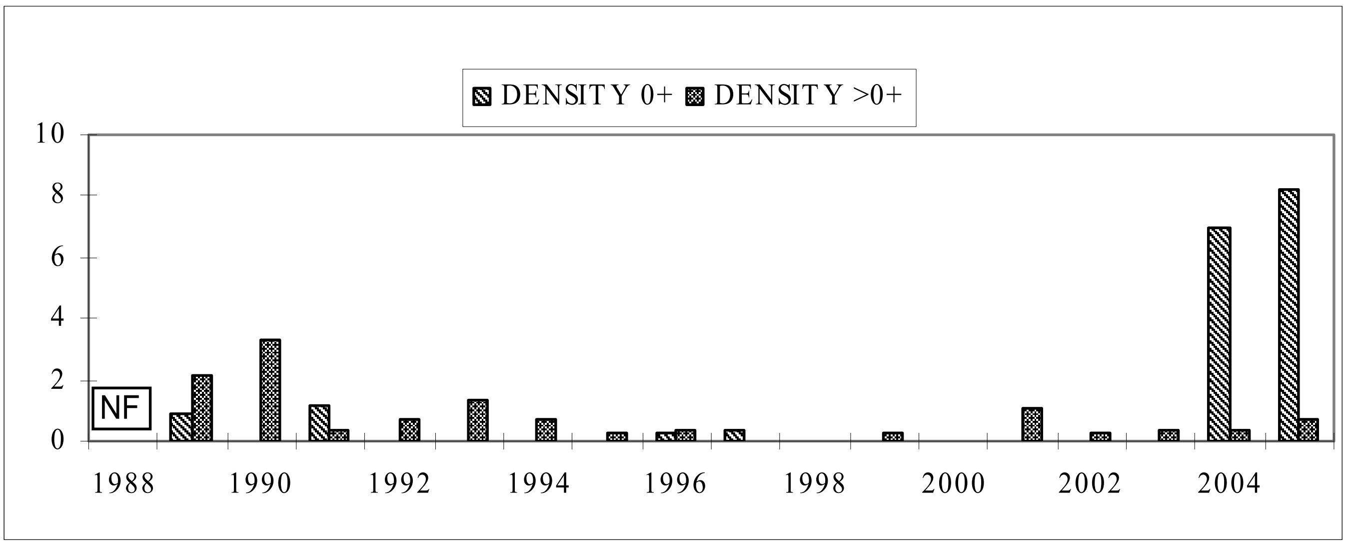


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.6.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Loch Tinker

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1250.36	154	49.1	50.9	0.09	0.55	0.001	0.022
Invertebrates	2024.49	49	63.6	36.4	0.07	0.34	0.001	0.135

Figure 4.6.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Loch Tinker



NF = Not fished

Figure 4.6.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Loch Tinker

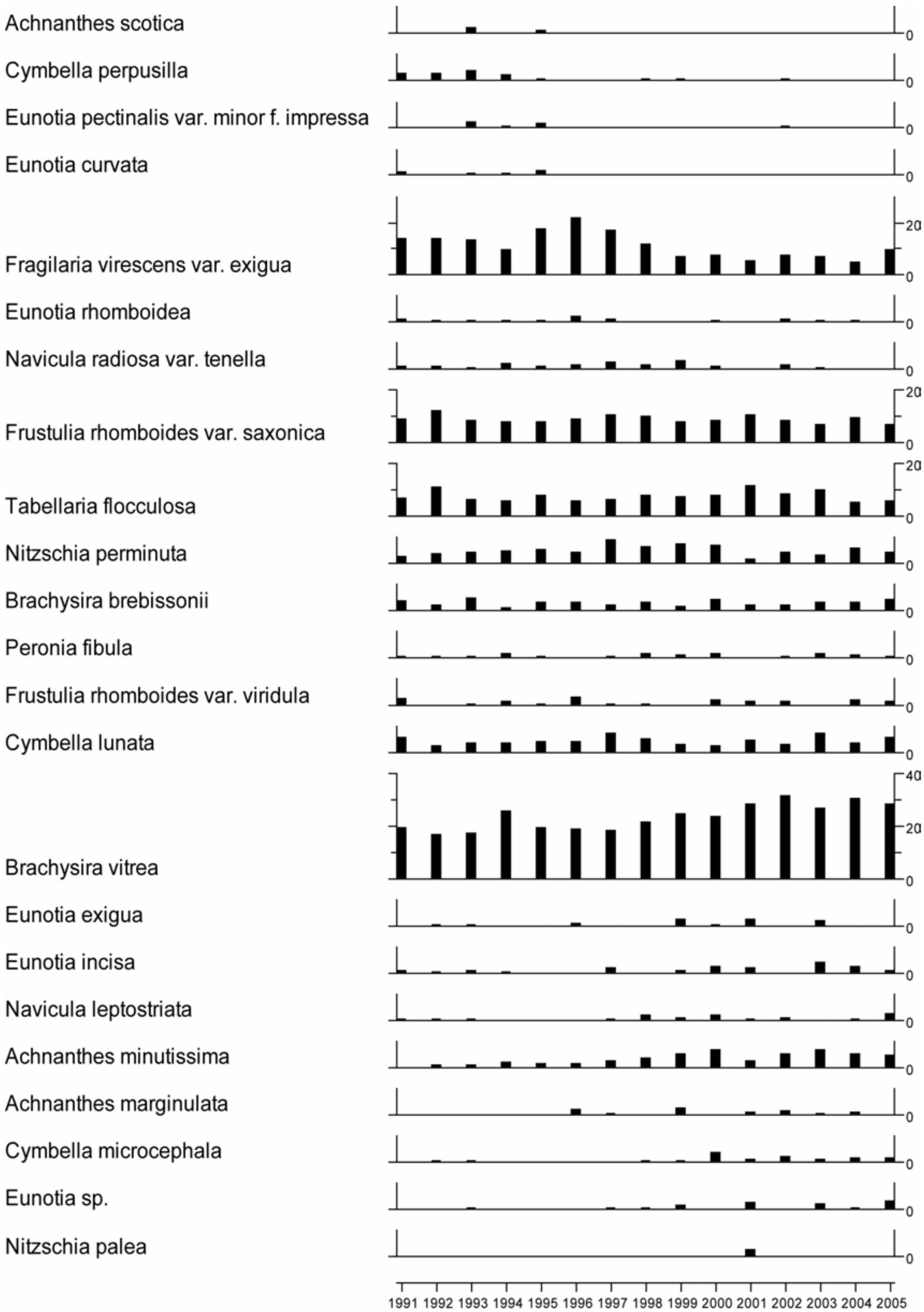
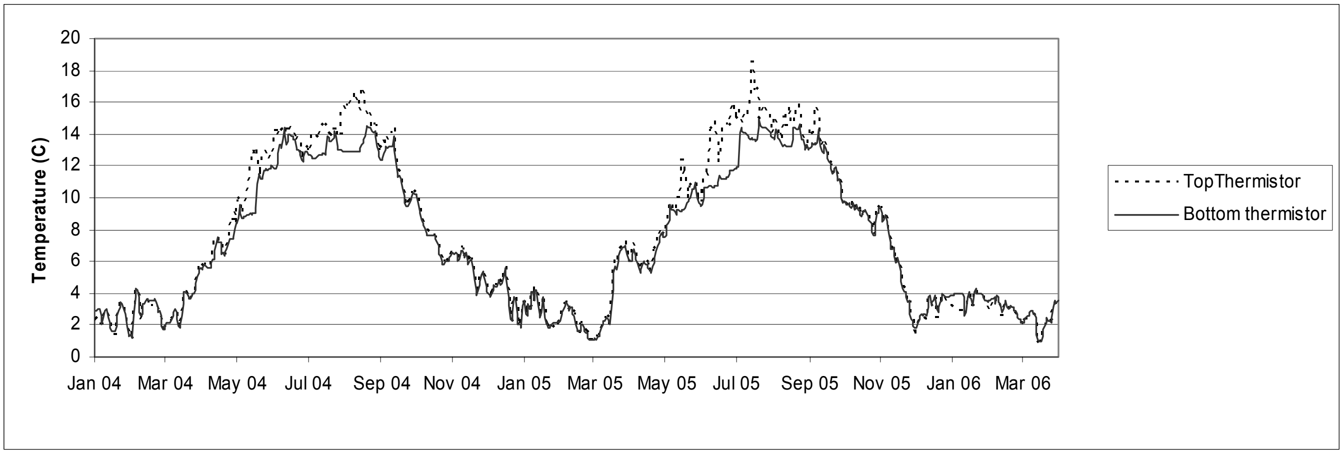


Figure 4.6.7 Thermistor Data: Loch Tinker



4.7 Round Loch of Glenhead

4.7.1 Water Chemistry Summary

The Round Loch of Glenhead is a naturally acidic and substantially acidified moorland loch situated on a granitic pluton in Galloway southwest Scotland. Over the first five years of monitoring mean pH was less than 5.0 and labile aluminium concentrations regularly exceeded 75 $\mu g\ l^{-1}$ - an upper threshold for likely toxicological effects on salmonids (Rosseland et al., 1990).

Over the course of monitoring xSO_4 concentration has fallen by circa 50% with most of the reduction occurring since 1996. However, concentrations still commonly exceed 25 $\mu eq\ l^{-1}$ and the 2003-2006 mean is approximately four times that for Loch Coire nan Arr (Site 1) in northwest Scotland.

Nitrate concentrations have increased slightly, although in terms of equivalence they remain at approximately one third of non-marine sulphate concentrations. In contrast to the first few years of monitoring, NO_3 concentrations have remained above the level of detection in all seasons since 1993. This is consistent with a progression in nitrogen saturation stage (cf. Stoddard 1994) although similar patterns at several other Scottish sites make it seem more likely that climate has the dominant influence on this trend (Davies *et al.* 2005). It is possible that the below-detection levels before 1993 were due to a series of unusually warm winters and consequent increased retention of N by soil biota.

The high concentrations of chloride between 1989-1992 (associated with a period of very high North Atlantic Oscillation Index; Evans et al. 2001) have not recurred although relatively high peaks were recorded in 1999, 2000 and 2002.

Dissolved organic carbon concentrations have almost doubled, and preliminary time series analysis suggests the change can be explained entirely by reductions in SO_4 and Cl concentration (i.e. reductions in anthropogenic sulphur and seasalt deposition) over the same period (see Section 5.4.5).

Ion balance ANC has increased gradually, and significantly is now approaching zero (2003-2006 mean = -0.7 $\mu eq\ l^{-1}$). The modest increase, relative to the change in xSO_4, results predominantly from the increase in DOC and NO_3 over the period, although there has also been a small reduction in base cation concentration of circa 15%.

pH has climbed steadily since xSO_4 began to fall and the 2003-2006 mean of pH 5.2 is 0.3 pH units higher than the mean for the first ten years. Perhaps of greater biological significance, labile aluminium levels have more than halved, and three samples since 2001 have been below the limit of detection. Alkalinity also shows marked improvement and slight positive values (indicating trace levels of bicarbonate) have been recorded three times since 2001.

4.7.2 Biology Summary

The epilithic diatom community of the Round Loch of Glenhead has undergone substantial and statistically significant change over the monitoring period, shifting from an assemblage dominated by the acidobiontic species *Tabellaria quadriseptata* (SWAP pH optima = 4.9), and to a lesser extent *Eunotia* *incisa* (SWAP pH optima = 5.1), to one increasingly dominated by *Navicula leptostriata* (SWAP pH optima = 5.1). *N. leptostriata* was not recorded in 1988 and 1990, but by 2006 comprised circa 30% of the entire assemblage. These taxonomic shifts are also reflected in the sediment trap material, although here *E.incisa* shows a slight increase in relative abundance.

Aquatic macrophyte composition has remained relatively constant, with the exception of the recent detection of the acid-sensitive elodeid species *Myriophyllum alterniflorum*. This species was detected in one open water location only in 2003 but has since spread around much of the lake perimeter. The establishment of this species, one of few oligotrophic macrophytes that form open-water stands, is likely to have a wider influence on the ecology of the loch, by providing an additional substrate for epiphytic algae and a source of food and shelter from predation for aquatic invertebrates.

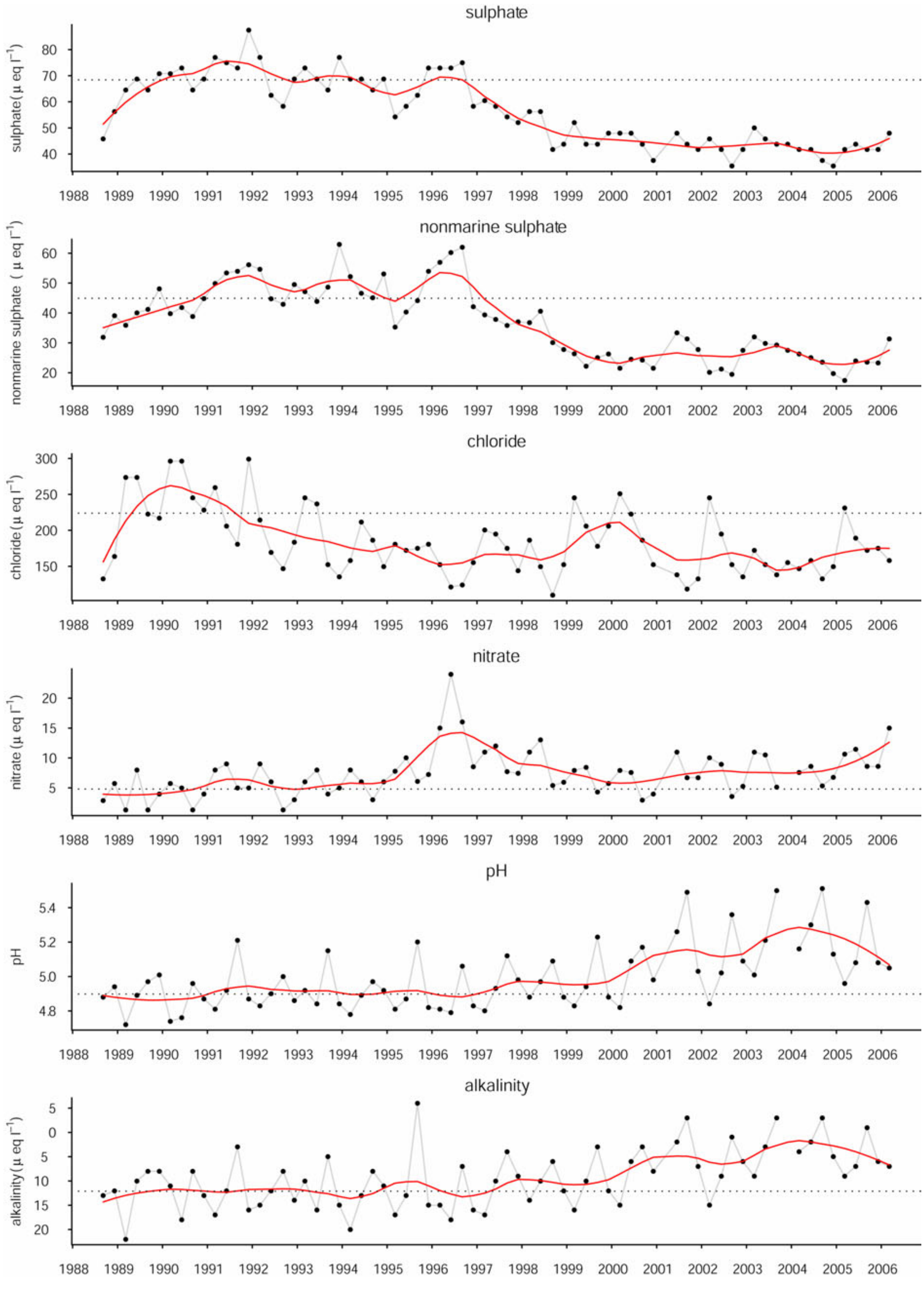
Perhaps surprisingly, given the substantial changes in water chemistry and aquatic flora, the macroinvertebrate assemblage shows no significant linear trend and remains relatively species poor and dominated by chironomid larvae. Importantly, however, the snail *Lymnaea peregra* was detected for the first time in 1996 and has since been detected in most years. This species was found to recolonise a formerly acidified streams in southern Norway that had been subjected to liming (Raddum and Fjellheim 2003) and is therefore considered to be a recovery indicator.

Brown trout have occurred at very low densities in the loch outflow burn throughout the monitoring period. However, the density of new recruits has increased slightly since 2000, providing evidence consistent with a gradual improvement in water quality.

4.7.3 Conclusions

Water chemistry data for the Round Loch of Glenhead demonstrate a reduction in acidity in response to a large reduction in xSO_4. All biological groups provide some indication of gradual biological recovery consistent with the increase in pH and decline in labile aluminium concentration, although the macroinvertebrate trend is not statistically significant using the more robust test statistic. The recent rise in NO_3 concentration gives cause for concern and requires further investigation, although SO_4 remains the dominant anthropogenic acid anion. Concentrations of xSO_4 remain four times higher than those for the cleanest site in the Network (Loch Coire nan Arr: Site 1).

Figure 4.7.1 Water Chemistry Summary Plots: Round Loch of Glenhead



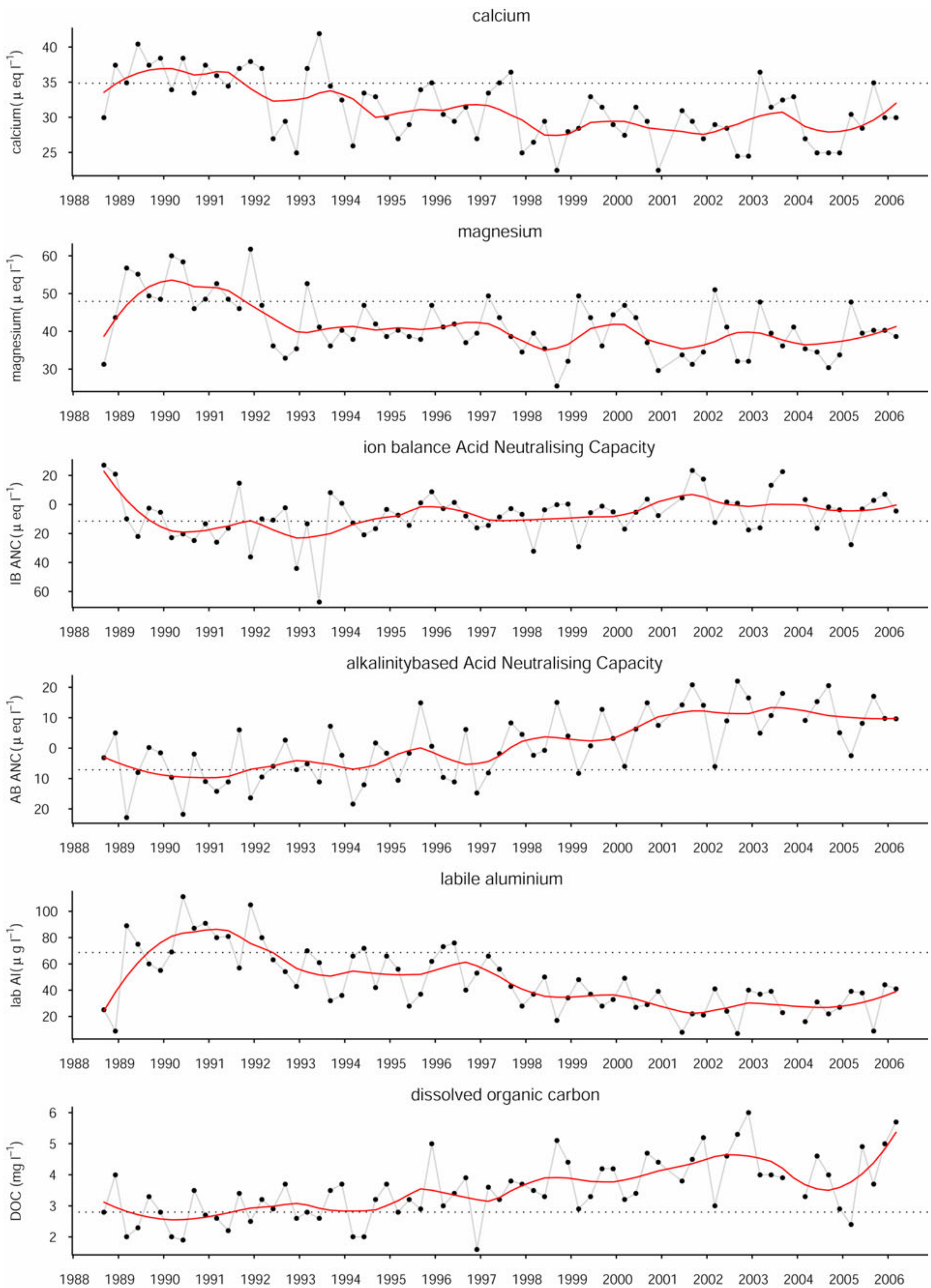

calcium
calcium(µ eq l⁻¹)
magnesium
magnesium(µ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC(µ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC(µ eq l⁻¹)
labile aluminium
lab Al(µ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.7.1 Water Chemistry Summary Data and Trend Statistics: Round Loch of Glenhead

Determinand / **period**		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	CB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Sep 1988 - Mar 1993	mean	45.1	4.8	223.9	4.90	-12.1	-11.4	-7.1	39.4	34.9	47.9	193.9	9.0	98.5	68.6	2.8
	st. dev	6.8	2.6	51.7	0.11	4.4	18.0	8.1	7.0	4.2	9.0	35.5	2.8	21.5	25.4	0.6
	min	32.0	1.3	132.6	4.72	-22.0	-44.1	-22.9	28.0	25.0	31.3	139.2	2.6	69.0	9.0	1.9
	max	56.3	9.0	299.0	5.21	-3.0	27.1	6.0	49.0	40.4	61.7	248.0	13.3	146.0	111.0	4.0
Apr 1993 - Mar 1998	mean	46.8	9.2	169.5	4.91	-11.9	-10.7	-3.1	33.9	31.5	40.6	153.3	7.0	90.8	51.5	3.2
	st. dev	9.1	4.8	29.3	0.13	6.1	16.6	8.7	3.1	4.2	3.7	14.7	2.0	17.7	15.9	0.8
	min	35.4	3.0	121.3	4.78	-20.0	-67.1	-18.3	28.0	25.0	34.5	130.5	2.6	55.0	28.0	1.6
	max	63.0	24.0	237.0	5.20	6.0	8.7	14.9	38.0	41.9	49.4	178.4	9.2	120.0	76.0	5.0
Apr 1998 - Mar 2003	mean	26.6	7.2	176.2	5.05	-7.7	-3.6	7.6	30.3	28.5	38.3	150.9	7.0	73.4	31.1	4.2
	st. dev	5.3	2.8	43.9	0.18	5.1	12.2	9.0	6.5	3.5	7.5	32.6	1.8	12.9	12.6	0.9
	min	19.6	2.9	110.0	4.82	-16.0	-29.1	-8.3	17.0	22.5	25.5	100.1	4.6	43.0	7.0	2.9
	max	40.7	13.0	251.1	5.49	3.0	23.5	22.1	42.0	36.4	51.0	208.8	11.0	96.0	50.0	6.0
Apr 2003 - Mar 2006	mean	25.1	8.9	163.1	5.18	-3.3	-0.7	11.0	30.2	29.4	38.1	139.6	7.4	73.5	29.9	4.0
	st. dev	4.1	2.9	26.6	5.59	4.1	13.5	6.6	4.8	3.4	4.4	16.7	1.3	16.4	11.4	1.0
	min	17.4	5.1	132.6	4.96	-9.0	-27.6	-2.5	25.0	25.0	30.4	113.1	5.4	37.0	9.0	2.4
	max	31.3	15.0	231.3	5.51	3.0	22.5	20.6	42.0	34.9	47.7	169.7	9.7	100.0	44.0	5.7
Seasonal-Kendall statistics	Sen-slope	-1.483	0.325	-3.174	0.016	0.450	0.756	1.329		-0.478	-0.388				-2.625	0.116
	P- val	**0.002**	**0.019**	**0.024**	**<0.001**	**<0.001**	**0.037**	**<0.001**		**0.009**	**0.008**				**<0.001**	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.7.2 Epilithic Diatom Percentage Abundance Summary: Round Loch of Glenhead

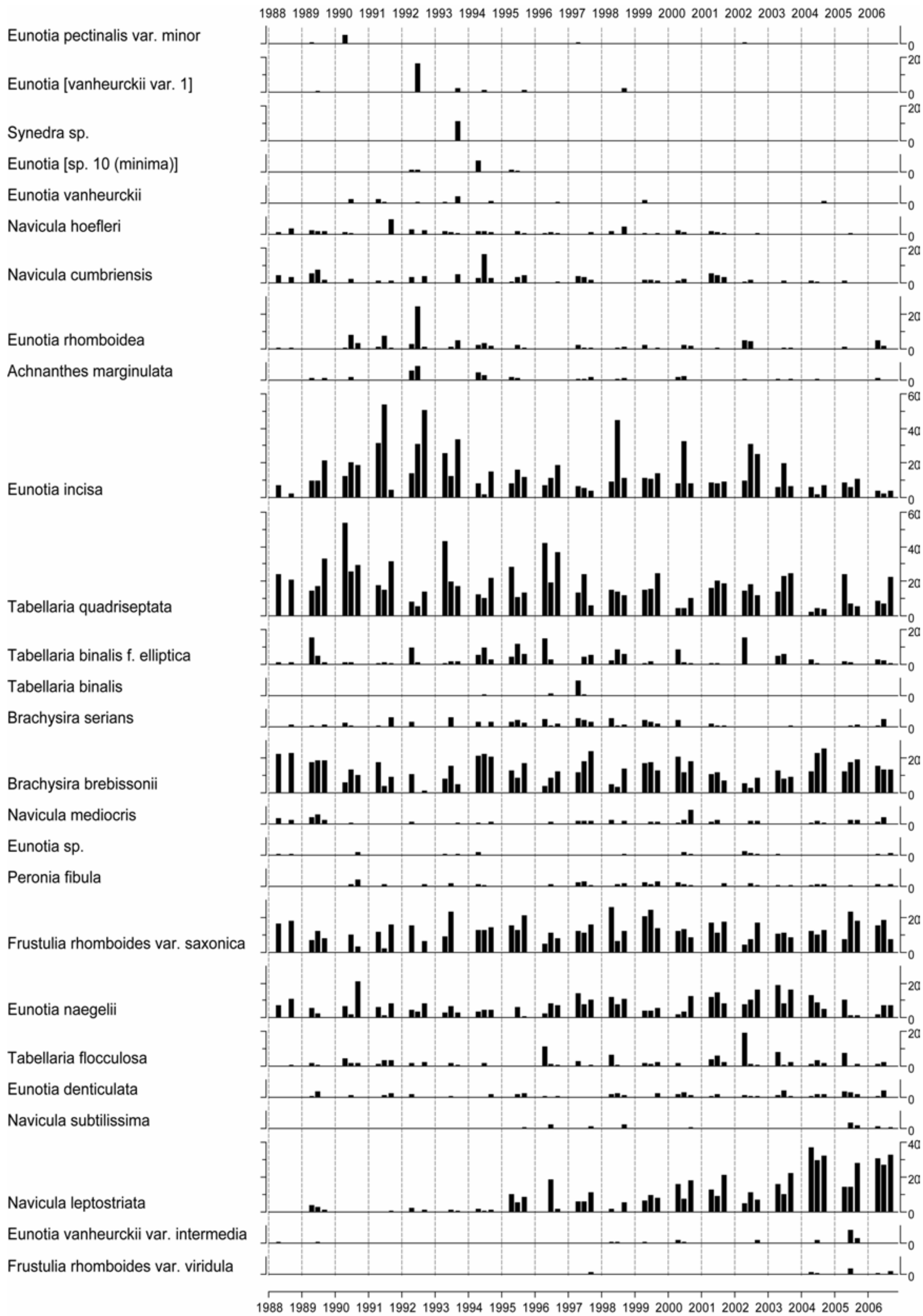


Figure 4.7.3 Aquatic Macrophyte Species Scores (1-5): Round Loch of Glenhead

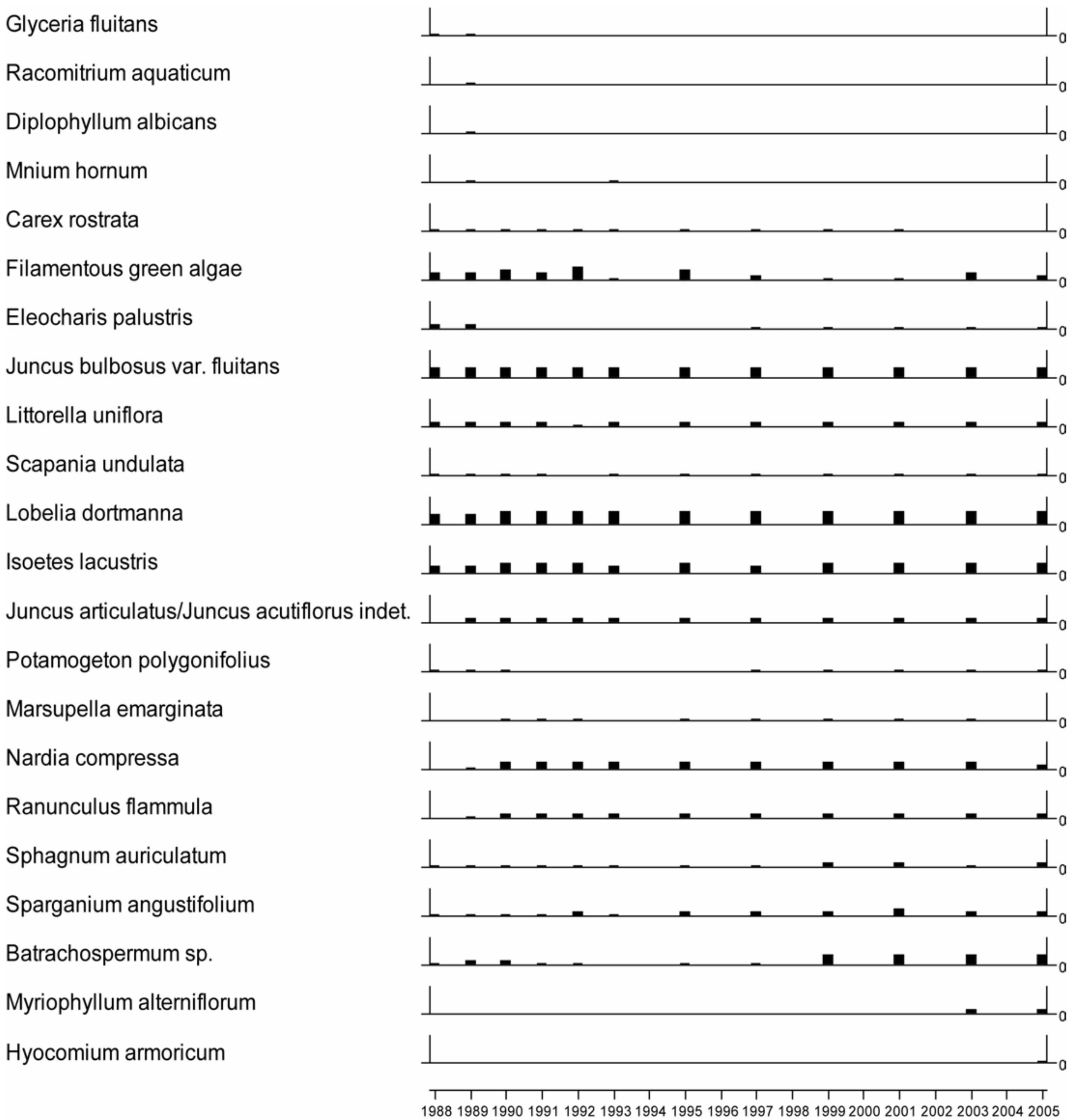
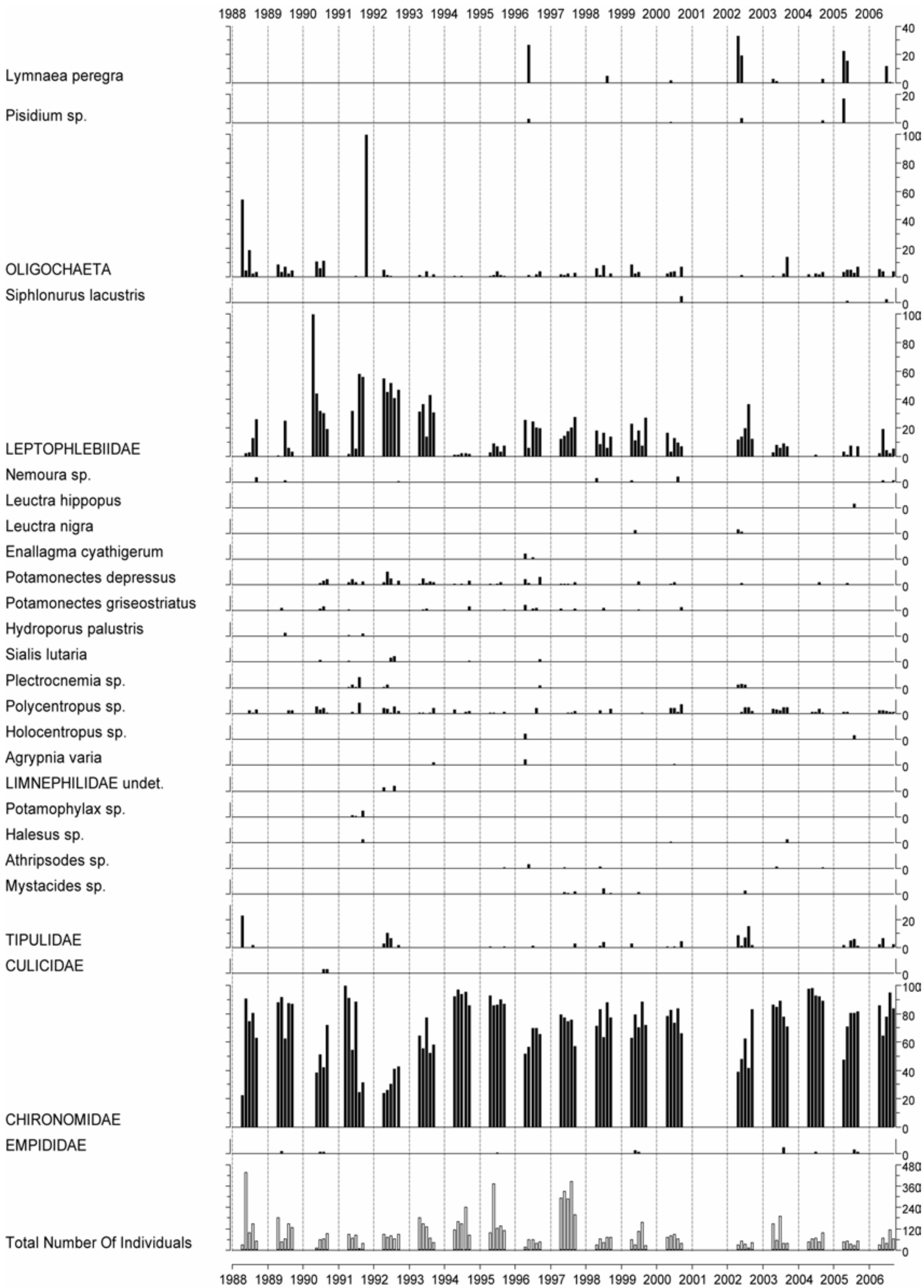


Figure 4.7.4 Macroinvertebrate Percentage Abundance Summary: Round Loch of Glenhead

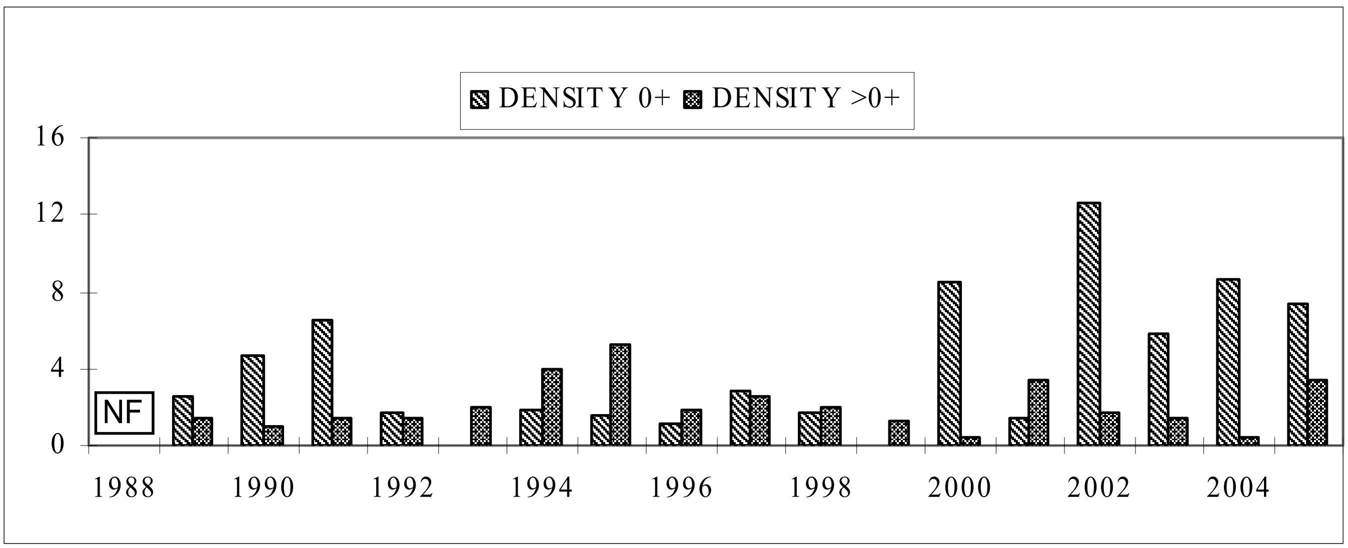


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.7.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Round Loch of Glenhead

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1088.28	94	44.6	55.4	0.18	0.97	0.001	0.022
Invertebrates	1476.98	37	59.9	40.1	0.06	0.17	0.004	0.161

Figure 4.7.5 Summary of Mean Trout Density (numbers $100m^{-2}$ for outflow stream): Round Loch of Glenhead



NF = Not fished

Figure 4.7.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Round Loch of Glenhead

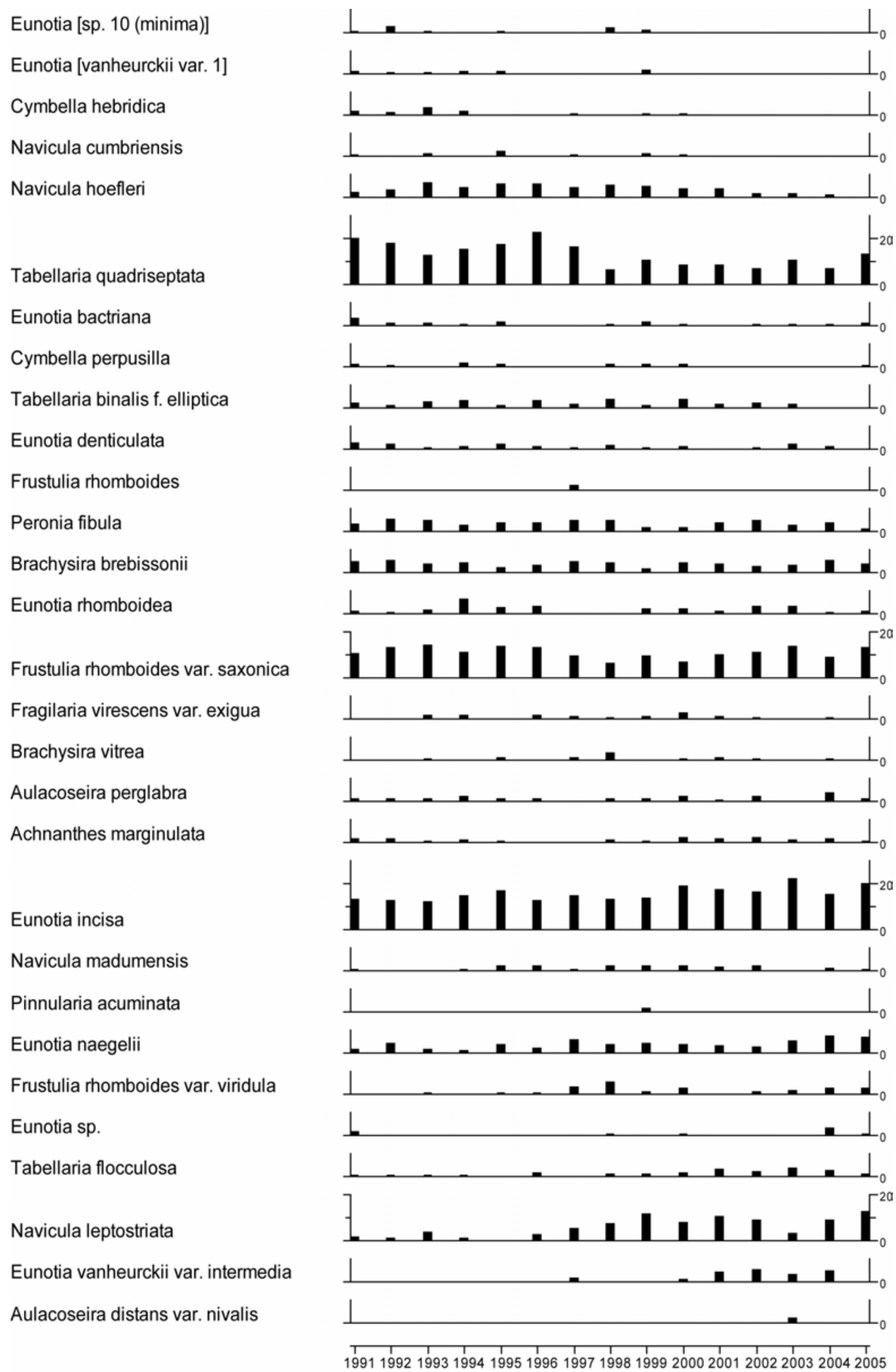
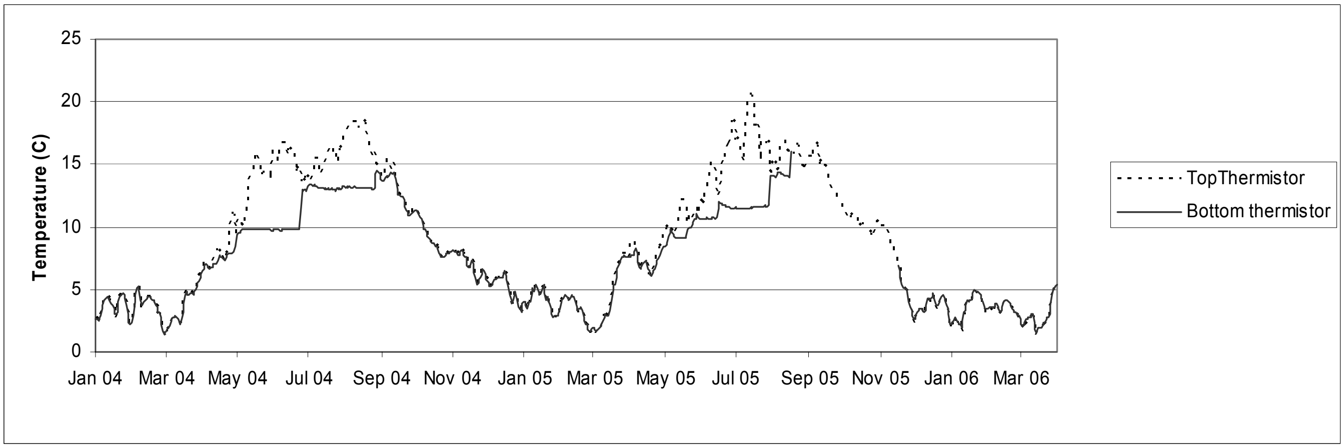


Figure 4.7.7 Thermistor Data: Round Loch of Glenhead



4.8 Loch Grannoch

4.8.1 Water Chemistry Summary

Loch Grannoch is a relatively large afforested loch 15 km to the southeast of the Round Loch of Glenhead (site 7) in Galloway, southwest Scotland and also lies on granitic bedrock.

At the onset of monitoring Loch Grannoch was one of the most acidic sites on the AWMN, with a 1988-1993 mean pH of 4.65, mean ANC of -43.5 μeq l^{-1} and an extremely high mean labile aluminium concentration of 246.1 μg l^{-1}, indicative of a severe level of toxicity to aquatic biota. The mean xSO_4 concentration of 68.5 μeq l^{-1} was approximately 50% higher than that of the Round Loch. It is likely that this difference results predominantly from the enhanced interception of pollutants by the forest canopy; concentrations of chloride, derived largely from seasalt, were also considerably higher for this reason. Nitrate showed a seasonal pattern with concentrations falling below the limit of detection occasionally during summer.

Over the course of monitoring xSO_4 concentration has fallen by circa 50%. Most of the decline occurred between 1996 and 2000, since when there has been no further reduction. After the first five years of monitoring NO_3 concentrations increased and, while a seasonal pattern has continued, concentrations have remained above the limit of detection throughout the year. Generally, NO_3 concentrations have remained much lower than xSO_4 in equivalence terms. However, between 1998-2003 NO_3 represented approximately one third of the acid load and in December 1999 concentrations of the two acid anions were roughly equal.

Chloride concentrations have shown the pattern of variation observed at most westerly sites from Galloway southward, with particularly high levels in the early 1990s, and a smaller peak between 1999 and 2000.

The downward trend in calcium and magnesium concentrations reflects the combined effects of reductions in seasalt inputs and anthropogenic sulphur in the early and late 1990s respectively. Ion balance ANC shows very large inter-seasonal variation, reflecting the large influence of seasalt deposition at this site. The effect of the large decline in xSO_4 in the late 1990s on ANC was masked by the increase in seasalt deposition over the same period. Between 2003-2006, the combination of relatively low levels of xSO_4 and seasalt deposition resulted in the highest mean ANC to date (-16.4 μeq l^{-1}) and the highest mean pH of 4.77.

Labile aluminium concentrations have declined dramatically over the 18 years, although the 2003-2006 mean of 73.4 μg l^{-1} is still very likely to exert toxic effects on fish. Concentrations are likely to increase again if rates of seasalt deposition rise again in future, unless xSO4 deposition falls further.

In common with most other AWMN sites DOC concentrations have increased markedly over the past 18 years. Most of the increase occurred in the 1990s as xSO_4 concentrations were declining most rapidly and changes are therefore consistent with a deposition control mechanism (see Section 5.4.5).

4.8.2 Biology Summary

The epilithic diatom assemblage in Loch Grannoch shows a significant long term trend although the cause of the main changes in species composition is currently unclear. At the onset of monitoring the assemblage was dominated by *Asterionella ralfsii* (SWAP pH optima = 4.9). An increase in the abundance of this species at the top of a sediment core taken from Loch Grannoch in the late 1980s had been attributed to the influence of fertiliser applied to sections of the forest in the mid-1980s (Flower et al., 1990). As monitoring progressed *A. ralfsii* declined proportionally as *Frustulia rhomboides* var. *saxonica* (SWAP pH optima = 5.2) and *Eunotia incisa* (SWAP pH optima = 5.1) increased temporarily. In 1993 the acidophilous species *Tabellaria quadriseptata* (SWAP pH optima = 4.9) became abundant in one sample, and since then this species has become dominant in most samples. Despite the considerable turnover of species and the reduction in labile aluminium concentration at this site, therefore, there is no clear evidence of a response in the diatom flora to the improvement in acidity.

The sediment trap data also demonstrate the upward trend in *T. quadriseptata* over the full period. Perhaps significantly, the key declining taxa, *A. ralfsii* and *T. quadriseptata* share the same SWAP pH optima of 4.9, indicating that the floristic changes may not be directly related to recovery from acidification.

The aquatic macrophyte flora of Loch Grannoch, dominated by isoetids, *Sphagnum* sp. and *Juncus bulbosus* var. *fluitans*, is typical of an acidified oligotrophic system and shows no indication of change over the monitoring period.

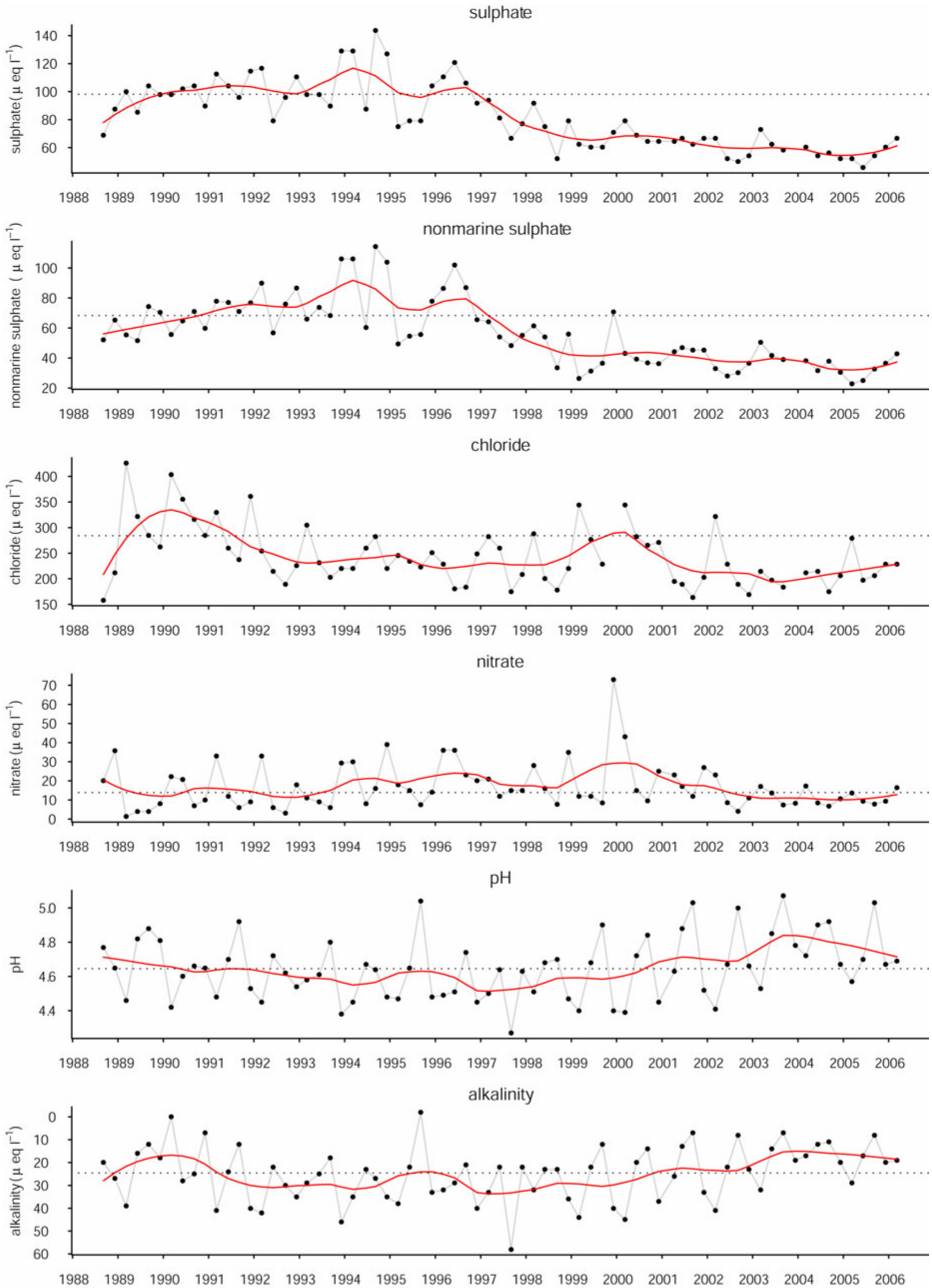
The macroinvertebrate fauna of Loch Grannoch has changed significantly over the 18 years. However, the main changes have been the apparent loss of the net spinning caddis *Oulimnius tuberculatus* (this species has increased in proportional abundance at other AWMN lakes that are showing clear chemical recovery) and an increased representation of chironomids. These trends, coupled with the observation of declining species richness (see summary) are indicative, therefore, of a slight deterioration in ecological condition.

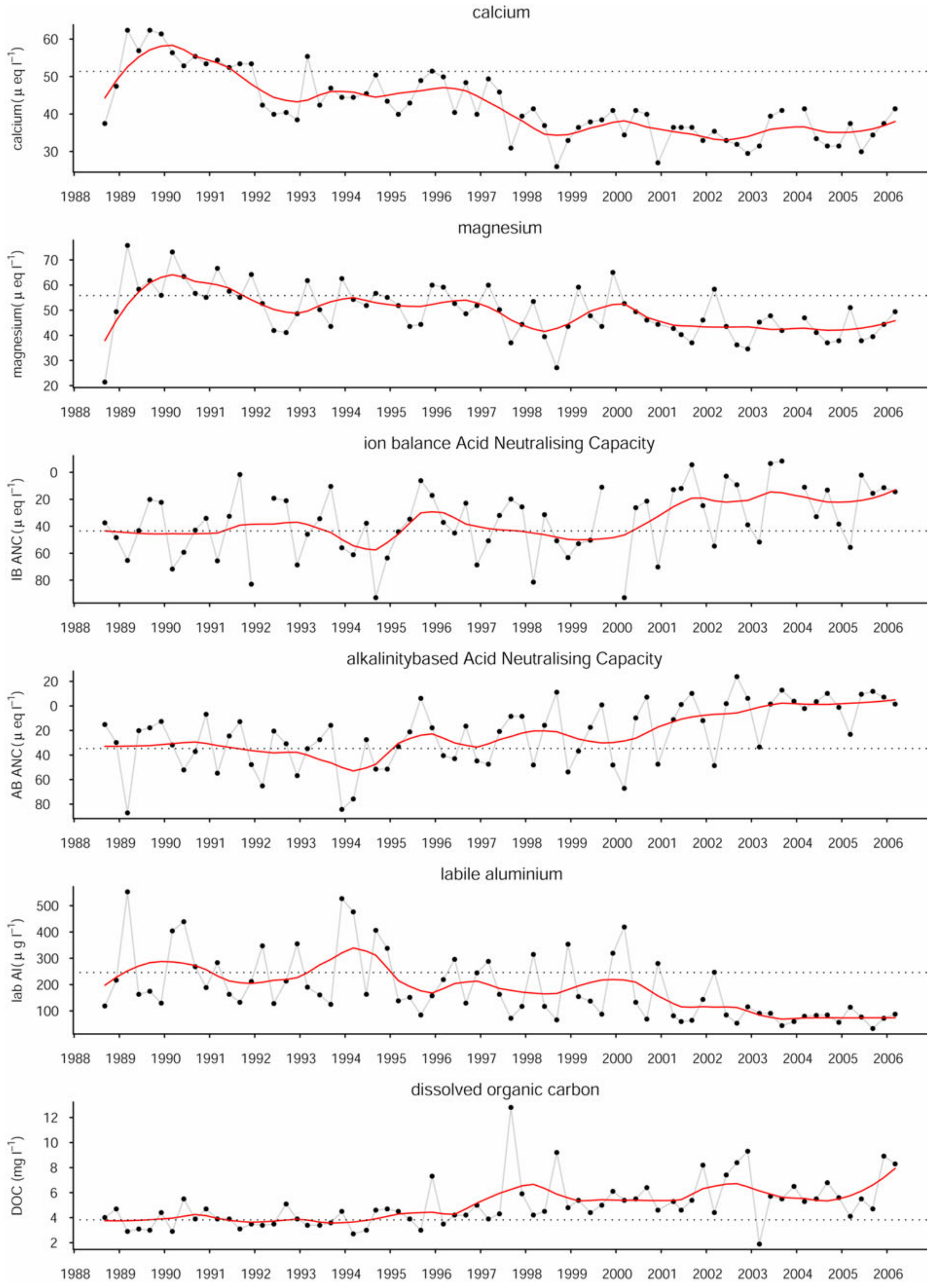
The outflow of the loch has yielded very few individual brown trout in relatively few years and provides no indication of any trend in these fish with time. A recent assessment of the AWMN fishing stretches, however, has concluded that these reaches are relatively poor physical habitats for fish and population responses to chemical change may not be expected.

4.8.3 Conclusions

Loch Grannoch is extremely acidic, as a result of geological sensitivity and the high interception of acidic pollutants by the forest canopy. The forest may also account for high seasalt inputs which dominate short term variability in ANC. Despite very large reductions in xSO_4 and consequent declines in labile aluminium concentration, levels of the latter remain potentially toxic to fish and the loch remains in a severely acidified condition. Changes in diatoms cannot be linked directly to any change in acidity, while the apparent deterioration of the macroinvertebrate assemblage requires further investigation.

Figure 4.8.1 Water Chemistry Summary Plots: Loch Grannoch





calcium
calcium (µ eq l^{-1})
magnesium
magnesium (µ eq l^{-1})
ion balance Acid Neutralising Capacity
IB ANC (µ eq l^{-1})
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l^{-1})
labile aluminium
lab Al (µ g l^{-1})
dissolved organic carbon
DOC (mg l^{-1})
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.8.1 Water Chemistry Summary Data and Trend Statistics: Loch Grannoch

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Sep 1988 - Mar 1993	mean	68.5	13.9	284.2	4.65	-25.9	-43.5	-34.7	53.2	51.4	55.8	239.3	4.7	316.4	246.1	3.8
	st. dev	11.2	10.8	71.9	0.15	10.7	22.2	21.2	12.6	8.0	12.3	45.3	2.8	148.9	121.3	0.8
	min	51.9	1.3	158.0	4.42	-42.0	-83.1	-87.3	31.0	37.4	21.4	147.9	2.6	153.0	118.0	2.9
	max	90.2	35.7	426.0	4.92	-7.0	-1.5	-6.7	78.0	62.4	75.7	313.2	10.7	715.0	552.0	5.5
Apr 1993 - Mar 1998	mean	74.9	19.9	232.2	4.57	-29.5	-42.1	-33.9	51.8	44.3	51.6	208.1	5.0	310.4	228.7	4.7
	st. dev	21.7	10.1	33.0	0.17	12.1	23.2	22.7	6.1	4.9	6.6	19.1	2.2	150.8	129.9	2.2
	min	48.4	6.0	174.9	4.27	-58.0	-92.9	-84.3	41.0	30.9	37.0	161.0	2.6	106.0	72.0	2.7
	max	114.3	39.0	287.7	5.04	2.0	-6.1	6.2	62.0	51.4	62.5	239.3	11.0	646.0	527.0	12.8
Apr 1998 - Mar 2003	mean	41.3	20.0	235.9	4.65	-26.1	-35.4	-17.0	45.5	34.8	45.1	202.3	5.4	248.6	153.7	5.8
	st. dev	10.9	15.8	57.2	0.20	11.9	26.0	26.0	10.8	4.2	8.9	44.7	1.3	124.6	109.3	1.9
	min	26.7	4.1	163.6	4.39	-45.0	-92.9	-67.3	25.0	25.9	27.1	126.2	3.1	107.0	53.0	1.9
	max	70.8	73.0	344.2	5.03	-7.0	5.5	23.9	64.0	40.9	65.0	278.4	7.9	556.0	419.0	9.3
Apr 2003 - Mar 2006	mean	31.6	10.7	211.6	4.77	-16.1	-16.4	3.0	41.6	36.2	43.1	178.4	5.1	159.4	73.3	6.0
	st. dev	11.7	3.6	27.9	5.25	6.1	19.3	9.6	6.1	4.3	5.0	16.6	1.0	30.6	22.2	1.4
	min	0.0	6.7	174.9	4.57	-29.0	-55.6	-23.2	34.0	29.9	37.0	152.3	4.1	77.0	33.0	4.1
	max	42.7	17.4	279.3	5.07	-7.0	8.3	12.9	56.0	41.4	51.0	200.1	7.2	196.0	114.0	8.9
Seasonal-Kendall statistics	Sen-slope	-2.323	-0.284	-3.013	0.005	0.375	1.657	2.293		-1.137	-0.953				-11.100	0.175
	P- val	**0.001**	0.437	0.080	0.380	0.281	**0.023**	**0.001**		**<0.001**	**0.004**				**<0.001**	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.8.2 Epilithic Diatom Percentage Abundance Summary: Loch Grannoch

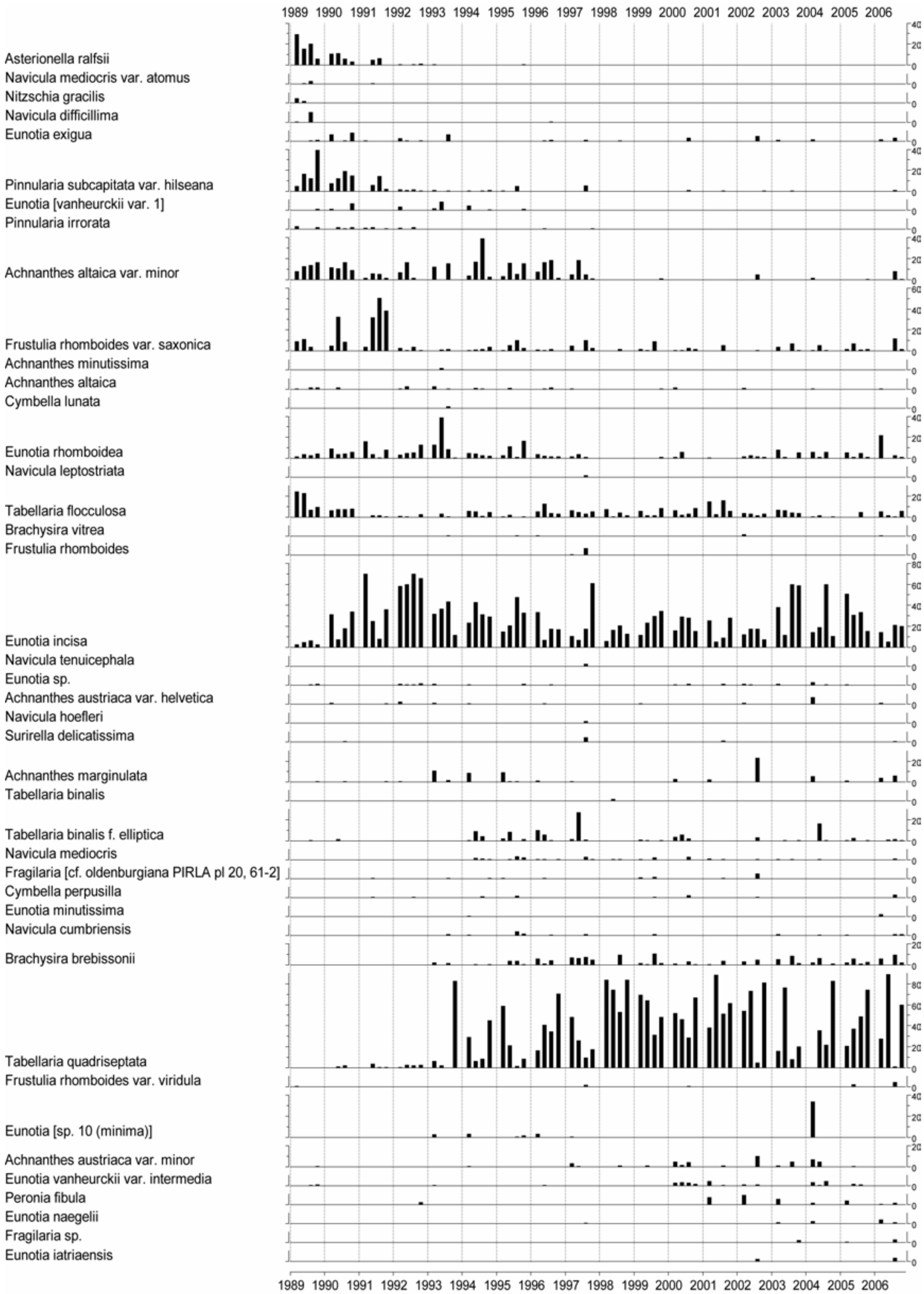
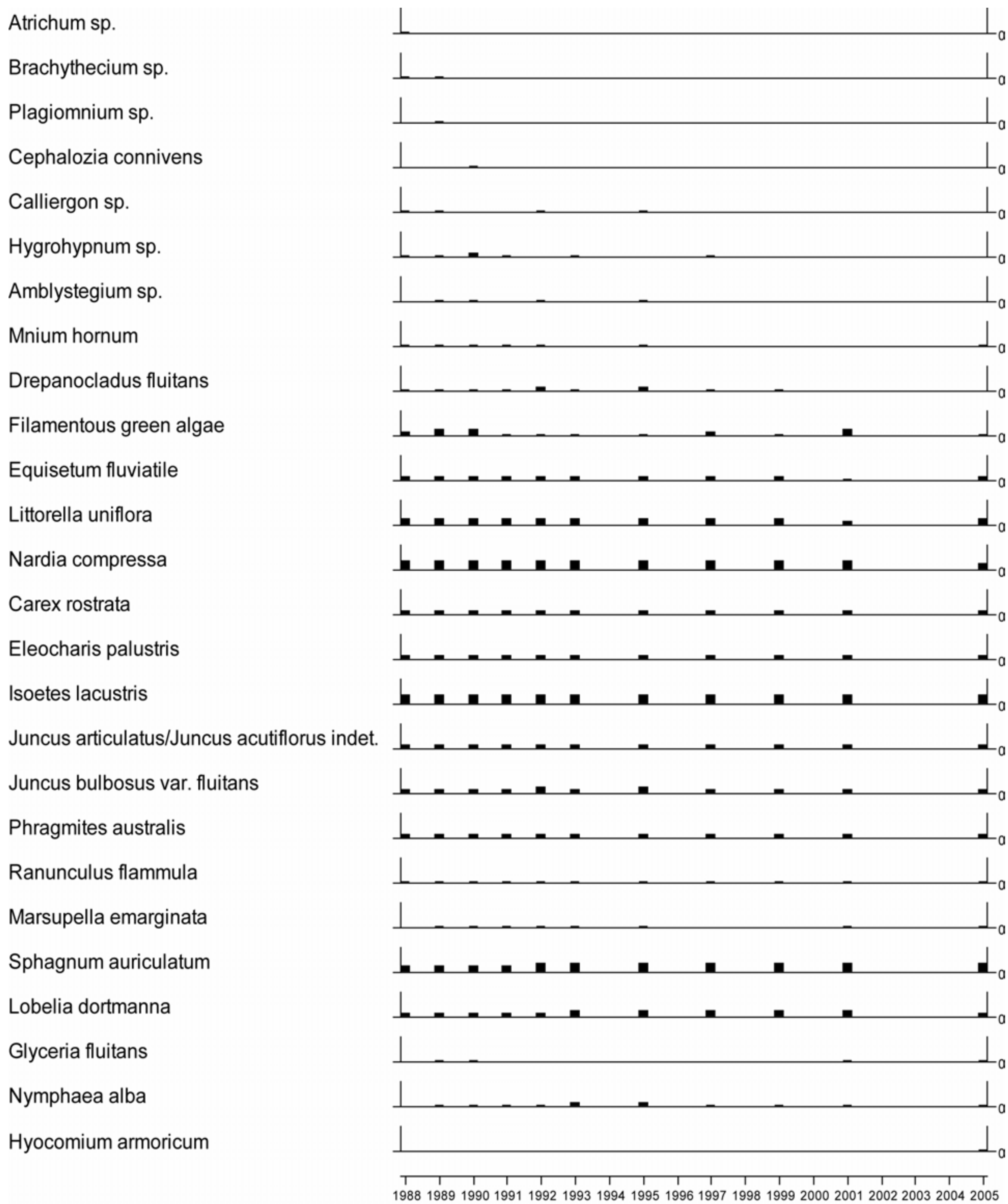
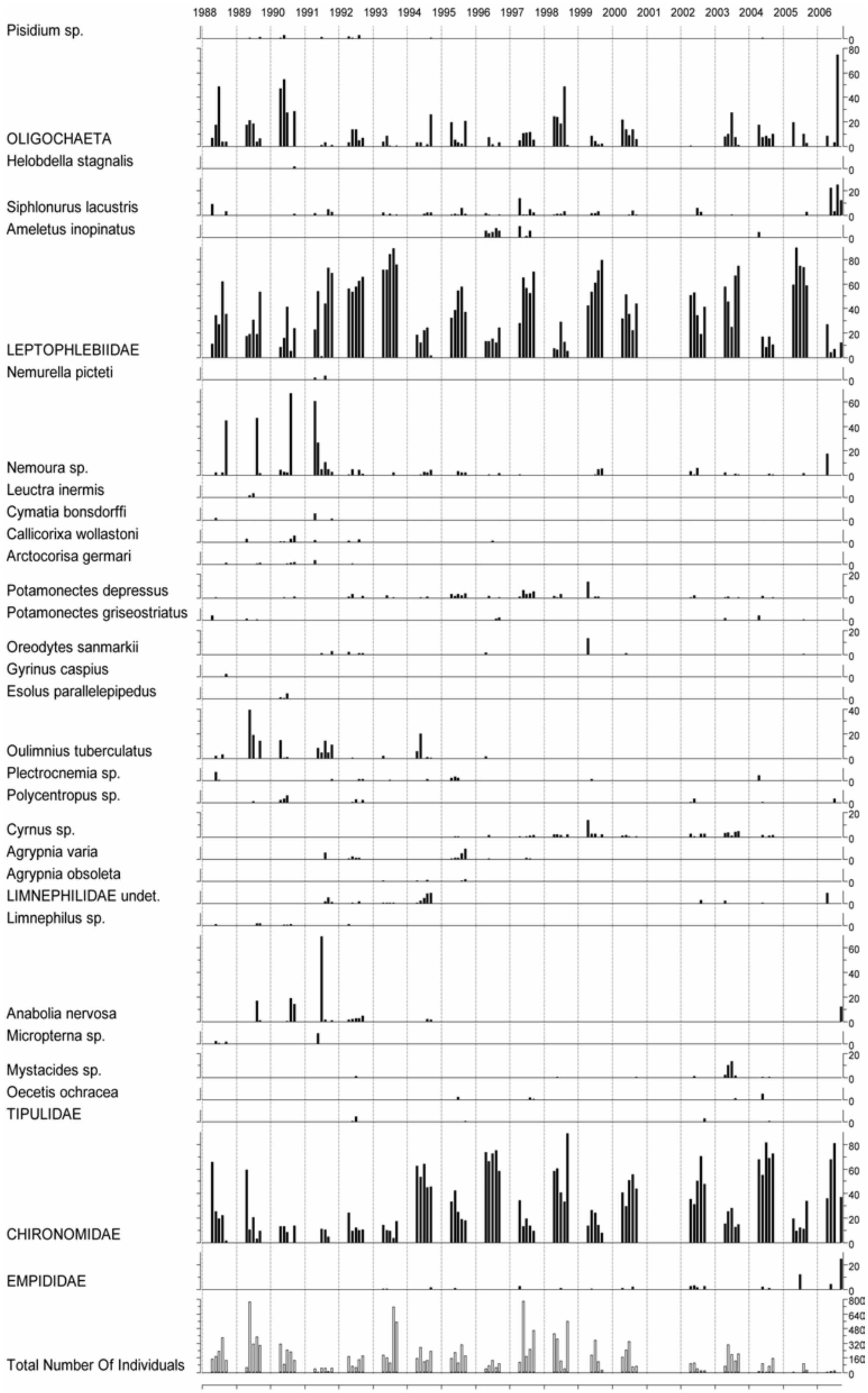


Figure 4.8.3 Aquatic Macrophyte Species Scores (1-5): Loch Grannoch



No aquatic macrophyte survey in 2003.

Figure 4.8.4 Macroinvertebrate Percentage Abundance Summary: Loch Grannoch

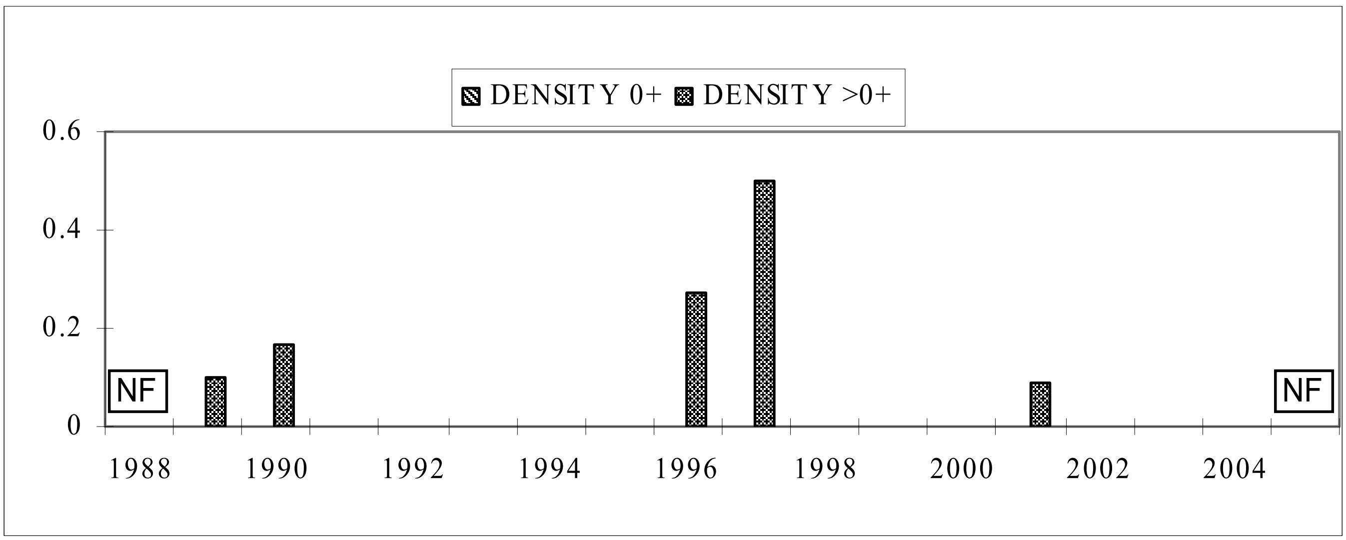


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.8.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Loch Grannoch

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	2363.70	103	46.3	53.6	0.21	0.86	0.001	0.015
Invertebrates	2538.10	55	47.1 001	52.9	0.08	0.28	0.001	0.161

Figure 4.8.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Loch Grannoch



NF = Not fished

Figure 4.8.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Loch Grannoch

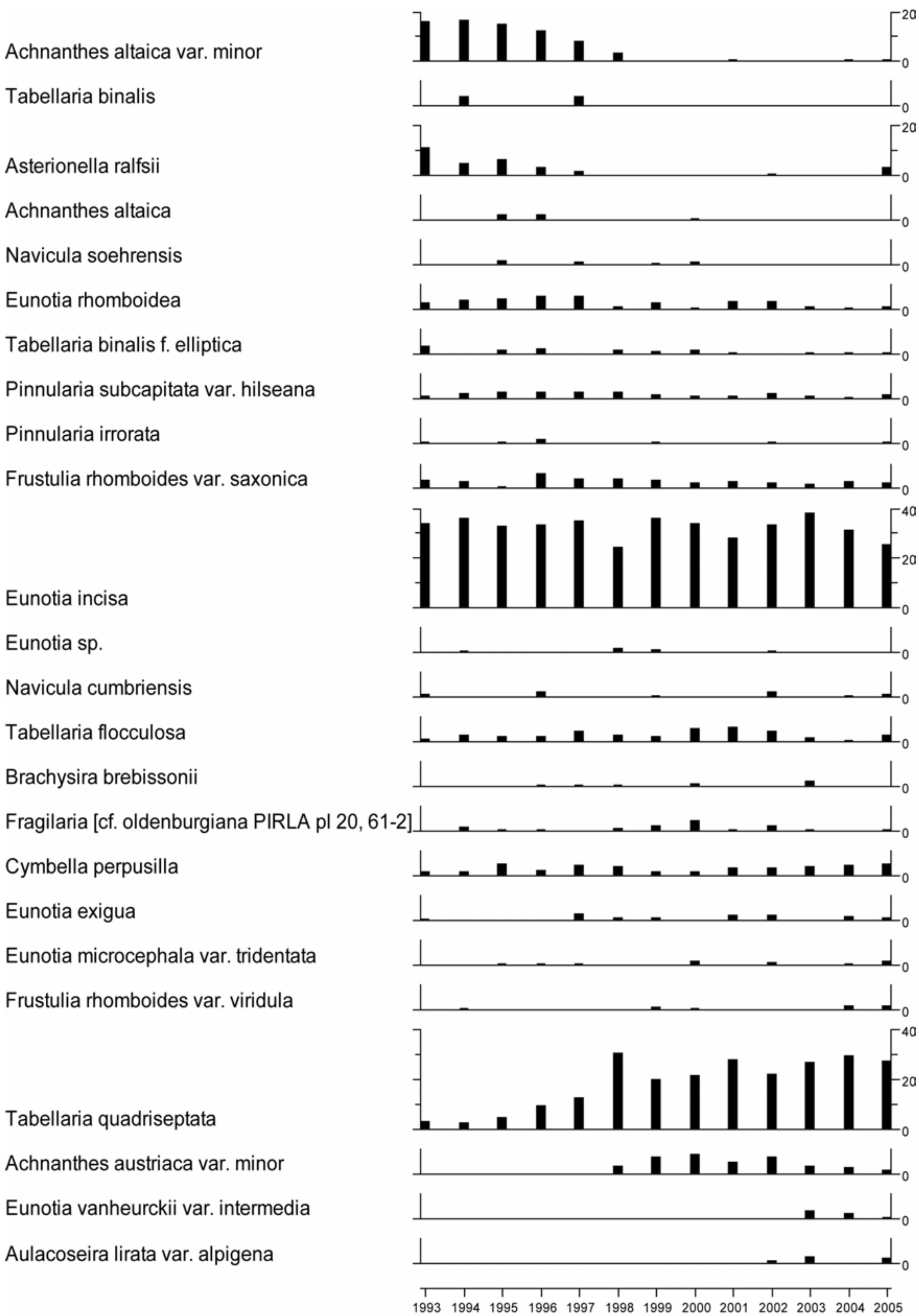
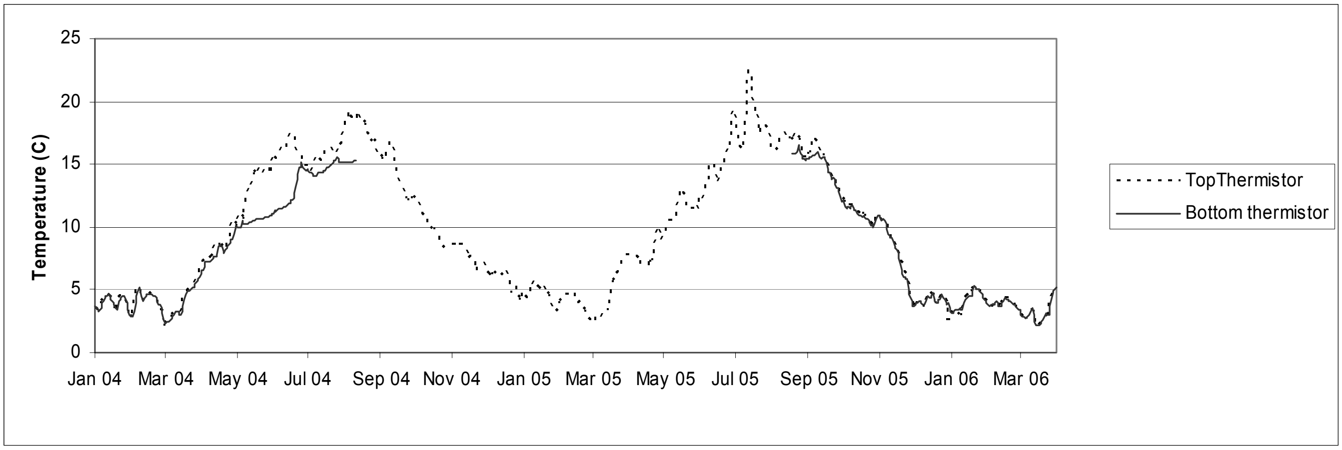


Figure 4.8.7 Thermistor Data: Loch Grannoch



4.9 Dargall Lane

4.9.1 Water Chemistry Summary

The Dargall Lane Burn is a small mountain stream draining moorland 2 km to the south of the Round Loch of Glenhead (site 7). Non-marine sulphate concentration is thought to be influenced by a geological source of sulphur (Giusti 1999) and this could explain the relatively high 1988-1993 mean concentration of 60.3 μeq l^{-1}. At the onset of monitoring NO_3 concentration showed a strong seasonal pattern and was below the limit of detection for two or three months each summer. Chloride concentration during the first five years was high due to prolonged periods of storminess and consequent elevated seasalt inputs experienced by many AWMN sites. Over the first five years mean pH was 5.44, mean ion balance ANC was fractionally negative (-2.2 μeq l^{-1}) and mean labile aluminium concentration (i39.9 μg l^{-1}) was within a range thought to represent moderate toxicological effects to aquatic biota.

Over the course of monitoring the reduction in xSO_4 has been relatively modest (circa 25%) with most of the decline occurring between 1996-2000. Since 2000 concentrations have risen again slightly. Nitrate concentrations have continued to show strong seasonality but no long-term trend, and inter-annual variation in peak concentrations appears to follow the regional pattern that has been linked to climatic variability (Monteith *et al.*, 2000). Chloride concentrations have shown a very similar pattern to neighbouring sites with the major peak in the early 1990s followed by a secondary peak between 1999-2000.

Since the mid-1990s pH has risen progressively with the clearest increase occurring in pH minima during periods of high flow or seasalt events. However, the most striking chemical response to declining sulphur inputs has been a steep fall in labile aluminium concentrations. By 2003-2006 concentrations had reached almost negligible levels (mean = 11.1 μeq l^{-1}). These very low levels in part reflect a reduction in seasalt deposition in recent years, and concentrations may rise again if the storminess experienced in the early 1990s returns. Mean ion-balance ANC for 2003-2006 was 12.6 μeq l^{-1}.

Dissolved organic carbon concentrations have increased slightly over the full monitoring period with most of the change occurring in the mid 1990s – coincident with the decline in xSO_4, and consistent with the hypothesis of a controlling effect of deposition chemistry on organic matter solubility (see Section 5.4.5).

4.9.2 Biology Summary

The epilithic diatom flora of the Dargall Lane Burn has changed significantly over the monitoring period. The main changes comprise a reduction in the relative abundance of *Eunotia naegelii* (SWAP pH optima = 5.0) and *Eunotia incisa* (SWAP pH optima = 5.1) and a rise in *Peronia fibula* (SWAP pH optima = 5.3) and *Tabellaria flocculosa* (SWAP pH optima = 5.4).

The aquatic macrophyte flora has been almost exclusively represented by acid tolerant liverworts. However, the cover of *Nardia compressa* (which is only dominant within the AWMN in the seasonally highly acidic Bencrom river) has declined, while the more ubiquitous *Scapania undulata* has increased. There has also been a slight increase in the cover of *Marsupella emarginata*.

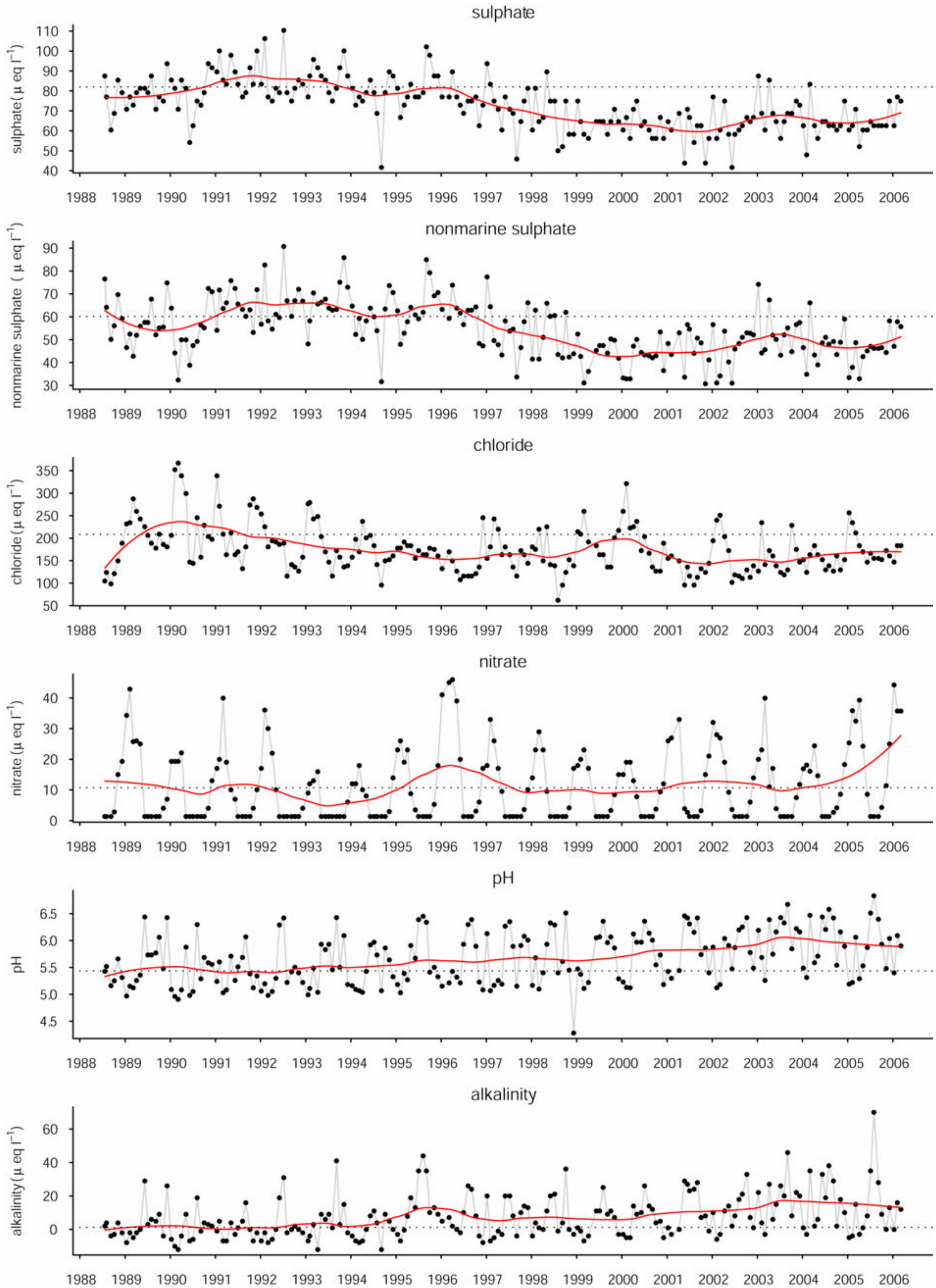
There are clear recent shifts in the macroinvertebrate fauna of the Dargall Lane Burn that are consistent with recovery responses although there is there is no statistically significant linear change in the full dataset, according to the most rigorous permutation test. The acid-sensitive stonefly grazer *Brachyptera risi* was first recorded in 1998 and is now detected at greater frequency, while the acid-sensitive stonefly predator *Isoperla grammatica* has increased in relative abundance. The more acid-tolerant shredder stonefly *Amphinemura sulcicollis* has also increased in relative abundance and is now the dominant taxa. The most significant decline has been in the proportion of the acid-tolerant collector-gatherer stonefly *Leuctra inermis*. The total number of individuals caught has risen from very low levels in the first five years, while species richness has also increased.

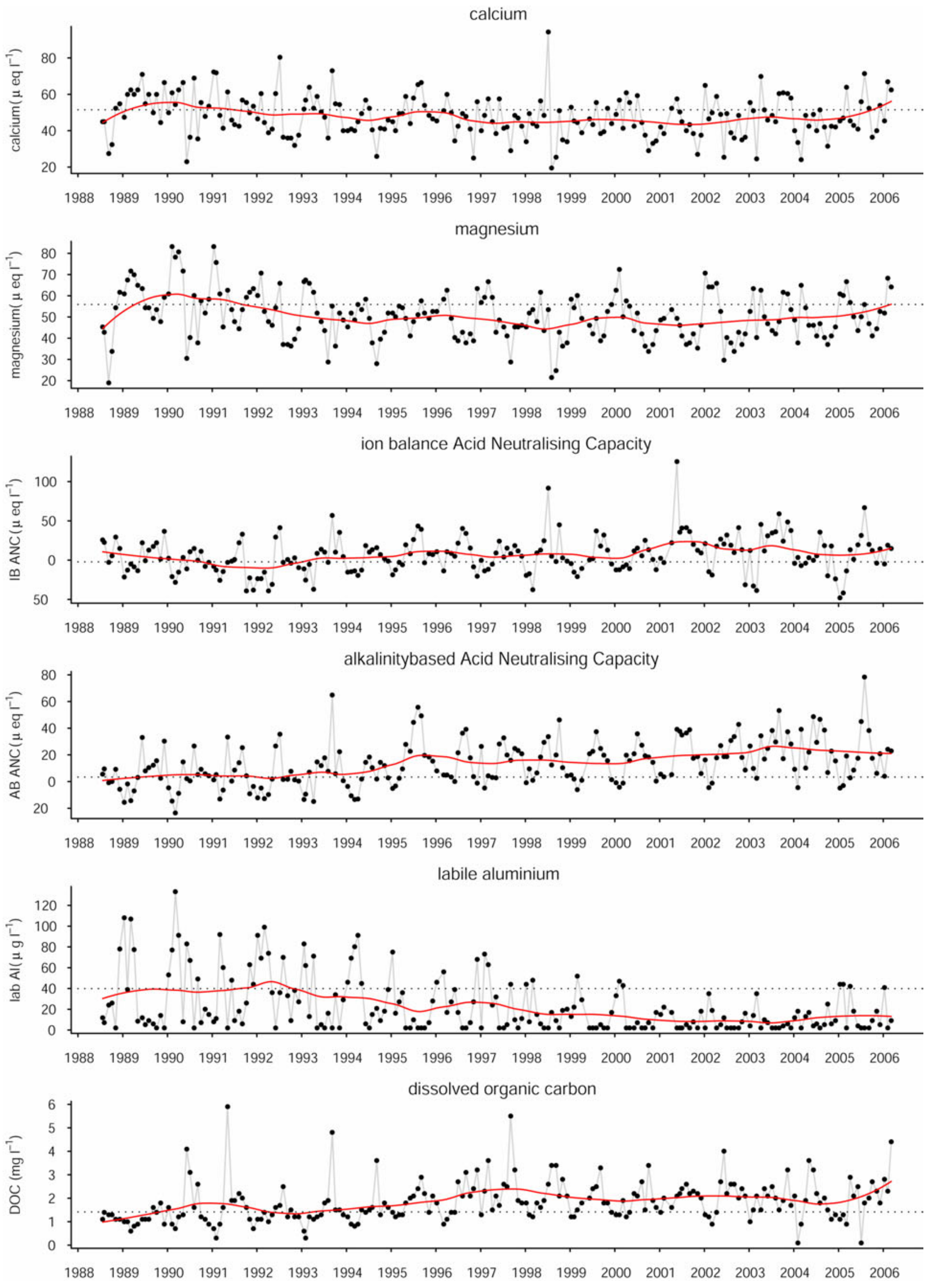
The brown trout data show oscillations in density but no obvious long term trend. Fishing could not be carried out in 2005 due to prolonged high flow conditions.

4.9.3 Conclusions

The Dargall Lane Burn has experienced a relatively moderate decline in xSO_4 over the monitoring period. This, in conjunction with an overall decline in seasalt deposition, has resulted in a slow but progressive increase in pH minima and a large reduction in labile aluminium concentration. Mean ANC remains slightly below 20 $\mu eq\ l^{-1}$, but there are clear indications of responses in the aquatic flora, and while the macroinvertebrate fauna shows no significant linear trend, species shifts are consistent with the early stages of biological recovery.

Figure 4.9.1 Water Chemistry Summary Plots: Dargall Lane





calcium
calcium (µ eq l^{-1})
magnesium
magnesium(µ eq l^{-1})
ion balance Acid Neutralising Capacity
IB ANC (µ eq l^{-1})
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l^{-1})
labile aluminium
lab Al(µ g l^{-1})
dissolved organic carbon
DOC (mg l^{-1})
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.9.1 Water Chemistry Summary Data and Trend Statistics: Dargall Lane

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Jul 1988 - Mar 1993	mean	60.3	10.7	208.2	5.44	ANC	-2.2	3.4	37.8	51.5	55.9	182.3	9.0	55.5	39.9	1.4
	st. dev	10.9	11.5	63.9	0.41	9.5	19.5	13.2	8.4	12.3	13.6	39.8	4.0	41.0	35.1	0.9
	min	32.6	1.3	98.7	4.91	-12.0	-39.2	-23.6	24.0	23.0	18.9	108.8	2.6	2.0	2.0	0.3
	max	90.7	42.9	366.7	6.44	31.0	41.2	35.5	59.0	80.3	83.1	282.8	17.1	143.0	133.0	5.9
Apr 1993 - Mar 1998	mean	60.4	11.1	165.5	5.60	7.1	4.9	13.0	32.9	47.1	48.5	155.4	8.3	43.2	25.3	1.9
	st. dev	11.1	12.3	34.7	0.45	12.7	18.9	16.5	4.7	9.3	8.4	21.0	3.1	30.2	24.8	0.9
	min	31.7	1.3	95.9	5.03	-12.0	-37.6	-14.9	21.0	25.0	28.0	91.4	2.6	2.0	2.0	0.8
	max	85.9	46.0	248.2	6.45	44.0	56.8	64.8	44.0	72.9	66.6	195.8	13.6	116.0	91.0	5.5
Apr 1998 - Mar 2003	mean	46.3	10.9	163.8	5.77	9.3	11.4	17.3	30.8	44.7	47.0	149.7	8.2	28.1	11.2	2.0
	st. dev	9.1	10.4	51.7	0.47	11.2	27.0	13.5	7.0	12.0	11.0	31.9	3.3	19.3	12.5	0.7
	min	30.8	1.3	62.1	4.28	-7.0	-38.5	-6.0	16.0	19.5	21.4	74.0	2.0	2.0	2.0	0.9
	max	74.2	40.0	321.6	6.51	36.0	125.4	46.3	50.0	94.3	72.4	252.3	15.3	75.0	52.0	4.0
Apr 2003 - Mar 2006	mean	48.5	14.2	162.4	5.77	16.0	12.6	23.9	32.8	48.8	50.9	146.8	8.3	26.1	11.1	2.0
	st. dev	8.1	13.1	31.5	0.56	16.3	25.3	18.0	5.2	10.9	8.7	19.5	2.8	20.7	12.8	0.9
	min	32.8	1.3	118.5	5.19	-5.0	-47.9	-4.9	24.0	24.0	37.0	113.1	2.3	2.0	2.0	0.1
	max	67.4	44.3	256.7	6.83	70.0	67.0	78.4	46.0	71.4	68.3	187.1	13.3	80.0	44.0	4.4
Seasonal-Kendall statistics	Sen-slope	-1.006	0.286	-2.233	0.032	0.785	0.585	1.226		-0.128	-0.110				-1.697	0.049
	P- val	**0.004**	**0.042**	**0.034**	**<0.001**	**<0.001**	**0.009**	**<0.001**		0.092	0.068				**<0.001**	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.9.2 Epilithic Diatom Percentage Abundance Summary: Dargall Lane

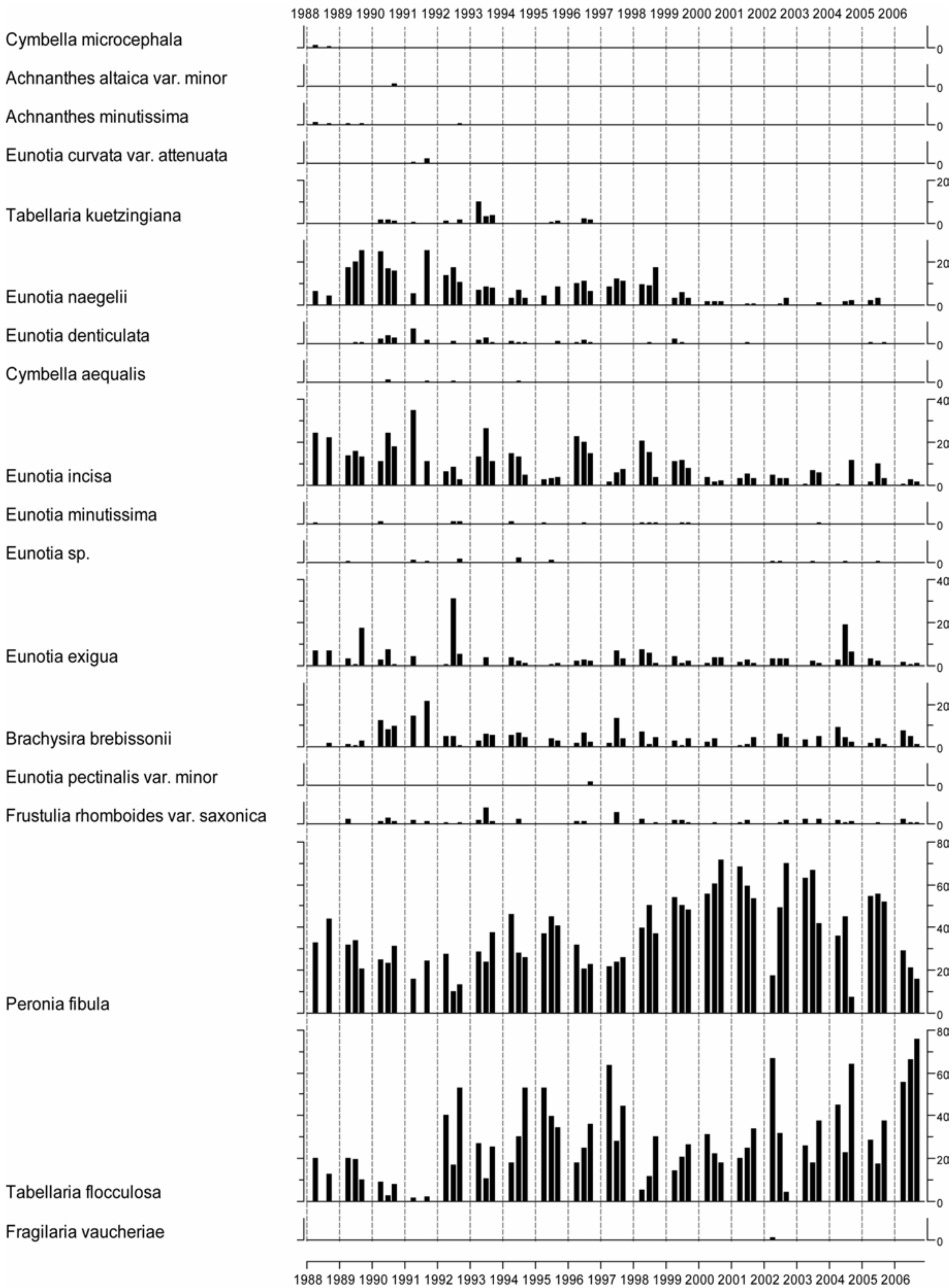
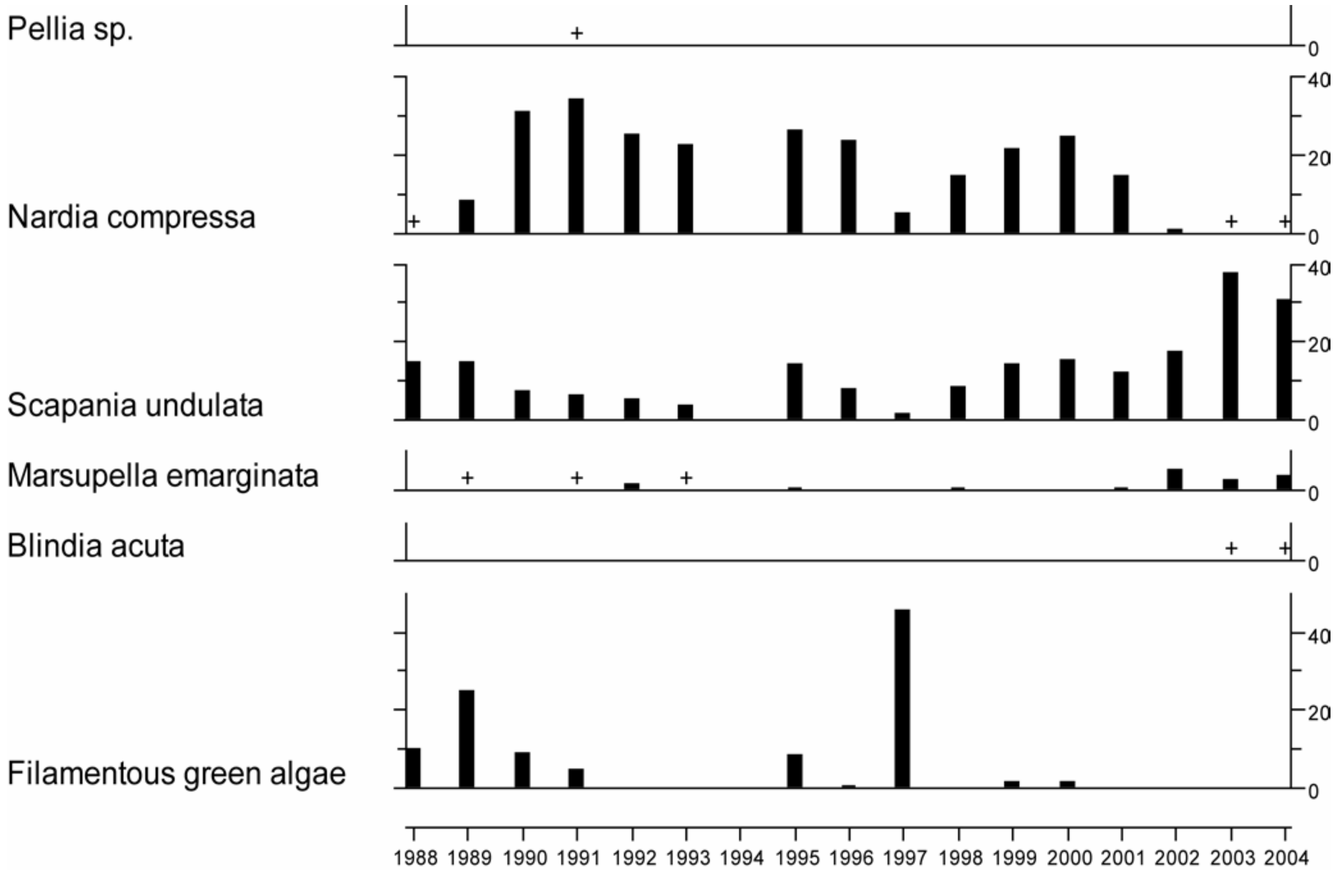
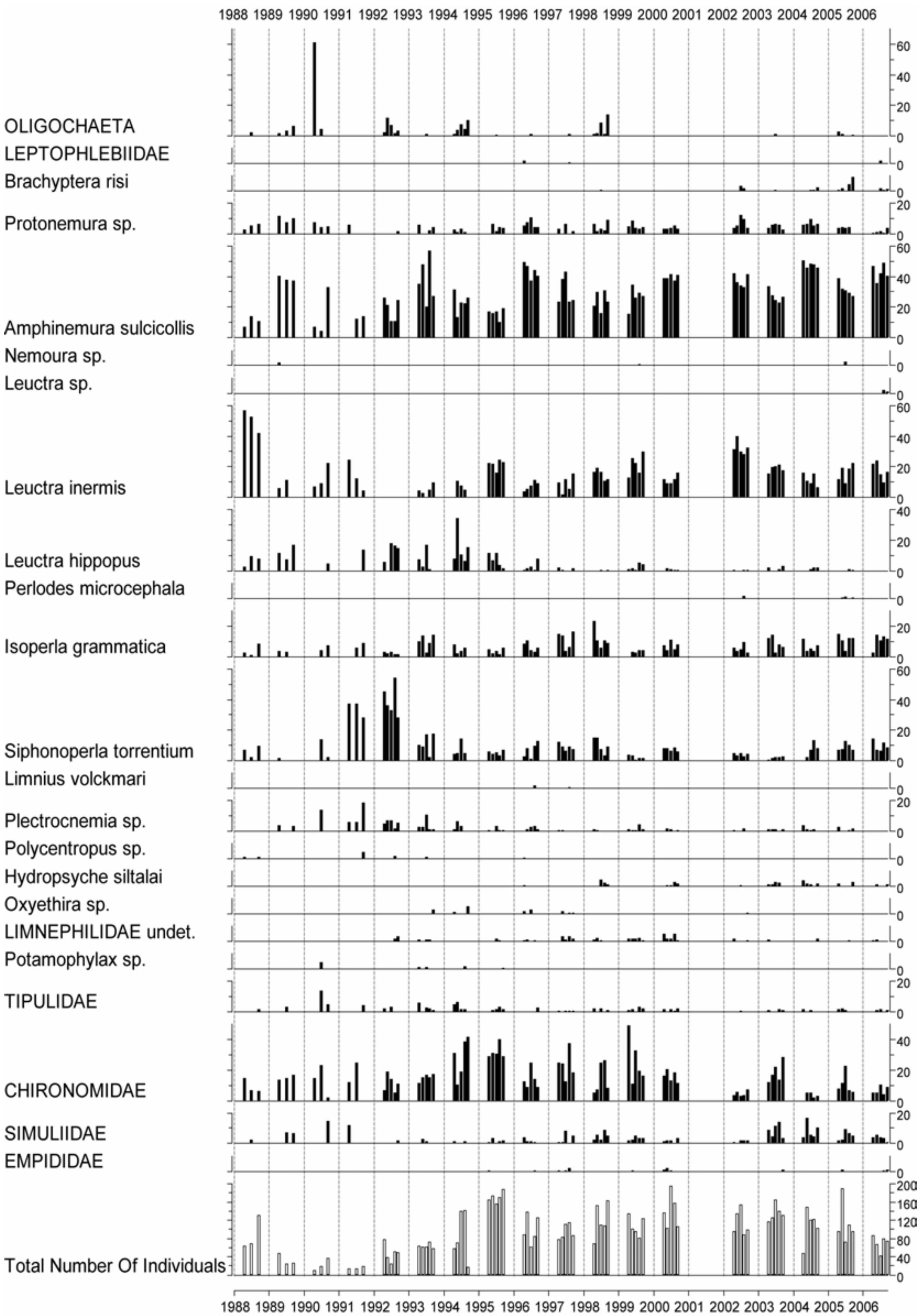


Figure 4.9.3 Aquatic Macrophyte Percentage Species Cover: Dargall Lane



+ Represents <0.1% abundance

Figure 4.9.4 Macroinvertebrate Percentage Abundance Summary: Dargall Lane

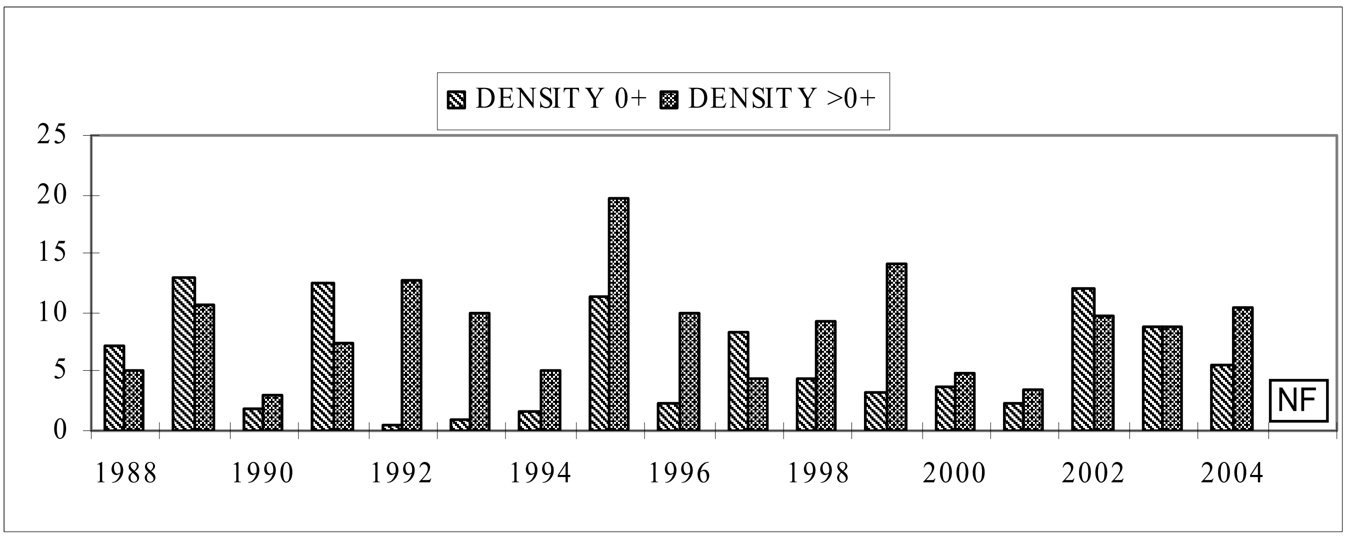


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.9.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Dargall Lane

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	772.8	84	36.5	63.5	0.21	0.90	0.001	0.015
Invertebrates	1579.43	33	40.5	59.5	0.13	0.67	0.001	0.083

Figure 4.9.5 Summary of Mean Trout Density (numbers 100m^{-2}): Dargall Lane



NF = Not fished

4.10 Scoat Tarn

4.10.1 Water Chemistry Summary

Scoat Tarn is the second highest lake on the AWMN (602 m a.s.l) lying on volcanic geology 7 km to the north of Burnmoor Tarn (Site 11) in the English Lake District. The lake water is exceptionally clear for an AWMN site as a result of its very low levels of DOC. Situated just 15 km from the west coast the water chemistry is influenced strongly by seasalt deposition which makes a significant contribution to the total sulphate load.

Over the first five years of monitoring (i.e. 1988-1993) mean xSO_4 and NO_3 concentrations were 39.2 μeq l^{-1} and 21.2 μeq l^{-1} respectively. The lake was highly acidic (mean pH = 5.0) and mean labile aluminium concentration (132.5 μg l^{-1}) was at a potentially highly toxic level for fish, with a maximum of 293.8 μg l^{-1} recorded in March 1990 following a seasalt episode. Mean ion-balance ANC was -16.9 μeq l^{-1}.

Throughout most of the record xSO_4 has shown a downward trend, although the relatively low concentrations in samples from the late 1980s results in a relatively gradual decline overall. By 2003-2006 mean concentrations had fallen to 33.4 μeq l^{-1} – a reduction of 15% on the first five year average. Current concentrations are more than six times higher than those for Loch Coire nan Arr (site 1) in northwest Scotland.

Nitrate concentrations vary seasonally throughout the record, although leaching occurs throughout the year. Inter-annual variation in spring peak concentrations has been shown to be linked to the North Atlantic Oscillation (Monteith *et al.*, 2000). There is evidence for a slight reduction in concentrations in recent years and concentrations have remained below the mean for the first five years since 2000.

Chloride concentrations follow those of many other western sites in the southern half of the Network with a very large peak (associated with a strongly positive North Atlantic Oscillation Index) in the early 1990s that has not recurred.

Base cation (calcium and magnesium) concentrations peaked in the early 1990s as a result of an increase in supply from marine sources and have since declined following reductions first in seasalt and later in xSO_4.

The combination of reductions in xSO_4, Cl and NO_3 have all contributed to a reduction in acidity over the monitoring period. The most striking effect has been on labile aluminium concentration which has fallen sharply from very high concentrations in the first five years to a 2003-2006 mean of 32.2 μg l^{-1}. However, a seasalt episode in March 2005 raised the concentration to 78.0 μg l^{-1}, suggesting that the lake water may still be periodically toxic to fish. Water pH has increased slightly (2003-2006 mean = 5.14), but there is no obvious trend in ion-balance ANC, for which variation is dominated by variation in seasalt inputs.

4.10.2 Biology Summary

The epilithic diatom assemblage shows a significant linear change over time. The clearest shifts in proportional abundance have been reductions in a number of acidophilous *Eunotia* species, including *Eunotia exigua* (SWAP pH optima = 5.1) and *Tabellaria binalis* (SWAP pH optima = 4.7), and increases in species with slightly higher optima e.g. *Peronia fibula* (SWAP pH optima = 5.3).

T. binalis forms a larger proportion of the species assemblage in the sediment trap samples, but again it has declined proportionally over the monitoring period. The clearest increases in the traps have been in *Aulacoseira tethera* (SWAP pH optima = 5.0) and *Aulacoseira distans* var. *nivalis* (SWAP pH optima = 5.0).

The aquatic macroflora of Scoat Tarn is typical for an upland oligotrophic and acidified lake, being dominated mostly by isoetid taxa, and shows no indication of change over the monitoring period.

The macroinvertebrate fauna is typical of acidified upland lakes, being low in diversity and dominated by chironomids. However, the assemblage has changed significantly. The most obvious shifts in species composition are an increasing proportion of the predatory net-spinning caddis, *Cyrnus* sp. and *Polycentropus* sp.. Neither of these species were recorded at the site prior to 1996. These species are increasing in proportional abundance in several other AWMN lakes that are recovering chemically (see Monteith et al., 2005) and, as predators, are indicative of an expansion of the aquatic food chain.

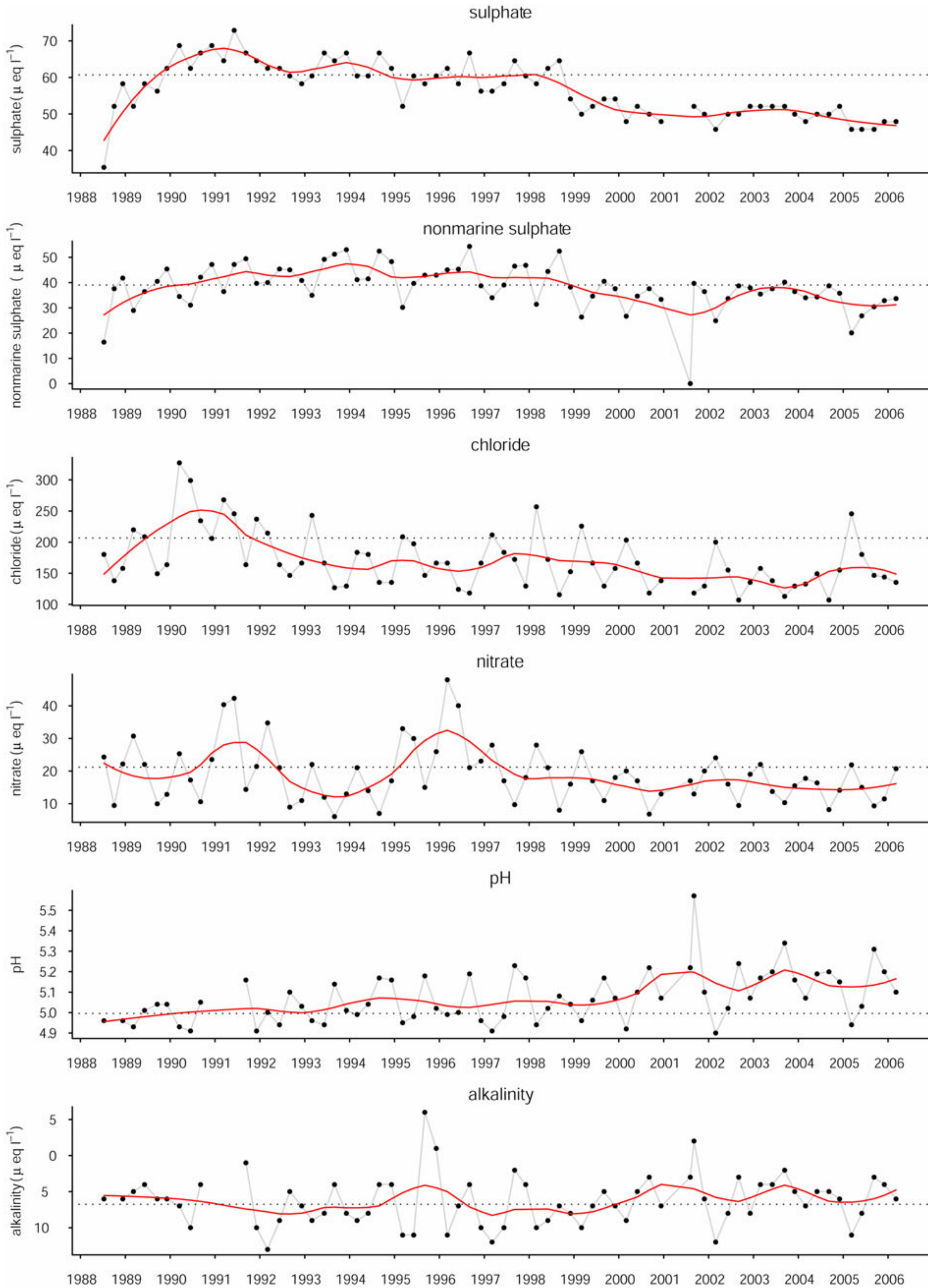
Brown trout densities in the outflow of Scoat Tarn have remained at very low levels throughout the monitoring period. However, juvenile fish have only been recorded in the outflow from 1998, since when they have been caught in all years other than 2001. This is indicative of recent spawning success in the locality. Juvenile brown trout have also been detected recently for the first time in the outflow of another strongly acidified AWMN lake, Blue Lough (Site 21).

4.10.3 Conclusions

Scoat Tarn was in an extremely acidified condition at the outset of monitoring, due in part to the strong contribution from NO_3 to the total acid load. A reduction in xSO_4 over the period, in conjunction with falling seasalt inputs and recent low NO_3 levels, has resulted in a large drop in labile aluminium concentration and a slight increase in pH. However, water chemistry is vulnerable to large seasalt deposition events that cause large oscillations in labile aluminium, pH and ANC. Mean ANC remains substantially below zero.

Although the lake remains acidified there are indications of gradual biological improvement. Diatom species with relatively low pH optima are being replaced by species with higher optima, predatory net-spinning caddis are increasing in proportional abundance and juvenile brown trout are now being recorded regularly, albeit in very low numbers, in the lake outflow.

Figure 4.10.1 Water Chemistry Summary Plots: Scoat Tarn



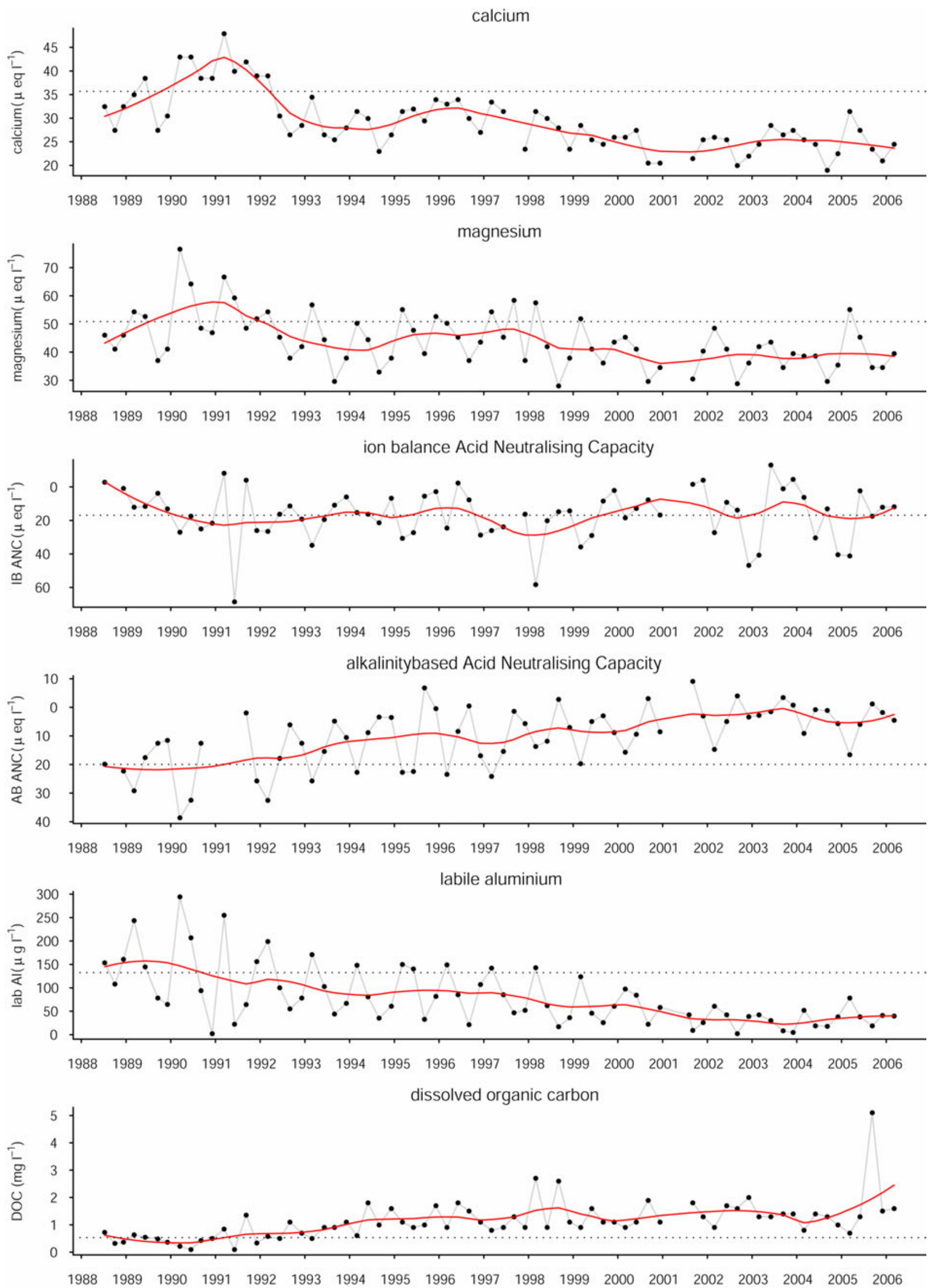

calcium
calcium (µ eq l⁻¹)
magnesium
magnesium (µ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (µ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l⁻¹)
labile aluminium
lab Al (µ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.10.1 Water Chemistry Summary Data and Trend Statistics: Scoat Tarn

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		μeq l^{-1}	μeq l^{-1}	μeq l^{-1}		μeq l^{-1}	μeq l^{-1}	μeq l^{-1}	μS cm^{-1}	μeq l^{-1}	μeq l^{-1}	μeq l^{-1}	μeq l^{-1}	μg l^{-1}	μg l^{-1}	mg l^{-1}
Jul 1988 - Mar 1993	mean	39.2	21.2	206.6	5.00	-6.8	-16.9	-20.0	37.6	35.7	50.8	178.4	8.2	144.7	132.5	0.5
	st. dev	7.6	10.0	53.0	0.07	2.9	17.2	10.3	6.4	6.1	10.1	39.1	2.3	79.7	79.6	0.3
	min	16.6	9.0	138.2	4.91	-13.0	-68.5	-38.7	28.0	26.4	37.0	134.9	2.6	12.2	2.0	0.1
	max	49.6	42.3	327.2	5.16	-1.0	8.2	-2.0	49.0	47.9	76.5	265.4	13.0	300.0	293.8	1.4
Apr 1993 - Mar 1998	mean	43.8	21.3	165.3	5.05	-6.5	-18.2	-10.8	32.5	29.5	45.0	149.9	6.4	98.2	88.8	1.2
	st. dev	6.9	10.9	35.8	0.10	4.6	13.7	9.4	5.0	3.4	8.2	18.9	1.7	42.8	44.1	0.5
	min	30.3	6.0	118.5	4.91	-12.0	-58.3	-24.2	24.0	23.0	29.6	126.2	2.6	32.0	21.0	0.6
	max	54.3	48.0	256.7	5.23	6.0	2.3	6.8	41.0	33.9	58.4	187.1	8.9	160.0	150.0	2.7
Apr 1998 - Mar 2003	mean	36.4	16.5	152.8	5.11	-6.3	-17.4	-5.5	28.9	24.7	38.8	134.6	6.1	57.3	47.2	1.4
	st. dev	6.5	5.3	32.8	0.15	3.2	14.0	7.4	4.0	2.9	6.7	23.7	1.3	31.2	30.4	0.5
	min	25.0	6.8	107.2	4.90	-12.0	-46.8	-19.7	23.0	20.0	28.0	95.7	4.1	13.0	2.0	0.9
	max	52.5	26.0	225.7	5.57	2.0	3.9	9.1	37.0	29.9	51.8	178.4	7.7	134.0	124.0	2.6
Apr 2003 - Mar 2006	mean	33.4	14.5	148.1	5.14	-5.5	-13.2	-3.5	28.8	25.1	39.1	128.7	5.5	41.9	32.2	1.6
	st. dev	5.5	4.3	36.1	0.12	2.4	16.9	5.4	5.8	3.4	6.6	21.8	1.0	19.4	20.4	1.1
	min	20.1	8.1	107.2	4.94	-11.0	-41.1	-16.5	23.0	19.0	29.6	100.1	3.6	15.0	5.0	0.7
	max	40.2	21.9	245.4	5.34	-2.0	13.0	3.4	45.0	31.4	55.1	178.4	7.2	82.0	78.0	5.1
Seasonal-Kendall statistics	Sen-slope	-0.489	-0.214	-3.056	0.009	0.021	0.021	0.997		-0.606	-0.598				-6.818	0.067
	P- val	**0.010**	0.072	**0.002**	**<0.001**	0.181	0.577	**<0.001**		**<0.001**	**<0.001**				**0.000**	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.10.2 Epilithic Diatom Percentage Abundance Summary: Scoat Tarn

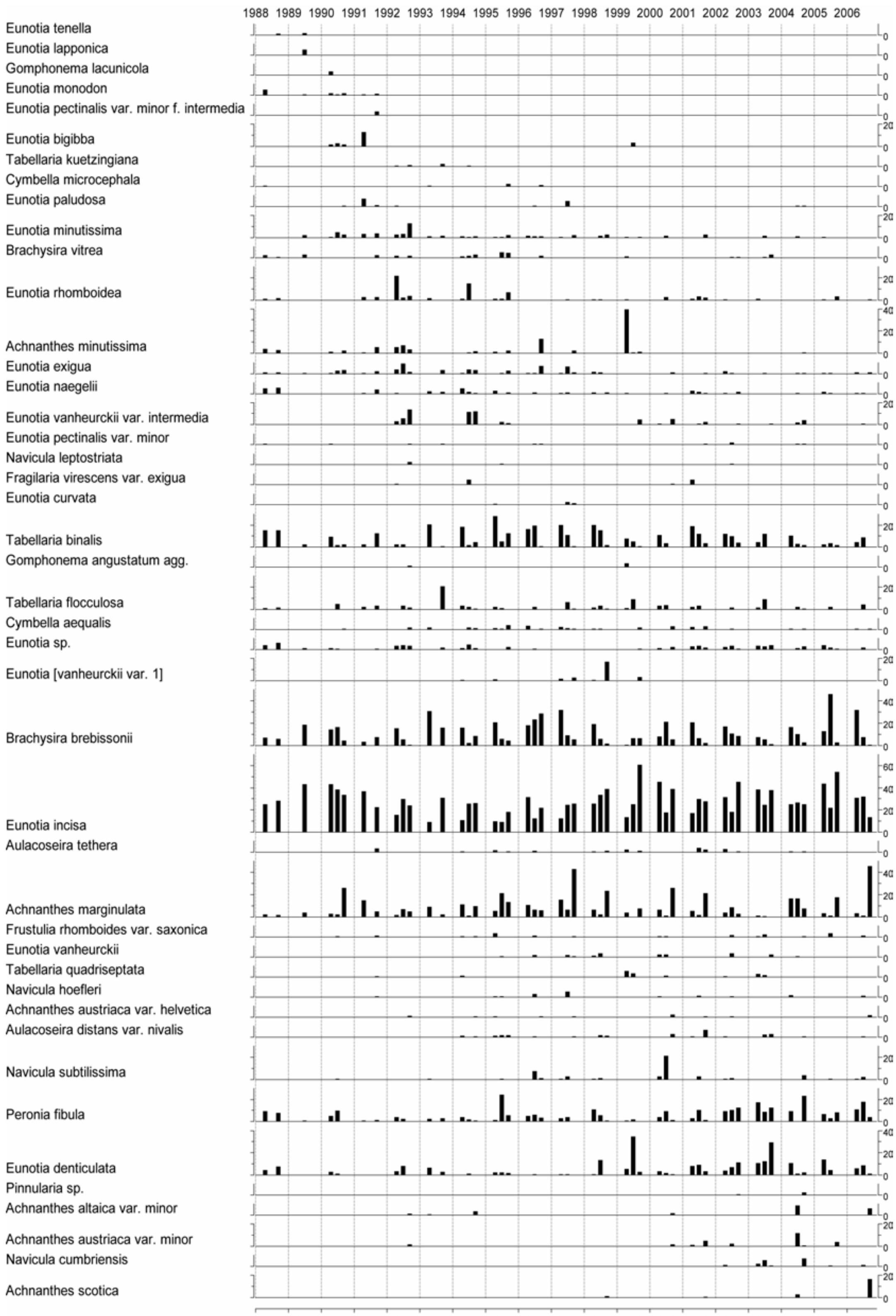


Figure 4.10.3 Aquatic Macrophyte Species Scores (1-5): Scoat Tarn

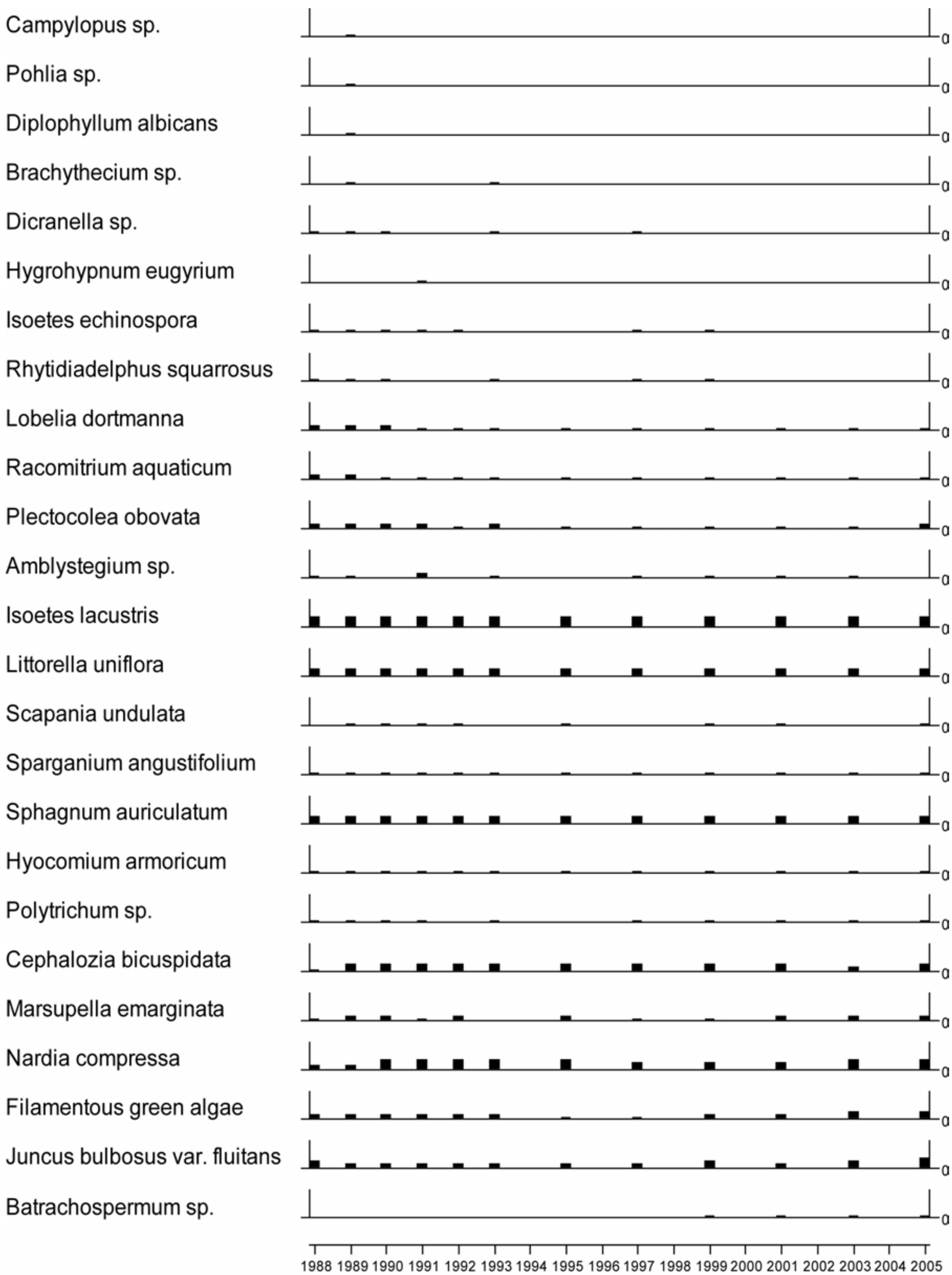
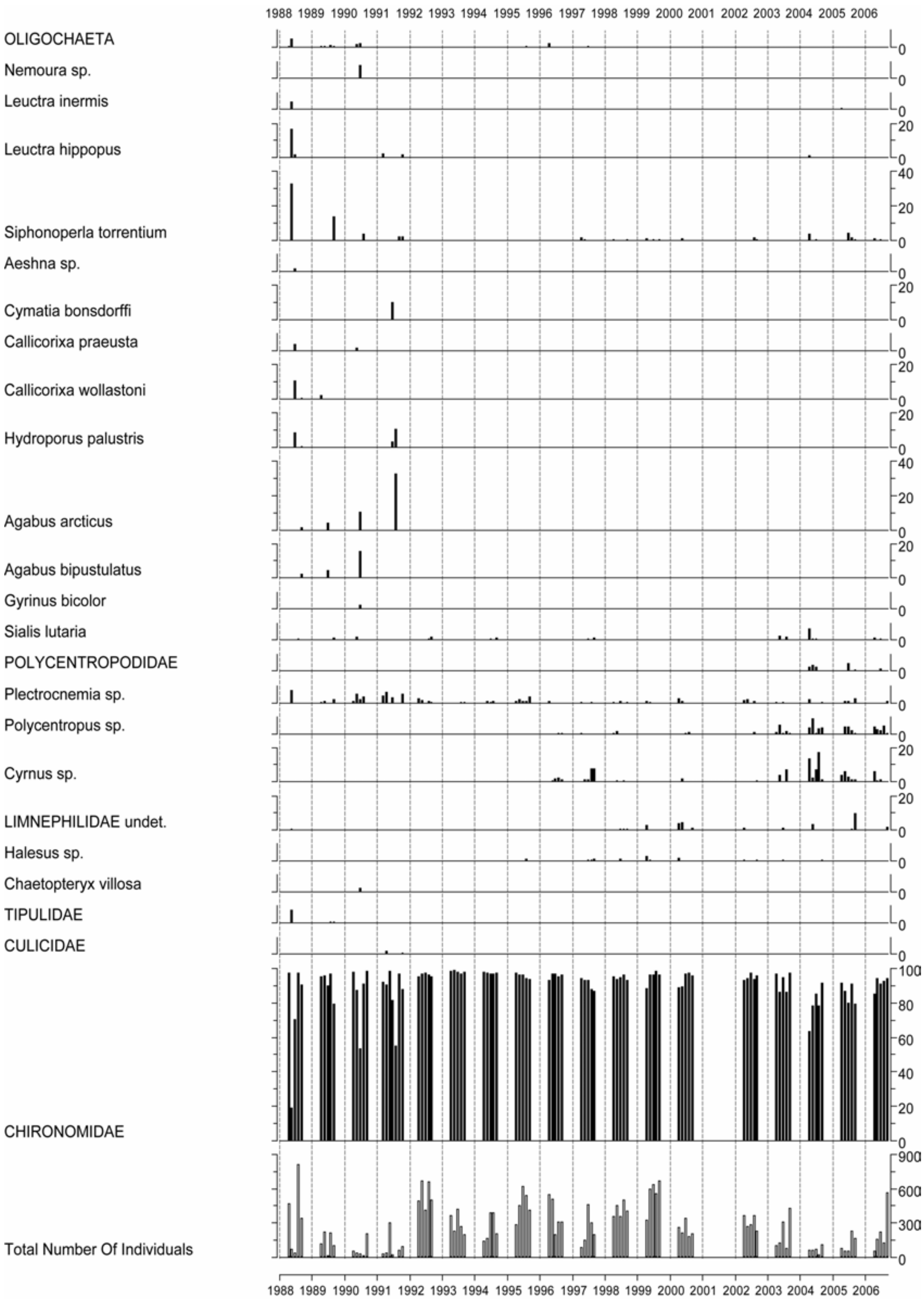


Figure 4.10.4 Macroinvertebrate Percentage Abundance Summary: Scoat Tarn

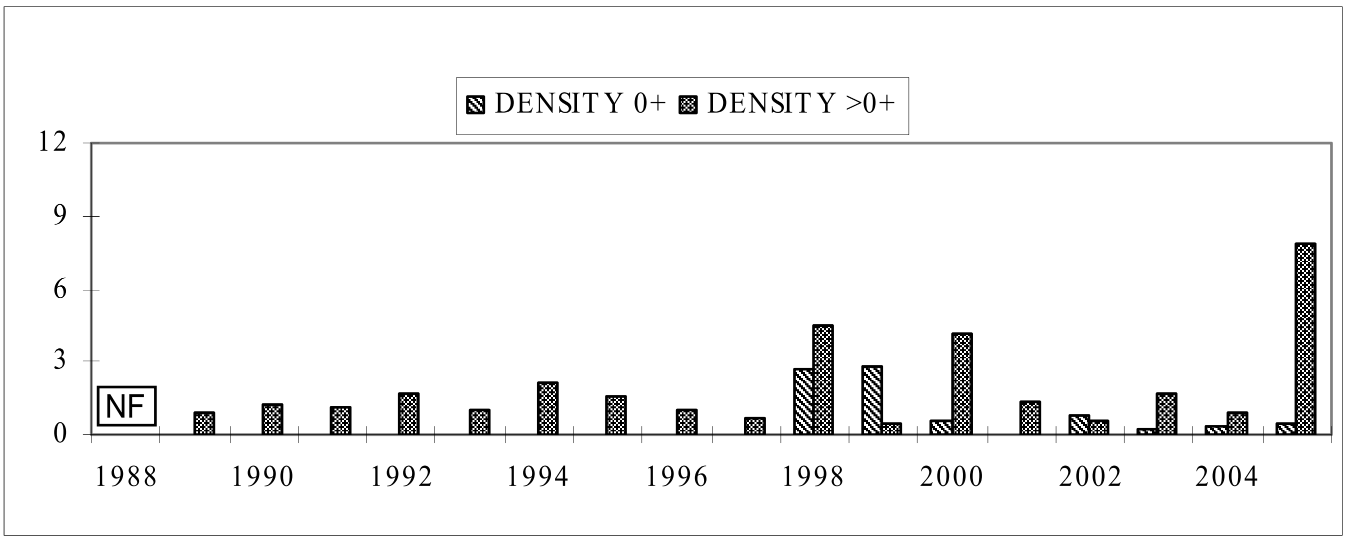


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.10.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Scoat Tarn

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1418.54	156	54.7	45.3	0.07	0.40	0.001	0.016
Invertebrates	605.86	45	65.7	34.3	0.15	0.73	0.001	0.009

Figure 4.10.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Scoat Tarn



NF = Not fished

Figure 4.10.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Scoat Tarn

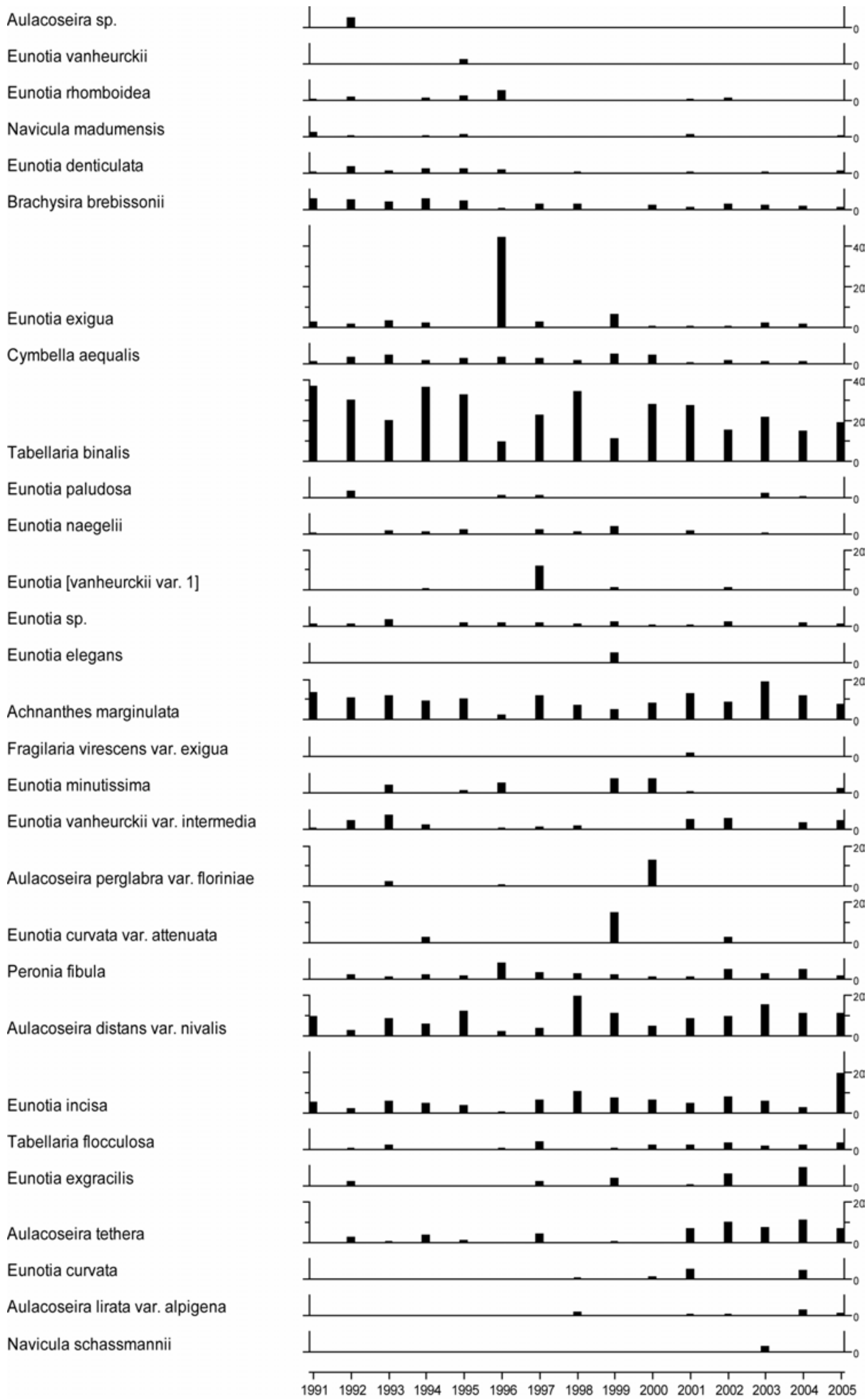
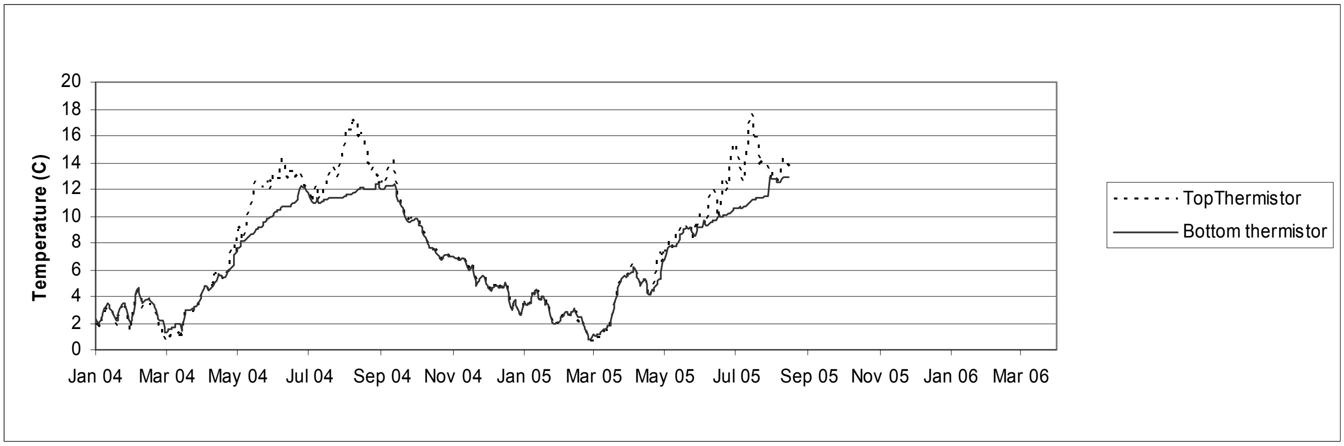


Figure 4.10.7 Thermistor Data: Scoat Tarn



2005/2006 thermistors still in situ – data pending.

4.11 Burnmoor Tarn

4.11.1 Water Chemistry Summary

Burnmoor Tarn lies 7 km to the south of Scoat Tarn (site 10) and is 350 m lower in altitude (i.e. 250 m a.s.l.). It was selected for the Network to provide a less acid-sensitive comparison with Scoat Tarn in this relatively high deposition region. Palaeoecological analysis provides no obvious indication that the lake has acidified significantly. Over the first five years of monitoring the mean calcium concentration was 95.8 µeq l^{-1} and mean alkalinity was 46.8 µeq l^{-1}. The mean 1988-1993 xSO_4 concentration of 57.1 µeq l^{-1} was almost 50% higher than for Scoat Tarn, while NO_3 concentrations were low, averaging 5.1 µeq l^{-1} and falling below the limit of detection each summer. Labile aluminium concentration was normally below the limit of detection.

Over the course of monitoring, xSO_4 concentration shows the pattern typical for the wider Network, with a substantial decline occurring in the second half of the 1990s. Since 2000 concentrations have stabilised and the 2003-2006 mean of 44.7 µeq l^{-1} is approximately 20% below that for the first five years. Nitrate concentrations have continued to show strong seasonality throughout the record and no long term trend.

Chloride concentrations follow those of many other sites in the southern half of the Network with a very large peak in the early 1990s that has not recurred. Base cations also peaked in the early 1990s reflecting additional input from marine sources. However, since then concentrations have remained relatively stable despite the reduction in xSO_4. This perhaps reflects a balancing effect provided by a rise in organic acids (DOC concentrations have more than doubled as SO_4 and Cl concentrations have declined). Ion balance ANC shows no long-term trend although the mean for the 2003-2006 period is the highest to date.

The main response to falling xSO_4 has been a gradual increase in alkalinity – averaging 71.9 µeq l^{-1} over the period 2003-2006. Burnmoor Tarn data therefore suggest that even sites that have not undergone significant pH change can show signs of recovery in acidity under a reduced sulphur load.

4.11.2 Biology Summary

The epilithic diatom flora has changed significantly over the monitoring period and this can be linked to recovery from acidification. Several species have increased in proportional abundance, particularly *Denticula tenuis* (SWAP pH optima = 6.8), *Cymbella microcephala* (SWAP pH optima = 6.3), *Cymbella cesatii* (SWAP pH optima = 6.4) and *Cyclotella kuetzingiana* var. *minor* (optima not known). The latter species is planktonic and its apparent expansion in the epilithon reflects the deposition of dead or dormant cells around the lake littoral. The clearest reduction in abundance is for *Nitzschia perminuta* (SWAP pH optima = 5.7). While the relative pH optima of increasing and declining species is indicative of a pH increase, the water chemistry data demonstrates that no such change has occurred. Rather it seems likely that these changes represent a response to an increase in bicarbonate alkalinity over the monitoring period.

While showing some common patterns with the epilithon data, the sediment trap data provide a clearer indication of planktonic changes within the lake; by 2003 *C. kuetzingiana* var. *minor* represented over half the cells in the assemblage. The most notable reduction has been in the deep water benthic species

Fragilaria virescens var. *exigua* (SWAP pH optima = 5.7). These data represent proportional abundance only and do not provide any indication of trends in productivity in individual taxa so it is not possible to conclude whether or not this switch in the relative abundance of benthic and planktonic taxa might indicate competition for light, with the expanding plankton shading out the deeper water species.

The aquatic macroflora of Burnmoor Tarn has been dominated throughout by isoetid taxa but has also included acid-sensitive species including *Myriophyllum alterniflorum* and the charophyte *Nitella flexilis* that are absent from the more acid lakes on the Network. A second sensitive charophyte, *Chara virgata*, was first recorded in 2003 and again in 2005.

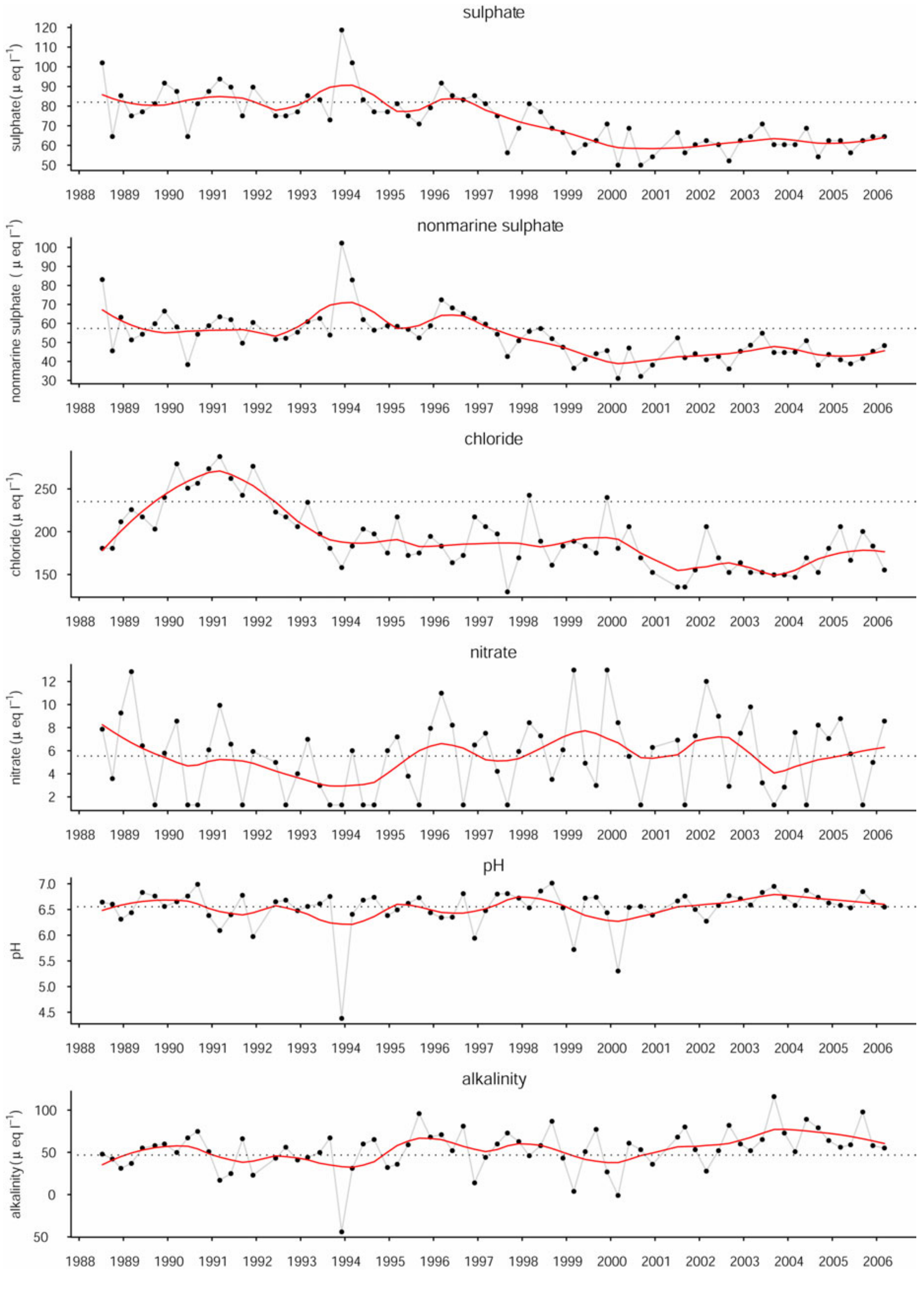
Littoral macroinvertebrates also show significant linear change. The data show three phases in the assemblage. Between 1988 and 1991 few individuals were caught and the assemblage was dominated by oligochaetes and chironomids. There then followed an increase in the total catch, with an increase in the acid-sensitive species *Gammarus lacustris*, and the acid-tolerant mayfly family the Leptophelbiidae. The acid-sensitive mayfly *Caenis luctuosa* was first recorded in 2002 since when it has formed a significant part of the assemblage. These data also demonstrate there has been a progressive increase in the total number of individuals caught, although there is no obvious change in total species richness.

Brown trout density in the outflow of Burnmoor Tarn has remained low throughout the monitoring period. This is surprising given the relatively benign chemistry of the lake. However, the outflow stream is affected periodically by highly acidic discharge when a stream draining Scafell spills into it during periods of high rainfall. The outflow population, therefore, are perhaps influenced by effects across a wider, more acid-sensitive, catchment than that of Burnmoor Tarn alone.

4.11.3 Conclusions

Burnmoor Tarn is a relatively well buffered lake that provided no clear indication of having acidified according to palaeoecological diatom-pH reconstructions. However, alkalinity has increased over the period that xSO_4 has fallen and this may account for a major structural shift in the algal (i.e. diatom) community of the site with a proportional increase in planktonic over benthic species. A second acid-sensitive charophyte was recorded only recently. Changes in the macroinvertebrate community are more ambiguous with regard to any link with changing acidity and there is no indication of any change in the brown trout population of the lake outflow that remains at low density.

Figure 4.11.1 Water Chemistry Summary Plots: Burnmoor Tarn



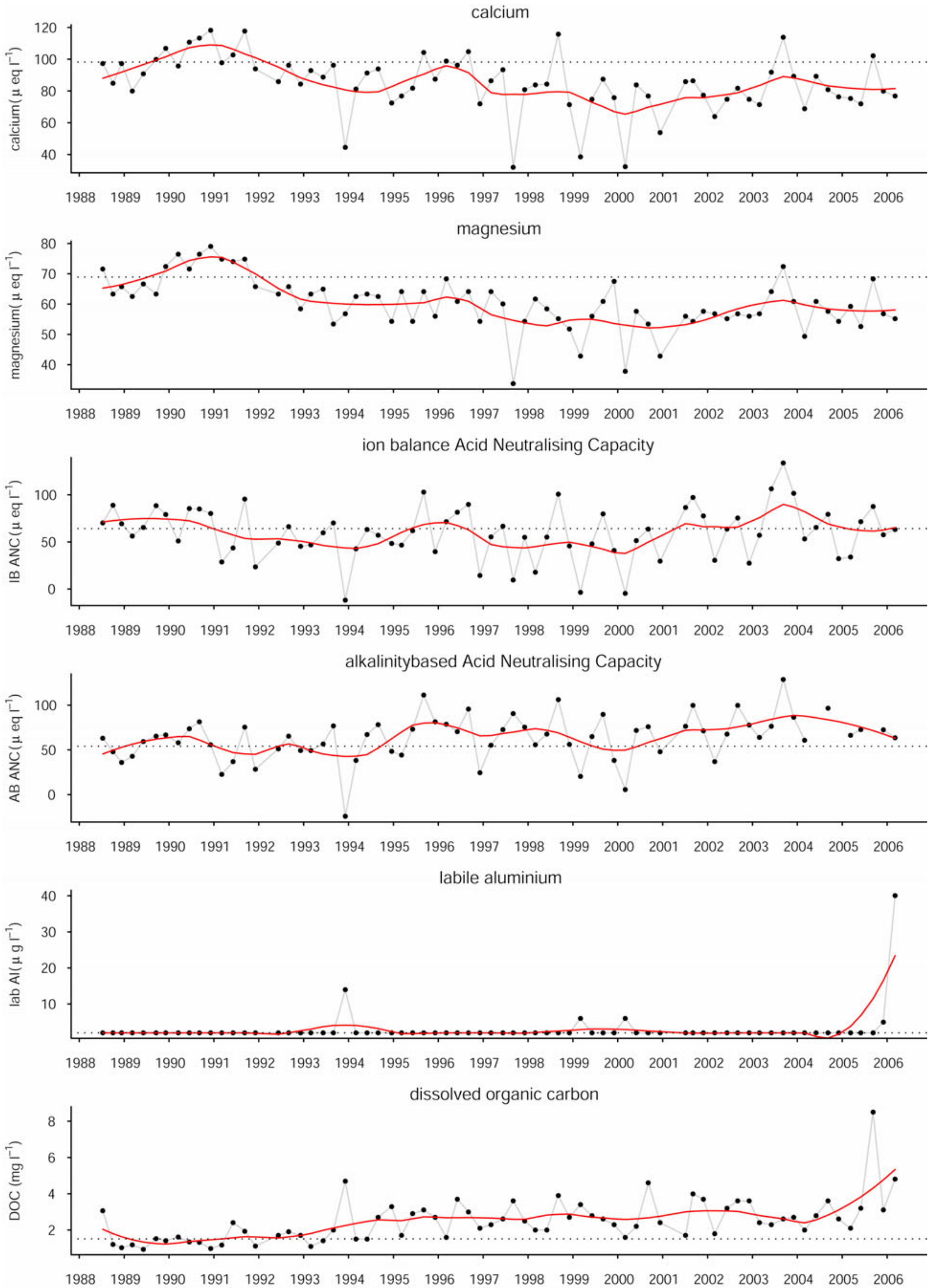

calcium
calcium(µ eq l^{-1})
magnesium
magnesium(µ eq l^{-1})
ion balance Acid Neutralising Capacity
IB ANC (µ eq l^{-1})
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l^{-1})
labile aluminium
lab Al(µ g l^{-1})
dissolved organic carbon
DOC (mg l^{-1})
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.11.1 Water Chemistry Summary Data and Trend Statistics: Burnmoor Tarn

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		µeq l^{-1}	µeq l^{-1}	µeq l^{-1}		µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µS cm^{-1}	µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µeq l^{-1}	µg l^{-1}	µg l^{-1}	mg l^{-1}
Jul 1988 - Mar 1993	mean	57.1	5.6	233.9	6.50	46.8	64.1	54.1	44.5	95.8	67.6	208.6	9.2	7.6	2.3	1.5
	st. dev	9.2	3.3	31.9	0.34	15.6	21.2	16.0	5.2	15.4	8.3	20.7	2.9	9.1	1.1	0.5
	min	38.4	1.3	180.5	5.50	17.0	23.6	22.6	37.3	49.4	42.8	169.7	2.6	2.0	2.0	0.9
	max	83.2	12.9	287.7	6.99	75.0	95.3	81.4	53.9	118.3	79.0	243.6	15.3	42.0	7.0	3.1
Apr 1993 - Mar 1998	mean	62.0	4.7	186.8	6.45	51.2	52.1	63.5	38.8	83.3	58.9	176.0	6.8	7.7	2.6	2.5
	st. dev	12.7	3.1	24.8	0.53	29.4	28.0	29.1	4.9	18.2	7.5	17.4	2.2	6.9	2.7	0.9
	min	42.7	1.3	129.8	4.38	-44.0	-11.8	-24.4	23.0	31.9	33.7	126.2	2.6	2.0	2.0	1.4
	max	102.2	11.0	242.6	6.81	96.0	103.1	111.3	48.0	104.8	68.3	208.8	10.2	27.0	14.0	4.7
Apr 1998 - Mar 2003	mean	43.5	6.8	173.6	6.51	51.1	53.8	65.1	35.6	74.3	54.4	160.0	7.1	8.4	2.4	2.9
	st. dev	6.8	3.6	25.9	0.40	24.3	29.7	26.5	3.7	18.3	6.8	20.3	1.2	7.6	1.3	0.9
	min	31.2	1.3	135.4	5.30	-1.0	-4.7	5.5	30.0	32.4	37.8	121.8	4.9	2.0	2.0	1.6
	max	57.4	13.0	239.8	7.01	87.0	100.6	106.3	43.0	115.8	67.5	213.2	8.9	33.0	6.0	4.6
Apr 2003 - Mar 2006	mean	44.7	5.1	167.6	6.69	71.9	73.8	80.5	37.2	84.7	59.3	157.7	7.1	7.3	5.4	3.4
	st. dev	4.9	3.0	20.6	0.40	20.0	30.0	21.3	3.1	13.2	6.6	11.3	0.8	11.7	10.9	1.8
	min	38.2	1.3	146.7	6.53	51.0	32.0	60.9	33.0	68.9	49.4	143.6	5.6	2.0	2.0	2.0
	max	54.8	8.8	205.9	6.95	116.0	133.9	128.8	44.0	113.8	72.4	174.0	8.7	43.0	40.0	8.5
Seasonal-Kendall statistics	Sen-slope	-1.145	0.078	-3.743	0.007	1.217	-0.097	1.438		-1.123	-0.711				0.000	0.128
	P- val	**0.002**	0.431	**<0.001**	0.315	**0.012**	0.793	**0.007**		**0.008**	**0.001**				0.069	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.11.2 Epilithic Diatom Percentage Abundance Summary: Burnmoor Tarn

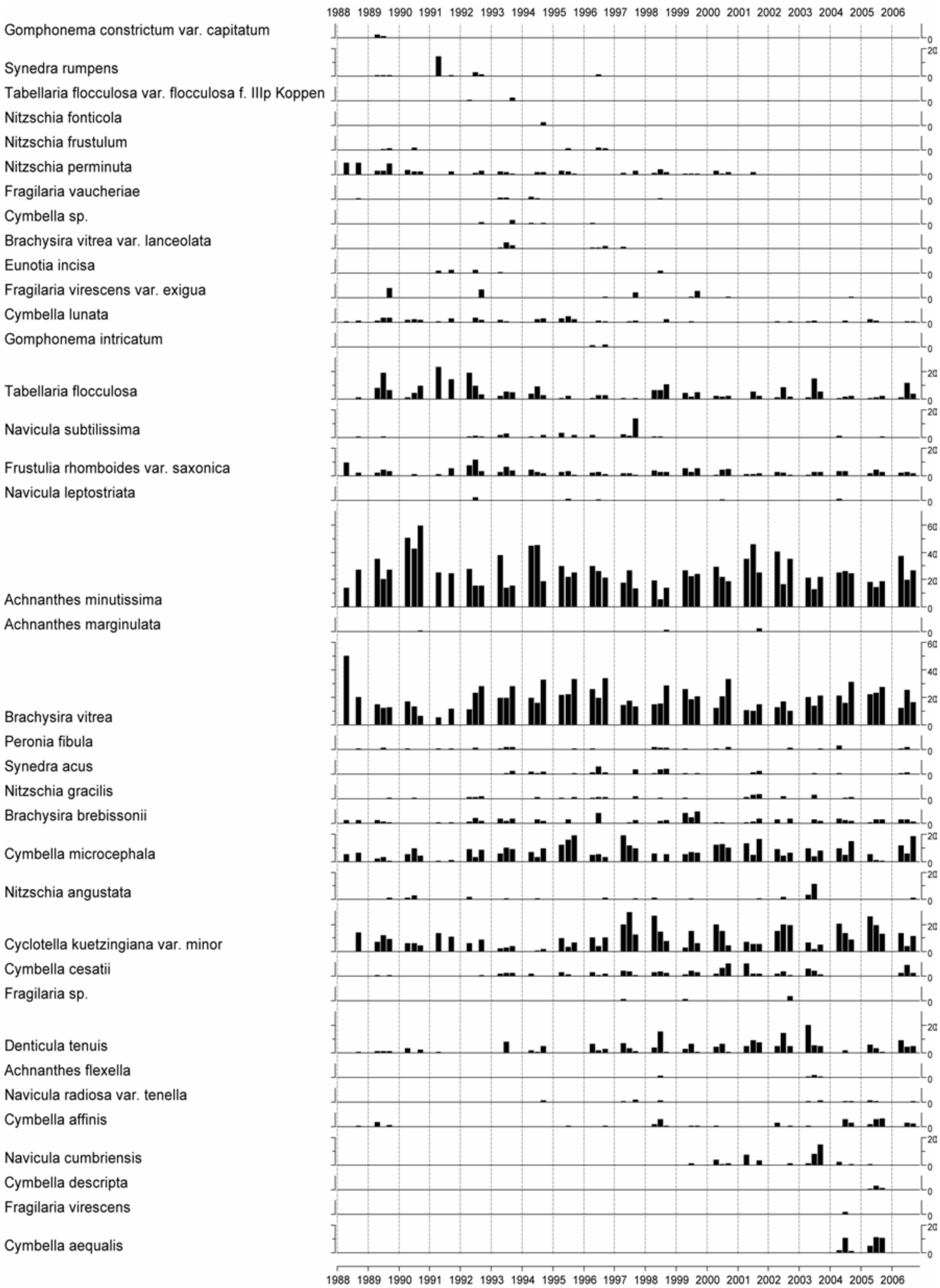


Figure 4.11.3 Aquatic Macrophyte Species Scores (1-5): Burnmoor Tarn

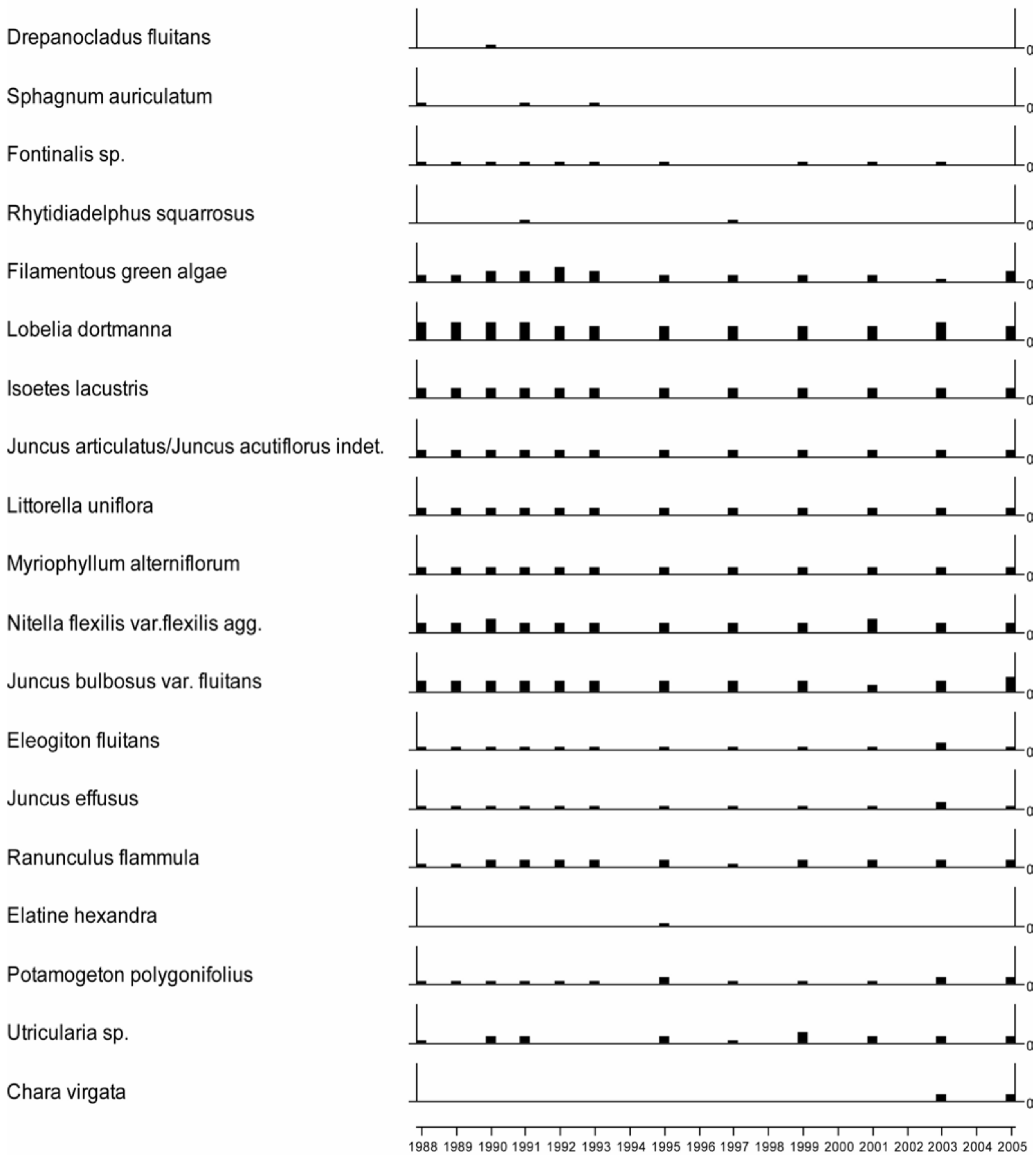
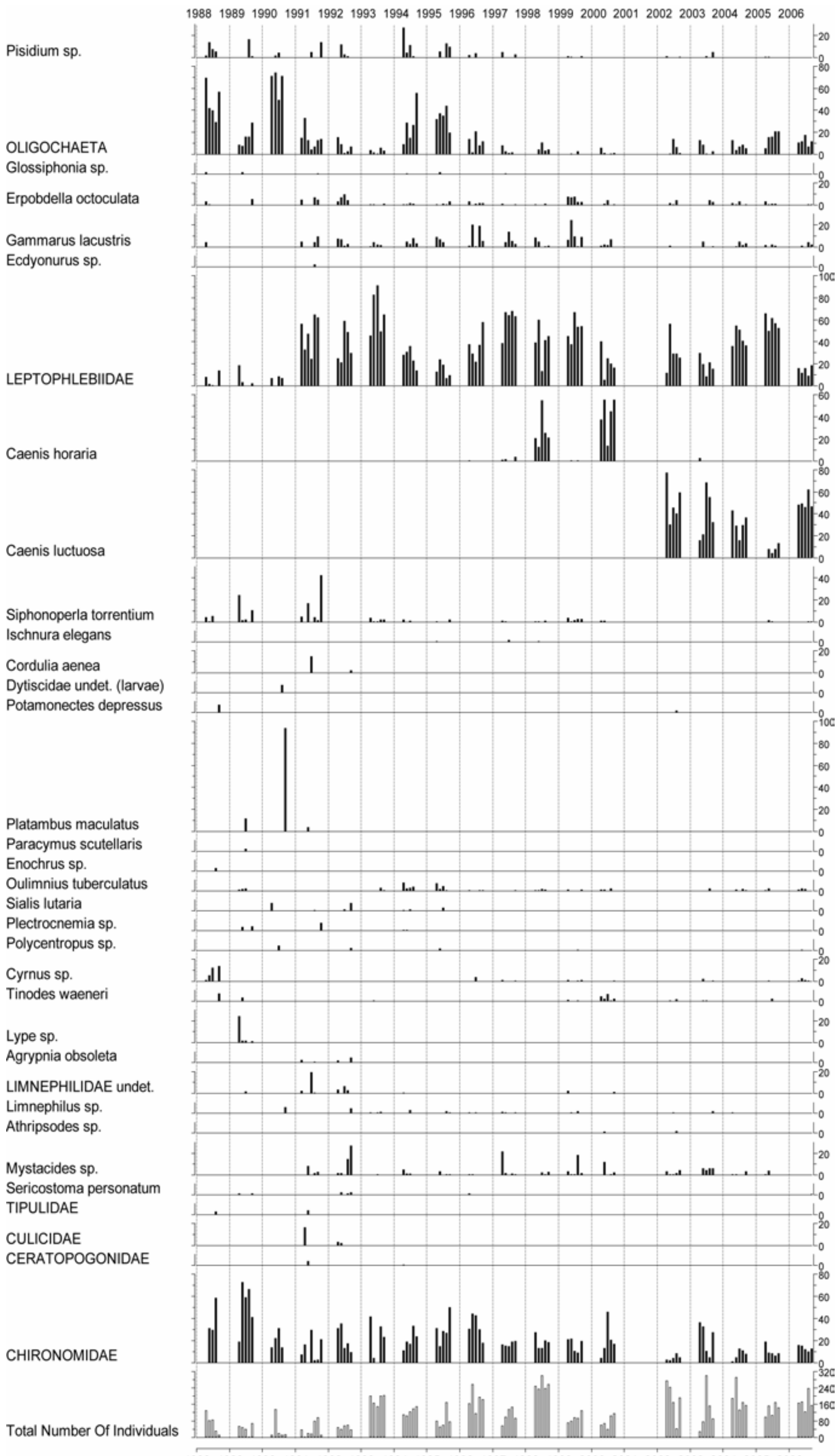


Figure 4.11.4 Macroinvertebrate Percentage Abundance Summary: Burnmoor Tarn

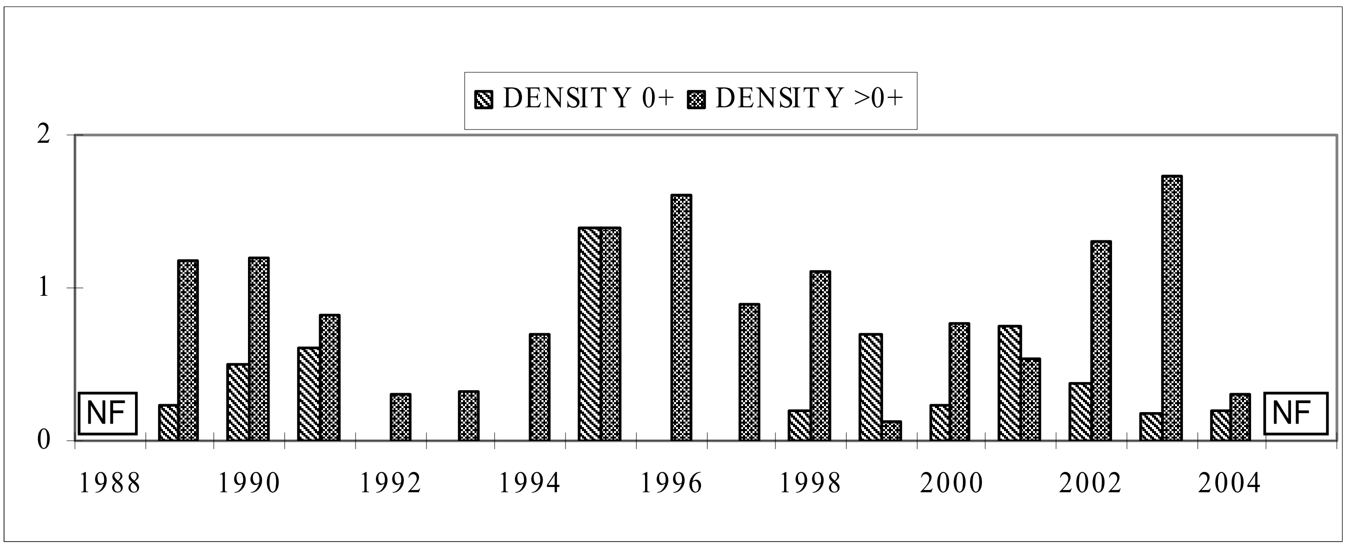


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.11.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Burnmoor Tarn

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1081.93	147	40.7	59.3	0.10	0.93	0.001	0.015
Invertebrates	3334.84	60	37.7	62.3	0.17	0.75	0.001	0.015

Figure 4.11.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Burnmoor Tarn



NF = Not fished

Figure 4.11.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Burnmoor Tarn

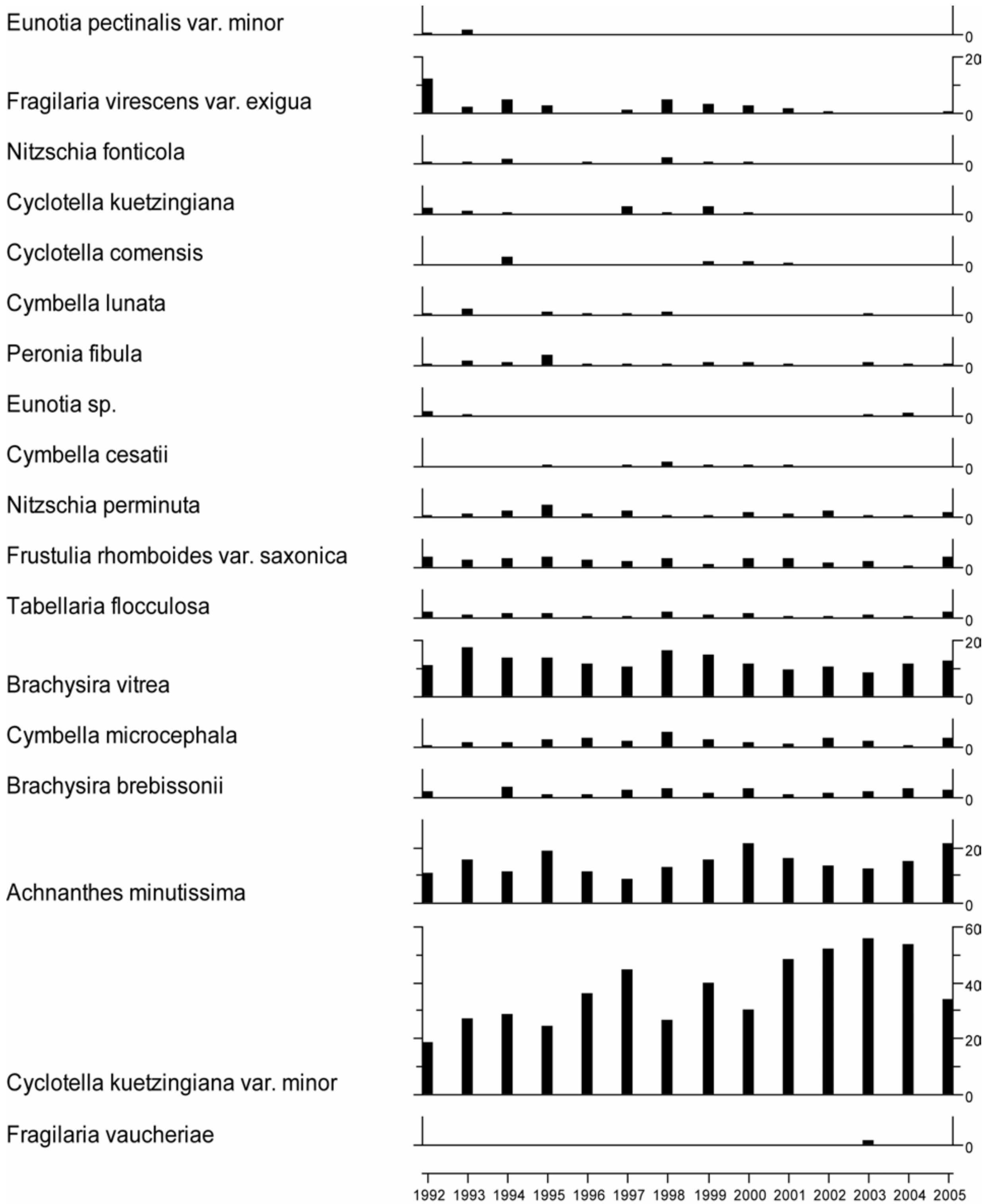
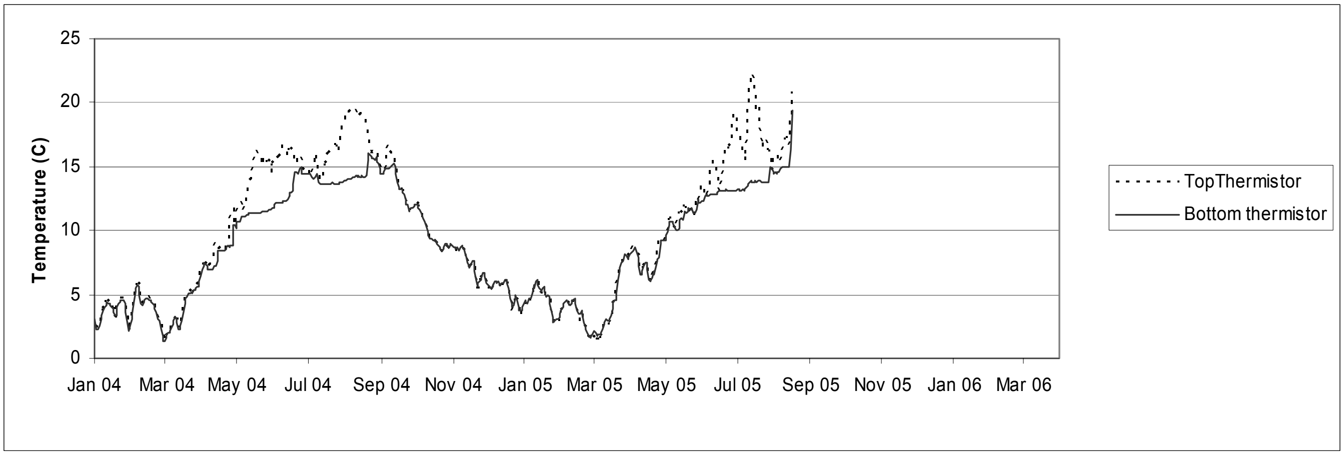


Figure 4.11.7 Thermistor Data: Burnmoor Tarn



2005/2006 thermistors still in situ – data pending

4.12 River Etherow

4.12.1 Water Chemistry Summary

The River Etherow is the most atmospherically impacted site on the AWMN, exhibiting higher concentrations of xSO_4 and NO_3 than any other site. It is also the most chemically variable site on the Network with pH varying from above 6.5, and alkalinity greater than 100 μeq l^{-1} during base flow conditions, to a pH of less than 4.5 and alkalinity substantially below 0 μeq l^{-1} during high flow. Mean xSO_4 and NO_3 concentrations for the 1988-1993 period were 257.7 and 44.4 μeq l^{-1}. While mean pH over the first five years was not unusual for AWMN sites, the minimum recorded pH was 3.79 and labile aluminium concentrations reached a maximum of 356.0 μg l^{-1}.

Unusually for AWMN sites, xSO_4 concentration has fallen roughly linearly over the past eighteen years and shows the strongest downward trend on the Network (i.e. 7.1 μeq l^{-1} yr^{-1}). However, mean concentration for 2003-2006 was still 168.2 μeq l^{-1}, almost thirty times higher than that for Loch Coire nan Arr in northwest Scotland.

The high NO_3 concentrations in the River Etherow show strong inter-annual variability but no overall trend. Despite these high concentrations NO_3 still only comprises around 20% of the net contribution of xSO_4 and NO_3 to acidity, although this contribution is climbing.

Chloride concentrations in the River Etherow are high for an inland site and may be influenced to an extent by road salt which may explain the relative lack of temporal variability.

Mean dissolved organic carbon concentrations have increased by about 50% over the period, from a mean of 4.6 mg l^{-1} over the first five years to 6.7 mg l^{-1} for the period 2003-2006. However, while concentrations at base flow (i.e. DOC minima) show only a gradual absolute increase, concentrations at high flow (i.e. DOC maxima) have increased substantially, with levels regularly exceeding 15 mg l^{-1} in the latter half of the record. This is consistent with a hypothesised control of sulphate deposition on the solubility of soil organic matter in the upper layers of the soil profile.

Base cation concentrations have declined progressively, although at slower rate than the reduction in xSO_4. Ion-balance ANC shows a steady increase and the 2003-2006 mean of 74.2 μeq l^{-1} yr^{-1} is more than 50 μeq l^{-1} higher than for the first five years. Despite this the River Etherow is still subject to severe acid episodes, as reflected by the minimum ANC during the 2003-2006 period of -89.9 μeq l^{-1}.

Mean pH shows no obvious trend over the period, but there has been a very clear rise in pH minima (associated with high flow events) since 1996, consistent with the period of strongest decline in xSO_4. pH has not fallen below 4.0 since 1998. Similarly, labile aluminium maxima have fallen dramatically, and have not exceeded 100 μg l^{-1} since 1998.

4.12.2 Biology Summary

The epilithic diatom community of the River Etherow shows greater inter-annual variability than any other site on the Network, reflecting the large hydrologically driven variability in acidity. Despite this the flora also provides clear evidence of a biological response to falling acidity levels. The most notable change has been a reduction in the acidophilous/acidobiontic species *Eunotia exigua* (SWAP pH optima = 5.1) in recent years and progressive increases in the more acid-sensitive species *Gomphonema angustatum* (SWAP pH optima = 5.8) and *Achnanthes saxonica* (SWAP pH optima = 5.7).

Like several of the more acidic streams on the Network the aquatic macrophyte flora in the survey stretch has been restricted largely to one acid tolerant and ubiquitous liverwort species, *Scapania undulata*. Its cover is sensitive to occasional very high flow events which scour the stream bed, and there is some indication of an overall downward trend over the full monitoring period that could result from an increased frequency of these episodes. Recently, however two acid-sensitive mosses have also been recorded. *Fontinalis antipyretica* was detected in 2000 and 2001 but disappeared following a major storm event (this species was recorded again in the same location in 2007). A very small amount of the acid-sensitive moss *Hygrohypnum ochraceum*, which is otherwise largely confined to the circumneutral AWMN streams, was first recorded in 2005 (and detected again in 2007).

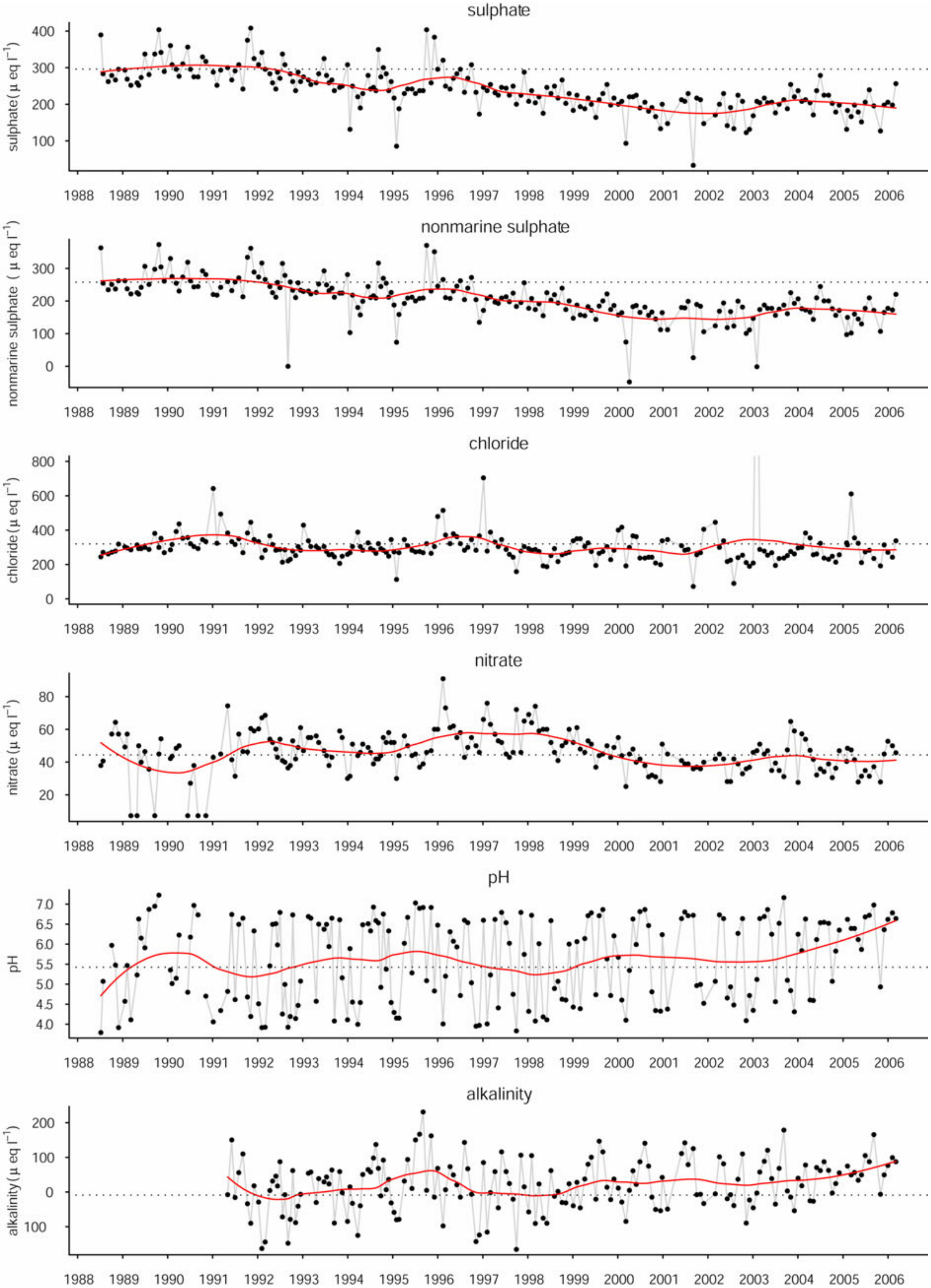
The macroinvertebrate community shows very clear and significant linear change over the monitoring period. The acid-sensitive stonefly grazer *Brachyptera risi* and the stonefly predator *Siphonoperla torrentium* occurred in low numbers in few samples only prior to 1995 but have become increasingly more common and relatively abundant since. There has also been an increase in the relative abundance of the stonefly grazer *Amphinemura sulcicollis*, which is generally considered to be more acid tolerant. Unusually for the Network there has been a sustained increase in the numbers of individual animals caught and a doubling in the number of species. The acid-sensitive mayfly species, *Baetis* sp., has been recorded sporadically throughout much of the monitoring period but has not persisted, perhaps due to the strong episodicity of the river. Overall, however, these observations are consistent with the early stages of biological recovery.

On sampling in 1989 the site was found to be fishless. As the site is situated above a fishless reservoir which prohibits any recolonisation from downstream, no further fish monitoring has been conducted.

4.12.3 Conclusions: River Etherow

The River Etherow is the most atmospherically contaminated and chemically variable site on the Network. Non-marine sulphate concentrations have declined sharply over the monitoring period and, while this has had little impact on mean pH, there has been a clear reduction in labile aluminium concentrations and in the severity of acid episodes during high flow periods. Nitrate concentrations have remained relatively high throughout the last eighteen years but remain less important than xSO_4 as an acidifying anion. The reduction in the severity of episodes appears to have had biological effects, with strong recovery responses evident in epilithic diatoms and macroinvertebrates, and evidence for the recent establishment of two acid-sensitive mosses. Despite these very obvious signs of biological recovery from acidification, the site remains heavily stressed by both sulphate and nitrate, and the rate of recovery is likely to remain firmly capped by peak acidity levels at high flow.

Figure 4.12.1 Water Chemistry Summary Plots: River Etherow



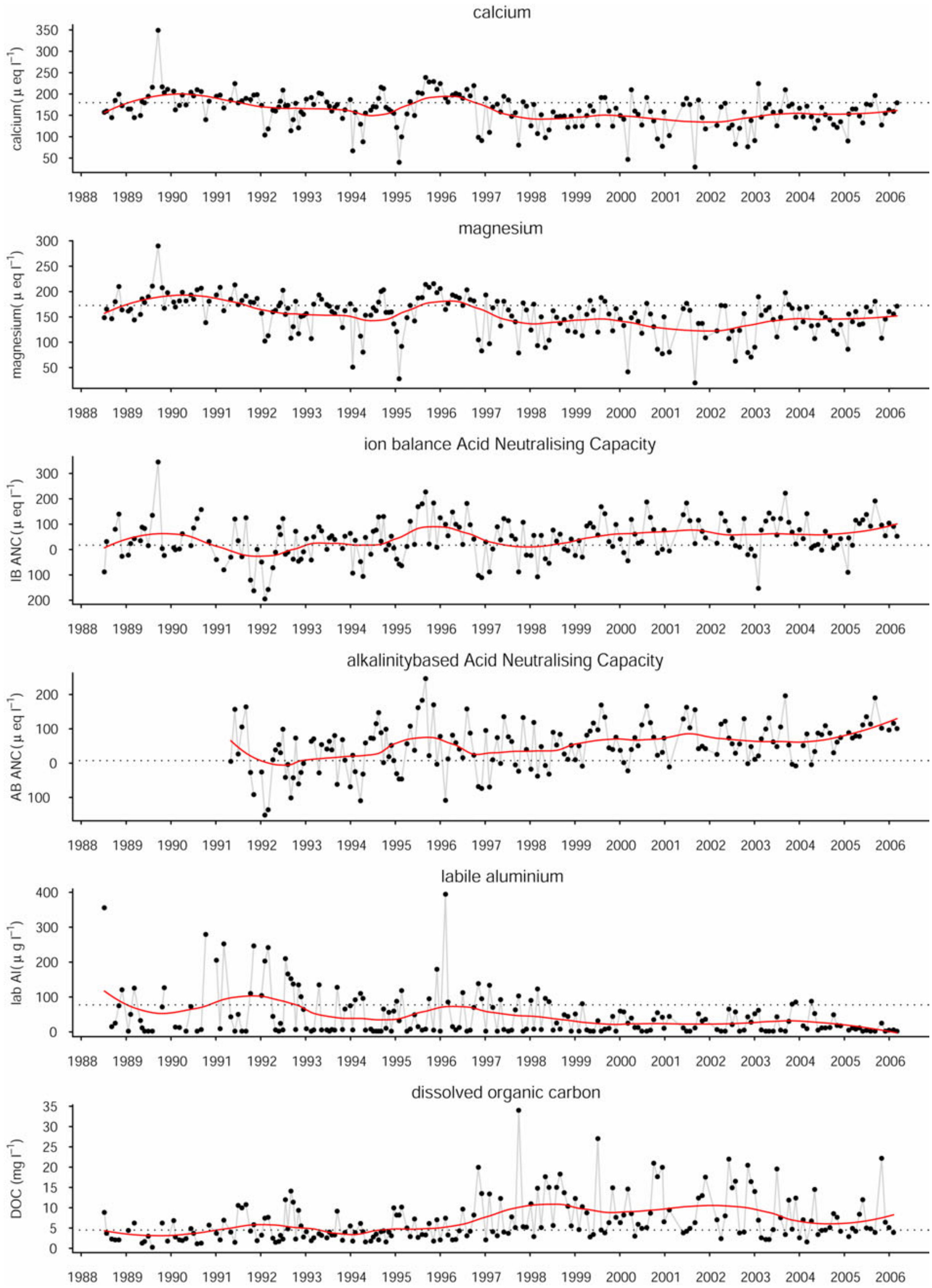

calcium
calcium (μ eq l^{-1})
magnesium
magnesium (μ eq l^{-1})
ion balance Acid Neutralising Capacity
IB ANC (μ eq l^{-1})
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l^{-1})
labile aluminium
lab Al (μ g l^{-1})
dissolved organic carbon
DOC (mg l^{-1})
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.12.1 Water Chemistry Summary Data and Trend Statistics: River Etherow

Determinand period		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Jul 1988* - Mar 1993	mean	257.7	44.4	319.9	5.43	-8.8	17.1	7.5	84.9	179.6	172.6	303.8	19.9	151.7	80.5	4.6
	st. dev	53.8	16.0	69.5	1.06	79.5	90.3	82.0	18.1	34.6	31.0	51.5	3.8	143.4	92.1	3.3
	min	-22.9	7.1	214.4	3.79	-163.0	-194.6	-151.9	32.8	103.8	102.0	213.2	11.0	2.0	2.0	0.3
	max	372.8	74.3	643.2	7.22	150.0	344.8	163.5	137.7	349.3	289.6	526.4	31.2	580.0	356.0	14.1
Apr 1993 - Mar 1998	mean	219.6	51.9	304.8	5.60	18.4	41.2	39.7	85.2	167.2	157.8	304.8	20.1	130.5	50.1	5.8
	st. dev	47.4	11.5	78.0	1.07	82.1	78.7	73.7	16.3	41.8	40.0	82.0	4.9	111.0	65.4	5.2
	min	73.6	30.0	112.8	3.83	-165.0	-110.8	-109.8	56.0	39.9	28.0	100.1	2.6	7.0	2.0	1.6
	max	370.5	91.0	705.3	7.03	231.0	227.8	246.6	161.0	238.5	215.5	648.2	32.2	565.0	394.0	34.0
Apr 1998 - Mar 2003	mean	162.8	43.6	303.4	5.52	18.8	49.8	62.4	80.4	141.3	133.1	300.0	17.0	121.9	26.7	10.1
	st. dev	44.7	8.8	244.3	0.98	63.6	66.1	50.0	41.4	38.1	37.8	199.1	4.4	75.6	25.5	6.1
	min	-0.1	25.0	73.3	4.09	-90.0	-153.5	-32.2	48.0	28.9	19.7	113.1	4.6	10.0	2.0	2.4
	max	239.8	61.0	2002.9	6.86	147.0	187.4	169.3	294.0	224.1	190.0	1666.1	24.5	296.0	96.0	27.0
Apr 2003 - Mar 2006	mean	168.2	40.3	283.2	5.27	52.1	74.2	83.4	73.3	154.5	146.9	281.4	18.7	85.9	19.1	6.7
	st. dev	43.3	11.5	73.7	0.96	53.2	60.7	46.6	11.7	23.7	23.8	62.8	3.2	77.3	24.9	4.8
	min	0.0	1.3	191.8	4.31	-54.0	-89.9	-7.6	56.0	89.8	86.4	195.8	11.0	4.0	2.0	1.6
	max	245.1	64.9	612.2	7.16	179.0	222.5	195.8	120.0	210.1	197.4	522.0	25.8	273.0	88.0	22.2
Seasonal-Kendall statistics	Sen-slope	-7.768	-0.308	-1.234	0.042	4.206	2.541	5.120		-2.317	-2.473				-3.880	0.273
	P- val	**<0.001**	0.131	**0.018**	**0.046**	**0.006**	**0.014**	**<0.001**		**0.007**	**0.002**				**0.007**	**0.003**

* Alkalinity and ANC records from May 1991.

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C); sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.12.2 Epilithic Diatom Percentage Abundance Summary: River Etherow

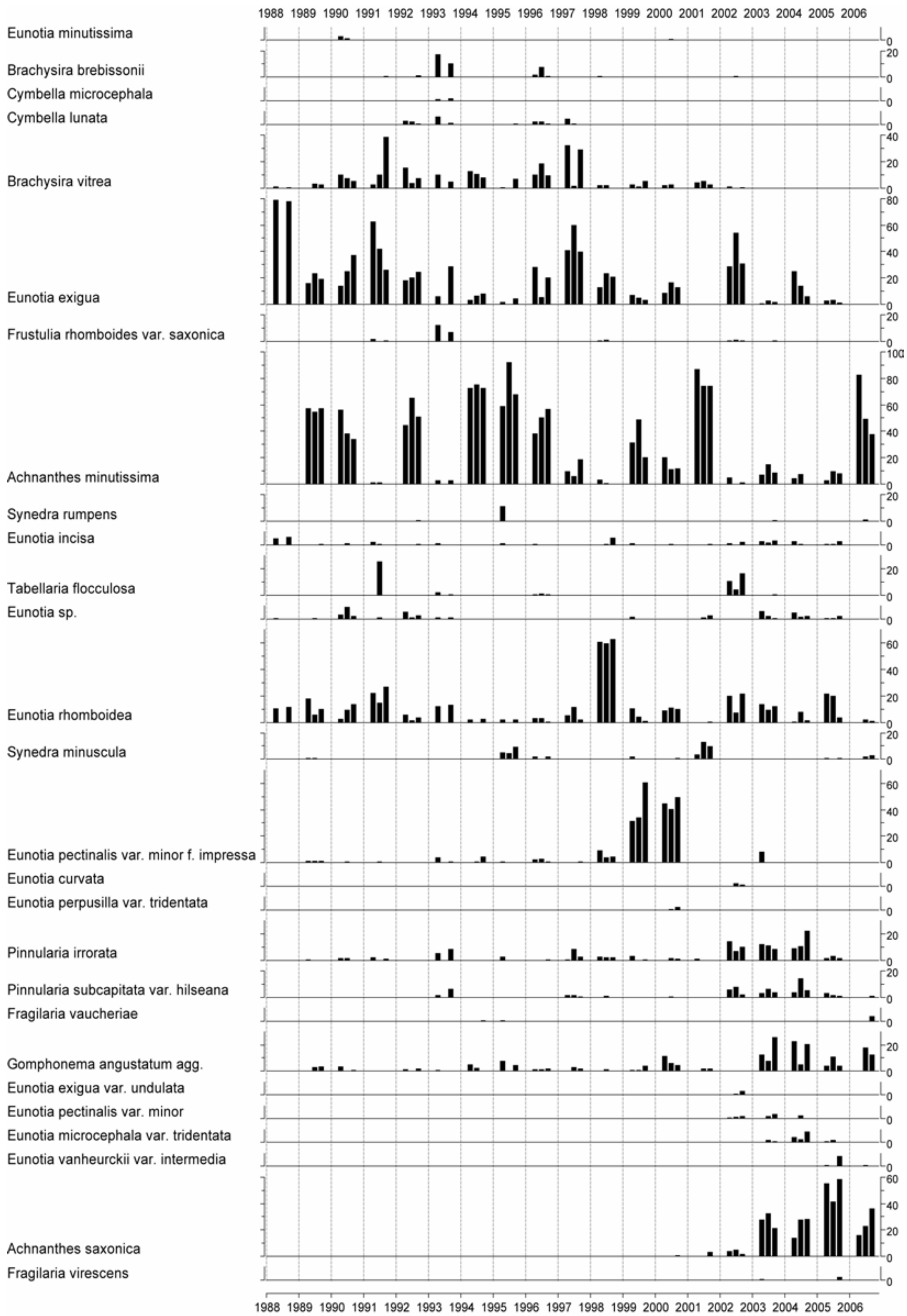
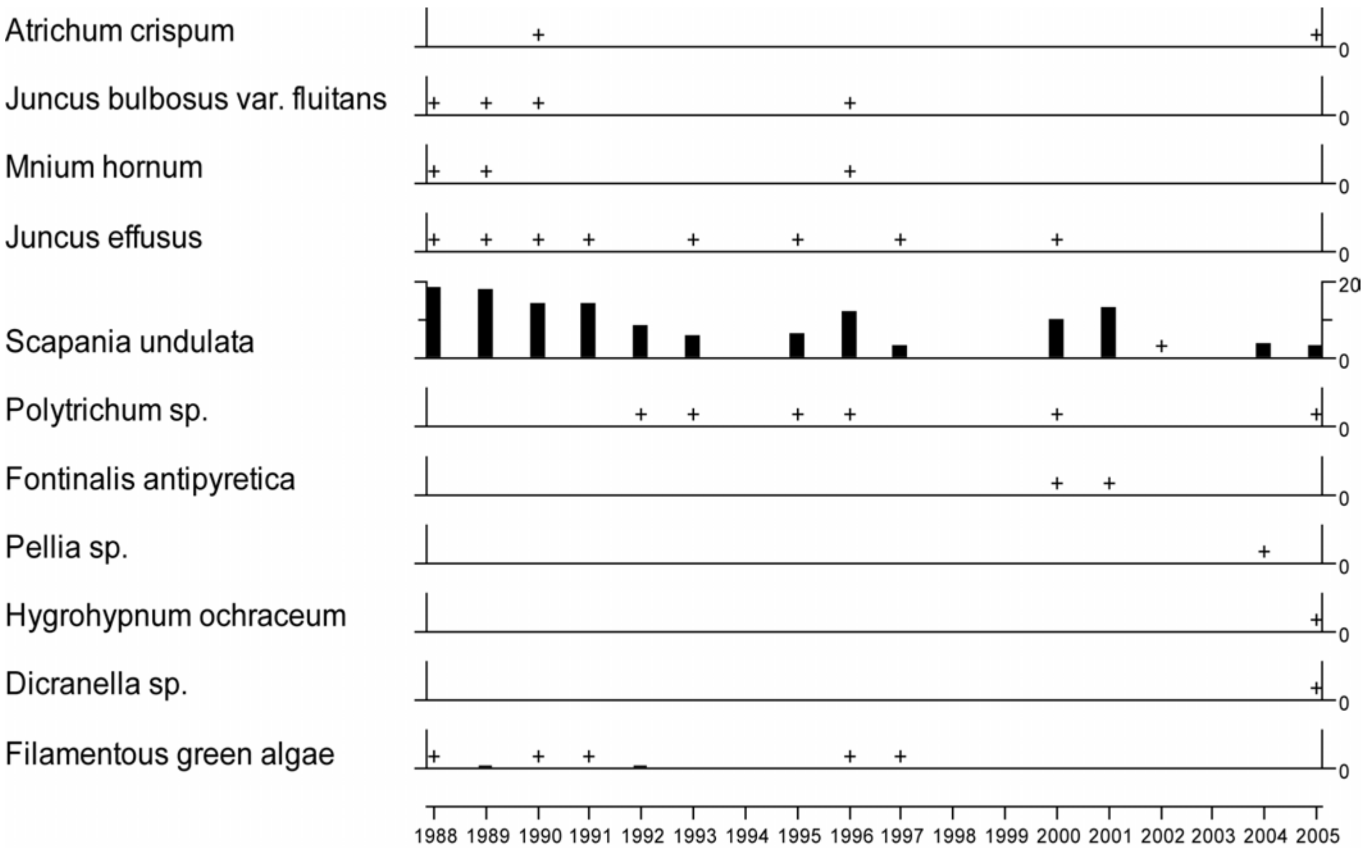


Figure 4.12.3 Aquatic Macrophyte Percentage Species Cover:: River Etherow



+ Represents <0.25% abundance

Figure 4.12.4 Macroinvertebrate Percentage Abundance Summary: River Etherow

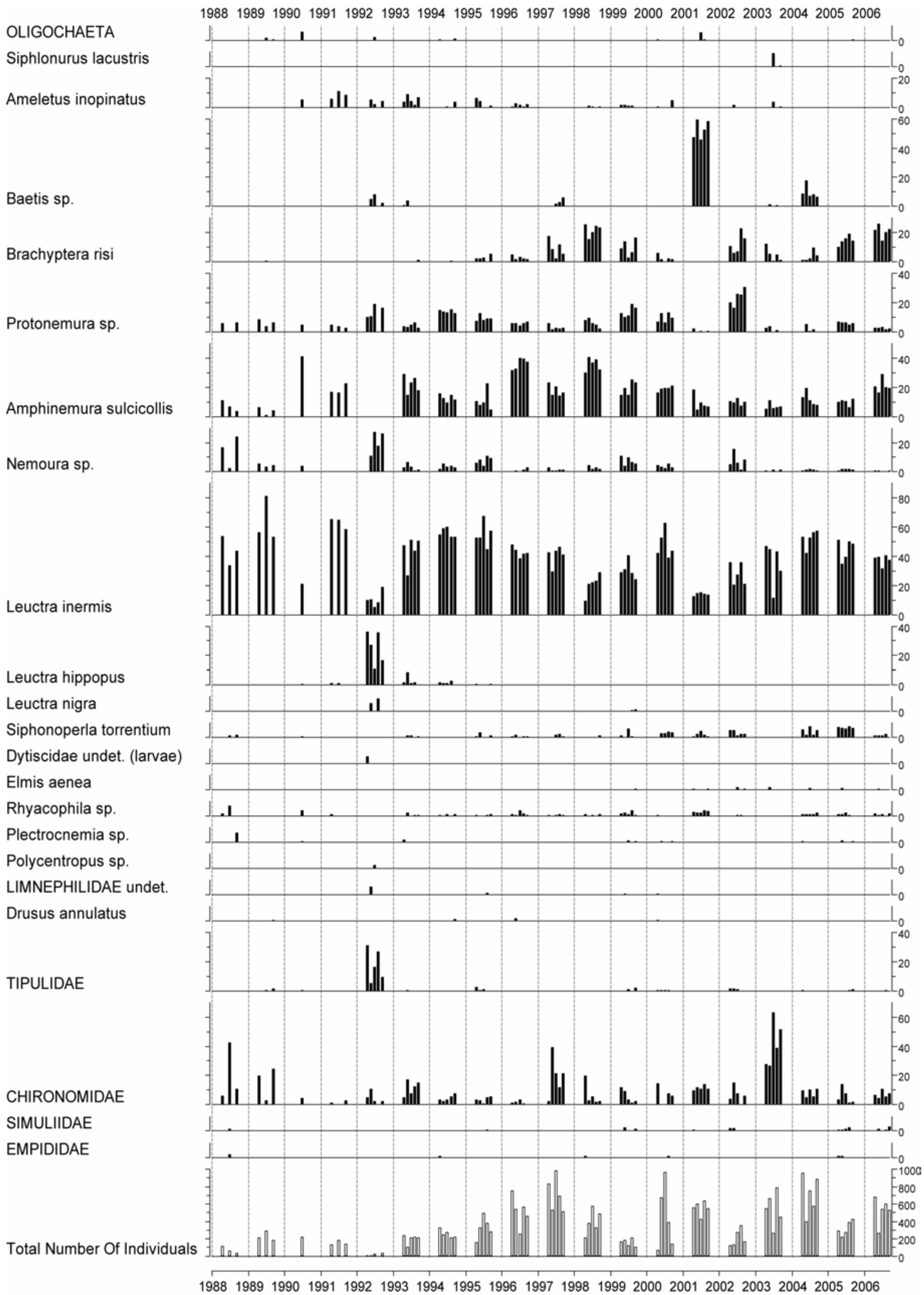


Table 4.12.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: River Etherow

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	2210.47	87	14.1	85.9	0.17	0.48	0.001	0.022
Invertebrates	1824.05	45	22.8	77.2	0.11	0.43	0.001	0.012

Fish: River Etherow

No fish are present in this reach of the river.

4.13 Old Lodge

4.13.1 Water Chemistry Summary

The Old Lodge stream, draining heathland on the Ashdown sands in southeast England, ranks behind the River Etherow (Site 12) only with respect to levels of xSO_4 on the AWMN. However, while the River Etherow is well buffered at baseflow, Old Lodge is a chronically acidic system. In the first phase of monitoring, mean xSO_4 (1988-1993) concentration was 225.1 μeq l^{-1}, average pH (1991-1993) was 4.55, the maximum pH recorded was 4.73, mean ion-balance ANC was -93.1 μeq l^{-1}, and mean labile aluminium concentration (1988-1993) was 223.1 μg l^{-1}. Most other major ions showed relatively high concentrations, due to factors including high pollutant deposition, geological influences, proximity to the English Channel (and hence vulnerability to seasalt episodes), low rainfall and relatively high rates of evaporation.

In common with the River Etherow, xSO_4 in Old Lodge has also fallen relatively linearly over the monitoring period, amounting to -6.5 μeq l^{-1} yr^{-1}. Mean concentrations also remain high; the 2003-2006 mean was 135.4 μeq l^{-1}, more than twenty times higher than that for Loch Coire nan Arr in northwest Scotland. However, in contrast to the Pennines site, xSO_4 shows very marked seasonality with concentrations falling to a very low level each summer while peaking in the spring.

Nitrate concentrations are considerably lower than in the River Etherow and therefore represent a negligible component of the total acidity load, but also show strong seasonality and inter-annual variability and no overall trend.

Chloride concentrations have remained high and, while the exceptional peak in concentrations around 1990 has not been repeated, there is substantial between sample variability and no clear long term trend.

Dissolved organic carbon concentrations have increased throughout most of the record but the largest change occurred between 1996 and 2003, coinciding with the clearest reduction in xSO_4. In the last three years concentrations have fallen back slightly as xSO_4 has increased again slightly.

Base cation concentrations largely follow the variation in total sulphate, reflecting variation in both anthropogenic and xSO_4 deposition. However, there is no indication of a long term trend, perhaps as a result of the increase in organic anion concentration in recent years. Ion balance ANC has increased substantially since 1991 to an average of -3.6 μeq l^{-1} between 2003-2006.

In the early years of monitoring the principal response to declining levels of xSO_4 was a large drop in labile aluminium concentration. Mean 2003-2006 labile aluminium concentrations were 67.0 μg l-1, less than one third that for the first three years. pH began to rise in around 1998 before stabilising again around 2001 as xSO_4 levelled out. Mean pH for the last three years was 5.0 and two samples have registered above pH 5.5.

4.13.2 Biology Summary

In common with the other more acidic streams on the Network the epilithic diatom assemblage of Old Lodge has been dominated by the acidophilous/acidobiontic species *Eunotia exigua* (SWAP pH optima = 5.1) throughout most ot the record. There is no significant linear trend in community structure, although there is some evidence that the assemblage has responded to the recent rise in pH that began circa 1999, with increases in *Frustulia rhomboides* var. *viridula* (SWAP pH optima = 5.3) and *Surirella linearis* (SWAP pH optima = 5.3), and generally lower abundances of *E. exigua* since 2002.

Similarly, the macroinvertebrate fauna of Old Lodge shows no significant linear trend and the assemblage remains in an impoverished condition indicative of a severely acidified system. It is feasible that the chronically elevated labile aluminium concentrations in Old Lodge continue to pose a barrier for recolonisation, although other restrictions may also be operating (see, for example, Monteith et al., 2005). The only potential links between the assemblage and water chemistry concern the relative abundance of the acid tolerant stonefly, *Nemoura* sp. (that was lowest during the early 1990s when labile aluminium levels were highest), and the recent reduction in the proportion of Simuliidae larvae that coincided with the period of increasing pH. There is, however, a slight indication of increasing diversity; in the six years since 2000 over 20 species have been recorded in all years but one (2003). Prior to 2000 this threshold was only exceeded once, in 1997.

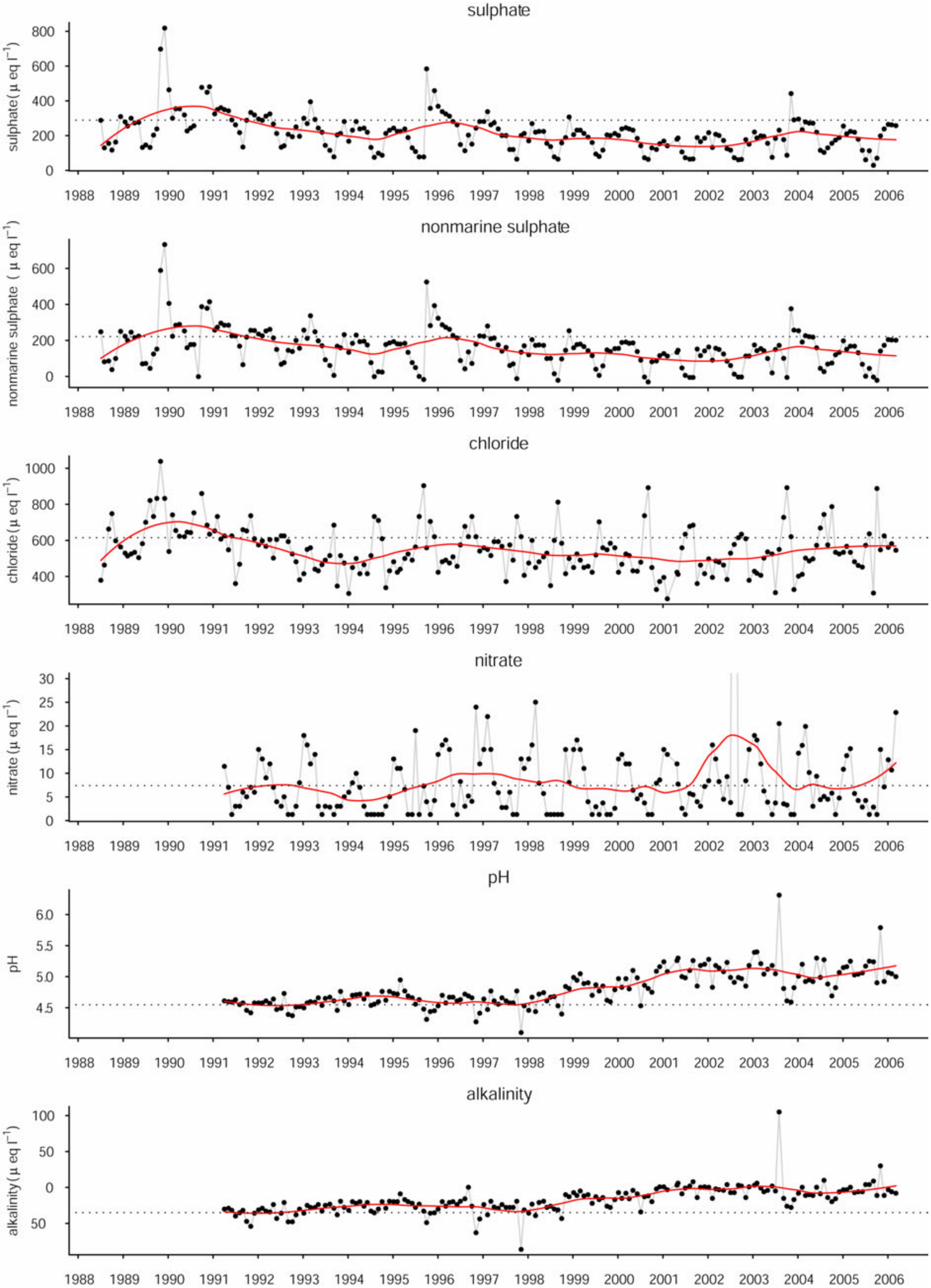
The macrophyte flora of the Old Lodge survey stretch has been dominated by the ubiquitous and acid-tolerant liverwort, *Scapania undulata*, throughout the monitoring period. Since 2000, however, small amounts of the aquatic moss *Hyocomium armoricum* have been recorded in permanently submerged locations in all years. The cover of filamentous algae has also declined from high levels in some years in the early 1990s.

Despite the limited evidence for biological improvement in most monitored groups, the salmonid data for Old Lodge show a dramatic improvement. No juvenile (< 1 year old) brown trout were caught in the first three years of electrofishing and densities of older fish were extremely low. However, juveniles have been recorded in all year but one from 1992, and since that time that has also been a gradual upward trend in the density of older fish. These trends therefore precede any obvious increase in pH but could be linked to the large reduction in labile aluminium concentration in the early 1990s.

4.13.3 Conclusions

Old Lodge is a chronically acidified stream that, unusually for AWMN streams, does not benefit from significantly more alkaline baseflow during times of low rainfall. Non-marine sulphate concentration has fallen substantially over the monitoring period and, until recently, the main effect of this has been to reduce levels of labile aluminium. Stream pH has only responded since around 1999. The biological impact of the xSO_4 decline appears generally muted, perhaps because labile aluminium levels remain at biologically toxic concentrations and ANC remains slightly negative. In this respect biological recovery lags behind almost all other sites on the AWMN. However, there has been a dramatic improvement in the density of brown trout and juveniles have been recorded in each year since. Further reductions in the xSO_4 load may be necessary before wider biological improvement becomes detectable.

Figure 4.13.1 Water Chemistry Summary Plots: Old Lodge



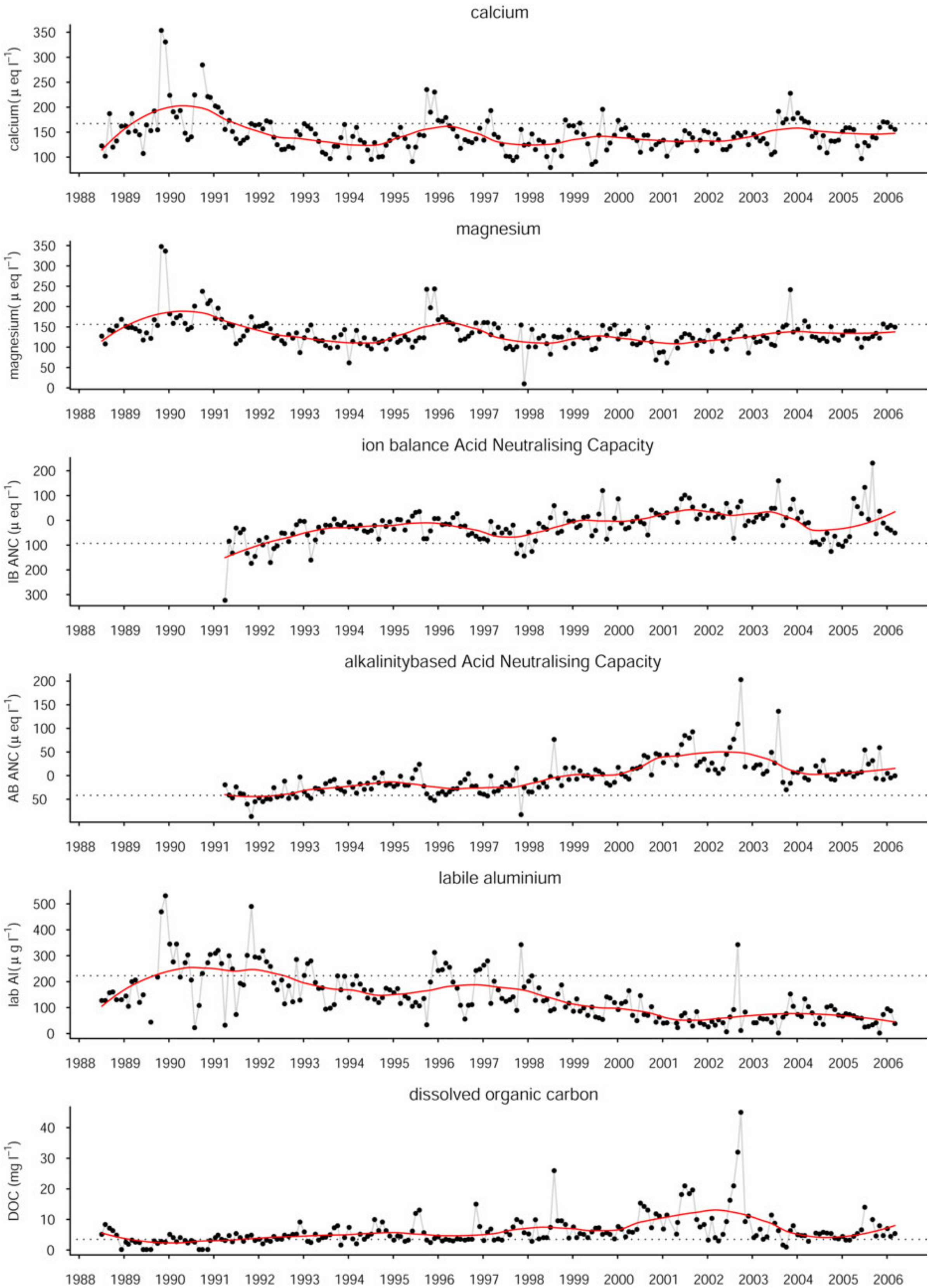

calcium
calcium (µ eq l⁻¹)
magnesium
magnesium (µ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (µ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l⁻¹)
labile aluminium
lab Al (µ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.13.1 Water Chemistry Summary Data and Trend Statistics: Old Lodge

Determinand / period		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Jul 1988* - Mar 1993	mean	225.1	7.4	615.1	4.55	-35.0	-93.1	-41.7	112.7	167.2	156.2	491.0	22.1	269.3	223.1	3.5
	st. dev	124.0	4.9	125.4	0.08	8.3	70.3	17.0	23.5	48.3	45.6	94.4	10.6	95.0	106.0	1.9
	min	38.8	1.3	361.1	4.37	-54.0	-322.6	-86.8	71.1	102.3	87.2	313.2	6.6	36.2	22.4	0.2
	max	731.7	18.0	1038.1	4.73	-21.0	-3.2	-2.9	201.6	353.8	347.1	813.5	55.5	533.0	530.5	9.2
Apr 1993 - Mar 1998	mean	163.1	7.5	531.7	4.61	-28.0	-35.2	-22.3	99.7	137.1	127.8	437.6	20.0	212.9	168.9	5.3
	st. dev	100.4	6.4	114.3	0.14	11.6	38.0	17.3	17.6	30.4	35.9	73.3	14.1	68.5	61.7	2.8
	min	-16.8	1.3	304.7	4.10	-86.0	-144.2	-82.6	63.0	91.3	9.9	269.7	6.6	61.0	34.0	1.7
	max	524.9	25.0	902.7	4.95	-9.0	36.1	23.7	152.0	235.5	243.5	617.7	110.5	411.0	342.0	15.0
Apr 1998 - Mar 2003	mean	109.0	9.6	503.3	4.95	-10.2	10.8	24.1	86.3	134.8	118.4	413.6	18.3	178.3	84.8	9.7
	st. dev	66.4	18.4	117.1	0.23	11.4	43.6	38.8	12.9	21.8	20.3	67.2	7.5	84.1	54.7	7.6
	min	-30.2	1.3	276.5	4.40	-43.0	-75.1	-24.5	43.0	79.3	61.7	261.0	4.3	54.0	7.0	3.0
	max	254.1	142.9	891.4	5.40	8.0	120.1	203.3	114.0	195.6	154.6	574.2	45.3	616.0	343.0	45.0
Apr 2003 - Mar 2006	mean	135.4	7.6	555.2	5.00	-2.9	-3.6	11.7	96.9	149.3	135.0	446.1	22.5	108.1	67.0	5.6
	st. dev	88.7	6.1	134.7	0.17	21.2	79.1	29.1	15.5	27.6	24.3	80.3	11.2	38.3	32.5	2.6
	min	-22.4	1.3	307.5	6.31	-28.0	-125.4	-29.9	54.0	97.3	99.5	295.8	7.7	19.0	2.0	1.0
	max	376.5	22.9	891.4	4.59	105.0	230.9	136.2	144.0	227.5	241.8	635.1	63.4	204.0	153.0	14.0
Seasonal-Kendall statistics	Sen-slope	-6.428	0.175	-4.299	0.045	2.649	6.396	4.374		-0.317	-1.320				-11.064	0.229
	P- val	**0.001**	0.557	**0.041**	**<0.001**	**<0.001**	**0.008**	**<0.001**		0.109	0.065				**<0.001**	**0.001**

* NO_3^-,pH, alk and ANC from April 1991

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C); sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.13.2 Epilithic Diatom Percentage Abundance Summary: Old Lodge

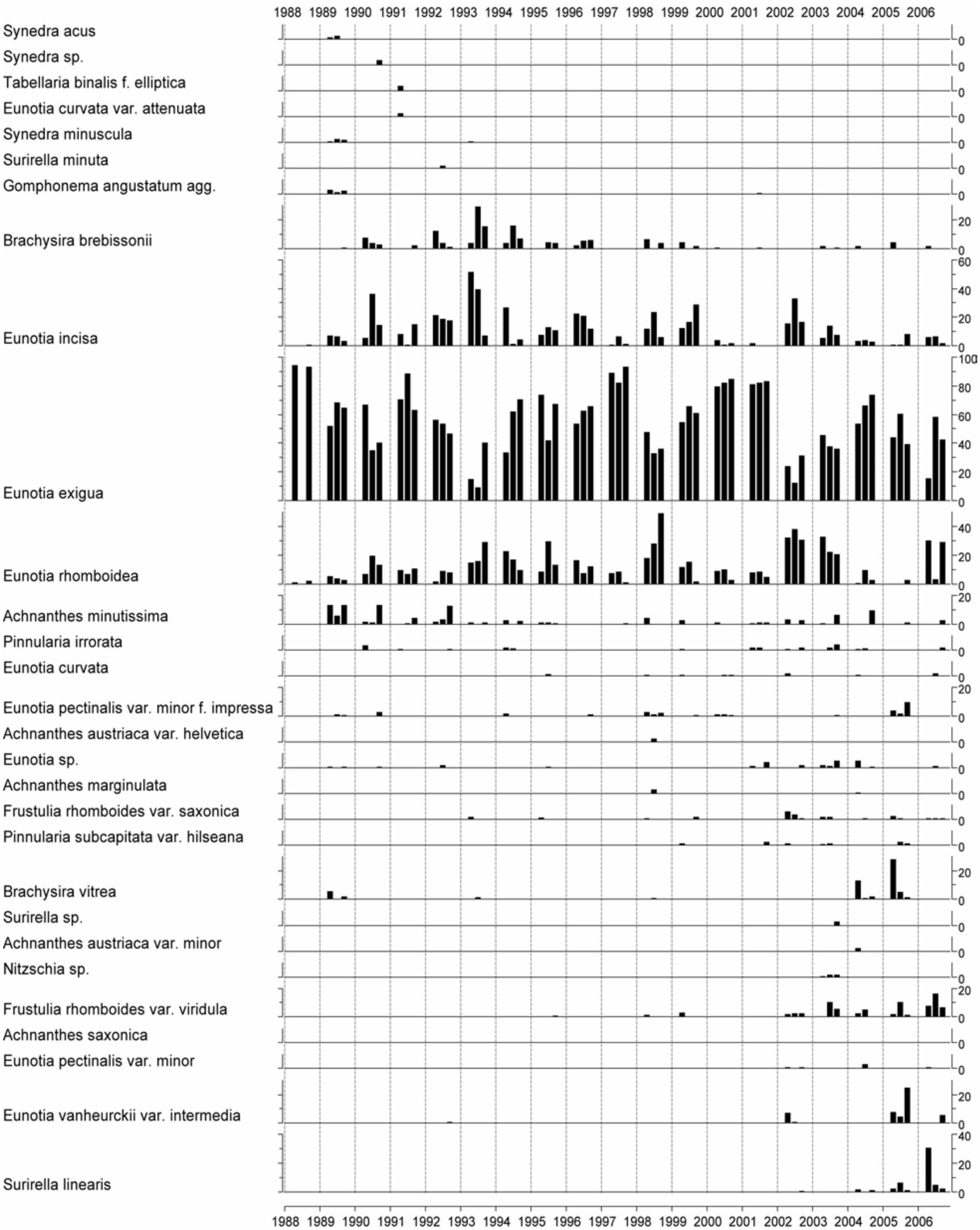
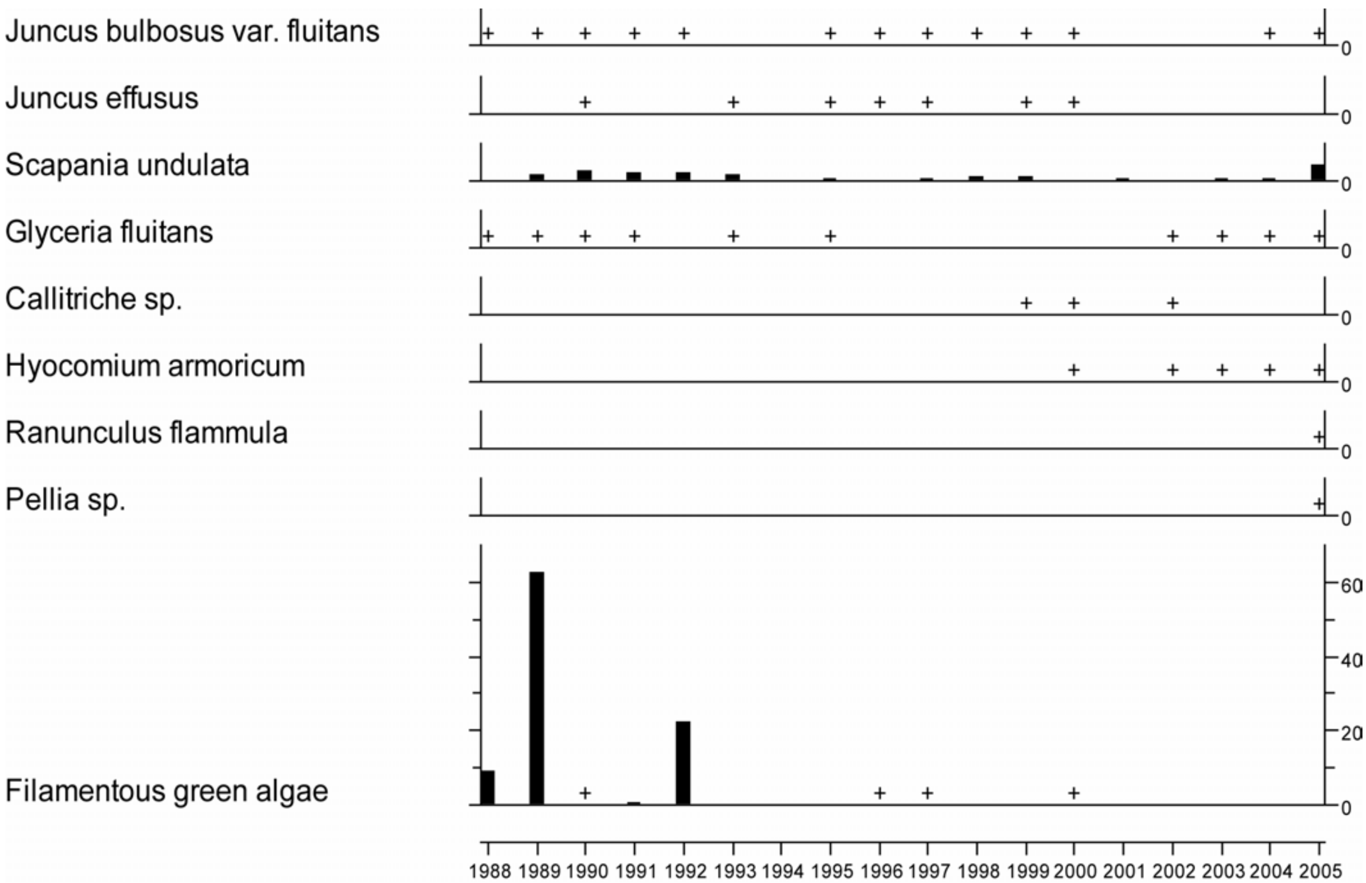


Figure 4.13.3 Aquatic Macrophyte Percentage Species Cover: Old Lodge



+ Represents <0.25% abundance

Figure 4.13.4 Macroinvertebrate Percentage Abundance Summary: Old Lodge

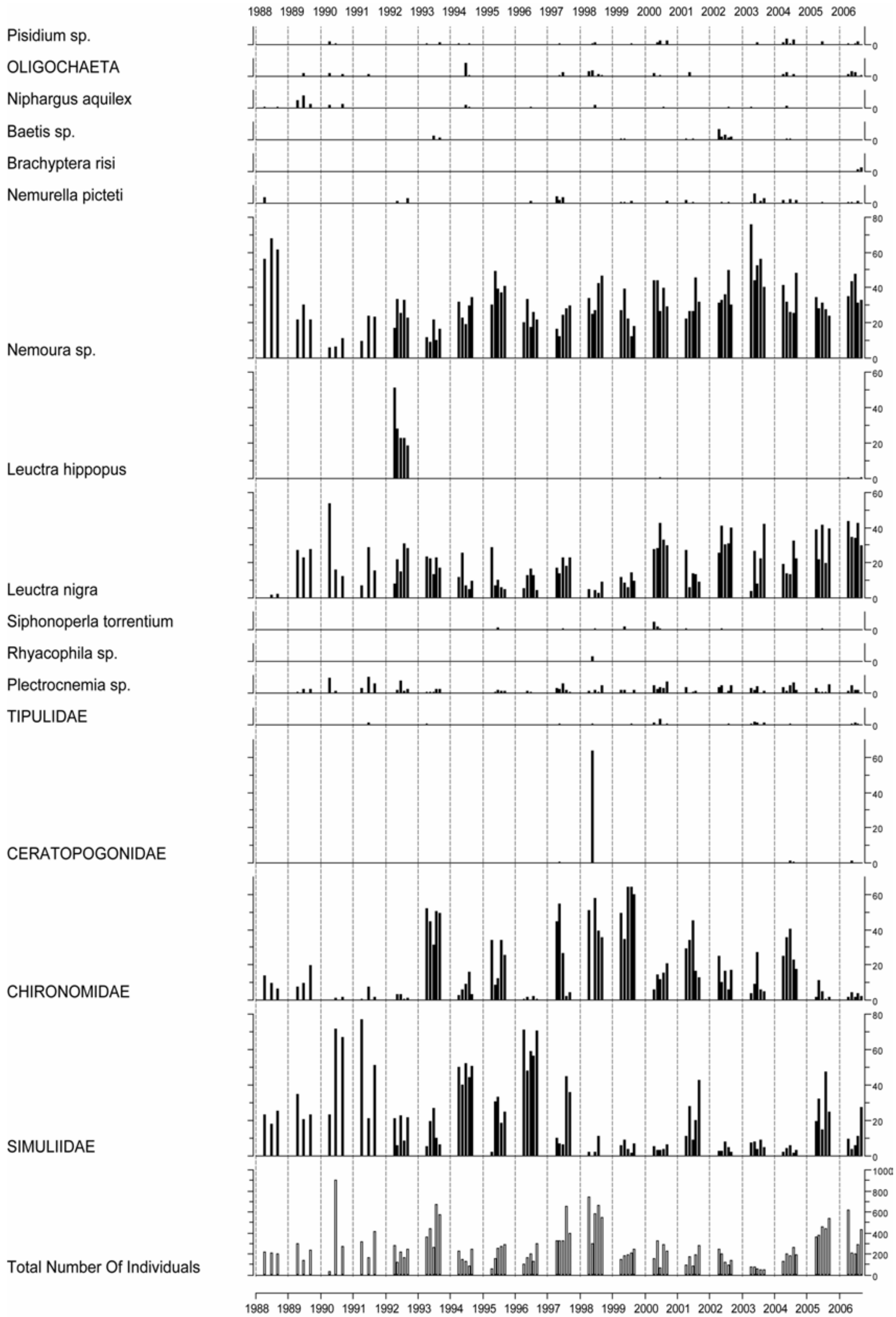
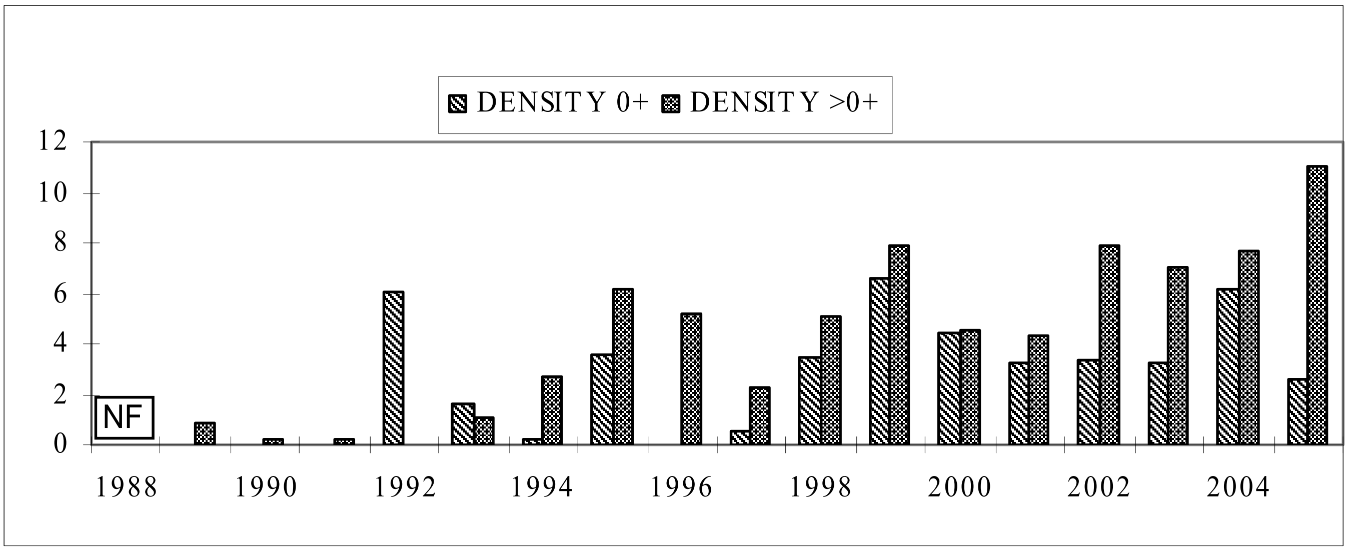


Table 4.13.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Old Lodge

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1036.99	102	35.1	64.9	0.09	0.29	0.001	0.116
Invertebrates	1621.55	45	32	68	0.09	0.25	0.001	0.150

Figure 4.13.5 Summary of Mean Trout Density (numbers 100m^{-2}): Old Lodge



NF = Not fished

4.14 Narrator Brook

4.14.1 Water Chemistry Summary

Narrator Brook drains moorland overlying granite and feeds the Burrator Reservoir in the Dartmoor National Park in southwest England. The chemistry sampling location was moved upstream in 1991 following a period of felling in the lower part of the catchment. Between 1991-1993, mean xSO_4 concentration was moderate for the Network (41.1 μeq l^{-1}) and NO_3 concentrations were low (mean = 6.1 μeq l^{-1}). Although the site is only 20 km from the south coast, the chloride time series does not show the large inter-sample variability shown by other Network sites that are prone to seasalt inputs, and this suggests a relatively long catchment residence time and perhaps a dominant influence on the water chemistry from groundwater.

Over the 1991-1993 period, the very low mean calcium concentration (34.5 μeq l^{-1}), mean pH of 5.69, mean labile aluminium concentration of 20.3 μg l^{-1}, and mean alkalinity and ANC of circa 10 μeq l^{-1} were indicative of an acid-sensitive site that was only mildly impacted by acid deposition.

Narrator Brook is unique amongst AWMN sites as it provides no indication of any reduction in xSO_4 concentration over the full monitoring period. Indeed, concentrations show a slight but significant upward trend (0.34 μeq l^{-1} yr^{-1}). Nitrate concentrations have remained low and show no indication of trend. Chloride concentrations declined between 1991 and 1996 but have remained relatively stable since, with occasional spikes indicative of specific seasalt events.

Despite no indication of decline in acid anion concentration, pH values showed an apparent upward step change between 1994-1995 and again between 2003-2006, and the overall trend is statistically significant. Conversely labile aluminium concentrations show a slight, but again significant, upward trend that broadly tracks the change in xSO_4.

Also unusually for the Network, DOC concentrations shown no clear indication of any long term trend, but appear to vary in a broadly inverse manner to variation in xSO_4. This relationship therefore provides strong support for the hypothesis that the more widely seen DOC increases across the Network are linked to changes in acid deposition (Section 5.4.5).

4.14.2 Biology Summary

The epilithic diatom flora of Narrator Brook shows strong interannual variation but no long-term trend, with the acid-sensitive *Achnanthes minutissima* dominant in most samples and most years. Between 1998-2003 *A. minutissma* relative abundance was depressed relative to *Eunotia vanheurkii* var. *intermedia* and *Suirella linearis* (species with considerably lower pH optima). These changes coincide with a period of higher xSO_4 and labile aluminium concentrations but no obvious change in pH.

The aquatic macrophyte community of Narrator Brook includes a diverse range of bryophytes including acid-sensitive moss species such as *Rhyncostegium riparioides*. There is no indication of any change in the community over the monitoring period.

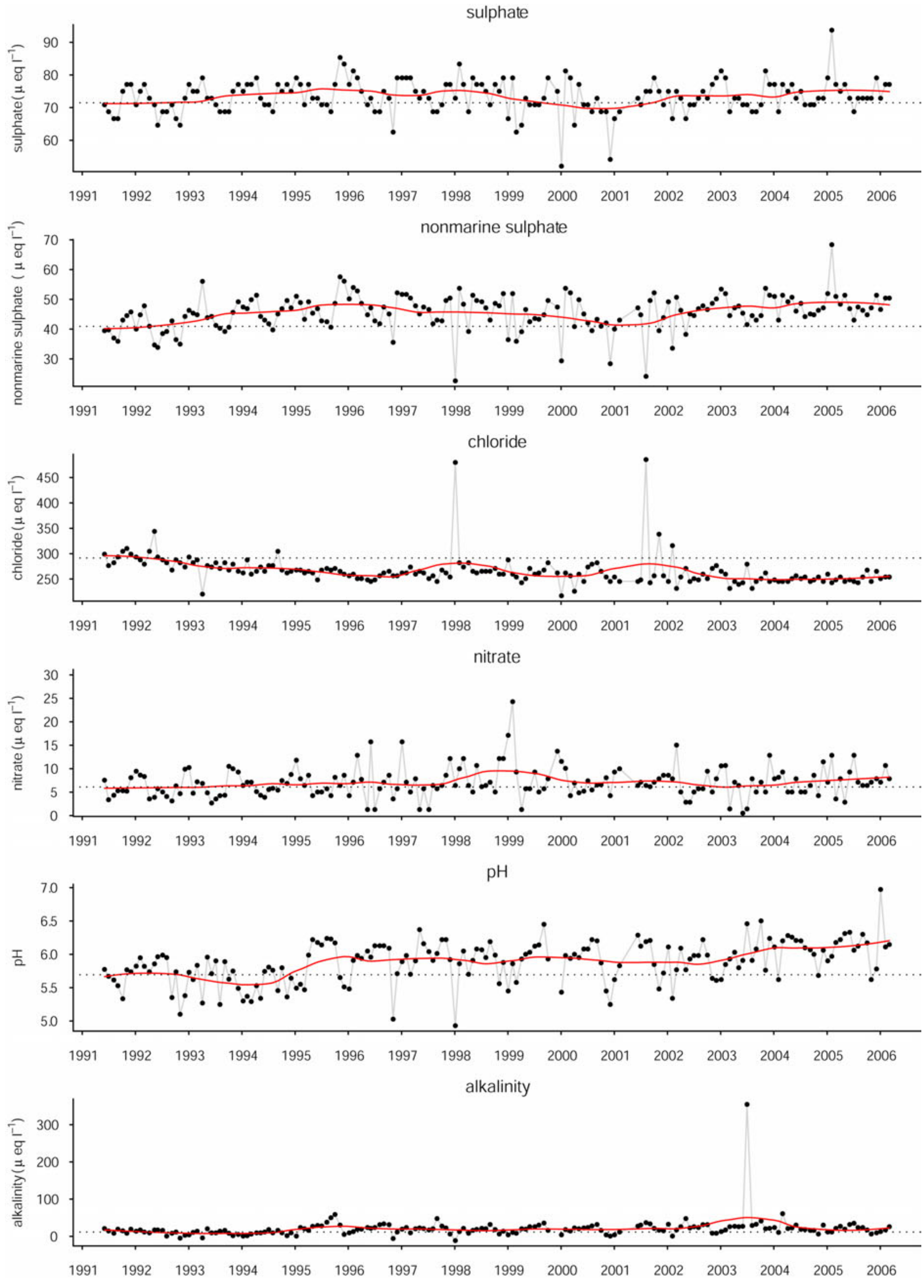
Similarly, the macroinvertebrate assemblage contains a diverse group of taxa including acid-sensitive species such as *Baetis* sp.. Redundancy Analysis demonstrates that there is a significant linear trend in the dataset but the changes are subtle. Two species, the acid-sensitive Mayfly *Ecdyonurus* sp. and the caddis *Chaetopteryx villosa* have only recently begun to be recorded regularly.

The brown trout population of the Narrator Brook is one of the highest on the AWMN and provides no indication of acid stress. There is no indication of trend in either juvenile or older fish.

4.14.3 Conclusions

Narrator Brook is a sensitive but only mildly deposition-impacted stream that, unusually for the AWMN, has not experienced a long-term decline in acid anion concentration. Curiously, however, pH has increased significantly, even though xSO_4 shows a subtle long-term increase. The biological communities of the brook all exhibit marked inter-annual variability in species composition but have remained relatively constant in the longer term.

Figure 4.14.1 Water Chemistry Summary Plots: Narrator Brook



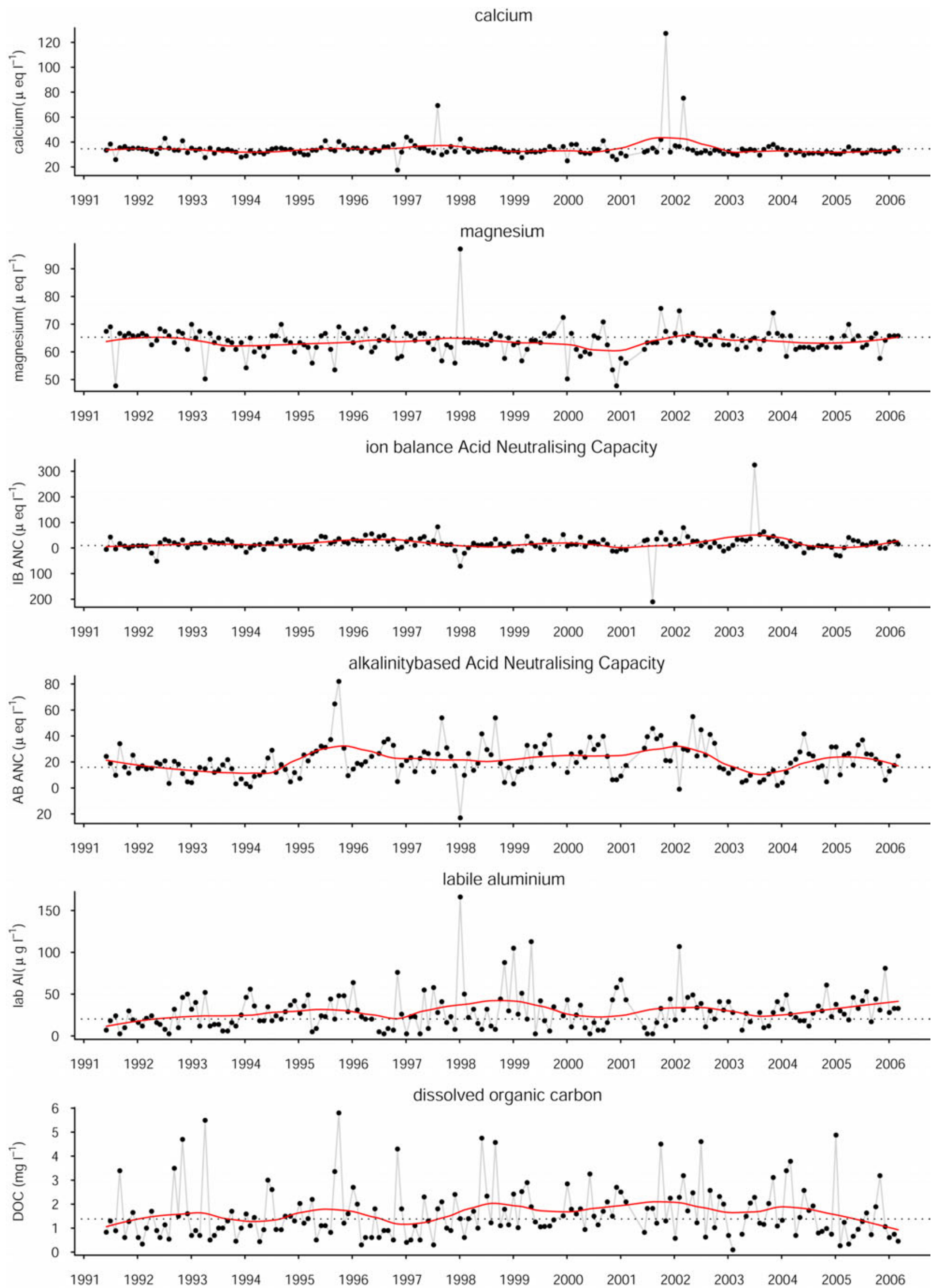

calcium
calcium(µ eq l^{-1})
120
100
80
60
40
20
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
magnesium
magnesium(µ eq l^{-1})
90
80
70
60
50
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
ion balance Acid Neutralising Capacity
IB ANC (µ eq l^{-1})
300
200
100
0
100
200
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l^{-1})
80
60
40
20
0
20
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
labile aluminium
lab Al(µ g l^{-1})
150
100
50
0
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
dissolved organic carbon
DOC (mg l^{-1})
6
5
4
3
2
1
0
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006

Table 4.14.1 Water Chemistry Summary Data and Trend Statistics: Narrator Brook

Determinand period		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ABC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
June 1991 - Mar 1993	mean	41.1	6.1	291.5	5.69	11.6	10.0	15.9	48.4	34.5	65.3	259.2	20.0	53.2	20.3	1.4
	st. dev	4.2	2.2	15.8	0.23	6.5	19.7	7.2	1.3	3.4	4.4	7.3	2.2	40.8	13.3	1.1
	min	34.0	3.1	268.0	5.10	-5.0	-51.3	3.5	45.5	25.9	47.7	248.0	16.4	11.0	2.5	0.3
	max	48.0	10.3	344.2	5.99	21.0	42.2	34.0	50.2	42.9	69.9	269.7	25.1	182.0	50.0	4.7
Apr 1993 - Mar 1998	mean	46.6	6.8	267.9	5.80	17.2	19.1	20.9	40.9	34.2	63.4	251.6	19.1	62.5	29.0	1.5
	st. dev	5.5	3.1	30.4	0.33	13.0	22.1	15.3	7.4	6.0	5.9	15.6	2.9	44.8	25.0	1.1
	min	23.0	1.3	220.0	4.93	-11.0	-71.4	-23.1	29.0	17.5	50.2	208.8	11.5	20.0	2.5	0.3
	max	57.8	15.7	479.6	6.37	58.4	82.1	82.1	58.0	69.4	97.1	335.0	27.1	236.0	166.0	5.8
Apr 1998 - Mar 2003	mean	44.8	7.7	264.5	5.90	19.8	13.5	25.5	34.9	35.3	63.3	240.1	19.2	78.1	31.7	1.9
	st. dev	6.3	3.8	35.7	0.26	10.3	35.9	13.0	4.9	14.1	4.9	14.8	2.8	49.2	25.6	1.0
	min	24.5	1.3	217.2	5.25	0.6	-209.9	-1.0	27.0	25.0	47.7	195.8	13.8	21.0	2.5	0.1
	max	53.9	24.3	485.2	6.45	48.0	79.7	54.9	47.0	127.2	75.7	274.1	33.5	202.0	113.0	4.8
Apr 2003 - Mar 2006	mean	48.1	7.1	250.3	6.03	32.0	25.3	18.2	40.6	32.6	63.9	240.8	19.7	62.8	30.8	1.5
	st. dev	4.6	2.9	8.7	6.26	56.3	55.2	10.5	5.1	2.0	3.1	55.8	2.3	28.7	15.1	1.1
	min	41.5	0.5	231.3	6.97	6.4	-31.1	2.0	34.0	29.4	57.6	208.8	14.3	23.0	7.0	0.3
	max	68.3	12.9	279.3	5.62	354.6	324.4	41.7	68.0	37.9	74.0	556.8	26.1	144.0	81.0	4.9
Seasonal-Kendall statistics	Sen-slope	0.339	0.122	-1.866	0.033	0.736	0.379	0.243		-0.066	0.046				0.801	0.012
	P- val	**0.011**	**0.037**	**<0.001**	**0.002**	**0.010**	0.705	0.237		0.053	0.207				**0.043**	0.127

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.14.2 Epilithic Diatom Percentage Abundance Summary: Narrator Brook

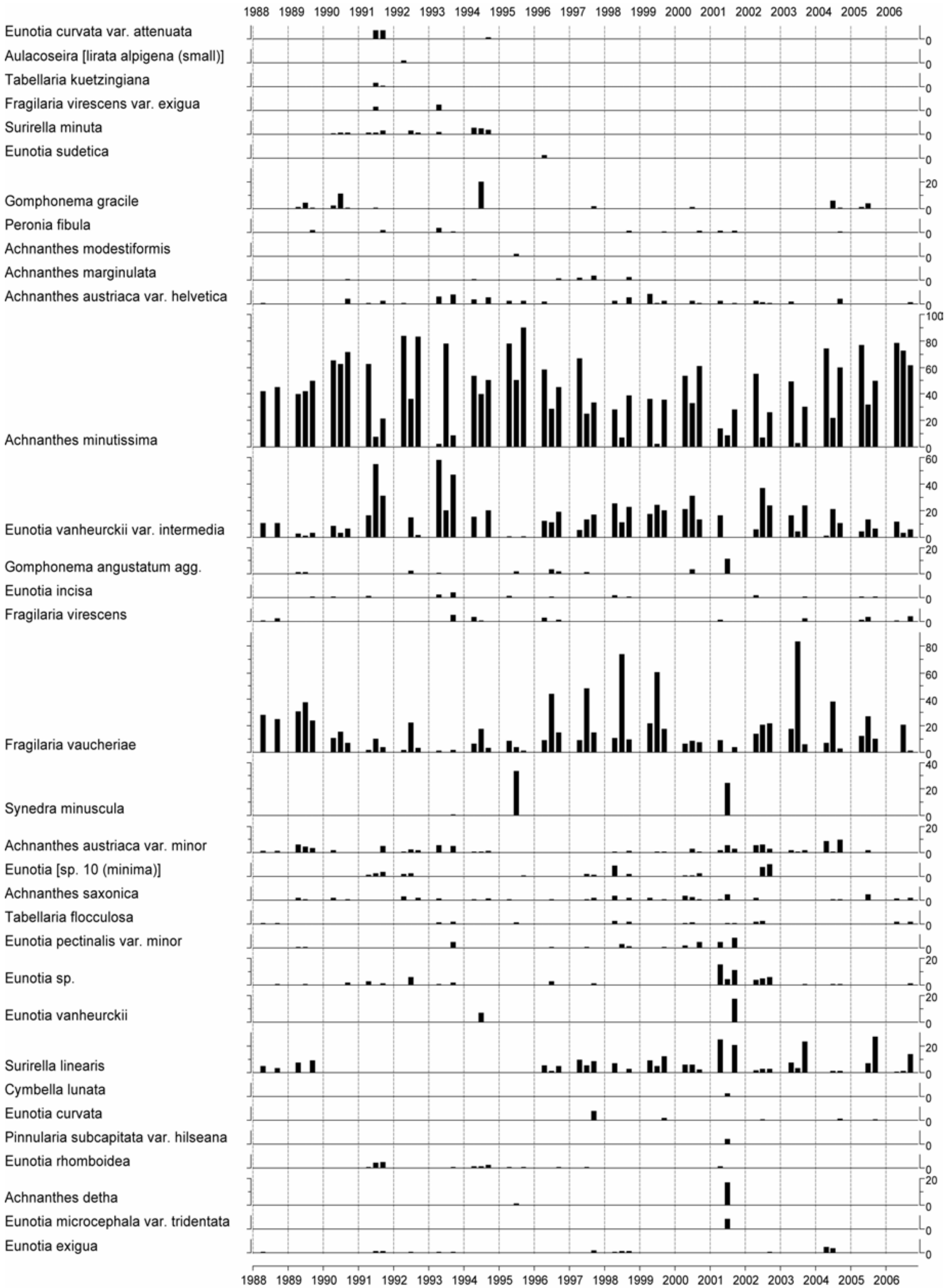
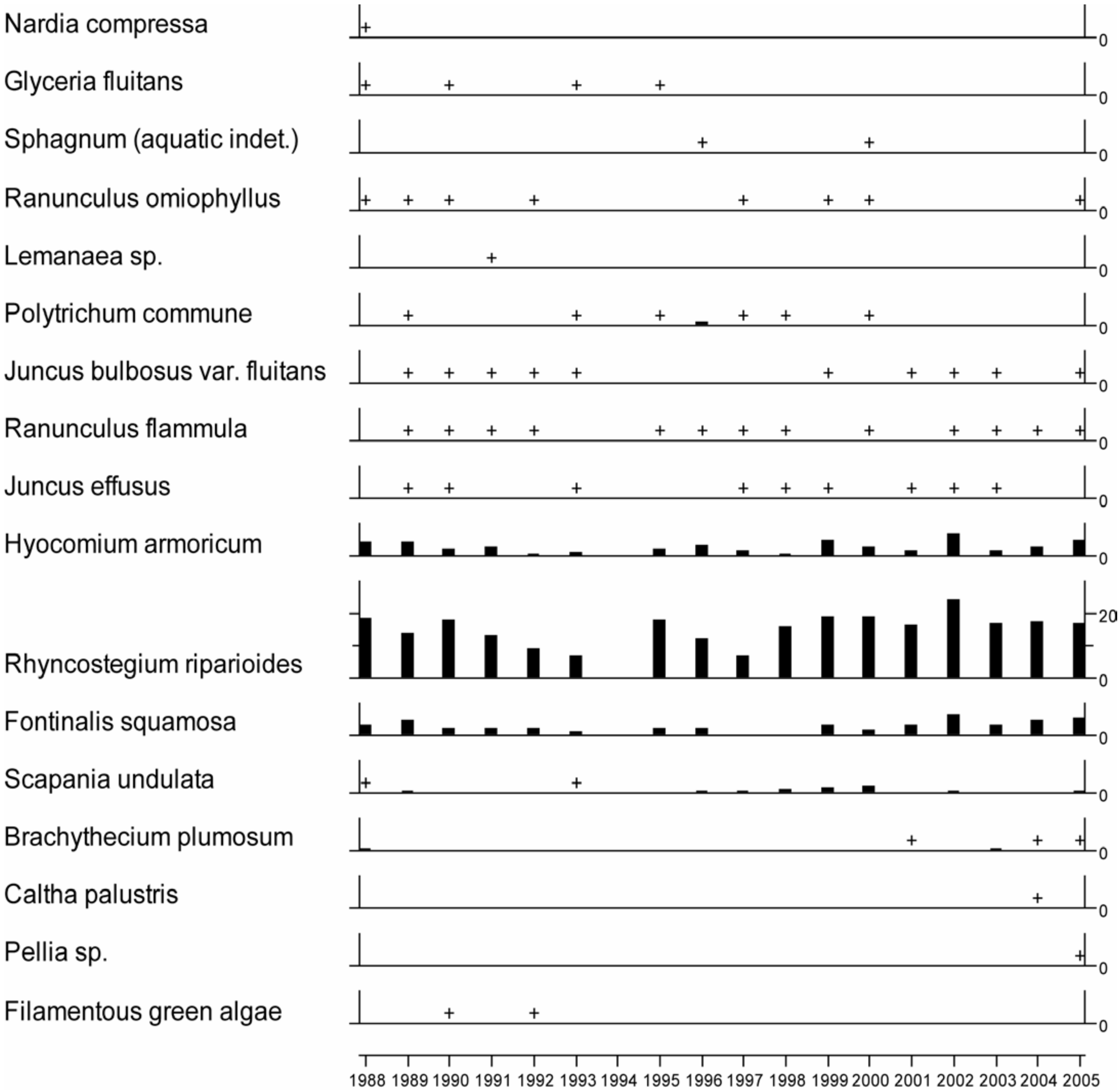
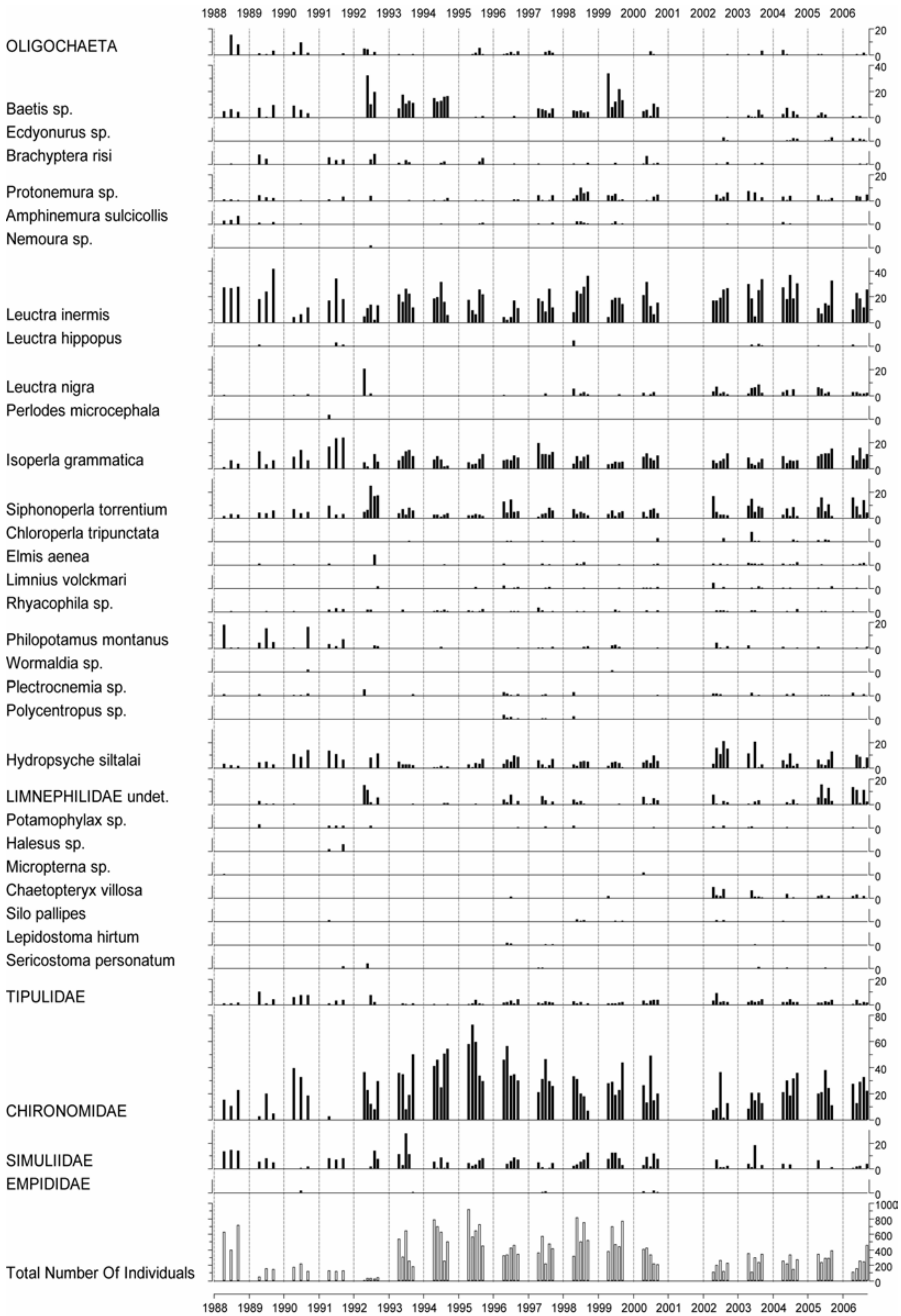


Figure 4.14.3 Aquatic Macrophyte Percentage Species Cover: Narrator Brook



+ Represents <0.25% abundance

Figure 4.14.4 Macroinvertebrate Percentage Abundance Summary: Narrator Brook

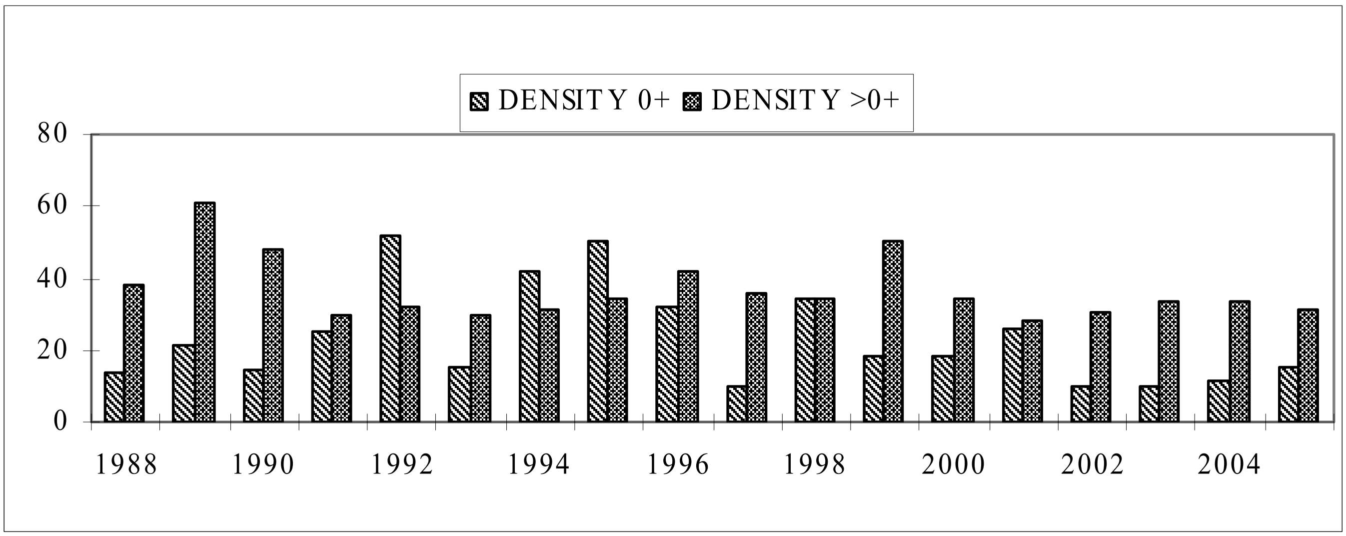


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.14.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Narrator Brook

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1470.00	97	47.8	52.2	0.03	0.12	0.065	0.580
Invertebrates	1594.76	65	51.3	48.7	0.08	0.34	0.001	0.010

Figure 4.14.5 Summary of Mean Trout Density (numbers 100m^{-2}): Narrator Brook



4.15 Llyn Llagi

4.15.1 Water Chemistry Summary

Llyn Llagi is a small upland corrie lake 7 km to the southeast of Snowdon in northwest Wales. Palaeoecological analysis suggest that Llyn Llagi began to acidify in the mid-1800s but acidification accelerated from around 1960 to the late 1980s.

Over the first five years of monitoring (1988-1993) the mean xSO4 concentration of 39.0 μeq l^{-1} was moderate for the Network, while NO_3 (mean 10.4 μeq l^{-1}) made a small but significant contribution to the total acid load. The mean pH of 5.23, mean ANC and alkalinity close to 0 μeq l^{-1}, and mean labile aluminium concentration of 42.6 μg l-1 was indicative of an acidified condition. The acidity of the lake was clearly sensitive to seasalt episodes and in the winters of 1990 and 1992 pH was recorded below 5.0 during periods of high seasalt inputs.

Non-marine sulphate concentrations remained relatively steady for the first 10 years of monitoring. However, pH increased gradually over this period as a result of the reduction in seasalt events. Non-marine sulphate began to fall sharply in 1997 and then stabilised in around 2002.

Nitrate concentrations, after showing strong inter-annual variability over the first ten years, have since fallen and have lost their seasonal structure.

Chloride concentrations continue to show a seasonal pattern due to the input of seasalt in winter, but the very high concentrations recorded in the early 1990s have not recurred.

The net effect of the fall in seasalt inputs and the reduction in xSO_4 and NO_3 in more recent years has been a progressive rise in pH and alkalinity and a concomitant fall in labile aluminium concentrations to negligible levels. Between 2003-2005 labile aluminium concentrations remained close to the limit of detection, but one extremely high measurement (182 μg l^{-1}) was recorded in the autumn of 2006. The reasons for this anomaly are as yet unclear but may be related to the release of ionic aluminium from organic complexes in the lake epilimnion following a prolonged period of stratification.

Base cation concentrations have fallen slightly in response to the decline in acid inputs. Dissolved organic carbon concentrations have risen slowly over the monitoring period in an apparent response to the decline in acid deposition and seasalt (Section 5.4.5).

4.15.2 Biology Summary

The epilithic diatom assemblage of Llyn Llagi was dominated by the acidobiontic species, *Tabellaria quadriseptata* (SWAP pH optima = 4.9) at the onset of monitoring. This species had shown a sharp increase in abundance in a sediment core from the lake in levels dated to the latter half of the 20th century, and remained abundant in the epilithon until around 1995 after which it declined rapidly. By 2003, *T. quadriseptata* was almost undetectable in the epilithon. Its decline was balanced by a rise in the relative abundance of *Nitzschia perminuta* (SWAP pH optima = 5.7), *Brachysira vitrea* (SWAP pH optima = 5.9) and *Cymbella minuta* (SWAP pH optima = 6.1).

The sediment trap data show very similar species changes, reflecting the importance of the epilithic community of Llyn Llagi for sediment species composition.

At the outset of monitoring the aquatic macrophyte community of Llyn Llagi was dominated by the acid-tolerant isoetids, *Isoetes lacustris*, *Lobelia dortmanna* and *Littorella uniflora*. The more sensitive *Callitriche hamulata* was first recorded in 1999 and is now well established. Another sensitive species, *Subularia aquatica*, was first recorded in 1993, and was found again in the 2003 and 2005 surveys. The spatial distribution of the acid-tolerant *Juncus bulbosus* var. *fluitans* appears to have expanded slightly over the full monitoring period.

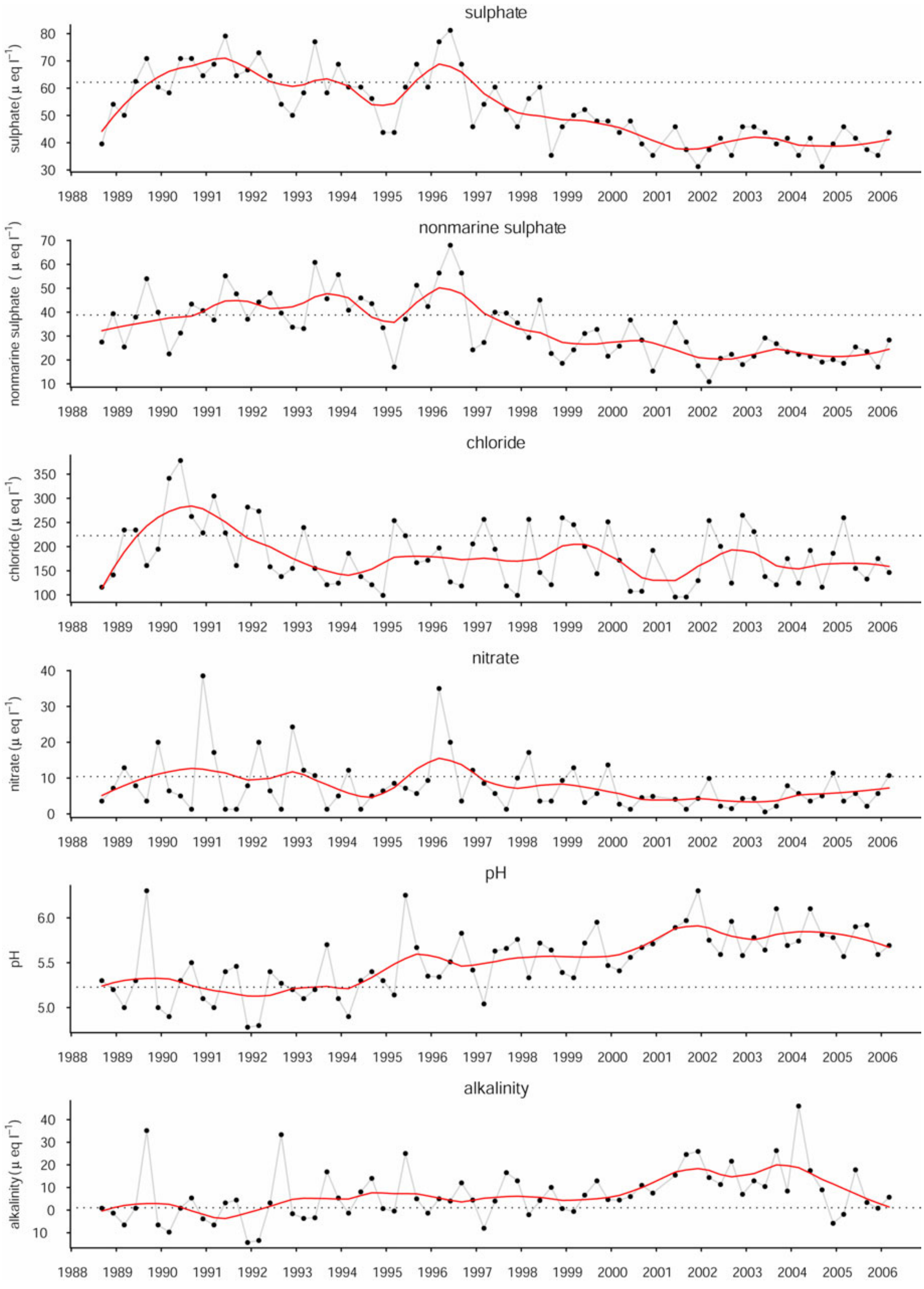
The macroinvertebrate community of Llyn Llagi shows significant linear change as a result of large changes in species composition. Representation of chironomids, that dominated the assemblage in the early years, fell in 1998 since when the assemblage has been comprised increasingly of caddis species such as *Mystacides* sp., *Oxyethira* sp. and *Oulimnius tuberculatus*, and the freshwater bivalve *Pisidium* sp.. Increases in the relative abundance of *O. tuberculatus* have been recorded in several of the chemically recovering AWMN lakes.

Brown trout density in the outflow of Llyn Llagi has have been at moderate levels over most of the monitoring period and shows no long term trend. However, densities of both juvenile and older fish have been low since 2003 and in 2005 no juvenile fish were recorded at all. The cause of these low densities is not clear and requires further investigation.

4.15.3 Conclusions

Llyn Llagi has undergone reductions in both xSO_4 and NO_3 concentration, while the additionally acidifying effects of seasalt were most severe in a series of stormy winters in the early part of the monitoring record. Lake pH has risen and labile aluminium concentrations have fallen substantially. This has resulted in a major change in diatom species composition and can also be linked to major changes in the macroinvertebrate community. Two acid-sensitive aquatic macrophytes, not recorded in early surveys, are now commonly found. The brown trout population of the lake outflow provided little indication of acid stress at the outset of monitoring and there is no evidence for any positive response to improving water quality in this indicator group. The relatively low densities recorded since 2003 needs to be investigated further.

Figure 4.15.1 Water Chemistry Summary Plots: Llyn Llagi



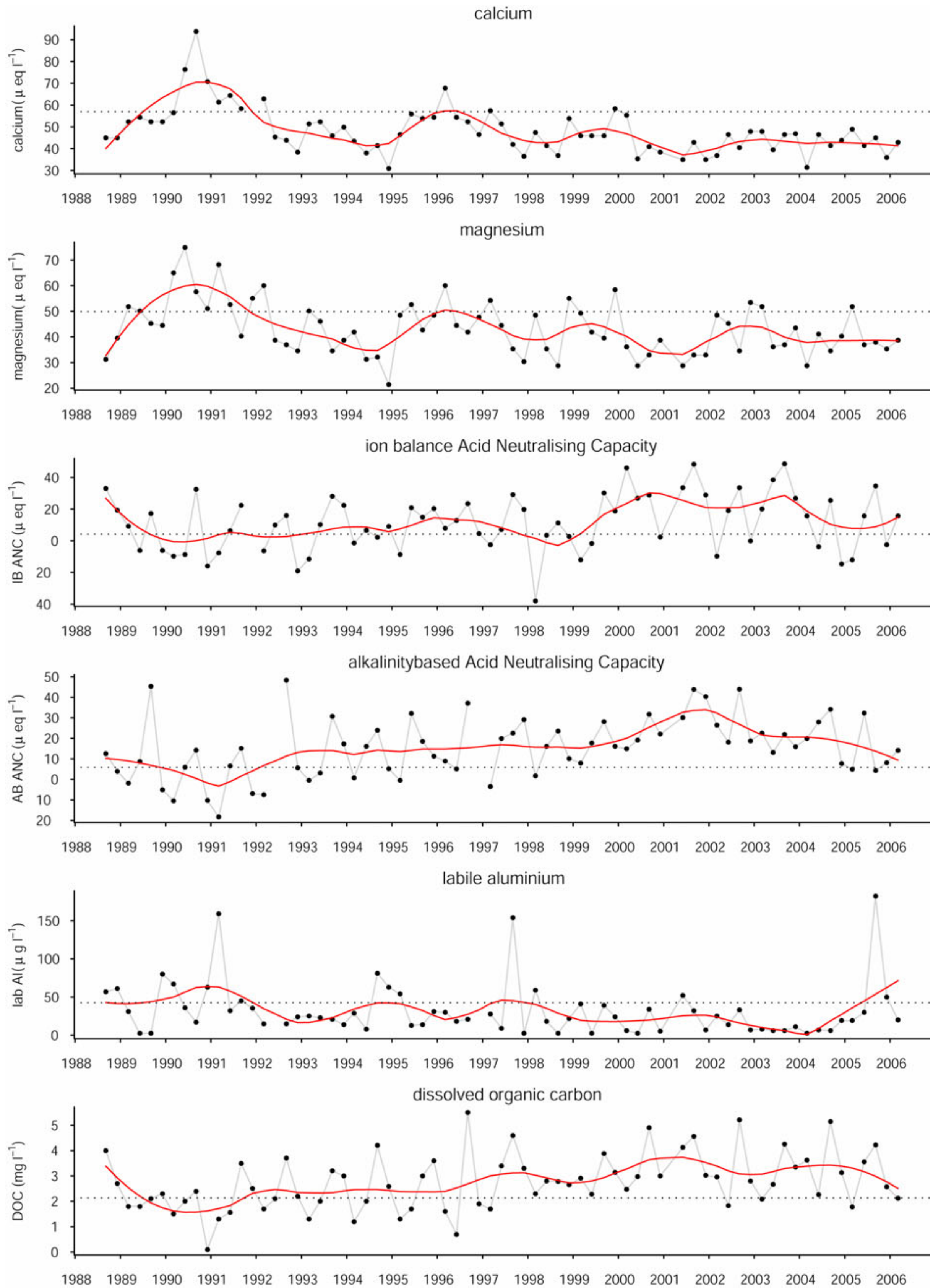

calcium
calcium(μ eq l⁻¹)
magnesium
magnesium(μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al(μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.15.1 Water Chemistry Summary Data and Trend Statistics: Llyn Llagi

Determinand / period		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Sep 1988 - Mar 1993	mean	39.0	10.4	222.7	5.23	1.0	4.2	5.6	36.3	56.9	49.9	187.5	3.6	75.8	42.6	2.1
	st. dev	8.8	9.8	72.9	0.34	13.0	16.4	17.1	9.1	13.5	11.8	49.3	1.6	38.6	36.7	0.9
	min	22.8	1.3	115.7	4.78	-14.3	-19.1	-18.4	23.0	38.4	31.3	113.1	2.6	5.0	2.5	0.1
	max	55.4	38.6	378.0	6.30	35.2	33.0	48.4	58.0	93.8	74.9	291.5	6.6	192.0	159.0	4.0
Apr 1993 - Mar 1998	mean	42.6	9.3	166.7	5.44	5.9	9.5	14.7	26.4	48.4	42.3	151.4	3.4	72.6	35.4	2.6
	st. dev	13.0	7.8	52.8	0.32	8.2	15.3	12.4	6.6	8.4	9.4	33.5	1.4	30.7	35.6	1.2
	min	17.3	1.3	98.7	4.90	-8.0	-37.9	-3.5	13.0	30.9	21.4	100.1	2.0	38.0	2.5	0.7
	max	68.0	35.0	256.7	6.25	25.0	29.3	37.2	36.0	67.9	60.0	200.1	6.6	193.0	154.0	5.5
Apr 1998 - Mar 2003	mean	25.2	5.1	175.9	5.70	10.6	17.4	23.8	24.1	43.7	40.7	153.9	3.7	74.2	19.7	3.2
	st. dev	8.3	3.7	61.4	0.24	7.5	17.9	10.5	8.2	7.0	9.6	39.4	2.0	23.5	15.3	0.9
	min	11.1	1.3	95.9	5.33	-0.6	-12.1	7.9	11.0	34.9	28.8	104.4	0.6	41.7	2.5	1.8
	max	45.1	13.7	265.2	6.30	26.0	48.3	44.0	36.0	58.4	58.4	208.8	7.7	116.0	52.0	5.2
Apr 2003 - Mar 2006	mean	23.0	5.3	160.1	5.76	11.5	15.7	17.1	25.7	42.5	38.5	137.0	2.9	72.2	29.9	3.2
	st. dev	3.9	3.3	40.7	0.20	14.1	20.4	10.3	3.9	5.0	5.6	22.5	1.3	51.3	49.7	1.0
	min	17.1	0.5	115.7	5.57	-5.8	-14.5	4.3	21.0	31.4	28.8	100.1	0.6	29.0	2.5	1.8
	max	29.2	11.4	259.5	6.10	46.0	48.6	34.1	35.0	48.9	51.8	191.4	4.9	224.0	182.0	5.2
Seasonal-Kendall statistics	Sen-slope	-1.189	-0.224	-2.233	0.038	0.638	0.579	0.838		-0.768	-0.544				-1.375	0.070
	P- val	**0.001**	0.087	0.104	**<0.001**	**<0.001**	0.104	**<0.001**		**0.008**	0.051				0.058	**0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.15.2 Epilithic Diatom Percentage Abundance Summary: Llyn Llagi

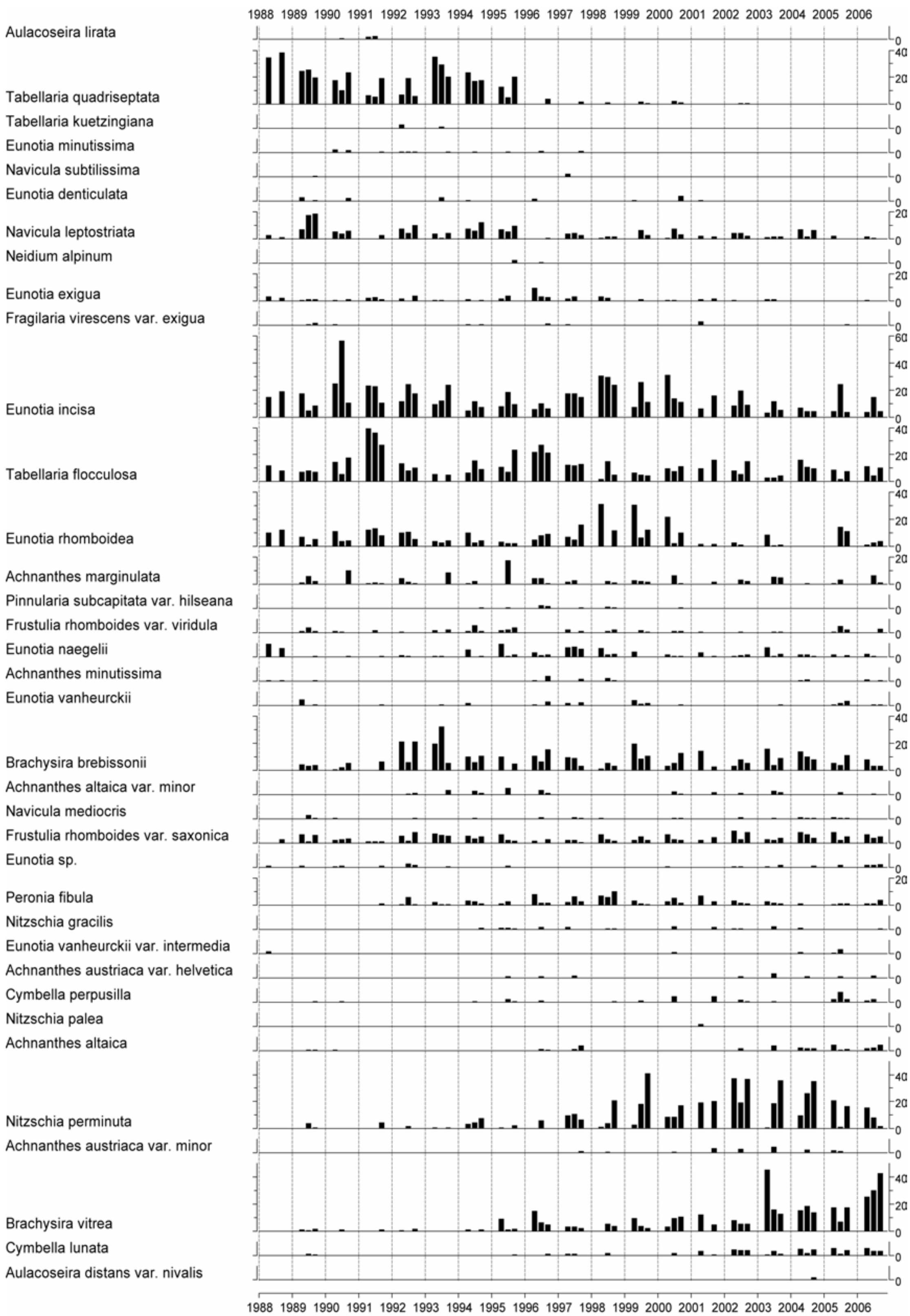


Figure 4.15.3 Aquatic Macrophyte Species Scores (1-5): Llyn Llagi

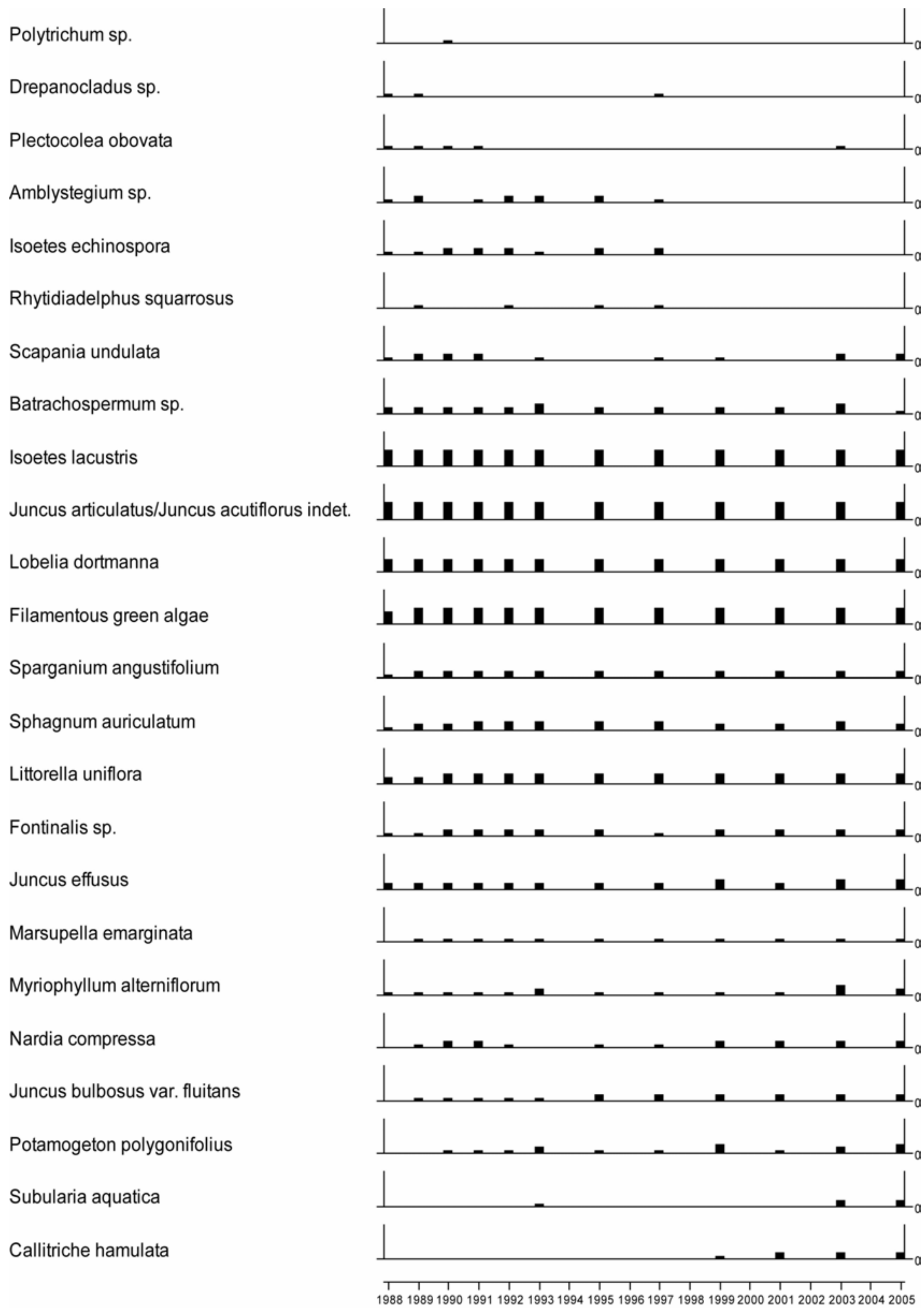


Figure 4.15.4 Macroinvertebrate Percentage Abundance Summary: Llyn Llagi

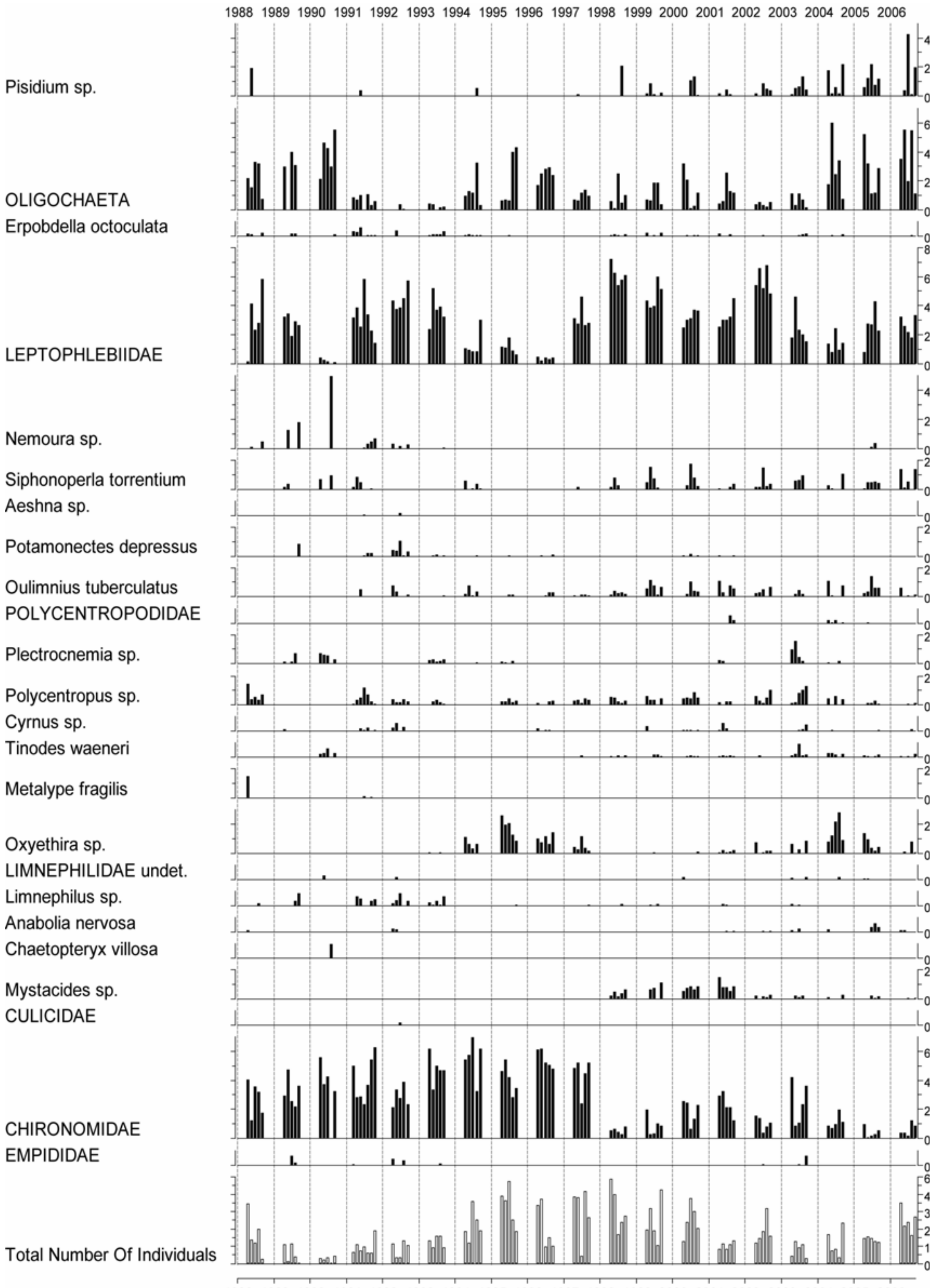
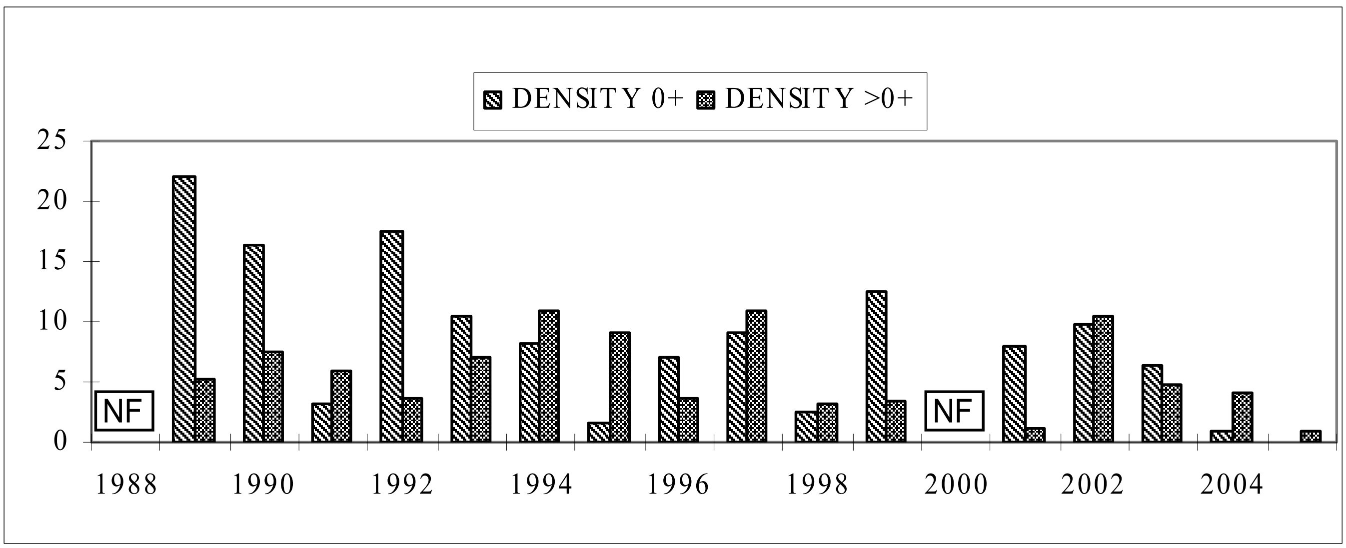


Table 4.15.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Llyn Llagi

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1550.03	144	36	64	0.28	2.70	0.001	0.015
Invertebrates	2465.24	51	39.1	60.9	0.16	0.57	0.001	0.022

Figure 4.15.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Llyn Llagi



NF = Not fished

Figure 4.15.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Llyn Llagi

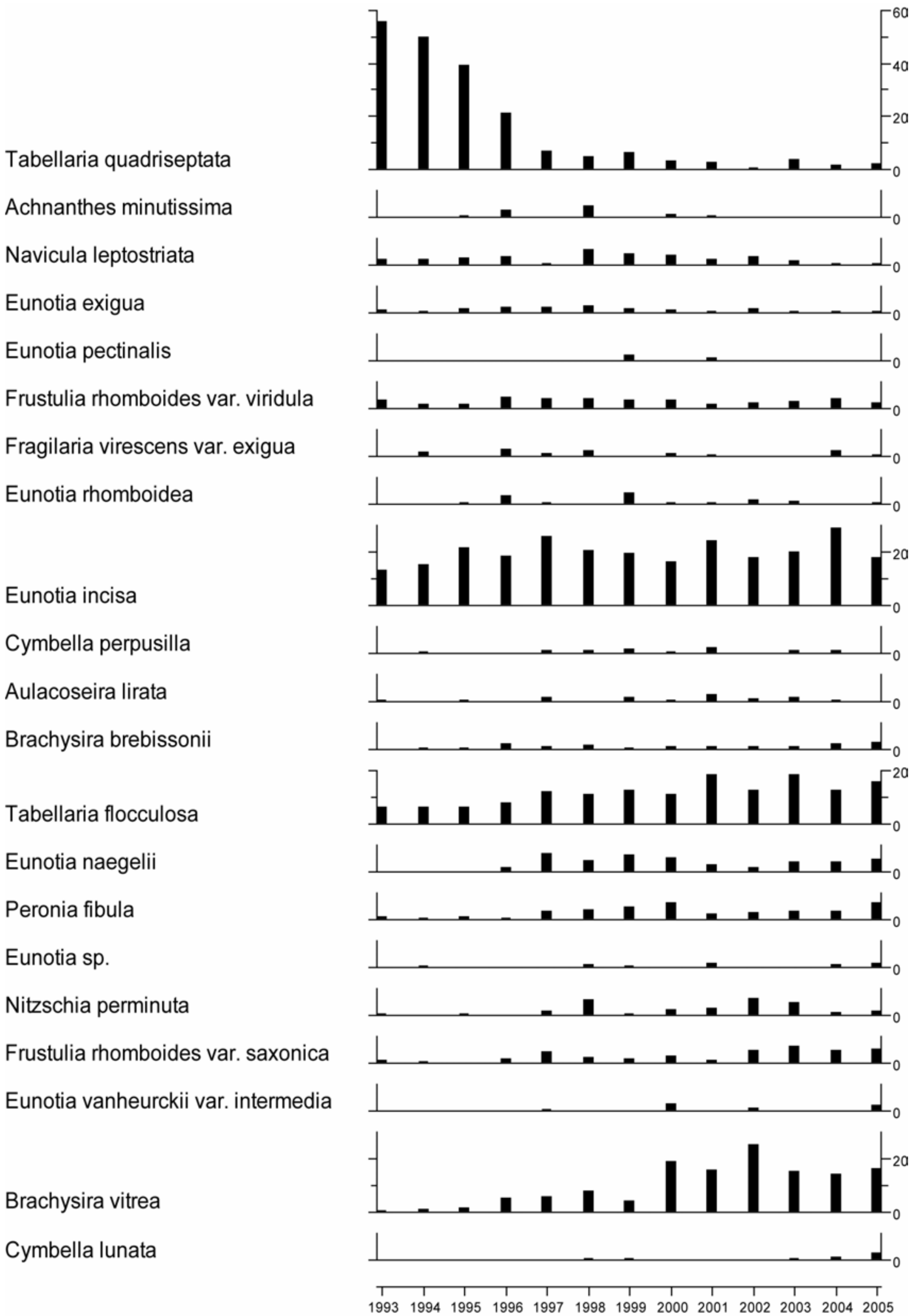
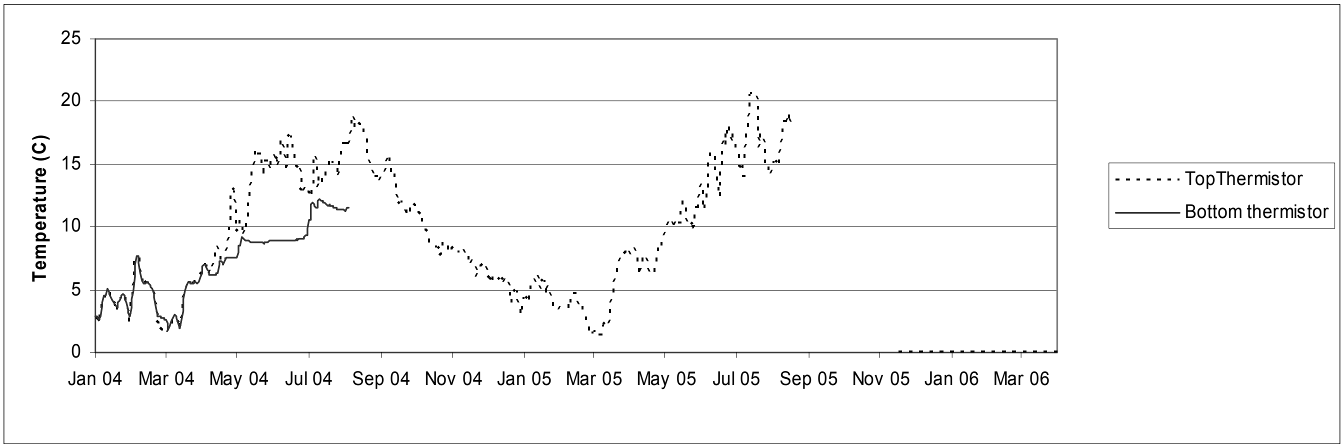


Figure 4.15.7 Thermistor Data: Llyn Llagi



2005/2006 thermistors still in situ – data pending

4.16 Llyn Cwm Mynach

4.16.1 Water Chemistry Summary

Llyn Cym Mynach is a small lake lying at 285 m altitude on Cambrian sedimentary lithology in the Rhinog Mountains, north Wales. The lake comprises two distinct basins, a 10 m deep basin to the north and a shallow macrophyte covered limb to the south. Over 50% of the catchment, including all land adjacent to the lake, is forested with Japanese larch, Lodgepole pine and Sitka spruce, which was planted in 1967.

Over the first 5 years of monitoring (1988-1993) the mean xSO_4 concentration of 52.4 $\mu eq\ l^{-1}$ was relatively high for an AWMN site and is likely to have been enhanced by the interception of sulphate aerosol by the forest canopy. Chloride concentrations were also relatively high and climbed above 500 $\mu eq\ l^{-1}$ as a result of very high inputs of seasalt in 1990. Mean NO_3 concentrations were low (9.6 $\mu eq\ l^{-1}$). The lake was moderately acidic with a mean pH of 5.38, mean alkalinity and ANC just above 0 $\mu eq\ l^{-1}$ and a mean labile aluminium concentration of 65.3 $\mu g\ l^{-1}$ – within the range where aluminium toxicity effects on salmonids are likely (Rosseland et al., 1990).

Over the monitoring period, Llyn Cwm Mynach has undergone a relatively small decline in xSO_4 concentration, with most of change occurring in the late 1990s. Mean concentration for 2003-2006 was 40.6 $\mu eq\ l^{-1}$ – approximately 25% below the average for the initial period. Nitrate and chloride concentrations have shown substantial inter-annual variability but no long-term trend.

There has been little indication of any change in pH or ion balance ANC. The mean labile aluminium concentration in 2003-2006 was 28% lower than for the first five years but the trend in this variable was not significant according to the Seasonal Kendall Test .

Unusually for the AWMN there is little indication of any long-term trend in DOC. Llyn Cwm Mynach is an exceptionally transparent lake – secchi disc depths are often greater than the maximum depth of the lake. However, the moderate DOC concentrations suggest that the molecular composition of DOC in Llyn Cwm Mynach differs from most other sites on the Network where DOC is predominantly in the form of coloured humic substances. The dominant DOC forms here may not be as responsive to changing deposition chemistry as most AWMN sites (Section 5.4.5).

4.16.2 Biology Summary

The epilithic diatom flora of Llyn Cwm Mynach has shown significant linear change over the monitoring period. The trend has been driven by a gradual replacement of *Eunotia rhomboidea* (SWAP pH optima = 5.1) and *Eunotia vanheurkii* var. 1 (SWAP pH optima = 5.1) with a range of species, including *Brachysira brebissonii* (SWAP pH optima = 5.3), *Frustulia rhomboides* var. *saxonica* (SWAP pH optima = 5.2) and *Navicula tenuicephala* (SWAP pH optima = 5.3). On balance therefore these changes are indicative of a slight increase in pH, and although there is no significant trend in pH there has been a tendency for fewer extremely low pH measurements in recent years.

The sediment trap data for Llyn Cwm Mynach is very different from the epilithic data and suggests that habitats other than the epilithon may be more important substrates at this site. The trends in species composition are also partly contradictory to those in the epilithon (with respect to acidity indicators), with reductions in the deep water benthic species *Fragilaria virescens* var. *exigua* (SWAP pH optima = 5.7) and a small increase in the acidobiontic species *Tabellaria binalis* (SWAP pH optima = 4.7). Clearly therefore, these trends cannot be linked with chemical improvement and are more likely due to changes in substrate availability (see below) over the monitoring period.

The aquatic macrophyte flora in Llyn Cwm Mynach is relatively diverse for an AWMN lake, partly as a result of the habitat heterogeneity, but the main basin is dominated by a range of oligotrophic species with varying sensitivity to acidity. The clearest change in the main basin has been a major expansion over the first few years of a blue green alga, *Plectonema* sp.. This species has a preference for high zinc levels, and may indicate an influence on water chemistry of some small abandoned metal mine workings within the catchment. *Plectonema* has formed a thick blanket over other submerged vegetation to the extent that *Juncus bulbosus* var. *fluitans* plants in parts of the lake have been killed and now form substantial rafts of decaying debris around the shore of the lake. Regardless of these apparently deleterious changes for the ecology of the lake, one acid-sensitive species, *Eleogiton fluitans*, was first detected in 1999 as has been found on each survey since.

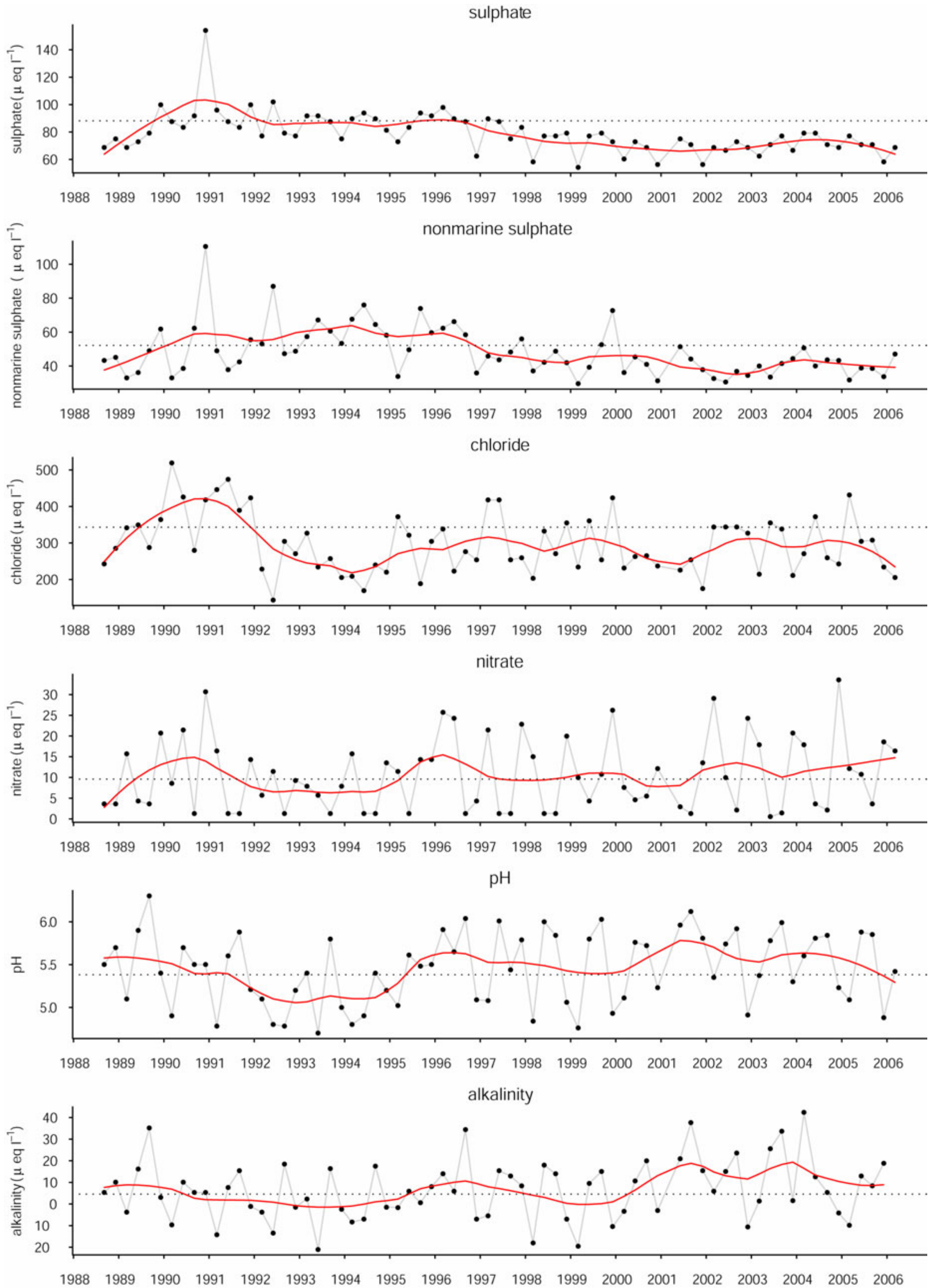
The macroinvertebrate community of Llyn Cwm Mynach has changed significantly over the monitoring period but there is no obvious link with the slight improvement in water chemistry. The main change has been a replacement of the acid-tolerant mayfly family Leptophlebiidae with chironomids, but as this latter group is not indentified to species level it is not possible to infer the likely driver. It is possible that the dominant influence on the assemblage has been the accumulation of decaying organic matter in the lake littoral and the subsequent loss of open stony habitats.

The outflow of Llyn Cwm Mynach has supported moderate densities of brown trout throughout the monitoring period. There is no trend in densities of juvenile or older fish over time.

4.16.3 Conclusions

Llyn Cwm Mynach is a forested site that has experienced a gradual decline in xSO_4 over the monitoring period. Labile aluminium concentrations have fallen in response but there is less evidence for a clear improvement in pH and alkalinity. Despite these modest changes there is an indication of a subtle improvement in the epilithic diatom flora. However, changes in the sediment trap diatom and macroinvertebrate data are difficult to interpret. Changes in these assemblages may have been complicated by the effects of a blue green algal mat at the site that has resulted in the die-back of some submerged aquatic plants. The brown trout population shows no trends in density with time.

Figure 4.16.1 Water Chemistry Summary Plots: Llyn Cwm Mynach



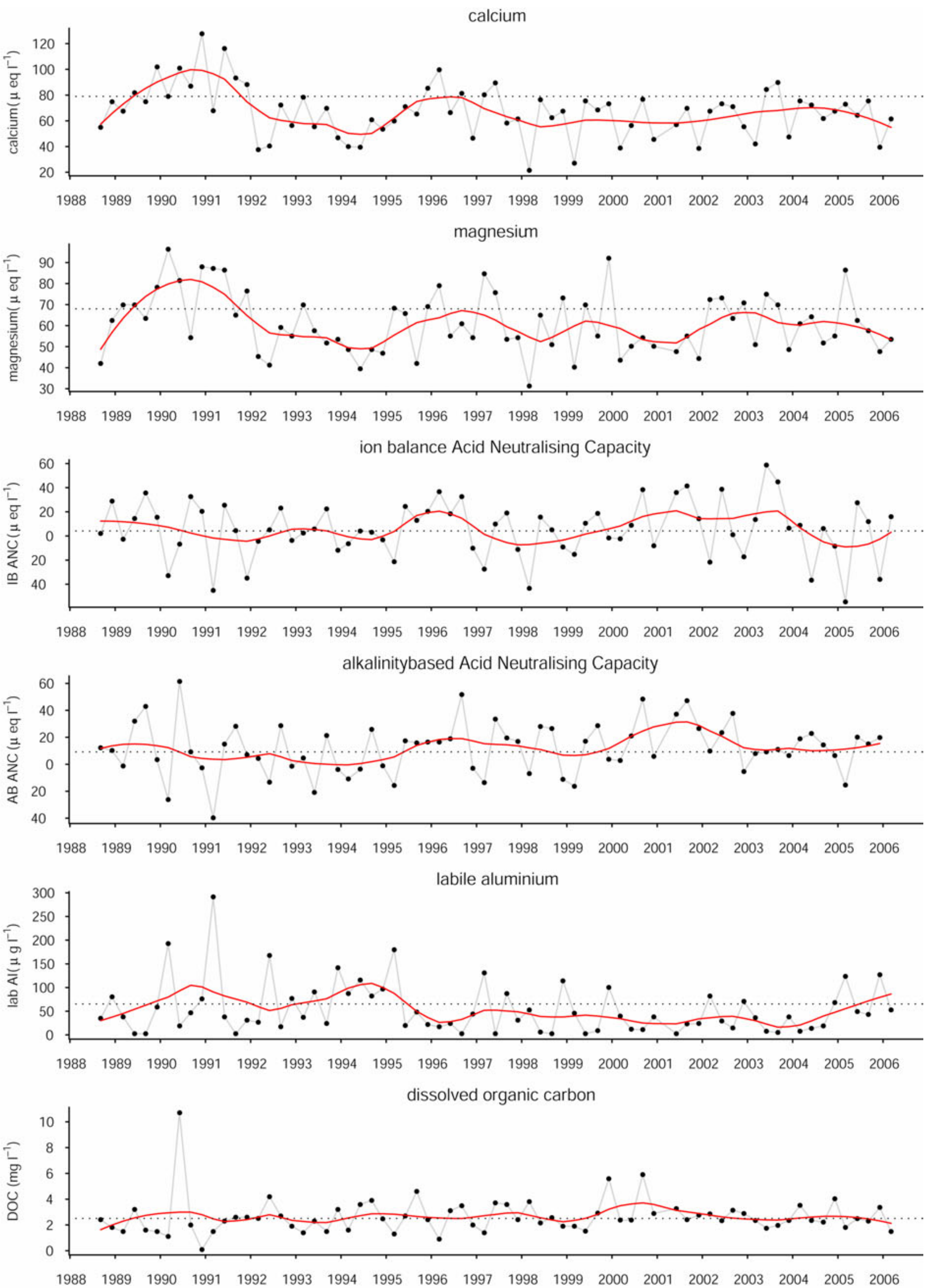

calcium
calcium(μ eq l⁻¹)
magnesium
magnesium(μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al(μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.16.1 Water Chemistry Summary Data and Trend Statistics: Llyn Cwm Mynach

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Sep 1988 - Mar 1993	mean	52.4	9.6	343.1	5.38	4.6	4.1	9.2	51.9	79.0	68.0	294.7	3.4	106.5	65.3	2.5
	st. dev	19.0	8.3	94.4	0.42	11.9	22.8	23.3	10.4	23.3	16.1	63.4	1.7	87.4	74.8	2.2
	min	33.2	1.3	143.9	4.78	-14.3	-45.2	-39.9	33.0	37.4	41.1	178.4	2.6	5.0	2.5	0.1
	max	110.6	30.7	519.1	6.30	35.2	35.6	61.5	72.0	127.7	96.2	404.6	7.4	378.0	291.0	10.7
Apr 1993 - Mar 1998	mean	56.1	10.3	268.3	5.36	3.4	3.8	8.7	40.4	62.6	57.0	243.4	3.4	127.6	65.1	2.7
	st. dev	12.2	8.7	72.3	0.42	13.2	20.7	18.6	10.6	19.0	13.5	51.6	1.3	65.6	50.5	1.0
	min	34.1	1.3	169.3	4.70	-21.0	-43.3	-20.8	24.0	21.5	31.3	174.0	2.3	25.0	2.5	0.9
	max	76.1	25.7	417.5	6.04	34.4	36.7	51.6	64.0	99.8	84.7	348.0	6.4	220.0	180.0	4.6
Apr 1998 - Mar 2003	mean	39.4	10.8	287.1	5.55	8.1	8.7	17.8	39.5	60.1	59.1	252.1	4.7	111.3	34.9	2.9
	st. dev	7.1	8.9	64.9	0.44	14.3	19.5	18.6	8.0	15.1	13.4	45.4	1.7	56.5	33.8	1.1
	min	28.9	1.3	174.9	4.76	-19.6	-21.8	-16.2	25.0	26.9	40.3	169.7	1.8	28.0	2.5	1.5
	max	52.7	29.1	423.2	6.12	37.6	41.3	48.3	53.0	76.8	92.1	348.0	7.2	220.0	114.0	5.9
Apr 2003 - Mar 2006	mean	40.6	11.8	294.6	5.41	13.4	3.7	11.7	44.4	67.7	61.1	248.3	4.5	101.8	46.3	2.5
	st. dev	5.7	10.1	69.8	0.43	15.8	33.4	10.6	7.1	14.2	11.5	48.0	1.3	59.4	42.2	0.8
	min	31.8	0.5	205.9	4.88	-9.8	-54.5	-15.4	36.0	39.4	47.7	182.7	1.8	21.0	5.0	1.5
	max	50.8	33.6	431.6	5.99	42.4	58.7	22.8	58.0	89.8	86.4	321.9	6.9	209.0	127.0	4.0
Seasonal-Kendall statistics	Sen-slope	-0.895	0.357	-2.116	0.006	0.459	-0.245	0.370		-0.817	-0.366				-2.383	0.011
	P- val	**0.025**	0.117	0.530	0.272	0.255	0.836	0.118		0.212	0.435				0.545	0.079

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.16.2 Epilithic Diatom Percentage Abundance Summary: Llyn Cwm Mynach

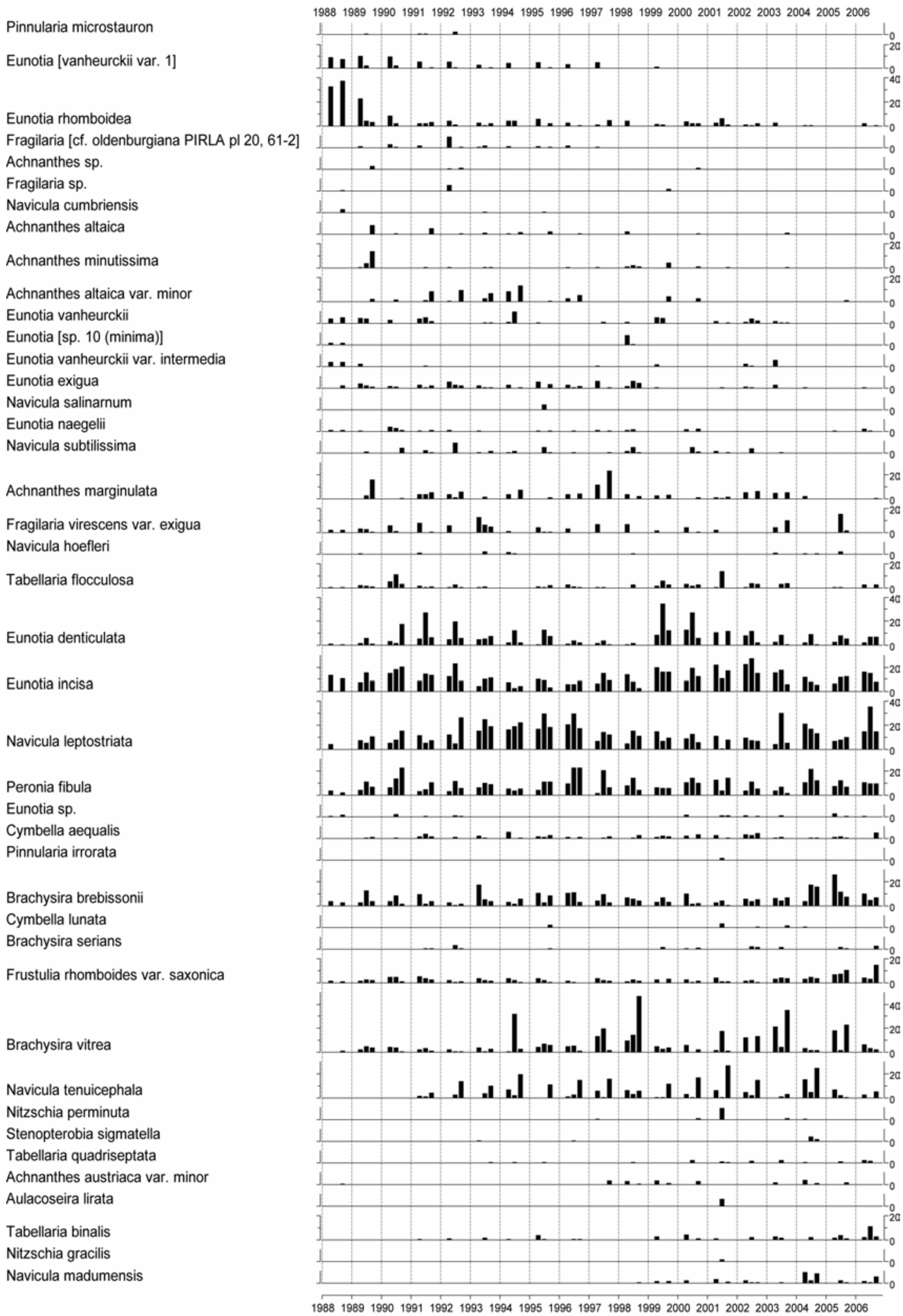


Figure 4.16.3 Aquatic Macrophyte Species Scores (1-5): Llyn Cwm Mynach

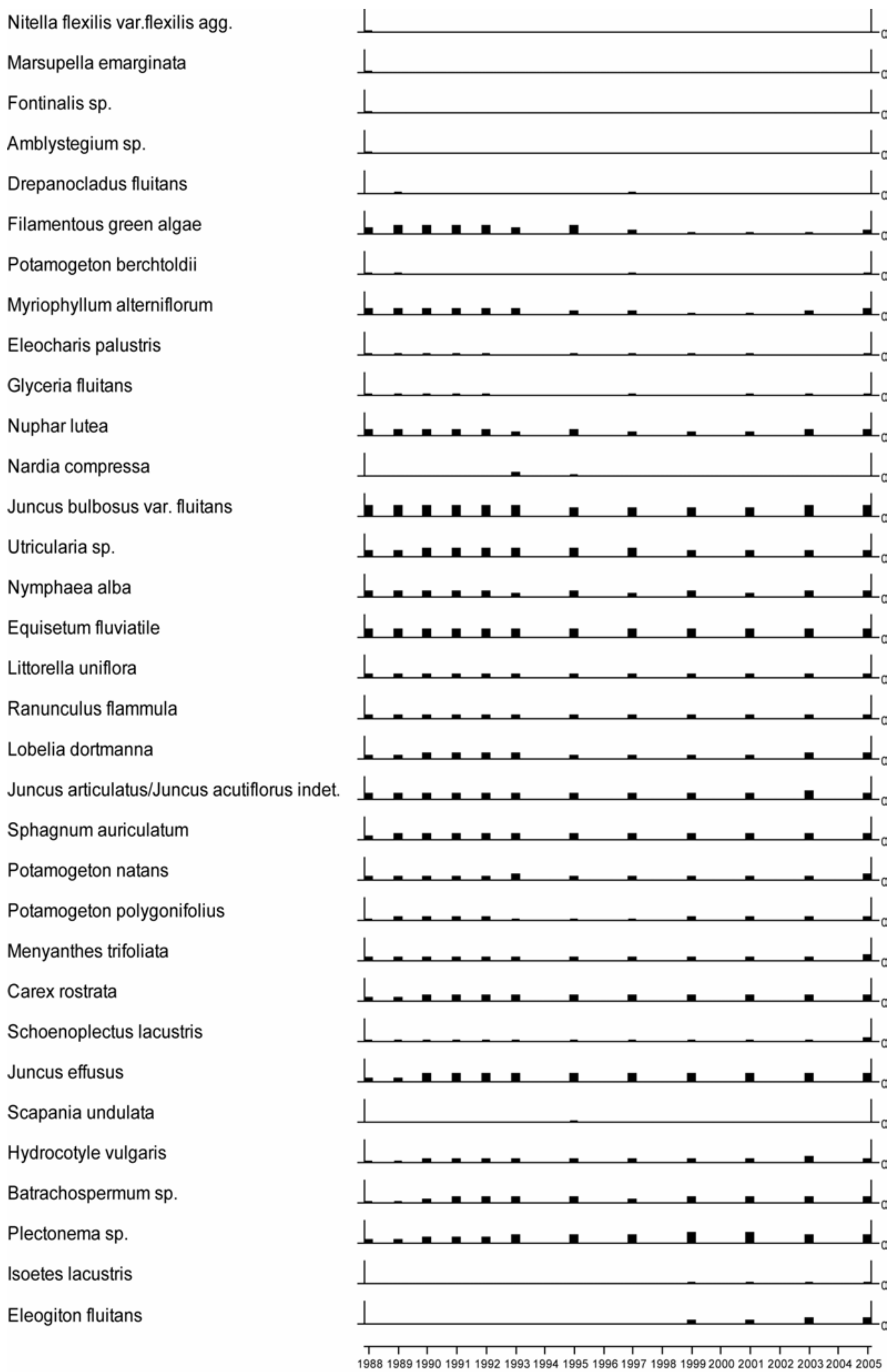


Figure 4.16.4 Macroinvertebrate Percentage Abundance Summary: Llyn Cwm Mynach

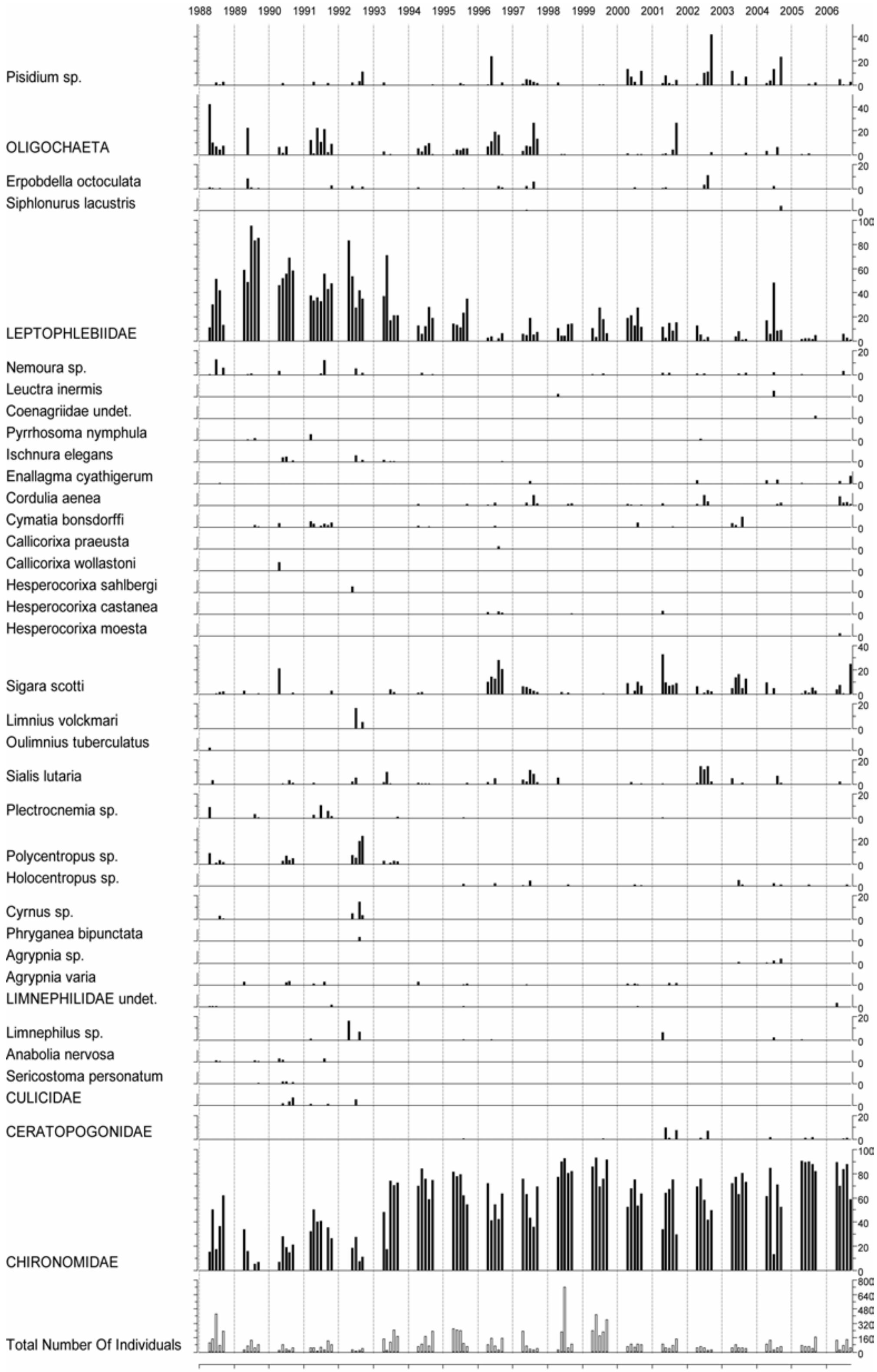
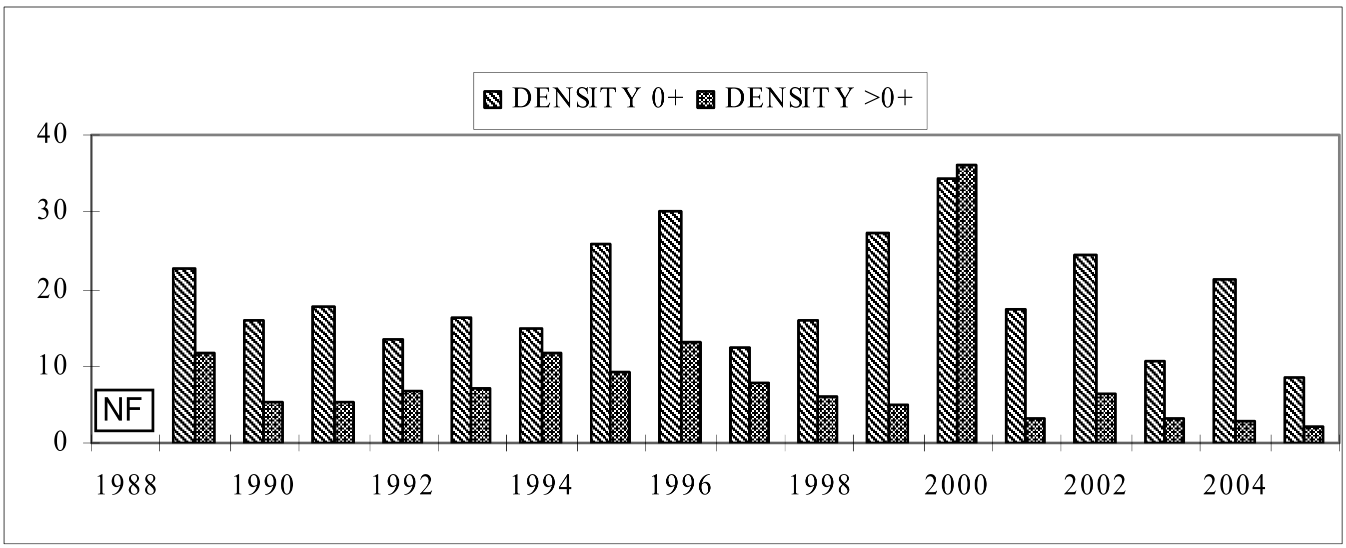


Table 4.16.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms): Llyn Cwm Mynach

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1474.48	128	51.7	48.3	0.10	0.74	0.001	0.022
Invertebrates	2446.31	56	41.6	58.4	0.25	1.27	0.001	0.011

Figure 4.16.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Llyn Cwm Mynach



NF = Not fished

Figure 4.16.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Llyn Cwm Mynach

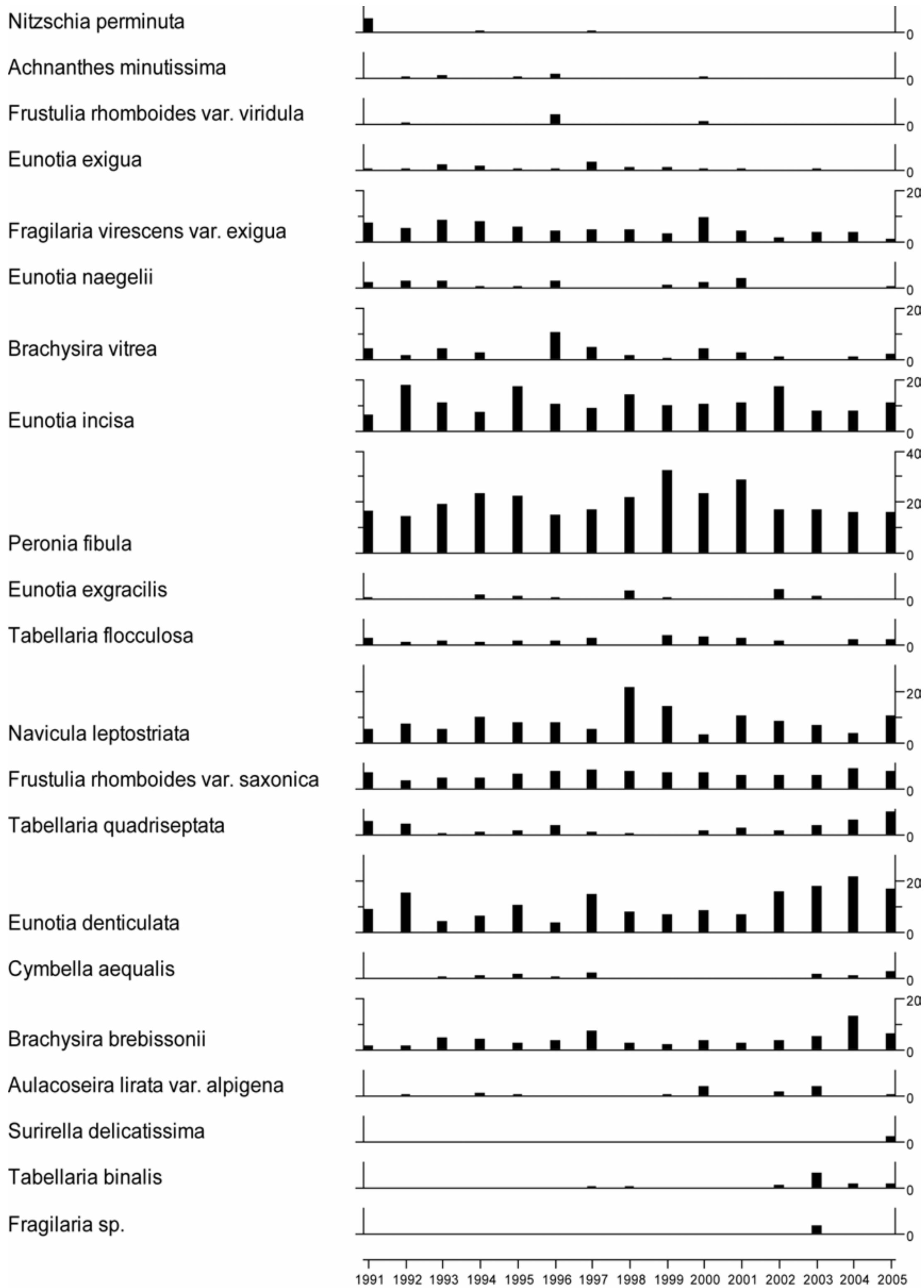
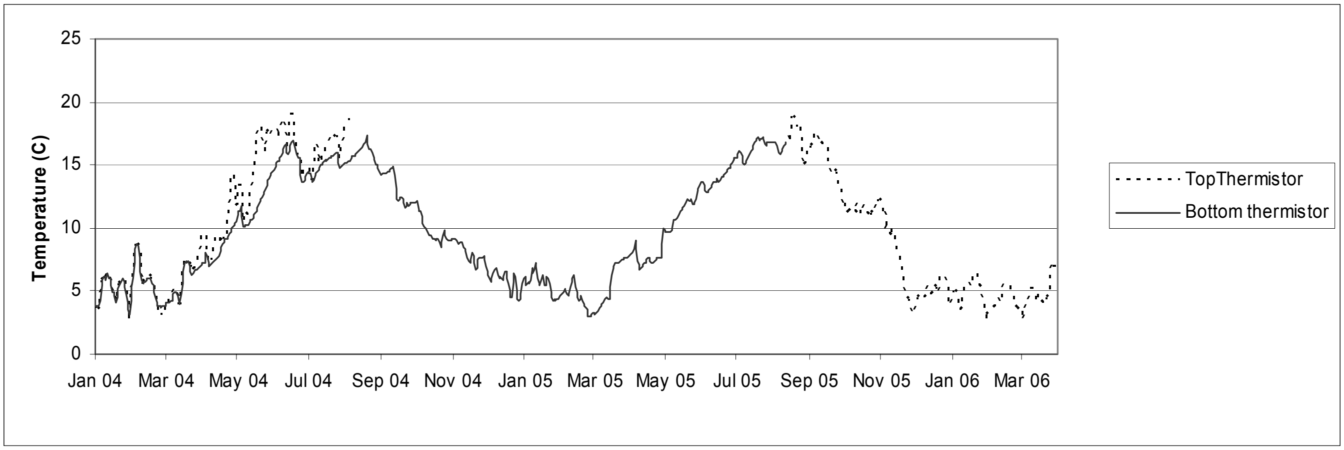


Figure 4.16.7 Thermistor Data: Llyn Cwm Mynach



4.17 Afon Hafren

4.17.1 Water Chemistry Summary

The Afon Hafren, the source of the River Severn, is an acidified stream draining a forested catchment on ordovician and silurian sedimentary geology in the Plynlimon region of mid-Wales. Water acidity is sensitive to variation in hydrology, with pH regularly falling below 5.0 at high flow and remaining above pH 6.0 at high flow. Over the first five years of monitoring (1988-1993) mean xSO_4 concentration was 59.5 μeq l^{-1}, 10 μeq l^{-1} higher than the nearby moorland stream the Afon Gwy (site 18). Mean NO_3 concentration was relatively high for an AWMN site at 20.4 μeq l^{-1}, again circa 10 μeq l^{-1} than for its non-forested neighbour. Mean pH was 5.27 and the minimum recorded in the first five years was 4.31. Mean labile aluminium concentration was 103.4 μg l^{-1}, suggesting levels would frequently exceed toxicological thresholds for salmonids.

Over the course of monitoring xSO_4 concentration has fallen by circa 20% with most of the reduction occurring between 1996 and 2000. Since 2002 levels have increased again slightly. The mean 2003-2006 concentration is almost six times higher than that for Loch Coire nan Arr (Site 1) in northwest Scotland.

Nitrate concentrations have shown strong inter-annual variability but no overall trend and, with the decline in xSO_4, NO_3 is an increasingly important source of acidity here.

In common with other westerly sites in the southern half of the UK, chloride concentrations were particularly elevated in the early 1990s, reflecting an increased input of seasalt during a period of intense and frequent coastal storms. However, comparatively large concentrations were also recorded in the winter of 2002-2003. In comparison with many of these sites, inter-sample variability in chloride appears dampened, perhaps due to interception and temporary retention of the seasalt aerosol within the forest canopy. There is no significant trend in chloride over the full period.

Dissolved organic carbon concentrations have increased slightly, mirroring the decline in xSO_4 (see Section 5.4.5), but there has been a much stronger increase in peak concentrations (that normally occur during periods of high flow), than in minima which tend to occur during drier periods.

Despite the reduction in acid anion loading, base cation concentrations show no indication of long term trends, perhaps as a result of the increase in organic anions over the period. Ion balance ANC has increased gradually from a slightly negative mean in the first five years and has remained largely above 0 μeq l^{-1} since 2001. However, these data demonstrate the continuing sensitivity of the Afon Hafren to periods of elevated seasalt e.g. during the winter of 2002-2003 where concentrations fell below -50 μeq l^{-1}.

Water pH shows no significant trend over the period although there has been a progressive increase in pH minima; average pH for the 2005-2006 year was the highest since monitoring began. The dominant acidity response to the reduction in sulphur loading has been a reduction in labile aluminium concentrations; the mean 2003-2006 concentration (65.1 μg l^{-1}) is 63% of the mean for the first five years.

4.17.2 Biology Summary

The epilithic diatom community of the Afon Hafren has been dominated by one acidophilous/acidobiontic species, *Eunotia exigua* (SWAP pH optima = 5.1), for almost the entire monitoring record but shows significant linear change indicative of recovery. In most samples in most years *E. exigua* has formed more than 70% of the assemblage. In 1989 and 1990, its abundance was down relative to *Achnanthes austriaca* var. *minor* (SWAP pH optima = 5.1), for reasons that are difficult to explain from the accompanying chemistry data. However, since 1998, *E. exigua* abundances have fallen progressively as *Tabellaria flocculosa* (SWAP pH optima = 5.4) has increased from trace amounts, until becoming the dominant species in 2006. This change is consistent with a gradual recent improvement in pH in response to falling S deposition. However, the strikingly high abundances of *T. flocculosa* in 2006 are also likely to reflect the influence on acidity of the low NO_3 concentrations and low seasalt inputs in the winter and spring of this year.

The aquatic macrophytes in the survey stretch have been restricted largely to one acid tolerant and ubiquitous liverwort species, *Scapania undulata*, which has shown no indication of long term changes in cover. The liverwort *Nardia compressa*, which is most common in some of the most acidic streams on the AWMN was found in trace amounts over most of the early years of monitoring but has not been recorded since 1998. The aquatic moss *Hyocomium armoricum* was found in one location in 2002 and has been recorded there every year since, but the acid-indicator value of this species is unclear.

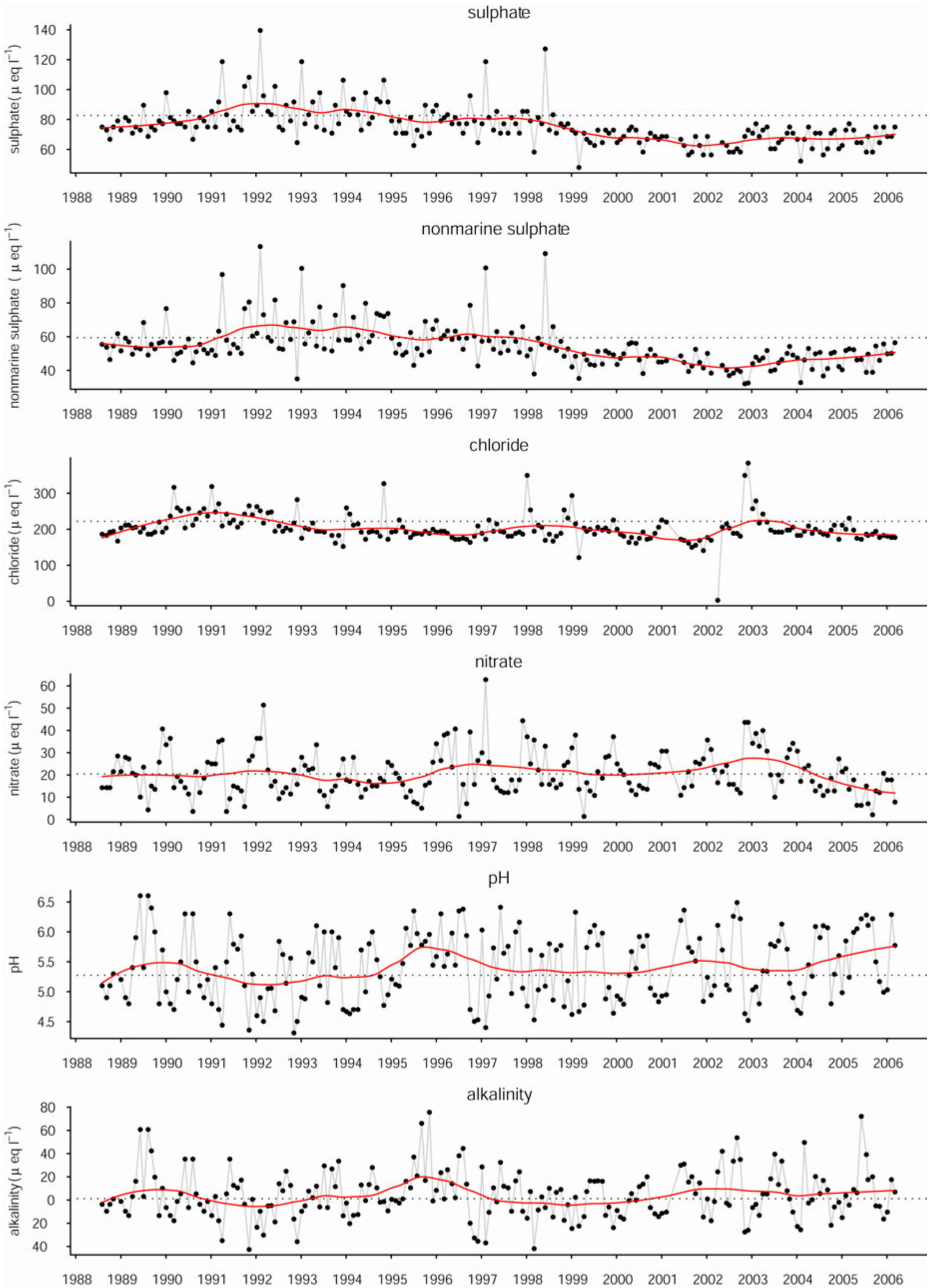
The macroinvertebrate assemblage shows a significant linear trend over the monitoring period which is driven predominantly by an increase in the abundance of the acid-sensitive predatory stonefly larva *Isoperla grammatica*. There is also an indication of an increase in another sensitive stonefly, *Siphonoperla torrentium*, although this species was also relatively abundant in 1991 and 1992.

Electrofishing of the Afon Hafren commenced only in 1995, when very low densities of brown trout were recorded. Densities of fish greater than 1 year old were relatively high in three of the last four years, and the highest number of juvenile fish were recorded in 2004. Currently, however, between-year variability in densities is too great to discern any obvious long term response to the gradual reduction in acidity.

4.17.3 Conclusions

The Afon Hafren is considerably more acidic than the neighbouring Afon Gwy, reflecting, at least in part, larger inputs of acidity due to the greater interception of pollutants by the forest canopy. However, the site is relatively well buffered by groundwater during periods of low precipitation. In common with the majority of AWMN sites xSO_4 concentration fell substantially in the late 1990s but more recently has shown a slight increase. The clearest long-term effect on acidity has been a decline in peak labile aluminium levels. Recent chemical improvement is reflected in a switch in the dominance of diatom taxa and an increase in acid-sensitive stoneflies. Despite this tentative evidence for the early stages of recovery the site remains vulnerable to seasalt episodes that are still capable of raising labile aluminium concentrations above severely toxic levels.

Figure 4.17.1 Water Chemistry Summary Plots: Afon Hafren



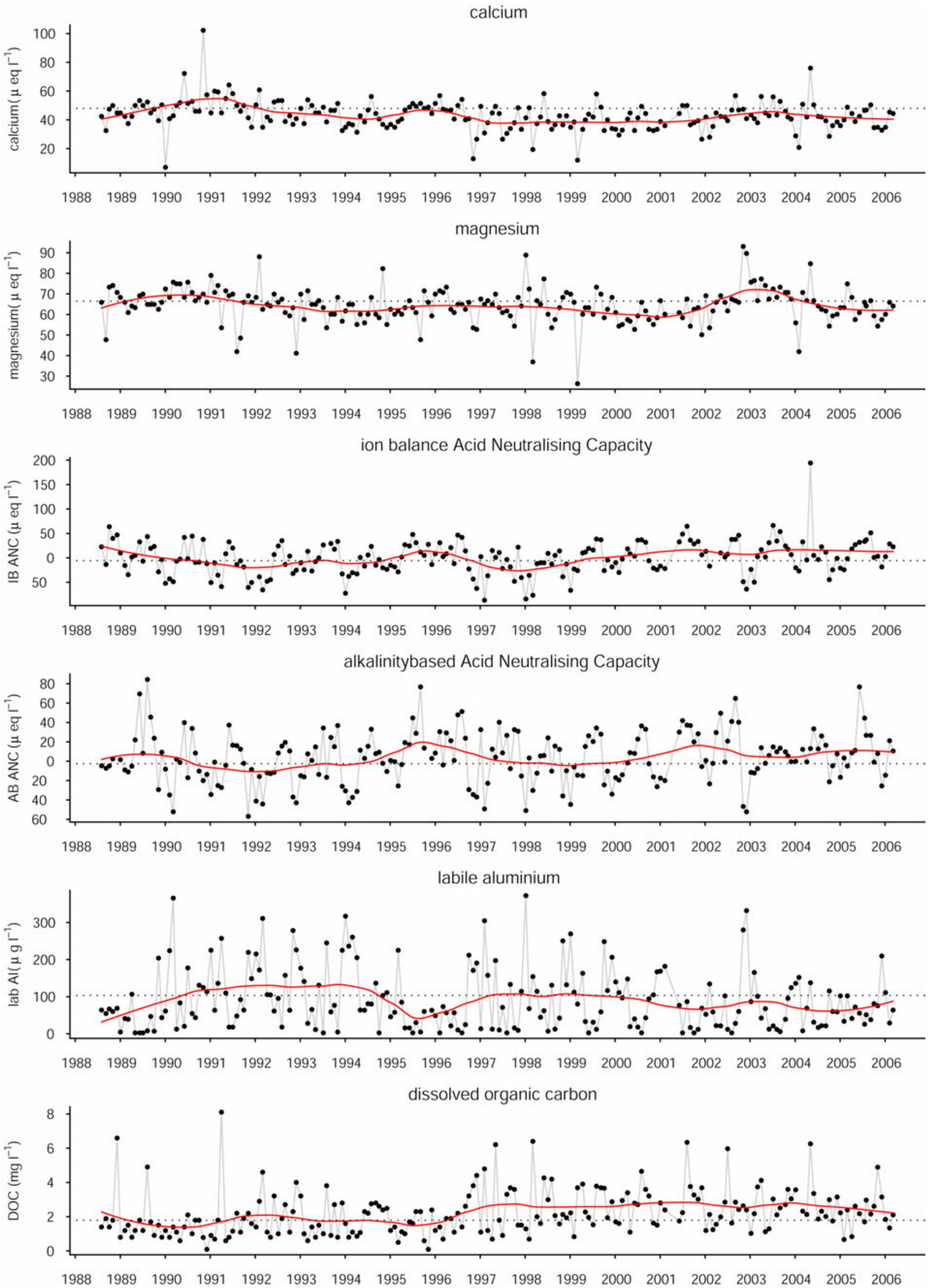

calcium
calcium(μ eq l⁻¹)
magnesium
magnesium(μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al(μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.17.1 Water Chemistry Summary Data and Trend Statistics: Afon Hafren

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Aug 1988 - Mar 1993	mean	59.5	20.4	222.1	5.27	1.1	-5.8	-13.8	41.5	48.0	66.5	201.1	3.2	172.4	103.4	1.8
	st. dev	13.9	9.9	32.7	0.58	21.0	32.2	23.5	10.6	12.0	8.2	17.3	2.1	113.0	86.7	1.4
	min	35.2	3.6	166.4	4.31	-42.6	-65.4	-57.1	34.0	7.0	41.1	174.0	2.6	5.0	2.5	0.1
	max	113.4	51.4	318.8	6.60	60.9	63.6	19.4	112.0	102.3	88.0	252.3	15.3	489.0	366.0	8.1
Apr 1993 - Mar 1998	mean	60.6	20.6	197.7	5.46	7.2	-7.7	4.9	34.9	41.9	63.1	183.1	3.4	172.6	94.9	2.0
	st. dev	11.3	11.3	33.3	0.57	22.3	32.2	27.6	7.4	8.7	7.5	22.7	1.5	124.4	92.7	1.3
	min	38.1	1.3	152.3	4.40	-42.0	-86.6	-51.1	20.0	13.0	37.0	134.9	2.3	27.0	2.5	0.1
	max	100.8	62.9	349.8	6.41	75.6	47.8	76.9	52.0	56.9	88.8	304.5	10.2	550.0	372.0	6.4
Apr 1998 - Mar 2003	mean	46.3	22.3	196.3	5.37	1.6	1.9	3.9	30.3	39.8	63.3	184.8	4.8	185.2	91.0	2.6
	st. dev	13.6	9.1	52.0	0.55	18.3	29.1	26.3	7.1	7.8	9.5	25.8	2.0	91.9	79.8	1.1
	min	1.8	1.3	2.8	4.52	-27.6	-66.6	-52.1	20.0	12.0	26.3	113.1	1.5	40.0	2.5	0.8
	max	109.4	43.6	383.7	6.49	53.6	64.4	64.8	58.0	58.4	93.0	295.8	11.8	425.0	332.0	6.3
Apr 2003 - Mar 2006	mean	47.1	18.2	193.7	5.30	7.4	16.3	9.7	33.8	42.8	64.9	183.9	4.0	144.0	65.1	2.5
	st. dev	5.8	8.6	15.7	0.44	20.7	39.4	18.7	2.9	9.5	7.7	24.8	2.0	80.8	47.6	1.1
	min	32.8	2.1	172.1	4.64	-25.8	-44.5	-25.6	29.0	21.0	42.0	156.6	1.8	47.0	6.0	0.7
	max	56.3	40.0	242.6	6.29	72.0	194.2	76.6	39.0	75.8	84.7	291.5	12.0	386.0	210.0	6.3
Seasonal-Kendall statistics	Sen-slope	-0.897	0.008	-1.432	0.019	0.328	1.002	0.752		-0.330	-0.183				-2.083	0.053
	P- val	**0.002**	0.995	0.053	0.100	0.674	0.087	0.068		**0.010**	0.280				0.376	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.17.2 Epilithic Diatom Percentage Abundance Summary: Afon Hafren

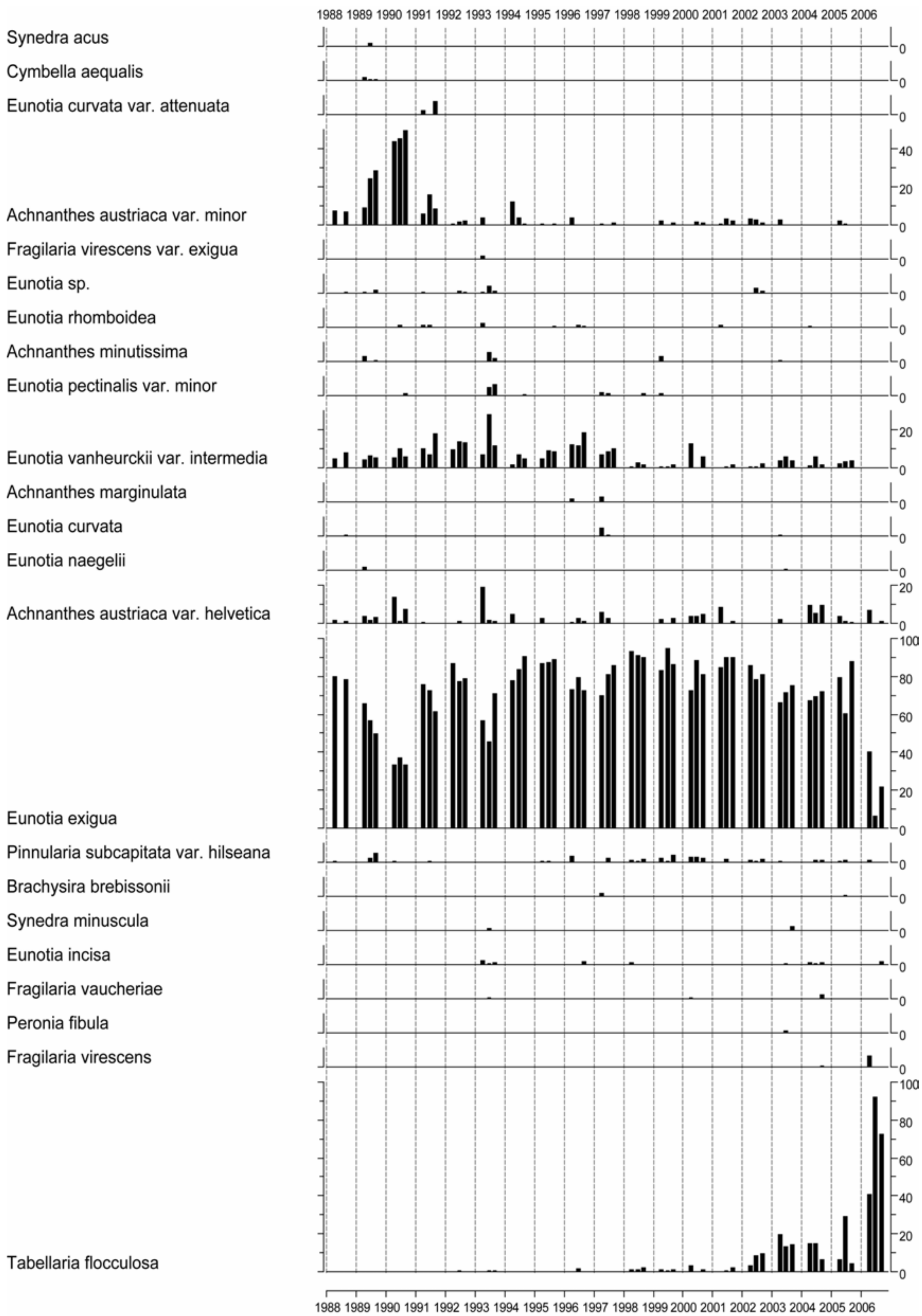
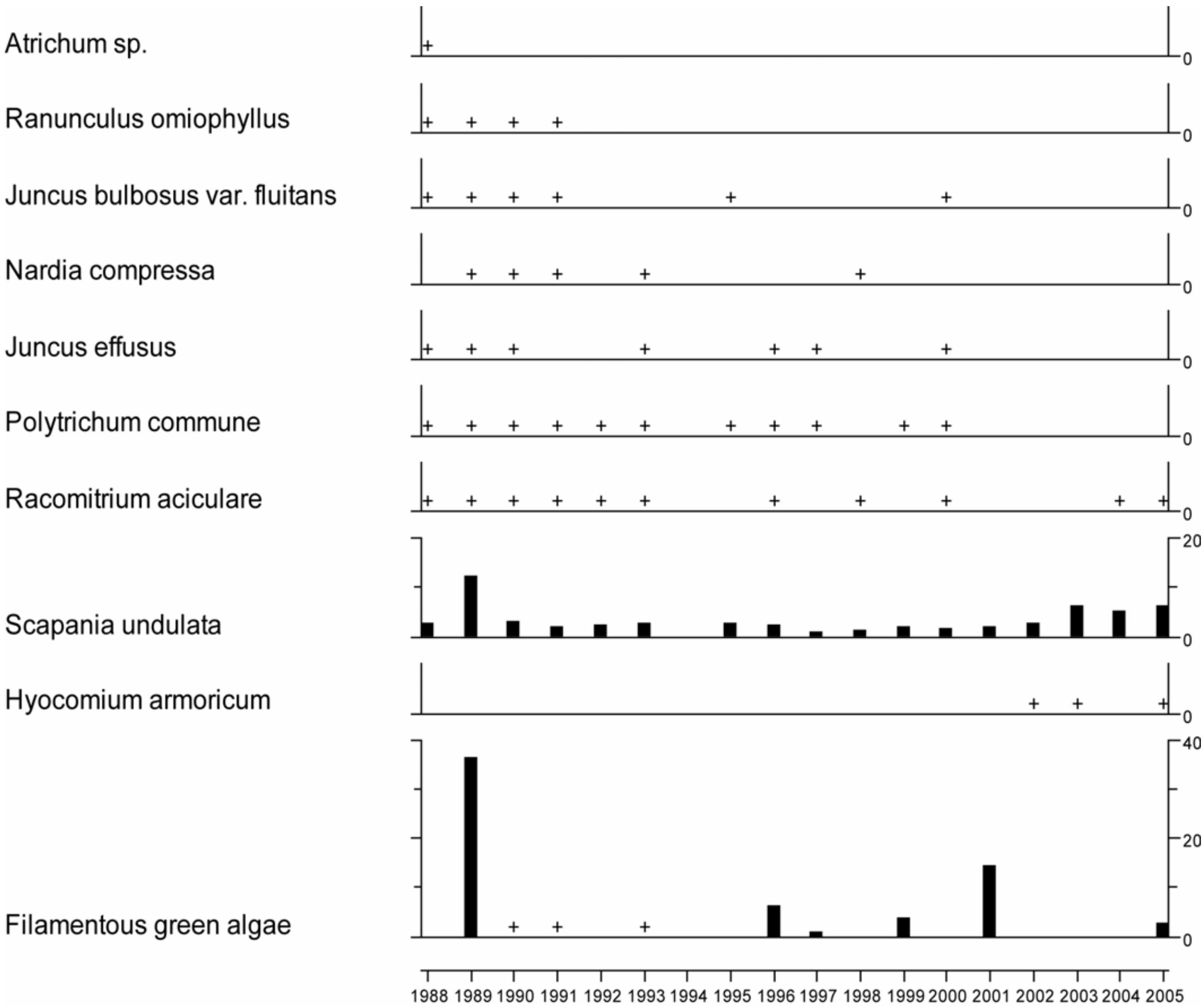
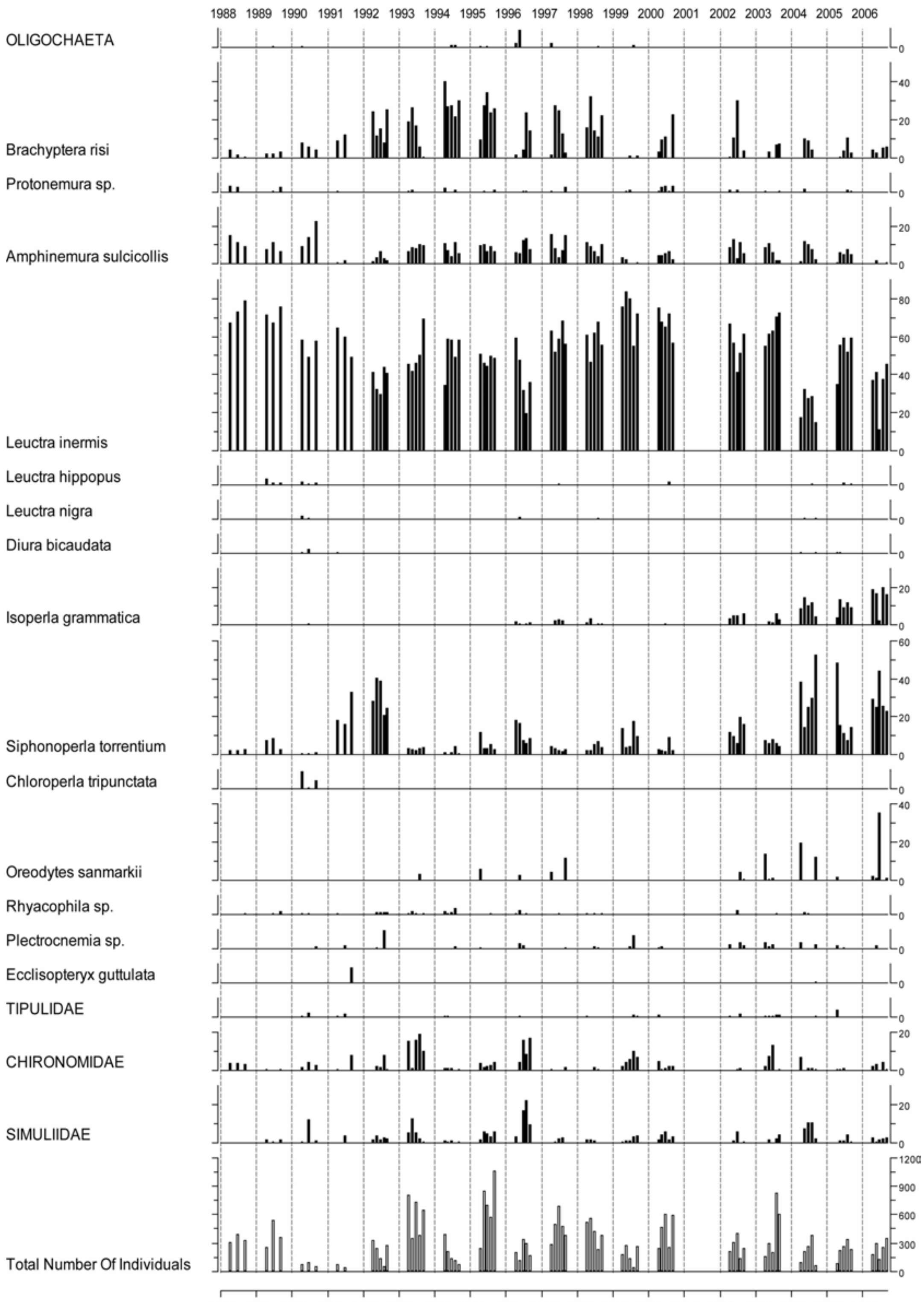


Figure 4.17.3 Aquatic Macrophyte Percentage Species Cover: Afon Hafren



+ Represents <0.25% abundance

Figure 4.17.4 Macroinvertebrate Percentage Abundance Summary: Afon Hafren

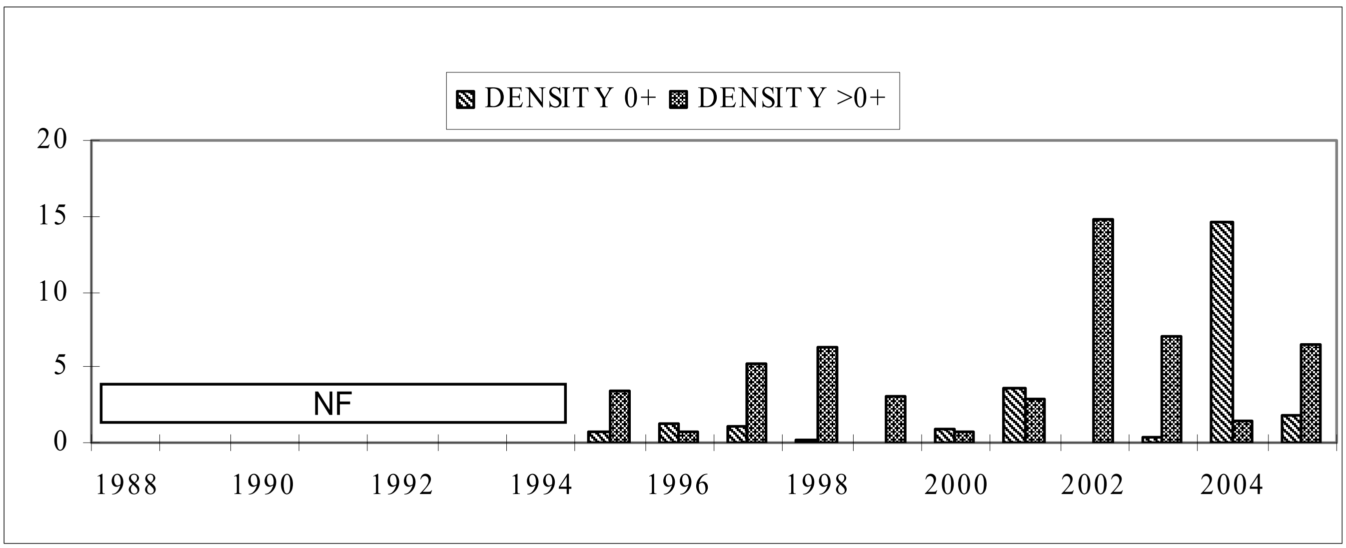


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.17.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Afon Hafren

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	854.77	69	22.7	77.3	0.29	1.24	0.001	0.022
Invertebrates	1294.80	37	41.8	58.2	0.14	0.51	0.001	0.010

Figure 4.17.5 Summary of Mean Trout Density (numbers 100m^{-2}): Afon Hafren



NF = Not fished

4.18 Afon Gwy

4.18.1 Water Chemistry Summary

The Afon Gwy, the source of the River Wye, is less acidic than the nearby afforested Afon Hafren (Site 17) but still exhibits severely acidic conditions during high flows and seasalt episodes. Monitoring only began at the site in 1991, and in the first two years mean xSO_4 concentration was 49.4 µeq l^{-1}, approximately four times that of NO_3. The mean labile aluminium concentration over this early period was 61.2 µg l^{-1} and reached a concentration potentially highly toxic to salmonids of 198 µg l^{-1} in one sample. Mean ion-balance ANC was close to zero and fell as low as -45.5 µeq l^{-1}.

Over the course of monitoring xSO_4 concentration has fallen by circa 25% with most of the reduction occurring between 1996 and 2000. Like the Afon Hafren, concentrations have increased again slightly since 2002. The mean 2003-2006 concentration was approximately seven times higher than that for Loch Coire nan Arr (Site 1) in northwest Scotland, and six times higher than Coneyglen Burn (Site 22) the stream site in the low deposition Sperrin region of Northern Ireland.

Nitrate concentrations have shown strong inter-annual variability throughout the monitoring periods but no overall trend, although there is an indication that the catchment soils are leaching NO_3 for a longer period of the year, with fewer samples registering "below detection limit" values in recent years.

Chloride concentrations show strong inter-sample variability, driven by occasional seasalt episodes. However, monitoring commenced after the stormy period around the turn of the 1990s that led to peak concentrations in several other sites including the Afon Hafren, and there is no long term trend in these data. The largest concentrations in the record were recorded in the winter of 2002-2003 coinciding with a large seasalt event in southern Norway which resulted in large fish kills (Larssen and Holme 2006).

Dissolved organic carbon concentrations have increased by approximately 50%, and show a roughly inverse pattern to the decline in xSO_4 (see Section 5.4.5). In contrast to the Afon Hafren there is little difference between the rate of change in basal and peak concentrations.

In common with the Afon Hafren, base cation concentrations provide little indication of a long term trend that often accompanies a reduction in sulphur loading, and this again is most likely accounted for by the increase in organic anions over the period. However, ion balance ANC has increased progressively to a mean of 26.4 µeq l^{-1} over the 2003-2006 period.

Mean pH has remained remarkably similar between periods, but pH minima associated with high flow have increased steadily (as demonstrated by Evans *et al.* in press). Peak labile aluminium levels also provide some indication of a long term decline, although the major seasalt events in the winter of 2002-2003 pushed concentrations to potentially severely toxic levels beyond 150 µg l^{-1} (approximately half that experienced in the Afon Hafren).

4.18.2 Biology Summary

The epilithic diatom community of the Afon Gwy shows clear and significant linear change over the monitoring period. As at the Afon Hafren (Site 17), early years of monitoring were dominated by the acidophilous /acidobiontic species, *Eunotia exigua* (SWAP pH optima = 5.1). However, abundances have declined from peak levels in the late 1990s, while *Tabellaria flocculosa* (SWAP pH optima = 5.4), again in common with the Afon Hafren, has increased from very low abundances in the early 1990s. While this change is consistent with a gradual recent improvement in pH in response to falling sulphur deposition it is interesting to note that there has been a general decline in representation of less common taxa.

Again in common with the Afon Hafren, the aquatic macrophyte flora in the survey stretch of the Afon Gwy is restricted largely to one acid tolerant and ubiquitous liverwort species, *Scapania undulata* which has shown no indication of long term changes in cover. There are no records of acid-sensitive mosses in the survey stretch, however the acid-sensitive red alga, *Lemanea* sp., which is common in the circumneutral AWMN streams, the Allt a'Mharcaidh (Site 2) and Narrator Brook (Site 14), was recorded for the first time in several locations in 2006.

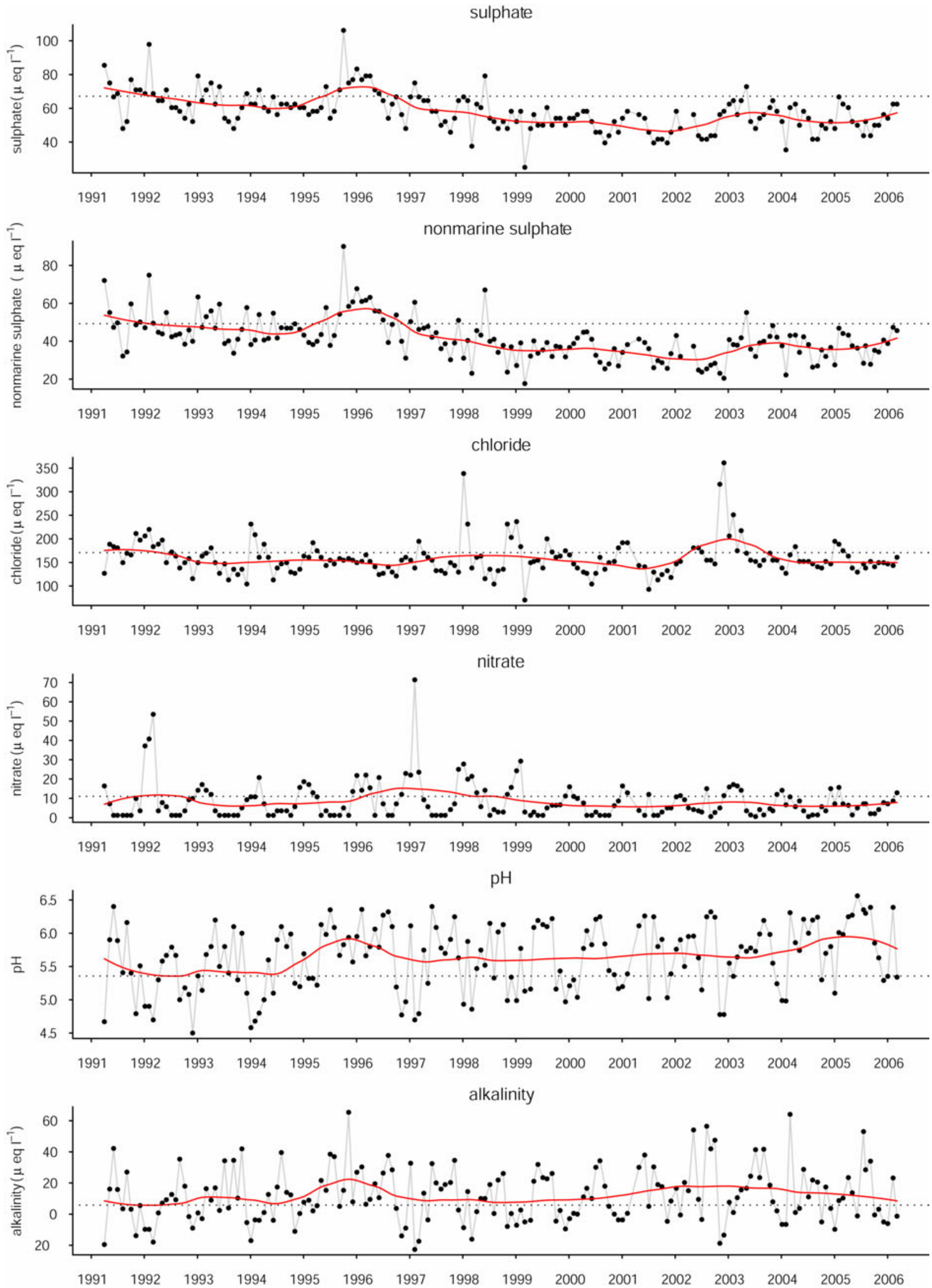
The macroinvertebrate assemblage of the Afon Gwy also shows a significant linear trend over the monitoring period and, again in common with the Afon Hafren, this is driven predominantly by an increase in the abundance of the acid-sensitive predatory stonefly larva *Isoperla grammatica*. Unlike the Afon Hafren however, there is no indication of any increase in the stonefly *Siphonoperla torrentium* which has remained relatively abundant throughout the monitoring period.

Brown trout densities are low in the survey stretch and do not show a long term trend. However, a few juvenile Atlantic salmon (a highly acid-sensitive species) were recorded in the stretch in 2006. It is important to determine whether the appearance of salmon may be linked to any recent changes in stocking practice immediately downstream before any conclusions can be drawn with respect to possible recovery.

4.18.3 Conclusions: Afon Gwy

The Afon Gwy is less acidic than the neighbouring Afon Hafren but is still subject to severe acid episodes. Nevertheless, pH minima have increased progressively over the monitoring period while extremes in labile aluminium are now confined only to occasional seasalt events. Early stages of biological recovery are very clear in the diatom flora and macroinvertebrate fauna, and there is also very recent evidence for improvement in the aquatic macrophyte flora through the arrival of *Lemanea* sp.. The detection of Atlantic salmon in the survey stretch in 2006 is potentially highly pertinent with respect to recovery, but requires further investigation.

Figure 4.18.1 Water Chemistry Summary Plots: Afon Gwy



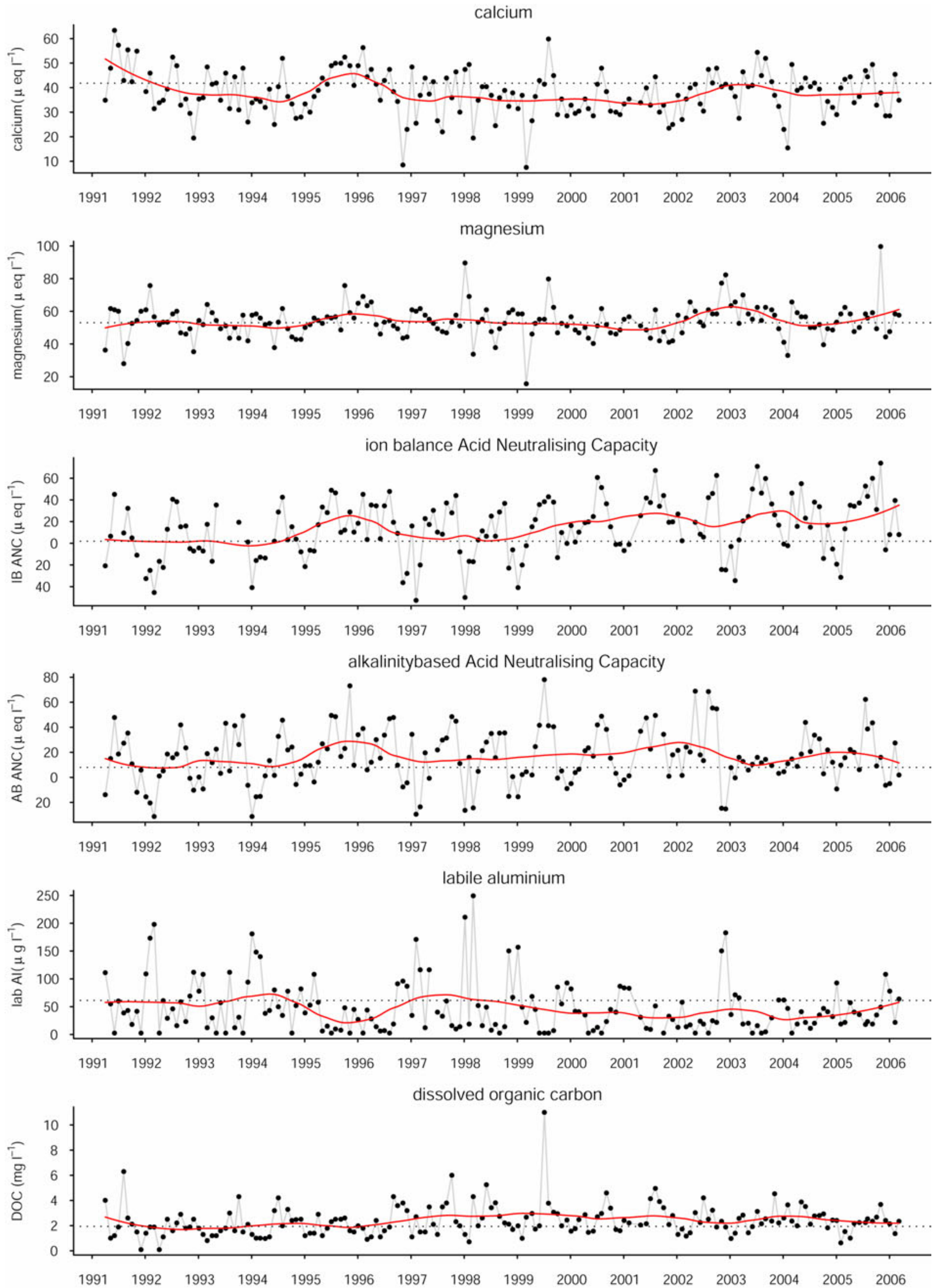

calcium
calcium (μ eq l^{-1})
magnesium
magnesium (μ eq l^{-1})
ion balance Acid Neutralising Capacity
IB ANC (μ eq l^{-1})
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l^{-1})
labile aluminium
lab Al (μ g l^{-1})
dissolved organic carbon
DOC (mg l^{-1})
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006

Table 4.18.1 Water Chemistry Summary Data and Trend Statistics: Afon Gwy

Determinand / period		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Apr 1991 - Mar 1993	mean	49.4	11.0	170.8	5.36	5.8	1.9	8.0	30.3	41.8	53.0	153.7	4.0	115.6	61.2	1.9
	st. dev	10.4	13.9	26.3	0.49	15.7	24.3	20.1	4.5	10.6	10.5	17.8	3.3	72.5	51.8	1.3
	min	32.3	1.3	115.7	4.50	-19.5	-45.5	-31.4	24.0	19.5	28.0	113.1	2.6	5.0	2.5	0.1
	max	75.0	53.6	220.0	6.40	42.3	45.1	48.0	44.1	63.4	75.7	195.8	16.4	256.0	198.0	6.3
Apr 1993 - Mar 1998	mean	47.3	10.0	154.1	5.63	12.5	8.9	16.7	26.3	38.3	53.9	143.3	3.3	110.9	54.1	2.2
	st. dev	10.9	11.4	35.0	0.50	17.6	25.6	23.0	6.8	9.5	9.0	19.9	2.4	70.0	56.0	1.1
	min	23.1	1.3	104.4	4.58	-22.6	-52.5	-31.3	16.0	8.5	33.7	113.1	0.6	24.0	2.5	0.7
	max	90.0	71.4	338.5	6.40	65.4	49.0	73.1	44.0	56.4	89.7	239.3	16.1	366.0	249.0	6.0
Apr 1998 - Mar 2003	mean	33.5	7.5	158.6	5.63	12.3	15.7	19.6	22.0	35.3	53.5	145.1	3.0	109.6	42.4	2.7
	st. dev	10.0	6.3	52.6	0.45	16.9	24.2	23.3	6.9	7.8	10.3	29.5	2.3	46.6	42.1	1.5
	min	1.8	0.5	2.8	4.78	-18.6	-41.0	-25.2	13.0	7.5	15.6	69.6	0.6	34.5	2.5	1.0
	max	67.1	29.3	361.1	6.32	56.4	67.2	78.1	49.0	59.9	82.3	274.1	12.0	235.0	183.0	11.0
Apr 2003 - Mar 2006	mean	37.9	6.3	155.2	5.63	14.5	26.4	16.0	26.8	38.6	55.4	145.2	2.9	87.7	34.8	2.4
	st. dev	7.1	4.4	18.5	0.47	17.6	25.3	15.1	2.7	8.4	10.7	16.3	2.0	37.5	25.1	0.8
	min	22.1	0.5	126.9	4.98	-9.8	-31.3	-9.3	20.0	15.5	32.9	113.1	0.6	18.0	2.5	0.6
	max	55.2	15.7	217.2	6.56	64.2	73.9	62.2	32.0	54.4	99.5	191.4	8.7	161.0	108.0	4.5
Seasonal-Kendall statistics	Sen-slope	-1.073	-0.070	-0.309	0.023	0.325	1.328	0.253		-0.207	0.231				-0.801	0.026
	P- val	**0.002**	0.336	0.362	**0.006**	0.109	**0.007**	0.086		0.298	0.698				0.153	**0.023**

(AB-ANC, see Chapter 5); cond = Conductivity (20 °C); sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.18.2 Epilithic Diatom Percentage Abundance Summary: Afon Gwy

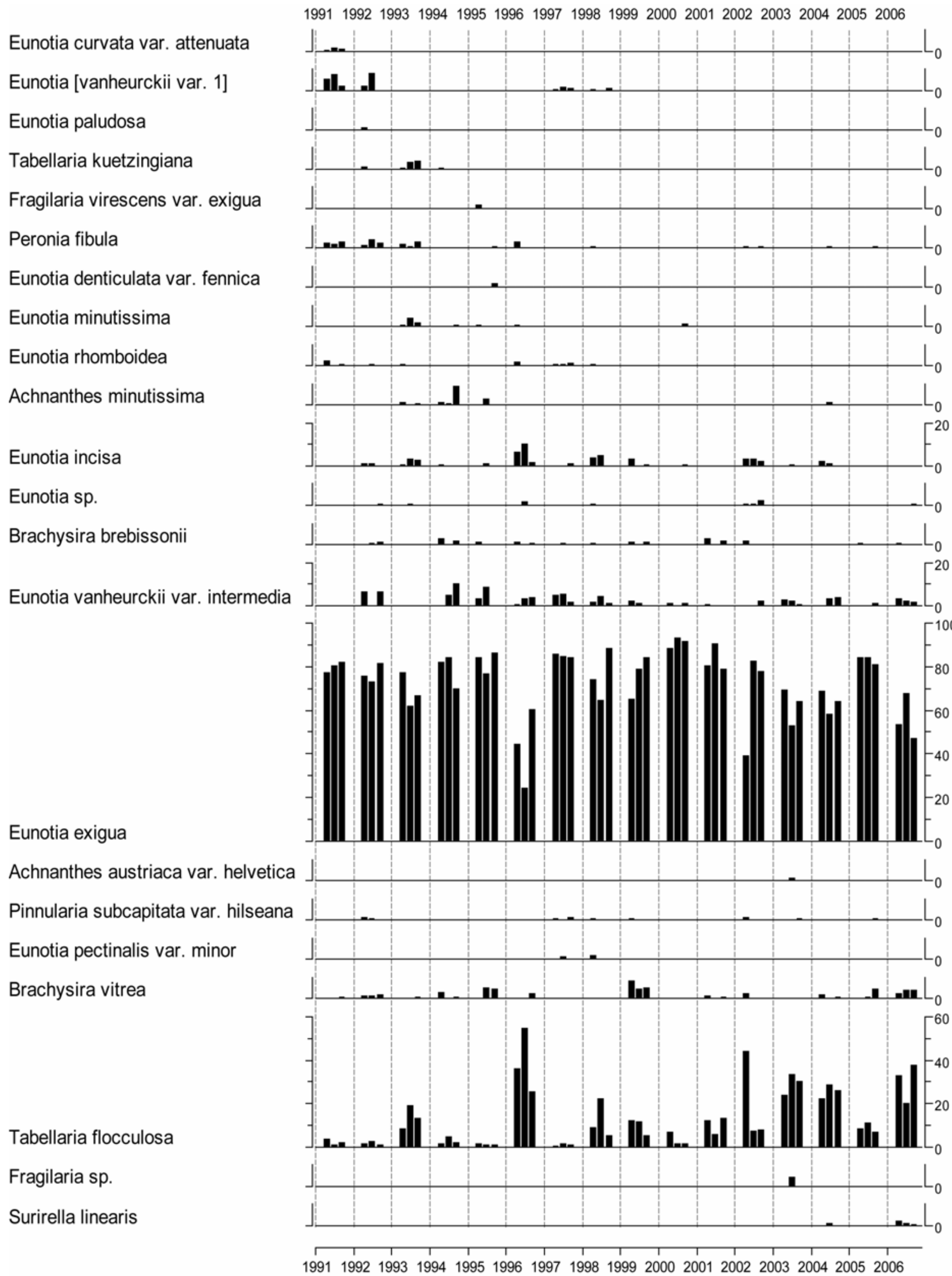
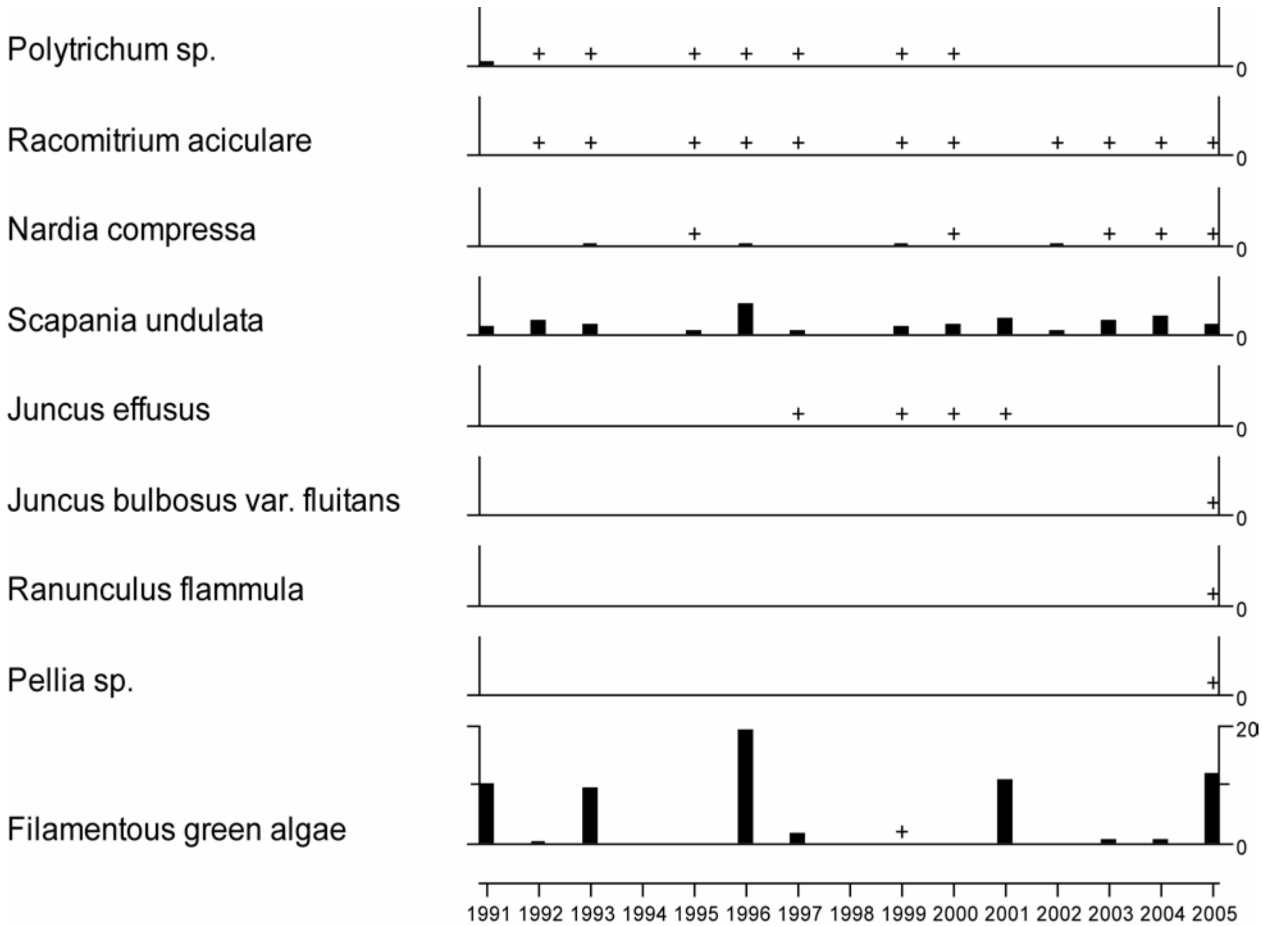
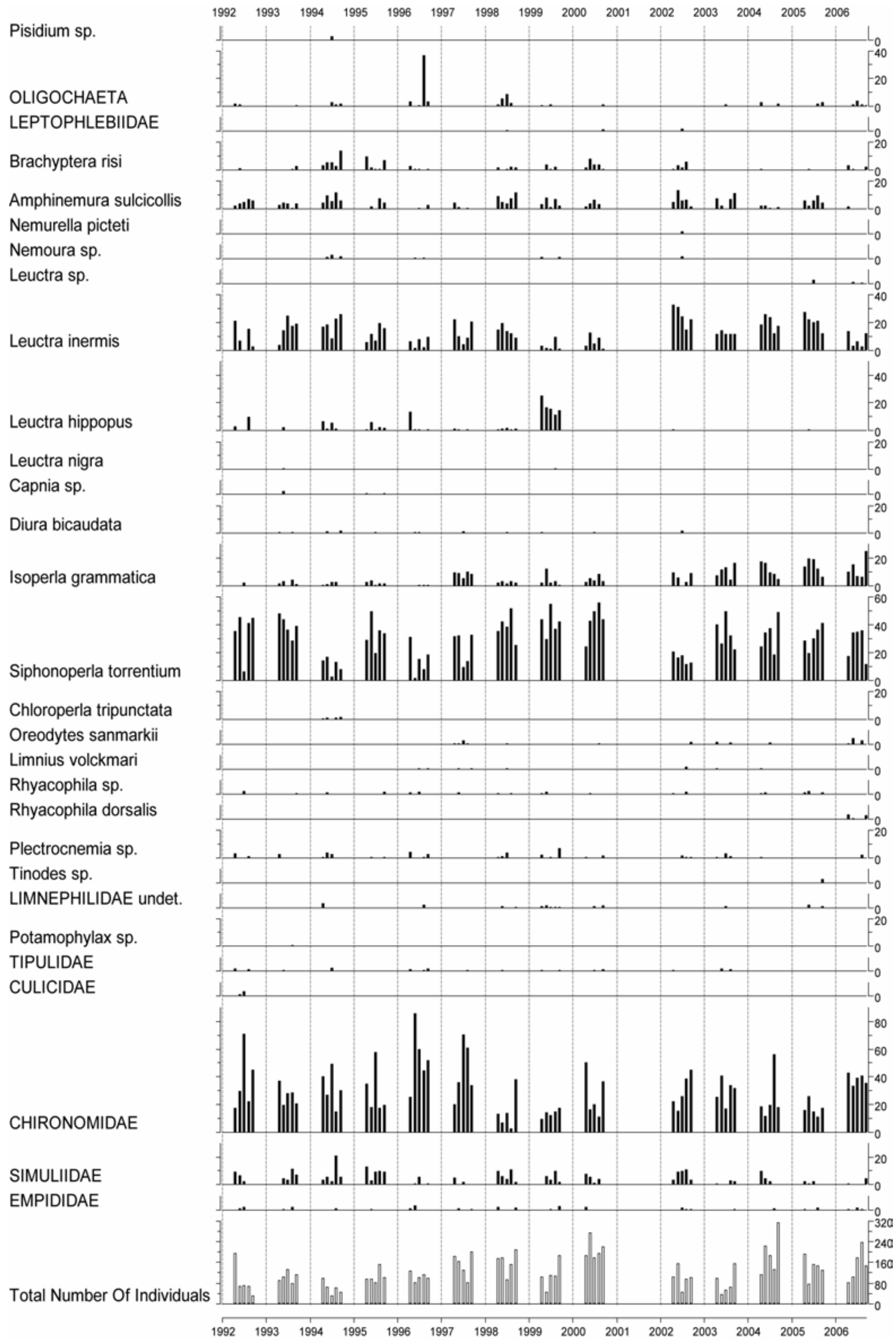


Figure 4.18.3 Aquatic Macrophyte Percentage Species Cover: Afon Gwy



+ Represents <0.25% abundance

Figure 4.18.4 Macroinvertebrate Percentage Abundance Summary: Afon Gwy

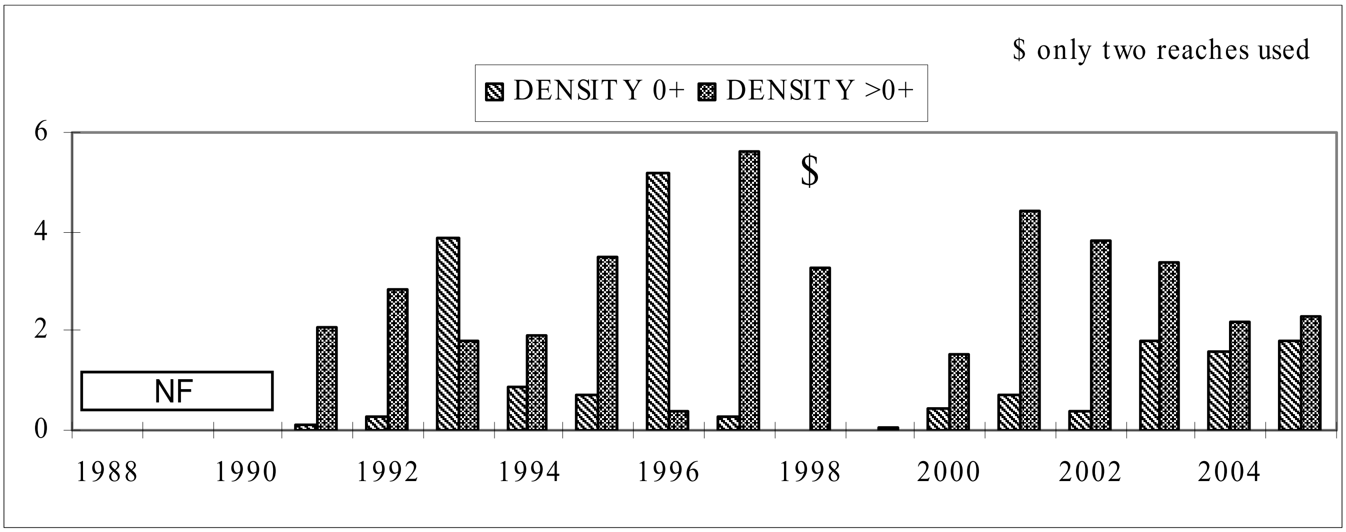


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.18.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Afon Gwy

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA / λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	519.42	64	36.9	63.1	0.14	0.46	0.001	0.026
Invertebrates	1465.92	45	47.7	52.3	0.10	0.44	0.001	0.012

Figure 4.18.5 Summary of Mean Trout Density (numbers 100m^{-2}): Afon Gwy



NF = Not fished

4.19 Beaghs Burn

4.19.1 Water Chemistry Summary

Beagh's Burn is a steep hillside stream draining moorland overlying schists in the Glens of Antrim in northeastern Northern Ireland. Water chemistry time series reflect a very episodic system with well buffered baseflow. Over the first five years of monitoring (1988-1993) mean xSO_4 concentration was relatively low for the AWMN (38.4 μeq l^{-1}) and mean alkalinity was relatively high (43.9 μeq l^{-1}). Although mean pH (5.76) and labile aluminium concentration (12 μg l^{-1}) were indicative of benign levels of acidity, pH fell as low as 4.36 and labile aluminium concentration rose as high as 60 μg l^{-1} during seasalt episodes. Mean NO_3 concentration was very low (3.1 μeq l^{-1}) and levels fell below the limit of detection during the middle of the year.

Non-marine sulphate concentration fell sharply between 1996-2000 before stabilising at low levels; the mean 2003-2006 concentration was 7.3 μeq l^{-1} and never exceeded 20 μeq l^{-1} during this period. These levels are comparable with those for Loch Coire nan Arr (Site 1), the most northerly site on the Network and an effective low deposition reference site. Nitrate has continued to show regular seasonality but no overall trend.

Chloride concentrations have continued to show marked variability, reflecting the susceptibility of the site to seasalt inputs. The acidity of the water during seasalt episodes has declined slightly, and although average Cl concentrations during 2003-2006 are similar to those during earlier periods of monitoring, labile aluminium concentration measurements have not exceeded 30 μg l^{-1} over this recent time. Concurrently the pH of episodic extremes has climbed gradually and did not fall below 4.50 between 2003-2006.

In common with most other sites on the AWMN, Beagh's Burn has experienced a large rise in DOC concentration. The sharp increase in DOC in 1994 corresponds with a brief period of lower than average seasalt inputs (inferred from Cl concentration) followed by a steep decline in xS04, and is therefore consistent with a hypothesis of a deposition chemistry control on organic carbon solubility (Section 5.4.5).

4.19.2 Biology Summary

The epilithic diatom flora of Beagh's Burn does not show significant linear change over the monitoring period. However, there has been a striking recent rise in the relative abundance of *Achnanthes saxonica* (SWAP pH optima = 5.7). This species was detected in a handful of samples only in the early years of monitoring and never exceeded 10% relative abundance prior to 1999. In 2006 it comprised over 60% of the two out of three replicate samples, and over 25% in the third. Few species show clear reductions in abundance, but the most obvious is *Pinnularia irrorata* (SWAP pH optima = 5.4) which now occurs only at trace levels.

The aquatic macroflora of Beagh's Burn has been dominated throughout by the ubiquitous liverwort, *Scapania undulata*. Reductions in the cover of this species in some years may reflect the physical effect of occasional major spates. There has been a decline in the cover of filamentous algae across the sampling stretch, while a trace amount of the acid-sensitive moss species *Hygrohypnum luridum* was recorded in 2003 only.

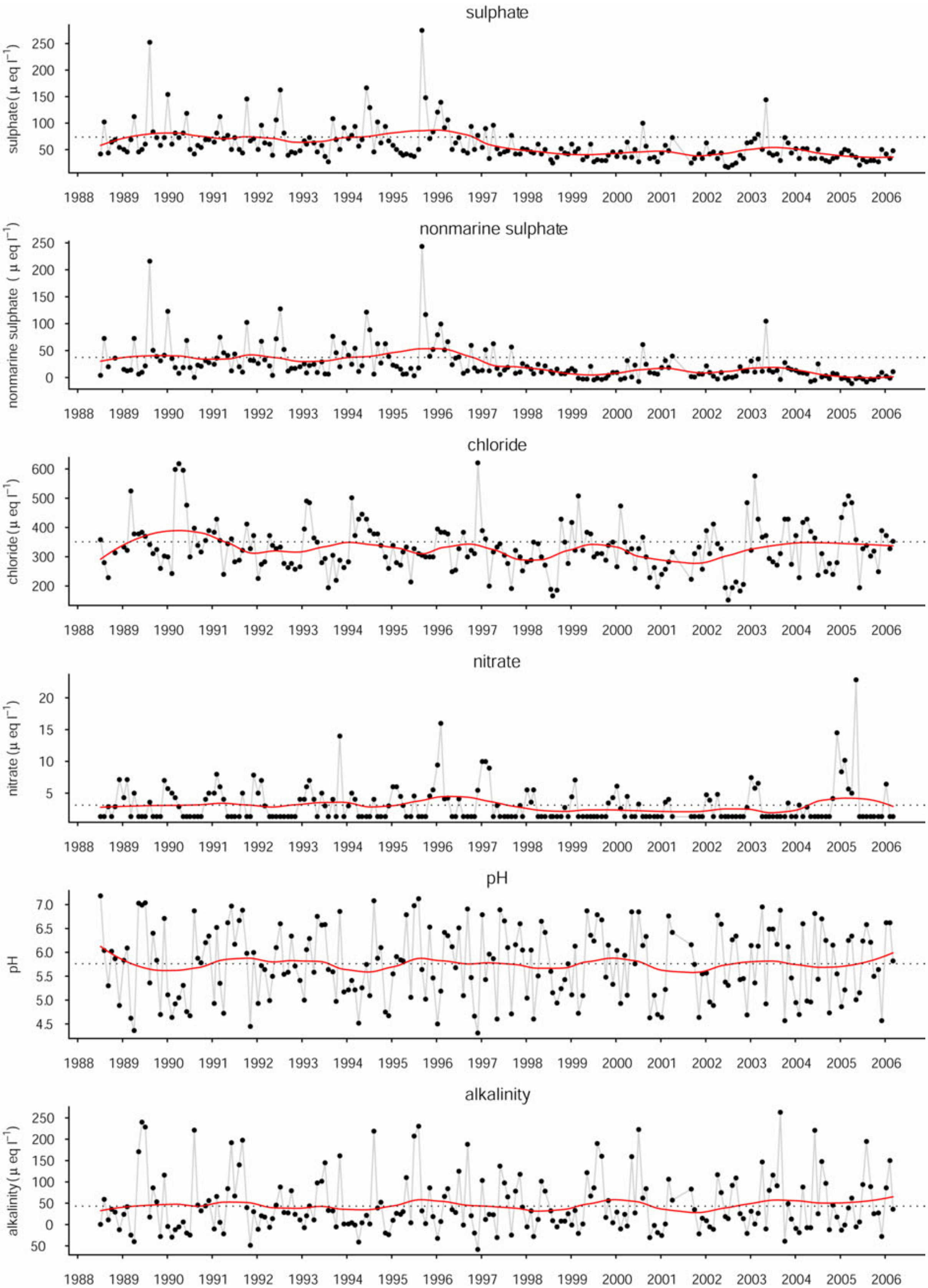
In common with the epilithic diatom data, the macroinvertebrate fauna also shows a significant linear trend in community structure over time. However, the main change observed, a proportional increase in Chironomidae, cannot be related to a reduction, since this group is not identified to a fine enough taxonomic level, and comprises taxa with a broad range of water chemistry preferences. There has been no change in the number of individual animals caught over time.

Brown trout density in Beagh's Burn has always been, and remains, low, possibly due to physical restrictions on habitat. There is no significant change through time in either 0+ or >0+ age groups.

4.19.3 Conclusions

Beagh's Burn is a well buffered, but episodically acidic, stream in a region of relatively low sulphur deposition that has experienced a substantial reduction in xSO_4 concentration over the monitoring period. It now shows some of the lowest levels of xSO_4 on the AWMN. Although the acidity of the site is highly variable, on account of sensitivity to changes in flow and seasalt inputs, there is some evidence that peak labile aluminum concentrations and pH minima have declined in recent years. This is reflected in a change in the epilithic diatom community to a less acidic flora, but there is no other clear evidence of biological improvement.

Figure 4.19.1 Water Chemistry Summary Plots: Beaghs Burn



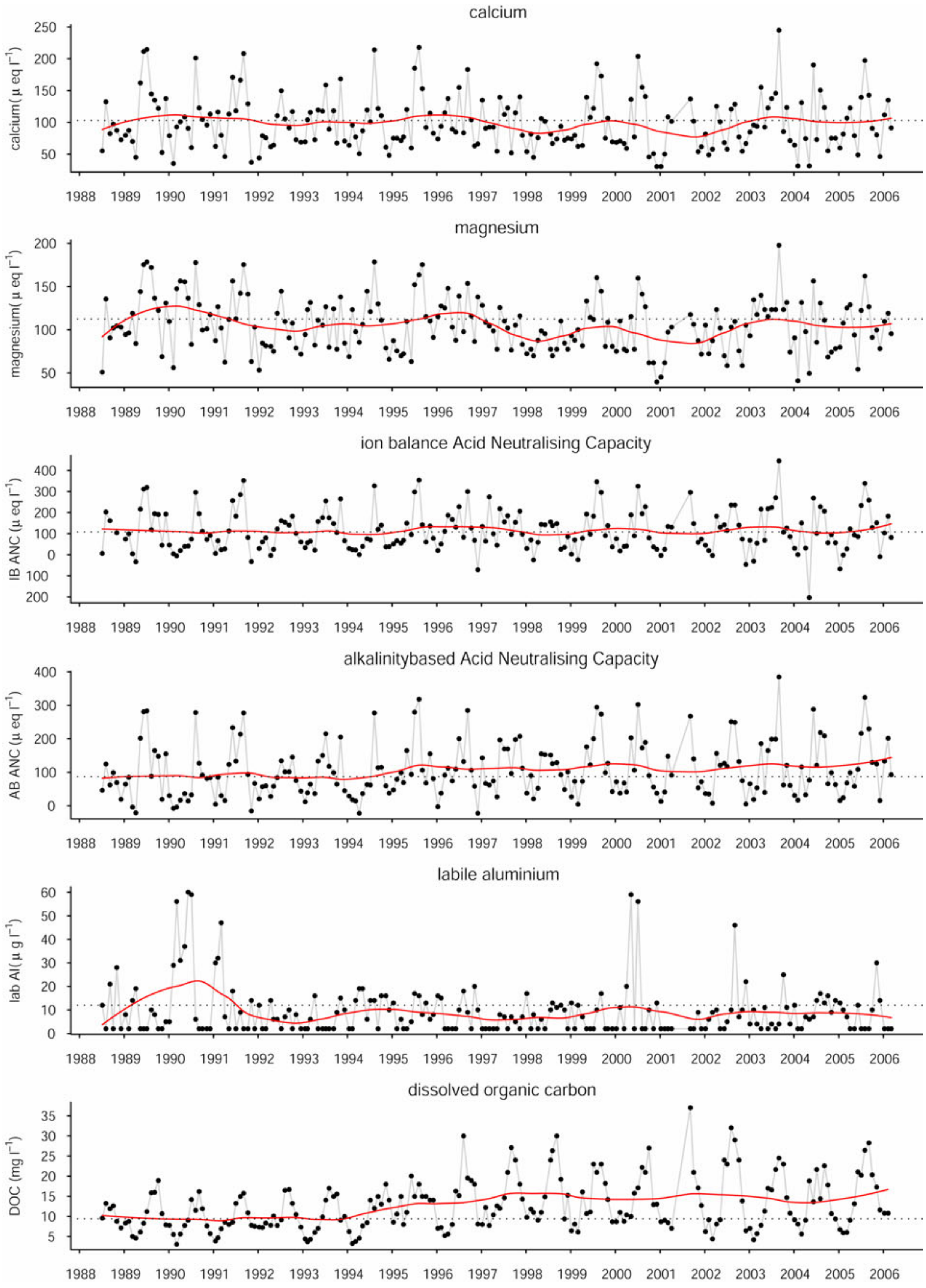

calcium
calcium(µ eq l^{-1})
magnesium
magnesium(µ eq l^{-1})
ion balance Acid Neutralising Capacity
IB ANC (µ eq l^{-1})
alkalinitybased Acid Neutralising Capacity
AB ANC (µ eq l^{-1})
labile aluminium
lab Al(µ g l^{-1})
dissolved organic carbon
DOC (mg l^{-1})
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.19.1 Water Chemistry Summary Data and Trend Statistics: Beaghs Burn

Determinand period		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Jul 1988 - Mar 1993	mean	38.4	3.1	351.0	5.76	43.9	107.9	87.0	60.3	103.0	112.5	306.9	11.3	57.7	12.0	9.4
	st. dev	36.7	2.2	89.8	0.77	69.3	95.5	78.1	11.9	44.0	33.6	53.3	3.7	21.8	15.2	3.8
	min	0.3	1.3	225.7	4.36	-49.0	-33.5	-21.4	43.0	35.4	51.0	204.5	2.6	2.0	2.0	3.1
	max	216.4	8.0	617.8	7.18	240.0	351.5	283.8	88.0	214.6	178.5	443.7	23.0	106.0	60.0	18.9
Apr 1993 - Mar 1998	mean	37.7	3.6	324.4	5.75	45.0	117.8	104.7	58.6	101.8	107.0	297.8	10.5	53.5	7.9	12.7
	st. dev	39.2	3.2	73.1	0.77	66.5	89.6	76.4	10.7	40.1	28.2	45.3	3.7	18.3	6.0	5.5
	min	3.4	1.3	191.8	4.31	-58.0	-71.2	-22.7	39.0	44.9	63.3	221.9	2.6	20.0	2.0	3.3
	max	243.1	16.0	620.6	7.12	230.0	353.8	318.2	96.0	218.1	178.5	408.9	21.5	96.0	20.0	30.0
Apr 1998 - Mar 2003	mean	11.2	2.3	310.1	5.72	40.5	107.4	110.3	52.5	89.7	94.7	269.3	9.6	53.2	8.8	14.8
	st. dev	13.0	1.7	88.8	0.69	56.6	89.8	76.8	11.7	37.5	26.6	48.7	3.4	23.1	12.0	7.9
	min	-7.0	1.3	152.3	4.63	-30.0	-45.6	5.1	33.0	30.4	39.5	165.3	3.1	13.0	2.0	4.2
	max	61.8	7.4	575.5	6.87	223.0	346.7	302.3	92.0	203.6	160.4	374.1	19.4	117.0	59.0	37.0
Apr 1998 - Mar 2003	mean	7.3	3.3	340.3	5.26	57.3	125.5	127.7	59.6	105.2	107.2	288.9	10.7	42.6	8.2	14.7
	st. dev	19.0	4.5	78.2	0.62	73.8	120.6	90.8	10.3	47.7	32.6	57.6	3.4	22.2	6.9	6.4
	min	-11.3	1.3	194.6	4.57	-39.0	-202.9	15.7	43.0	31.4	41.1	134.9	2.6	10.0	2.0	5.6
	max	104.7	22.9	507.8	6.95	263.0	444.8	385.1	83.0	245.0	197.4	387.2	19.4	114.0	30.0	28.3
Seasonal-Kendall statistics	Sen-slope	-2.349	-0.016	-0.353	0.003	0.999	-0.214	2.581		-0.490	-0.891				-0.273	0.333
	P- val	**<0.001**	0.100	0.258	0.858	0.547	0.431	**0.019**		0.443	0.176				0.950	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.19.2 Epilithic Diatom Percentage Abundance Summary: Beaghs Burn

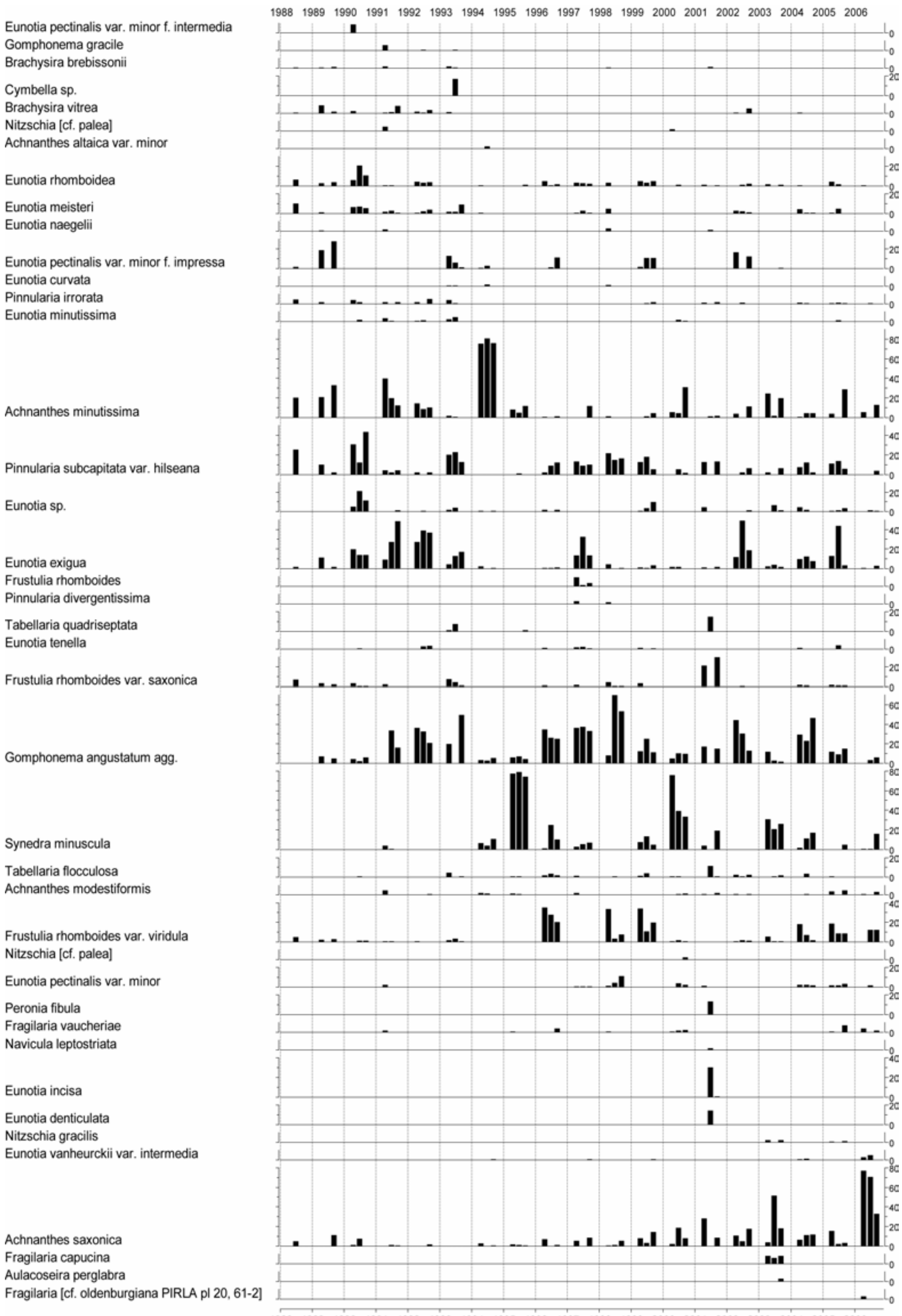
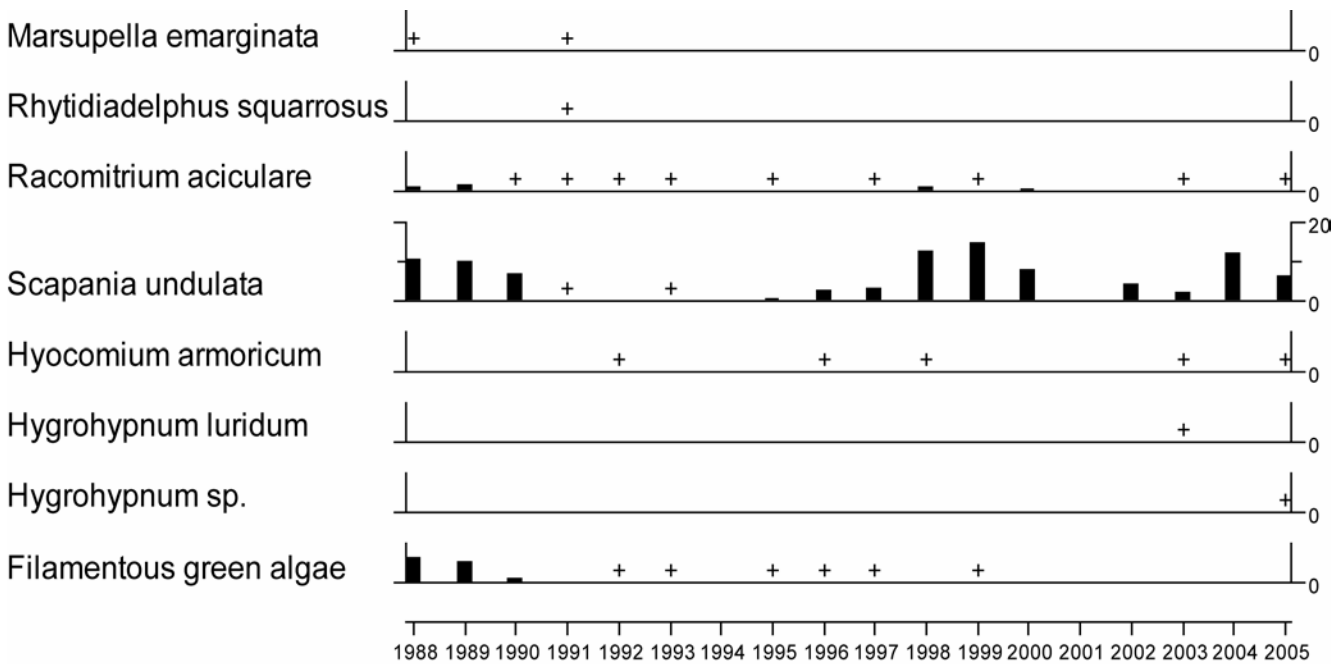


Figure 4.19.3 Aquatic Macrophyte Percentage Species Cover: Beaghs Burn



+ Represents <0.25% abundance

Figure 4.19.4 Macroinvertebrate Percentage Abundance Summary: Beaghs Burn

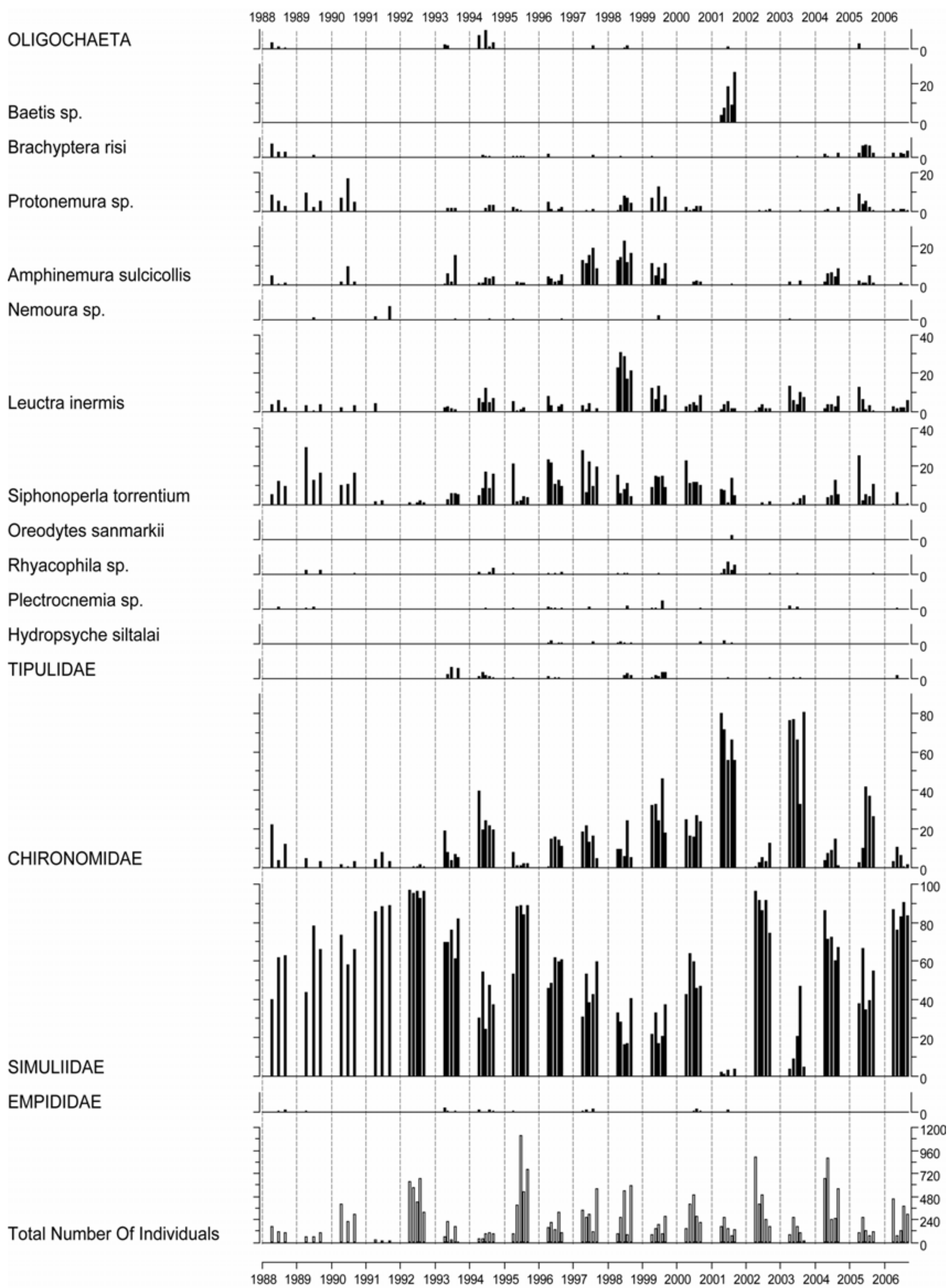
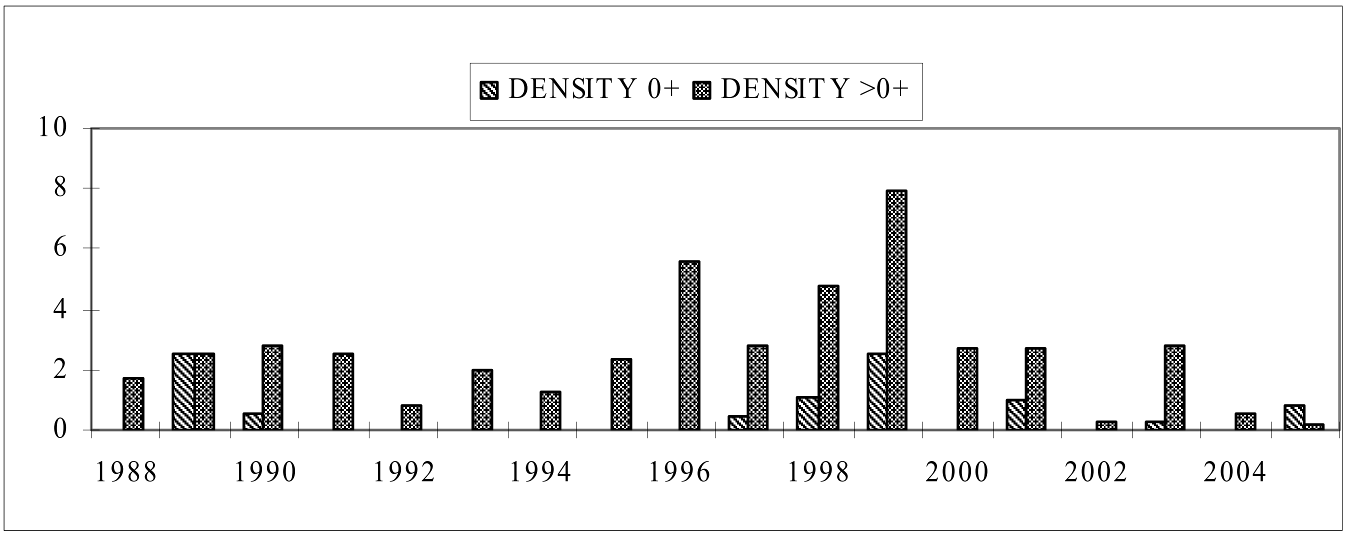


Table 4.19.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Beaghs Burn

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	2228.94	99	25.4	74.6	0.08	0.31	0.001	0.139
Invertebrates	1663.79	40	23.4	76.6	0.06	1.33	0.003	0.552

Figure 4.19.5 Summary of Mean Trout Density (numbers 100m^{-2}): Beaghs Burn



4.20 Bencrom River

4.20.1 Water Chemistry Summary

The Bencrom River drains moorland in the Mourne Mountains, 2 km to the west of Blue Lough (Site 21). The stream is relatively well buffered at baseflow, but in the early years of monitoring pH regularly fell below 4.5 during high flow, while labile aluminium concentrations often reached concentrations likely to be toxic to salmonids and rose occasionally above 200 µg l^{-1}.

Non-marine sulphate concentration during the 1988-1993 period (mean = 68.6 µeq l^{-1}) was relatively high for an AWMN site but similar to Blue Lough, reflecting the relatively high sulphur deposition regime in this region.

Over the same period NO_3 (mean concentration = 26.9 µeq l^{-1}) made a significant contribution to acidity. Nitrate concentrations showed distinct seasonality, with highest concentrations in the spring, but remained above the limit of detection throughout the year.

Non-marine sulphate concentration fell sharply from around 1996 to 2000, but has since increased again slightly. The mean 2003-2006 of 51.4 µeq l^{-1} represents a relatively modest overall reduction of circa 25%. Unusually for AWMN sites, NO_3 concentrations appeared to lose seasonal structure from around 2000 and have largely remained above the first five year mean in the most recent period. Also atypically, DOC concentrations have fallen substantially in recent years. Calcium and alkalinity data indicate that there was an abrupt hydrological change in the Bencrom River that cannot be explained by changes in deposition chemistry.

Because of uncertainties surrounding the cause of recent changes the recent improvement in pH cannot be linked to changes in deposition at this stage. Despite the recent reduction in acidity, labile aluminium concentrations still frequently exceed levels deemed potentially toxic to salmonids and have often been recorded above 100 µg l^{-1}.

4.20.2 Biology Summary

The epilithic diatom flora of Bencrom River has remained dominated by *Eunotia naegelii* and *Brachysira brebissonii* throughout the monitoring period. There is, however, a subtle and statistically significant linear trend in the data, resulting in part from a gradual increase in the relative abundance of *Frustulia rhomboides* var. *saxonica* (SWAP pH optima = 5.2) and a gradual reduction in the acidobiontic *Tabellaria quadriseptata* (SWAP pH optima = 4.9).

The aquatic macrophyte flora of Bencrom River has been dominated throughout the monitoring period by the liverwort *Nardia compressa* that thrives in acidic streams. There is no evidence for any change in the assemblage over time.

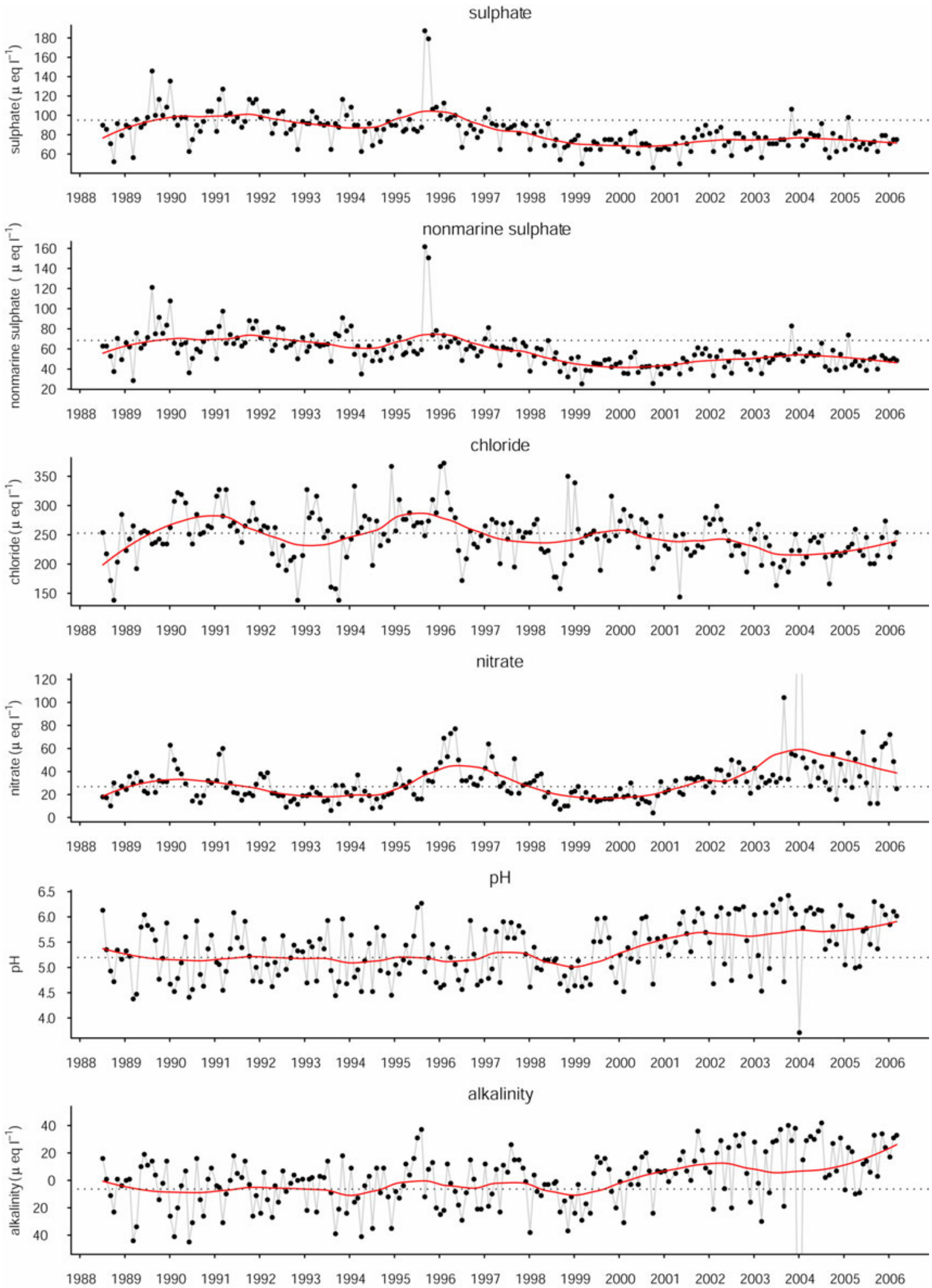
The macroinvertebrate data also show significant linear change over time, but here the changes in the community are clearer than for diatoms, with a progressive increase in the relative abundance of the acid-sensitive stonefly *Siphonoperla torrentium*, and a cocommitant decline in the acid tolerant stonefly *Protonemura* sp.

Brown trout density in Bencrom River has remained low throughout the monitoring period although some recruitment is apparent in all years. In the last three years (2003-2006) densities have been particularly low.

4.20.3 Conclusions

Bencrom River is an episodically acidic stream, acidified by both xSO_4 and NO_3. While xSO_4 declined substantially in the late 1990s, NO3 concentrations have increased in recent years and now represent close to half of the acid load. There is some evidence for an improvement in epilithic diatom and macroinvertebrate communities. However, water chemistry data indicate a hydrochemical disruption to the stream catchment in around 2001, leading to a greater contribution from groundwater. This could account for at leat some of the biological changes observed. Investigations into the cause of these chemical changes are underway.

Figure 4.20.1 Water Chemistry Summary Plots: Bencrom River



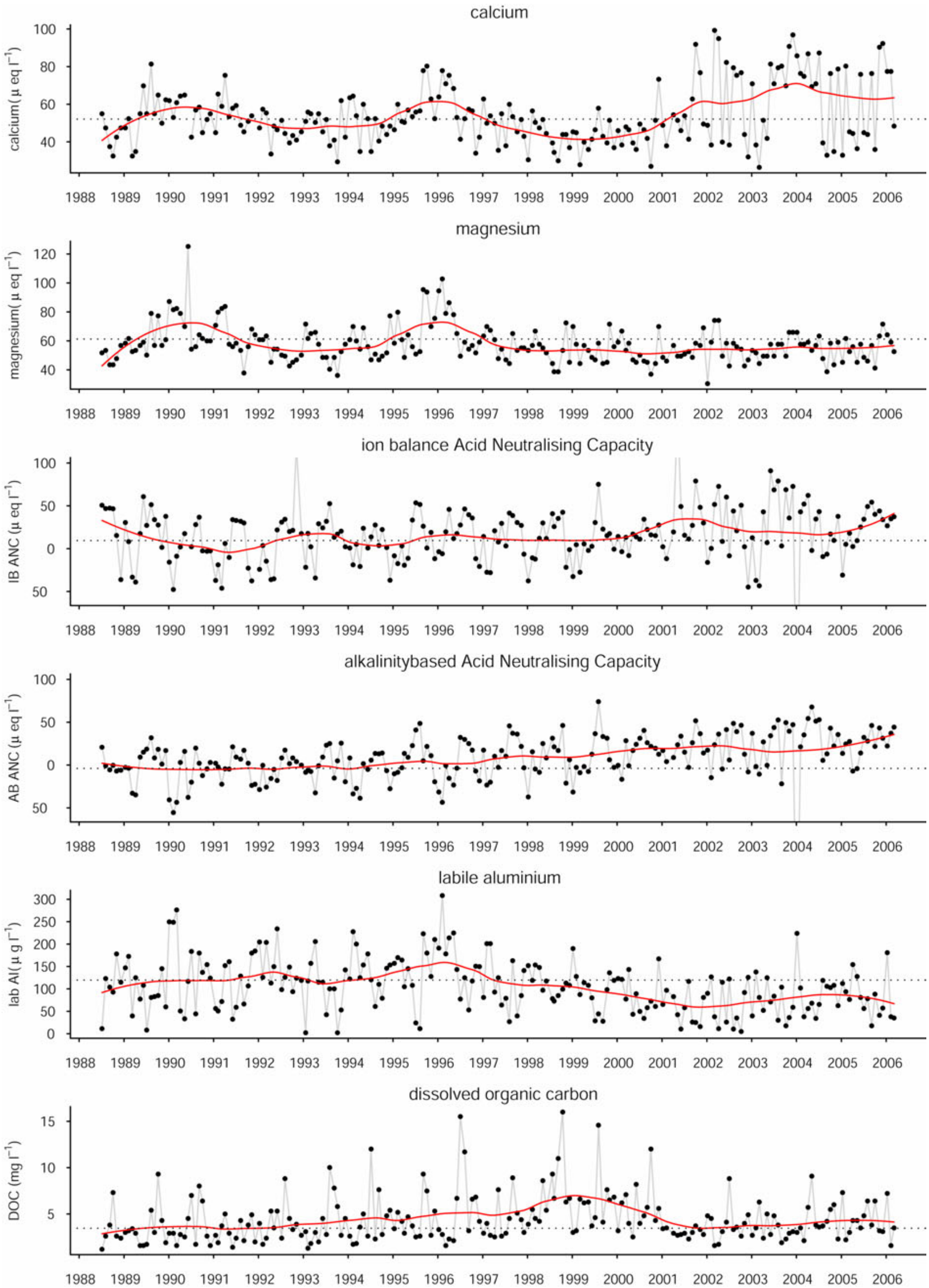

calcium
calcium (μ eq l⁻¹)
magnesium
magnesium (μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al (μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.20.1 Water Chemistry Summary Data and Trend Statistics: Bencrom River

Determinand period		xSO_4^{2-} µeq l^{-1}	NO_3^- µeq l^{-1}	Cl^- µeq l^{-1}	pH	alk µeq l^{-1}	IB-ANC µeq l^{-1}	AB-ANC µeq l^{-1}	cond µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	Na^+ µeq l^{-1}	K^+ µeq l^{-1}	sol. Al µg l^{-1}	lab._Al µg l^{-1}	DOC mg l^{-1}
Jul 1988 - Mar 1993	mean	68.6	26.9	252.7	5.20	-6.7	9.5	-3.9	49.5	52.1	61.2	259.9	11.6	199.9	119.7	3.5
	st. dev	15.8	11.7	42.9	0.47	16.6	32.7	18.4	7.1	10.1	14.5	30.5	2.3	88.7	62.1	1.9
	min	28.6	9.0	138.2	4.38	-45.0	-47.5	-55.6	36.0	32.4	37.8	182.7	6.6	9.0	2.0	1.2
	max	121.4	62.9	327.2	6.13	19.0	120.2	32.0	68.0	81.3	125.0	317.6	17.4	390.0	276.0	9.3
Apr 1993 - Mar 1998	mean	65.1	30.6	259.0	5.19	-4.5	9.9	2.5	51.3	52.4	60.9	266.8	11.5	204.2	130.5	4.7
	st. dev	19.9	15.4	46.0	0.49	18.0	23.8	22.4	8.0	11.5	14.0	38.3	3.2	73.7	61.0	2.8
	min	35.2	6.0	138.2	4.44	-41.0	-37.6	-43.6	36.0	29.4	36.2	178.4	5.4	41.0	2.0	1.6
	max	161.6	77.0	372.4	6.27	37.0	53.5	48.8	80.0	80.3	102.8	352.4	25.3	400.0	308.0	15.5
Apr 1998 - Mar 2003	mean	45.9	24.4	241.6	5.37	1.4	18.1	16.3	45.8	49.6	52.8	242.5	10.3	149.4	81.3	5.2
	st. dev	9.0	10.5	39.2	0.53	18.1	33.3	20.8	5.9	16.8	9.5	30.6	2.2	62.5	43.6	2.9
	min	25.3	4.1	143.9	4.52	-37.0	-44.7	-31.6	35.0	26.4	30.4	165.3	6.1	24.0	5.0	1.6
	max	68.4	50.0	349.8	6.20	36.0	165.3	73.8	64.0	99.3	74.0	295.8	15.9	256.0	190.0	16.0
Apr 2003 - Mar 2006	mean	51.4	49.9	222.0	5.09	12.4	25.4	22.5	49.6	66.1	55.1	238.8	12.0	133.5	80.6	4.1
	st. dev	9.1	48.8	24.5	0.49	44.2	50.0	48.8	15.0	20.4	7.7	25.2	2.3	62.6	45.2	1.7
	min	38.8	12.1	163.6	3.71	-227.0	-220.0	-238.4	36.0	32.9	38.7	161.0	7.4	38.0	18.0	1.6
	max	82.9	312.9	273.6	6.42	42.0	90.8	67.9	132.0	96.8	71.6	282.8	17.6	318.0	224.0	9.1
Seasonal-Kendall statistics	Sen-slope	-1.403	1.116	-1.959	0.040	1.274	0.909	2.012		0.823	-0.183				-2.917	0.048
	P- val	**0.001**	0.272	**0.030**	**0.002**	**0.002**	**0.030**	**<0.001**		0.647	**0.050**				**0.005**	0.090

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.20.2 Epilithic Diatom Percentage Abundance Summary: Bencrom River

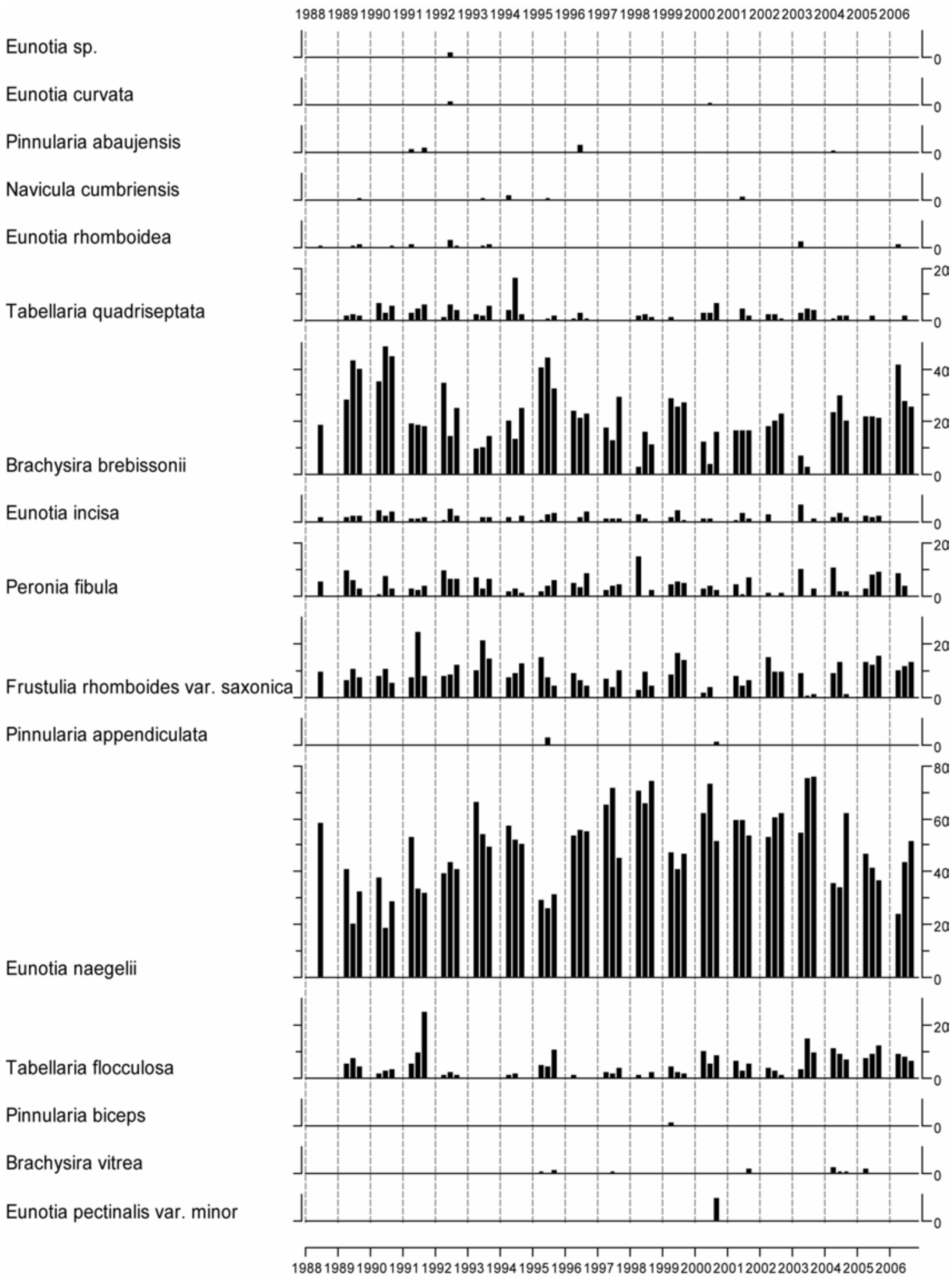
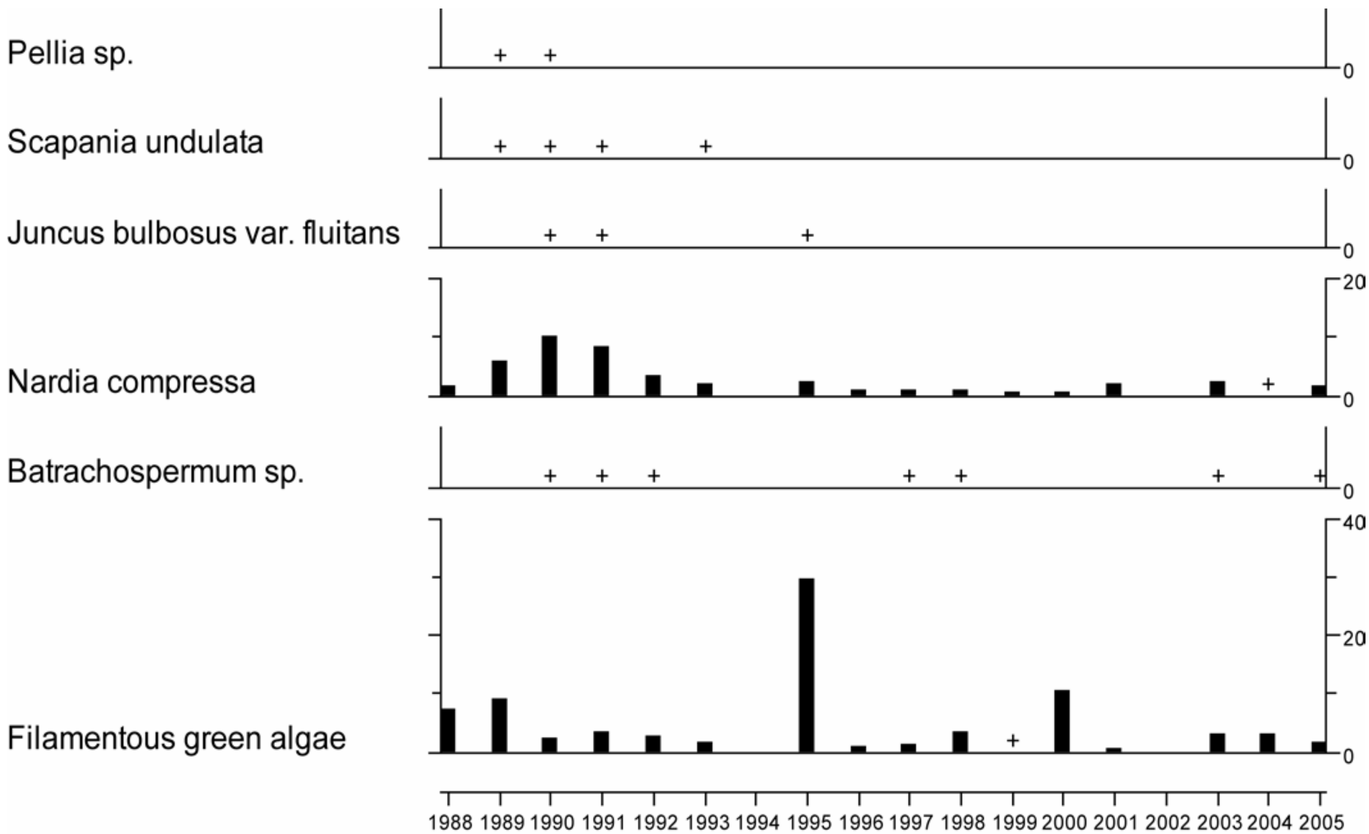


Figure 4.20.3 Aquatic Macrophyte Percentage Species Cover: Bencrom River



+ Represents <0.25% abundance

No survey undertaken in 2002 due to spate conditions.

Figure 4.20.4 Macroinvertebrate Percentage Abundance Summary: Bencrom River

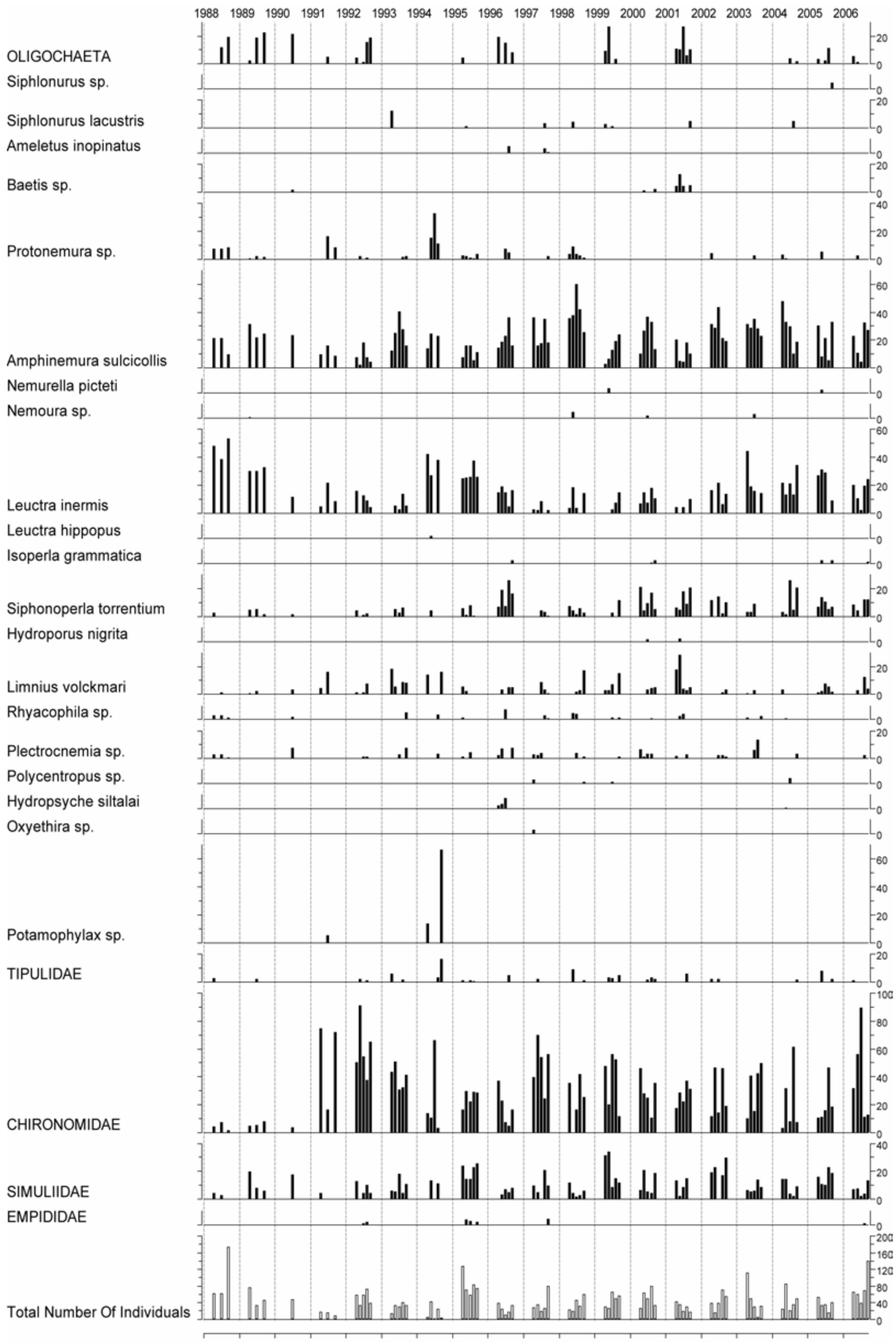
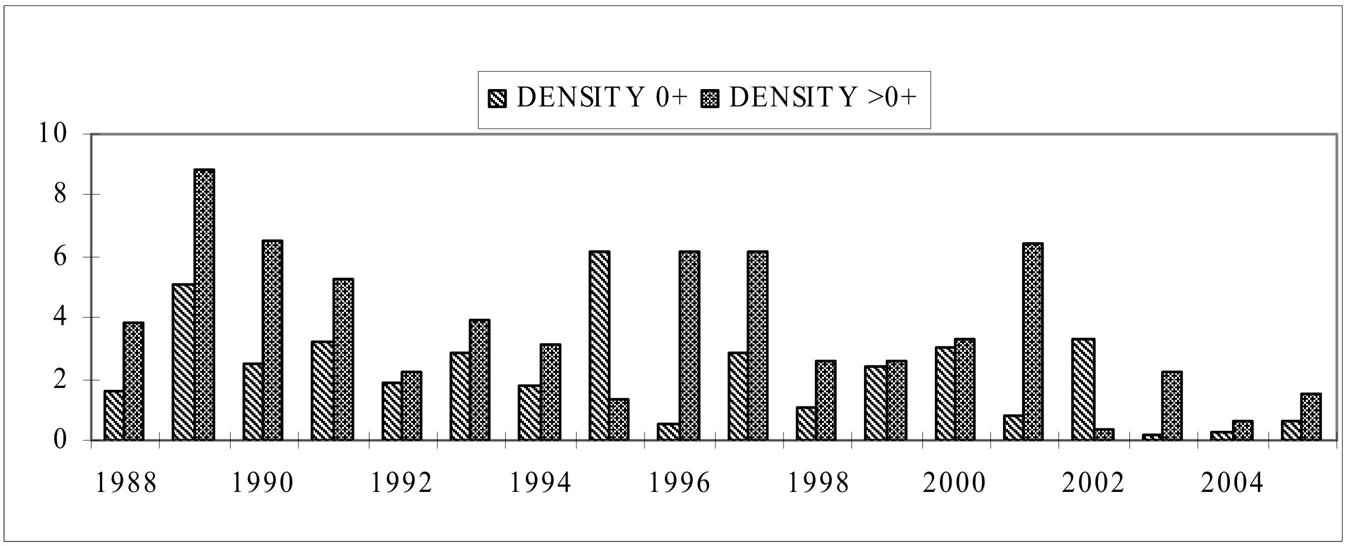


Table 4.20.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Bencrom River

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	488.70	60	39.8	60.2	0.68	0.22	0.003	0.273
Invertebrates	2189.32	27	57.9	42.1	0.04	0.15	0.003	0.051

Figure 4.20.5 Summary of Mean Trout Density (numbers 100m^{-2}): Bencrom River



4.21 Blue Lough

4.21.1 Water Chemistry Summary

Blue Lough is a small upland lake in the Mourne Mountains lying in a boggy col overlying granite, 2 km to the east of Bencrom River (Site 20). Over the early years of monitoring Blue Lough showed one of the highest concentrations of both xSO_4 and NO_3 on the Network. Despite similarities in these concentrations with the neighbouring stream, Blue Lough was considerably more acidic, with a mean pH of 4.67, mean labile aluminium concentration of 326.2 $\mu g\ l^{-1}$ and mean alkalinity of -24.7 $\mu eq\ l^{-1}$ (1990-1993 data).

Non-marine sulphate concentrations, in common with many other sites, remained relatively level until 1996 when they began to fall sharply. Unlike the majority of sites, however, concentrations have continued to fall slightly since 2000, and overall concentrations are now at about 50% of those in the first three years.

Nitrate concentrations have varied strongly between years, reflecting variability, and show no long term trend.

Concomitant with the reduction in non-marine sulphate concentration, labile aluminium concentration also fell sharply. However, despite an average decline of over 10 $\mu g\ l^{-1}\ yr^{-1}$, the mean concentration for 2003-2006 of 181.0 $\mu g\ l^{-1}$, is indicative of water that is still likely to be severely toxic for salmonids and other aquatic biota. Water pH began to rise in 1996 and averaged 4.87 in the most recent (2003-2006) period. Alkalinity and ANC both show significant increases but remain negative (i.e. mean 2003-2006 concentrations = -13.0 and -22.8 $\mu eq\ l^{-1}$ respectively. Calcium and magnesium concentrations parallel the decline in xSO_4.

4.21.2 Biology Summary

The epilithic diatom data show a significant linear trend over the monitoring period, driven primarily by reductions in the proportion of the acidobiontic species *Tabellaria binalis* (SWAP pH optima = 4.7) and an increase in the more sensitive *Brachysira brebissonii* (SWAP pH optima = 5.3). The other classic acidobiontic species *Tabellaria quadriseptata* (SWAP pH optima = 4.9), that dominated most samples in most years prior to 2004, has been at reduced abundances over the last three years.

The diatom composition of sediment trap samples has also changed significantly with time, but the change in species balance differs from that in the epilithon. This indicates that, in contrast with some other lakes on the AWMN, the sediment trap assemblage is dependent predominantly on diatoms from non-epilithic habitats. *Tabellaria quadriseptata* shows a clearer long term decline than in the epilithon, and is being balanced by *Semiorbis hemicyclus*, a species with a slightly lower pH optima than *T. quadriseptata* (i.e. SWAP pH optima = 4.8) but not very well represented in the SWAP dataset. There is no indication from the palaeoecological record for this site that *S. hemicyclus* was ever abundant in Blue Lough in the past, and the reason for its recent increase in sediment is currently unclear.

The aquatic macroflora of Blue Lough remains dominated by an acid tolerant assemblage of isoetid species and *Juncus bulbosus* var. *fluitans* and shows no indication of any change with time.

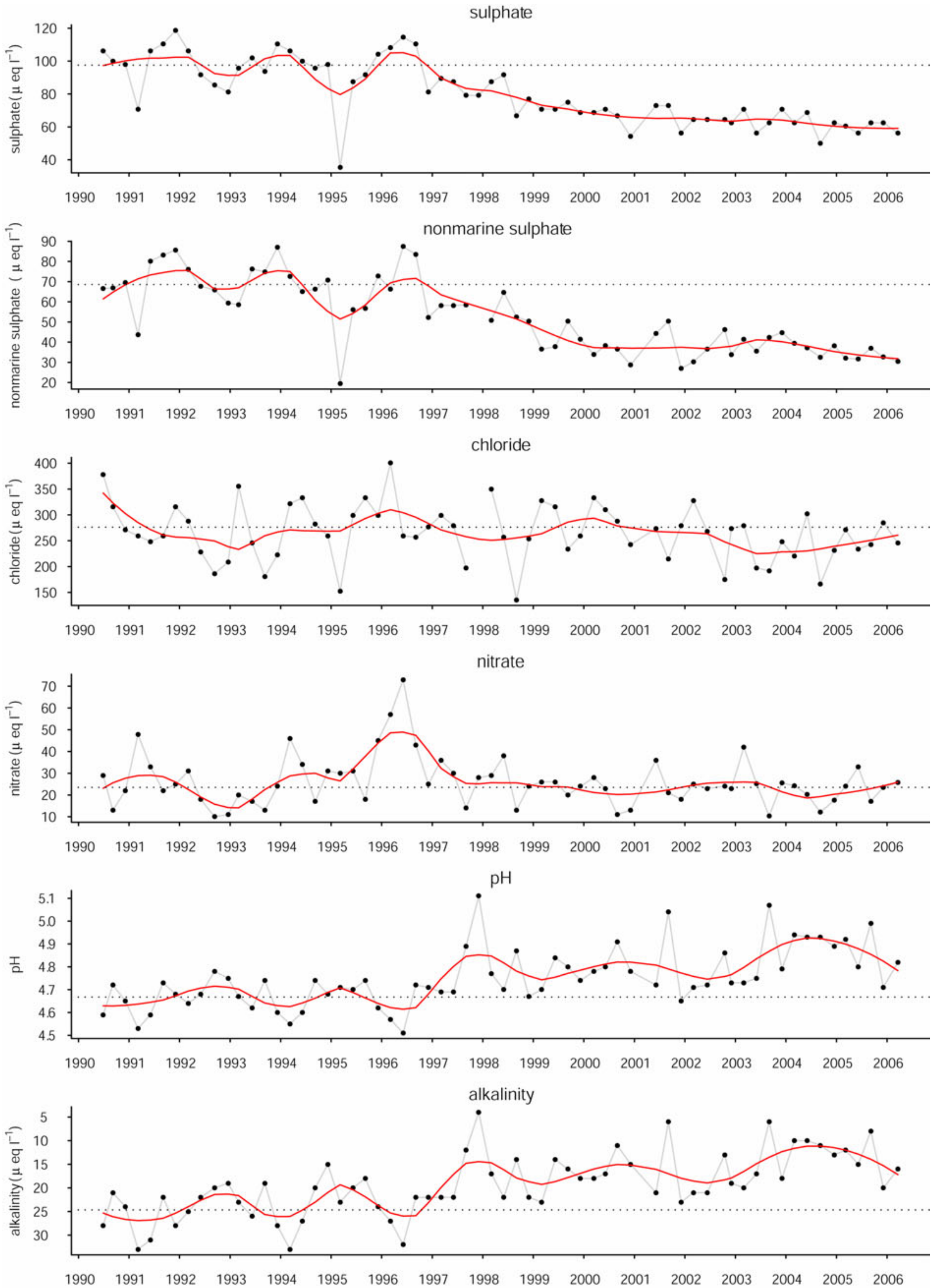
The macroinvertebrate community shows a strong linear trend, most clearly represented by a gradual increase in relative abundance of the predatory net spinning caddis, *Polycentropus* sp.– a species that is increasing also in other chemically improving AWMN lakes.

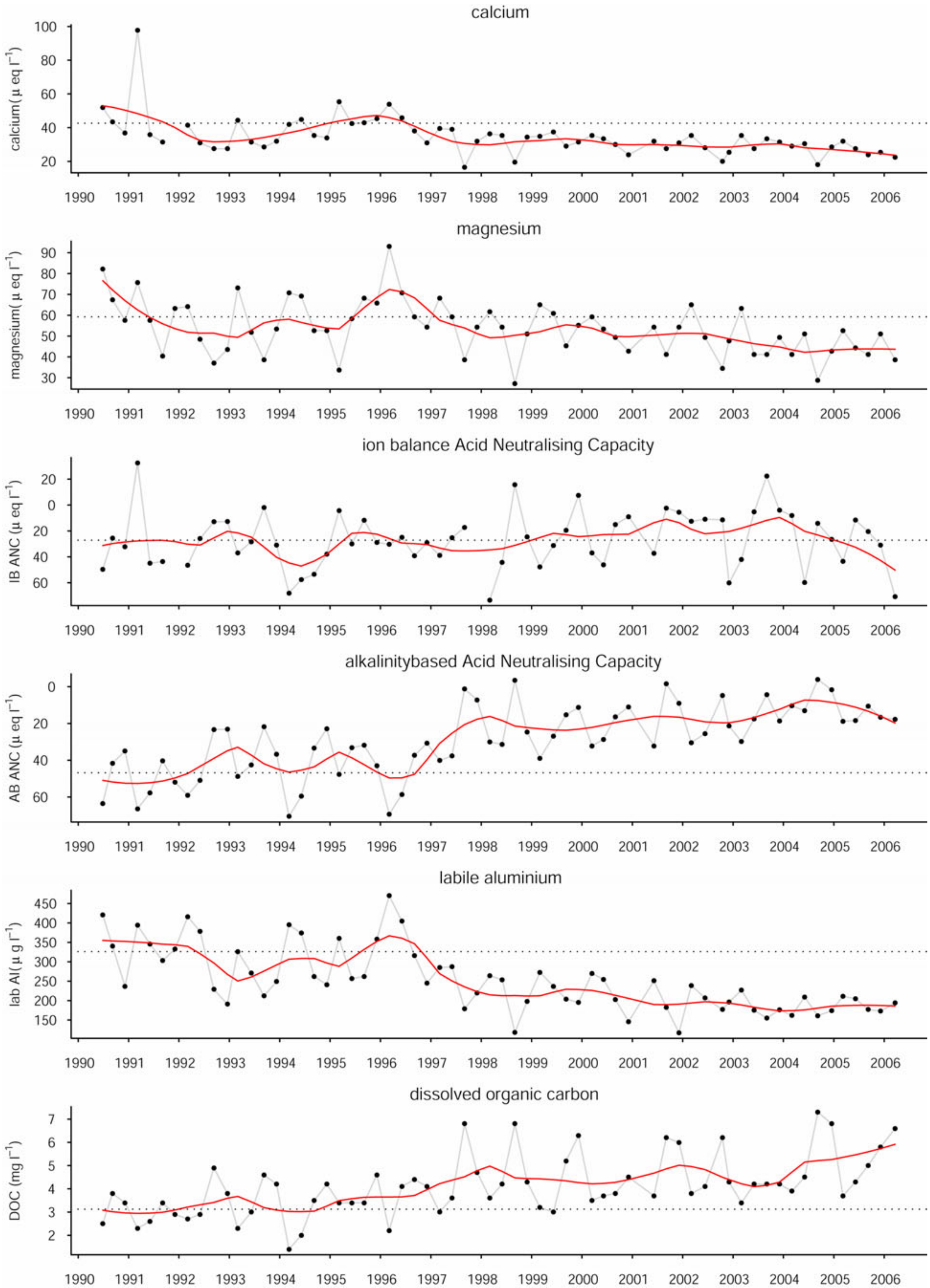
No fish were caught in the outflow of Blue Lough in most of the early years of monitoring. However, at least one fish has been recorded each year since 1997 and fish of less than one year old (indicative of local recruitment) were recorded first in 2000 and then in 2002 and 2004. Overall however, the brown trout density remains at a very low level.

4.21.3 Conclusions

Blue Lough is a naturally acidic but heavily impacted lake, with very low pH and high concentrations of labile aluminium. The water chemistry of the Lough has responded to a sharp reduction in xSO_4 since 1996, but while labile aluminum levels have fallen substantially they remain at levels thought to be toxic to fish and other components of the aquatic biota in softwater lakes. There is evidence for biological responses to chemical recovery to date in diatoms, macroinvertebrates and fish. However, brown trout density in the outflow remains at a very low level, while the change in diatom composition in the sediment involves a shift to a very different assemblage to that recorded in the deeper, pre-acidification sediments.

Figure 4.21.1 Water Chemistry Summary Plots: Blue Lough





calcium
calcium(μ eq l⁻¹)
magnesium
magnesium(μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al(μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.21.1 Water Chemistry Summary Data and Trend Statistics: Blue Lough

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Jun 1990 - Mar 1993	mean	68.8	23.5	276.2	4.67	-24.7	-27.1	-46.8	55.2	42.6	59.2	254.1	11.5	392.6	326.2	3.1
	st. dev	11.8	10.7	57.4	0.07	4.4	23.6	14.5	9.5	19.8	14.5	37.1	2.2	69.0	74.6	0.8
	min	43.8	10.0	186.2	4.53	-33.0	-49.8	-66.4	41.0	27.4	37.0	195.8	8.4	288.0	191.0	2.3
	max	85.8	47.9	378.0	4.78	-19.0	32.5	-23.1	73.0	97.8	82.3	313.2	16.1	511.0	421.0	4.9
Apr 1993 - Mar 1998	mean	65.8	32.0	276.2	4.70	-21.7	-33.3	-37.8	56.4	38.3	58.7	258.8	13.1	368.0	295.6	3.7
	st. dev	15.6	15.0	60.7	0.13	6.7	19.2	17.8	8.5	9.0	13.4	48.2	4.7	67.4	74.8	1.2
	min	19.6	13.0	152.3	4.51	-33.0	-73.4	-70.6	36.0	16.5	33.7	121.8	2.6	280.0	179.0	1.4
	max	87.5	73.0	400.6	5.11	-4.0	-1.9	-1.3	73.0	55.4	93.0	369.8	25.3	520.0	470.0	6.8
Apr 1998 - Mar 2003	mean	41.3	24.1	265.6	4.78	-17.6	-22.9	-20.3	48.7	30.5	51.2	241.8	12.4	281.2	207.9	4.5
	st. dev	9.5	8.0	51.2	0.10	4.6	20.6	12.3	6.5	5.3	10.0	30.6	1.9	34.0	46.4	1.2
	min	27.2	11.0	135.4	4.65	-23.0	-60.3	-38.9	33.0	19.5	27.1	169.7	9.2	212.0	117.0	3.0
	max	64.9	42.0	332.9	5.04	-6.0	15.8	3.5	59.0	37.4	65.0	291.5	15.6	331.0	273.0	6.8
Apr 2003 - Mar 2006	mean	36.2	21.5	236.3	4.87	-13.0	-22.8	-12.0	45.1	27.4	43.6	215.0	10.0	258.3	181.0	5.0
	st. dev	4.5	6.4	39.1	0.14	4.3	25.8	7.6	6.3	4.4	6.7	26.3	1.9	19.7	19.2	1.3
	min	30.5	10.4	166.4	4.71	-20.0	-70.8	-18.8	33.0	18.0	28.8	161.0	6.6	219.0	155.0	3.7
	max	44.8	32.9	301.8	5.07	-6.0	22.3	4.0	53.0	33.4	52.6	252.3	13.6	286.0	211.0	7.3
Seasonal-Kendall statistics	Sen-slope	-2.967	-0.203	-2.408	0.015	0.750	0.054	2.415		-1.215	-1.209				-10.405	0.171
	P- val	**<0.001**	0.334	0.237	**<0.001**	**<0.001**	0.243	**<0.001**		**<0.001**	**0.010**				**<0.001**	**<0.001**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C);
sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.21.2 Epilithic Diatom Percentage Abundance Summary: Blue Lough

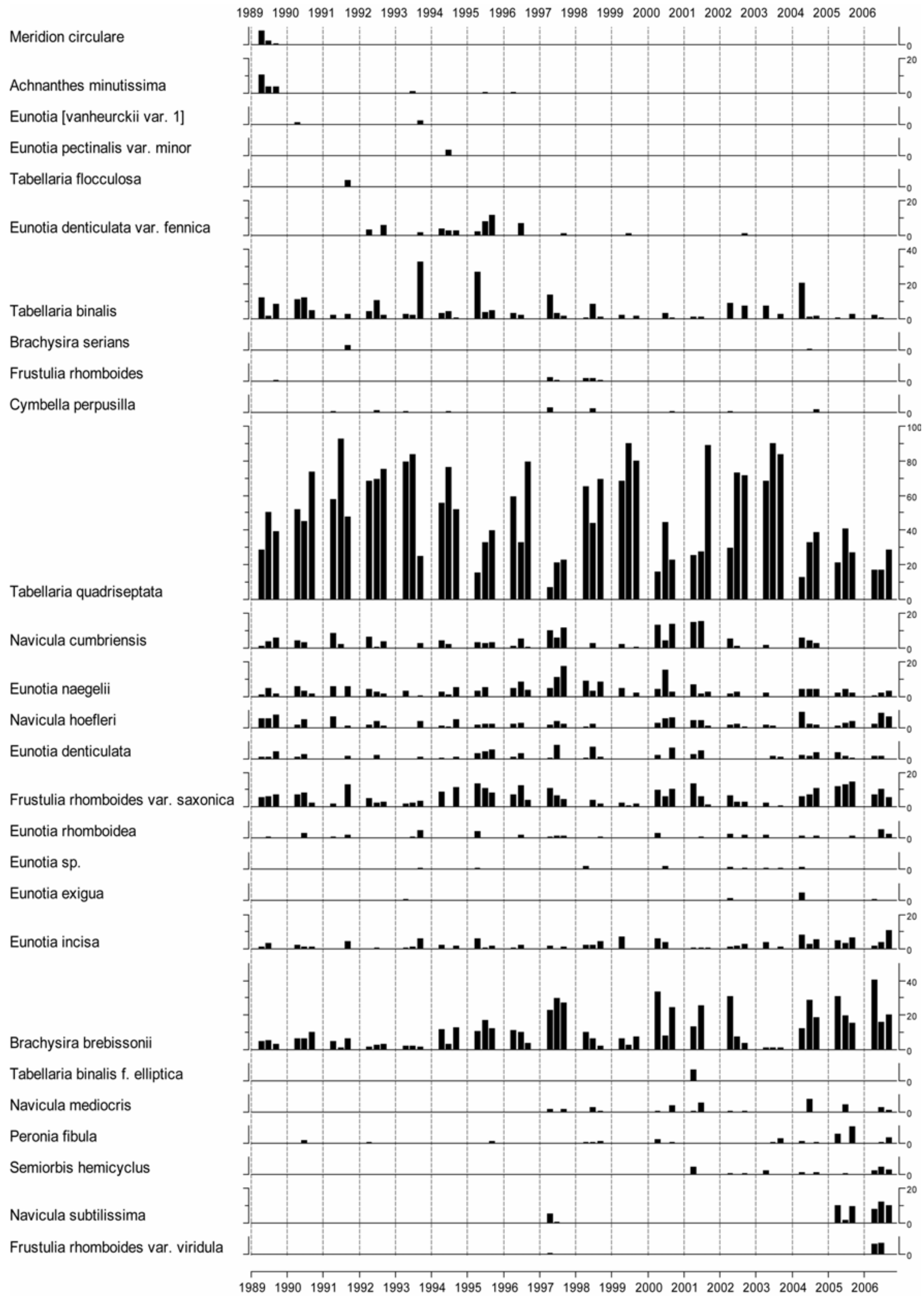


Figure 4.21.3 Aquatic Macrophyte Species Scores (1-5): Blue Lough

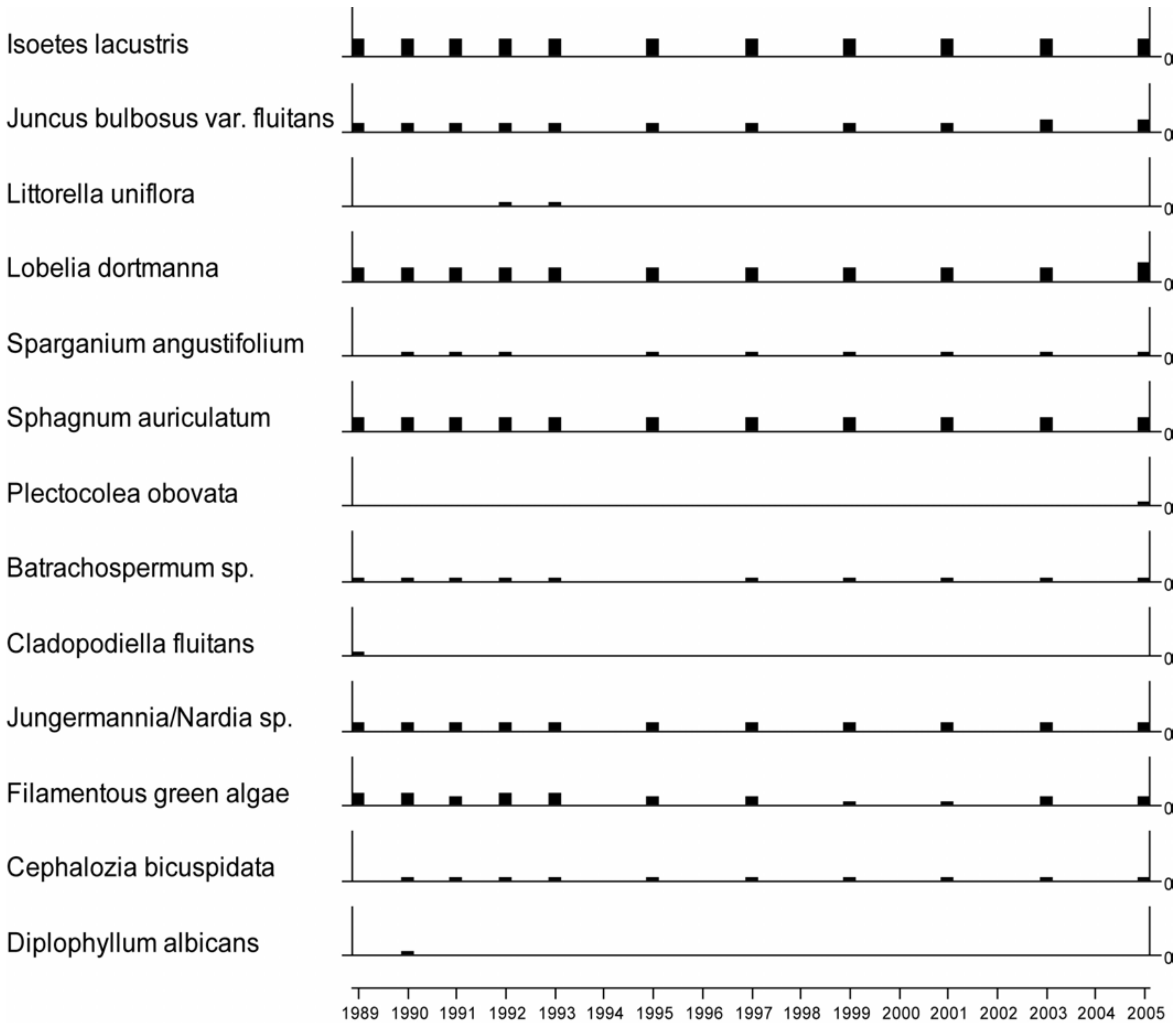


Figure 4.21.4 Macroinvertebrate Percentage Abundance Summary: Blue Lough

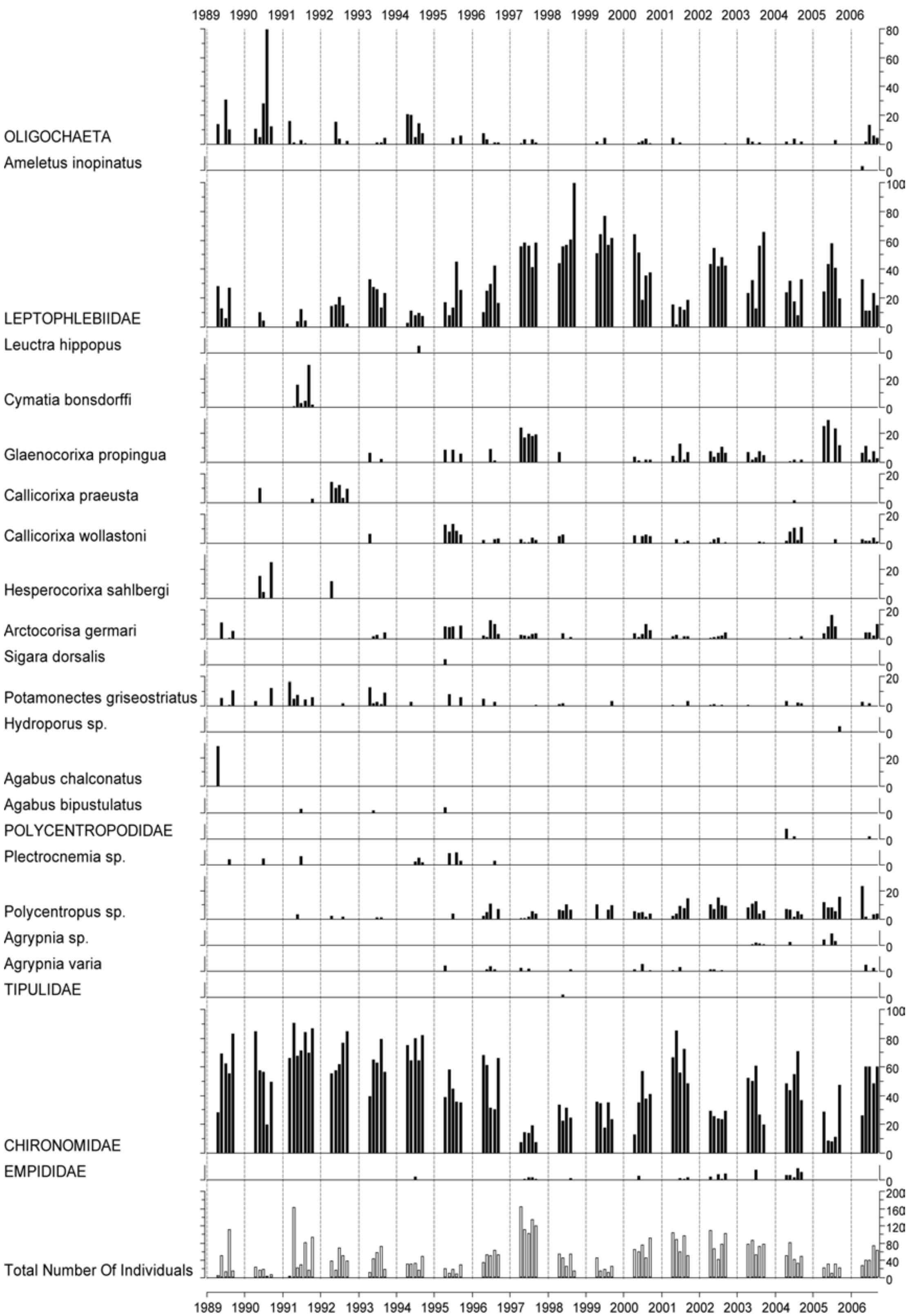
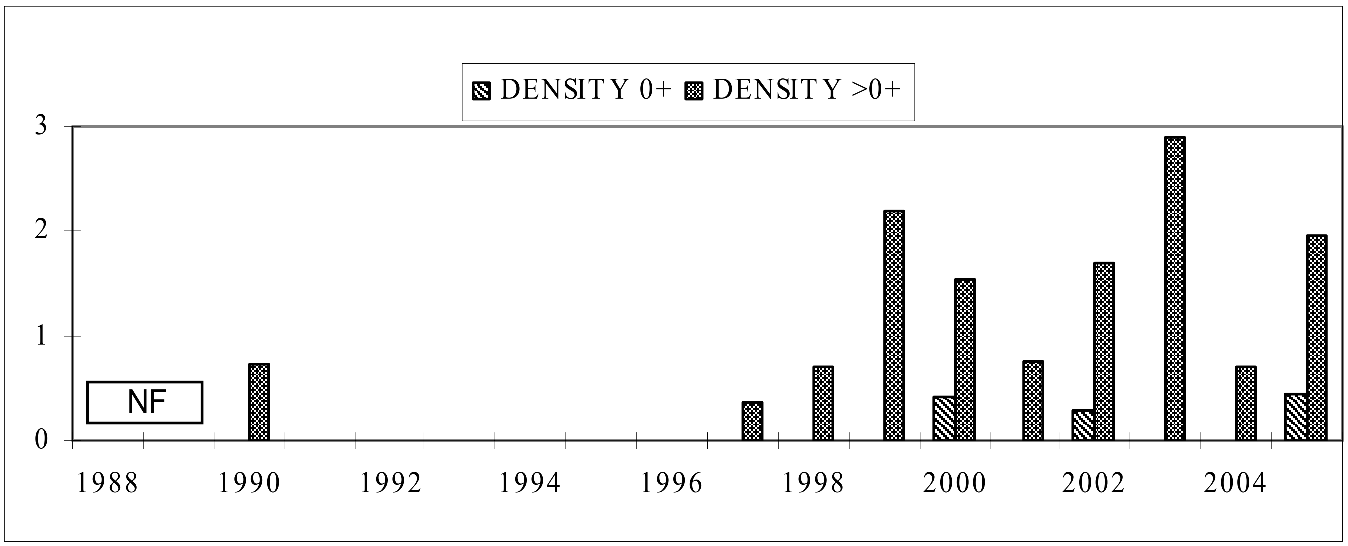


Table 4.21.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Blue Lough

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1000.87	93	43.1	56.9	0.10	0.32	0.001	0.022
Invertebrates	2190.49	30	47.1	52.9	0.20	0.70	0.001	0.037

Figure 4.21.5 Summary of Mean Trout Density (numbers 100m^{-2} for outflow stream): Blue Lough



NF = Not fished

Figure 4.21.6 Relative Percentage Frequency of Sediment Trap Diatom Taxa: Blue Lough

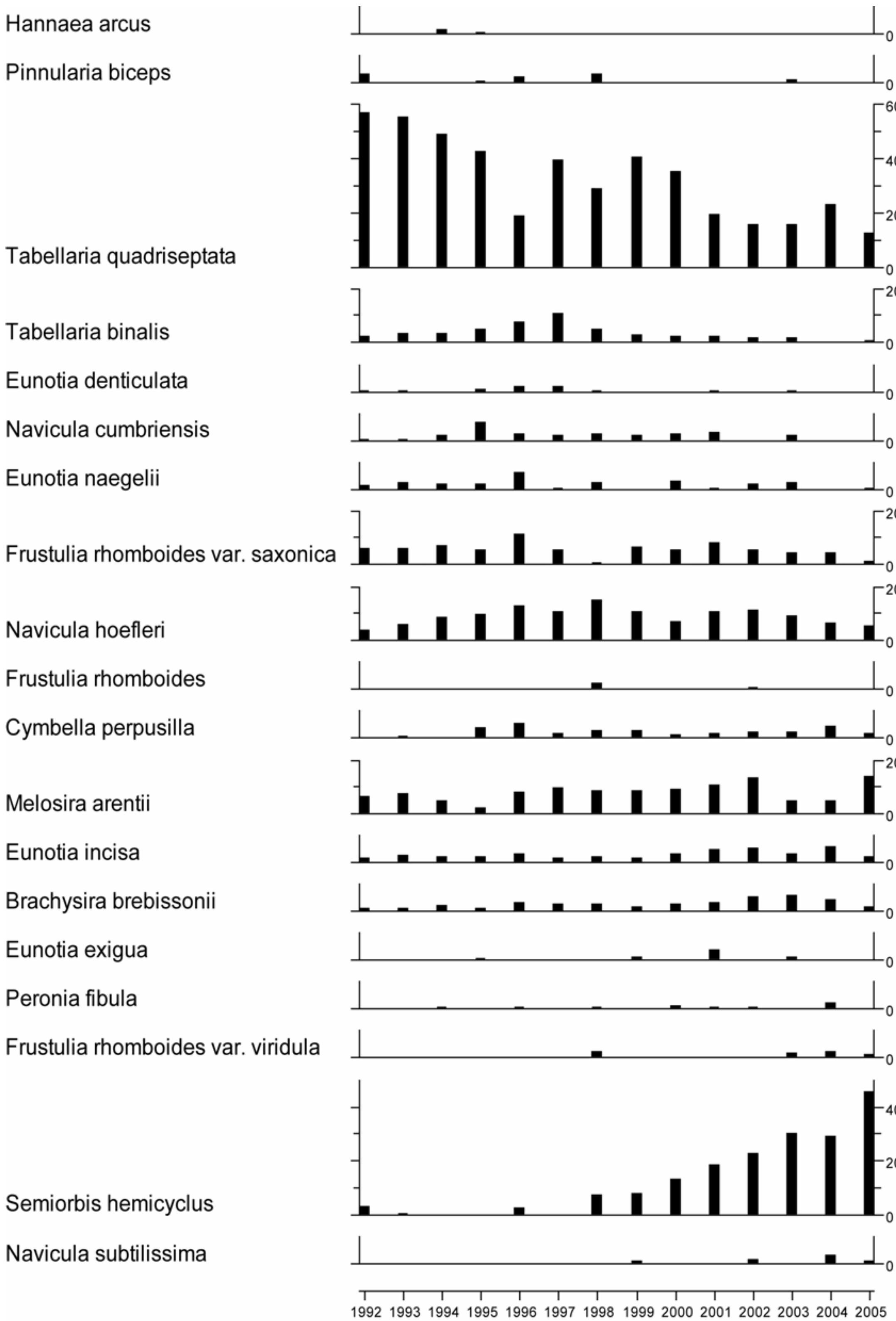
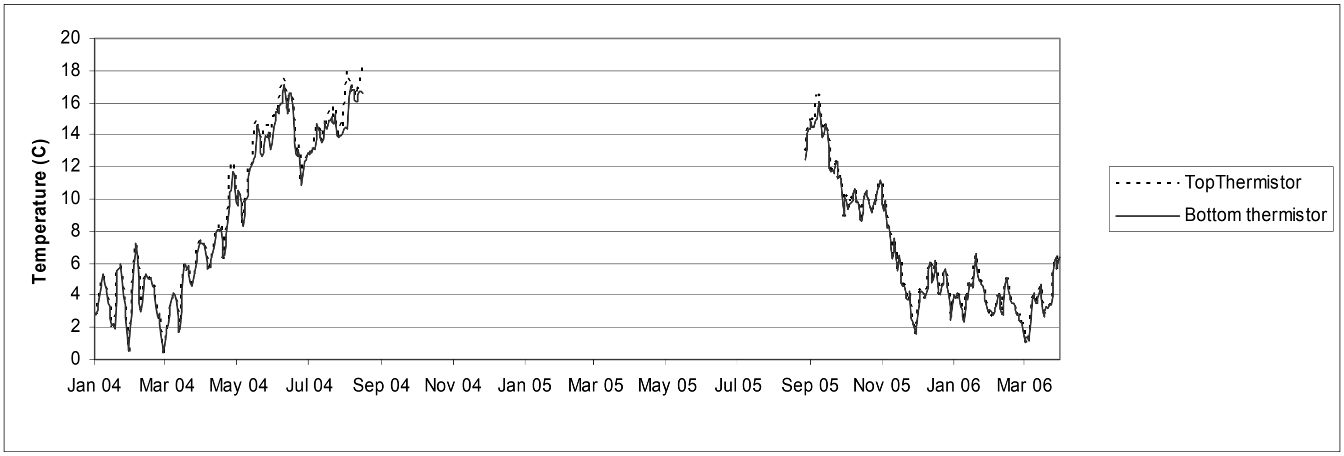


Figure 4.21.7 Thermistor Data: Blue Lough



2004/2005 thermistors not recovered.

4.22 Coneyglen Burn

4.22.1 Water Chemistry Summary

Coneyglen Burn drains a large area of moorland overlying schists in the Sperrin Hills of Northern Ireland. The lower stretches of the catchment were under coniferous forestry at the onset of monitoring, but a considerably larger part of the catchment has been planted with trees over the past five years. In contrast to the sites in the Mourne Mountains, 90 km to the south east, Coneyglen Burn is one of the least deposition-impacted sites on the AWMN; over the first three years (1990-1993) mean xSO_4 concentration was 26.5 μeq l-1, while NO_3 concentrations were normally below the limit of detection. Mean pH of 6.54 and mean alkalinity of 157.9 were indicative of a well buffered system although pH dropped occasionally below 5.0 during hydrological episodes. Labile aluminium levels were normally below the limit of detection and rarely exceeded 20 μg l^{-1}.

Despite relatively low initial concentrations of xSO4, there has been a significant decline in levels over the full monitoring period, with most of the change after a large, drought-related peak in 1996. Unusually for the AWMN, concentrations continued to fall after 2000 and the 2003-2006 mean was 13.5 μeq l^{-1}. Nitrate concentrations have shown some inter-annual variability but no long-term trend.

Chloride concentrations also show marked variability, demonstrating proximity to the west coast of Ireland, but no overall trend.

With the exception of DOC that shows an upward trend in common with most other sites on the Network, there are no other significant changes in water chemistry.

4.22.2 Biology Summary

The epilithic diatom data shows strong interannual variability reflecting strong interannual variability in water chemistry. However, there is no significant linear trend in the data. The only potential indication of recent change comes from a decline in *Eunotia exigua* (SWAP pH optima = 5.1) and a corresponding slight increase in *Cymbella lunata* (SWAP pH optima = 5.7).

The aquatic macrophyte survey stretch is characterised by several bryophytes and dominated by the acid-sensitive moss species *Hygrohypnum ochraceum* and *Fontinalis squamosa*. There is no indication of any change in relative or absolute species cover of the survey stretch over time.

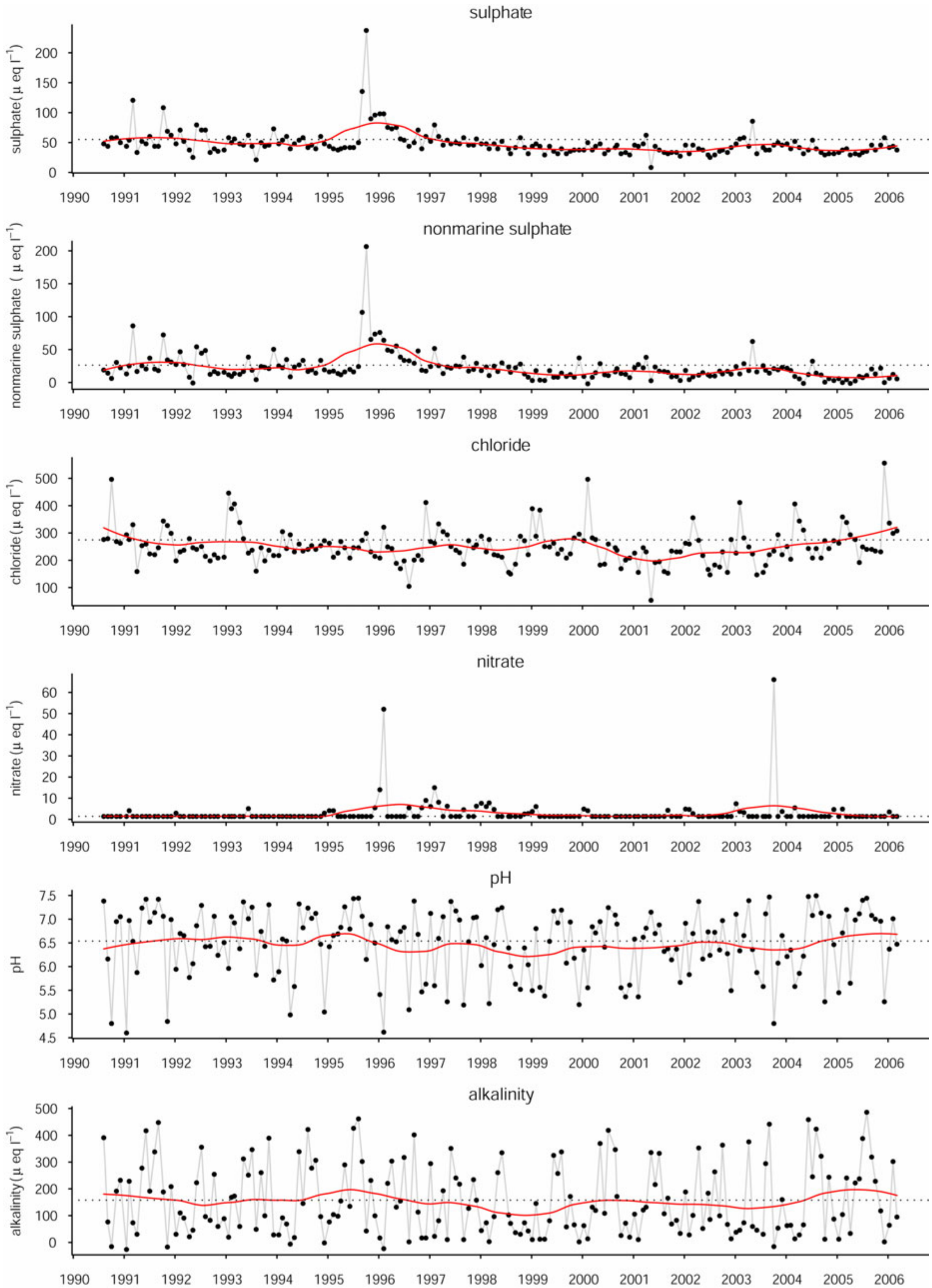
The macroinvertebrate assemblage has changed significantly over the monitoring period, largely as a result of an increase in the proportional abundance of the stonefly shredder *Leuctra inermis* and corresponding decline in the stonefly predator *Siphonoperla torrentium* that is generally considered to be more sensitive to acidity. There is no obvious link between these changes and changes in water chemistry.

Coneyglen Burn has supported relatively high densities of brown trout since the onset of monitoring. There is no trend in the density of juvenile or older fish over time.

4.22.3 Conclusions

Coneyglen Burn is a relatively insensitive stream exposed to relatively low levels of sulphur deposition. Nevertheless, xSO_4 concentrations have fallen significantly over the monitoring period. With the exception of DOC concentrations, that have increased substantially, there is no indication of other trends in chemical variables. Reasons for the gradual switch in relative abundance of two dominant stonefly taxa are currently unclear. Coneyglen Burn remains important to the AWMN as a low deposition “control” site.

Figure 4.22.1 Water Chemistry Summary Plots: Coneyglen Burn



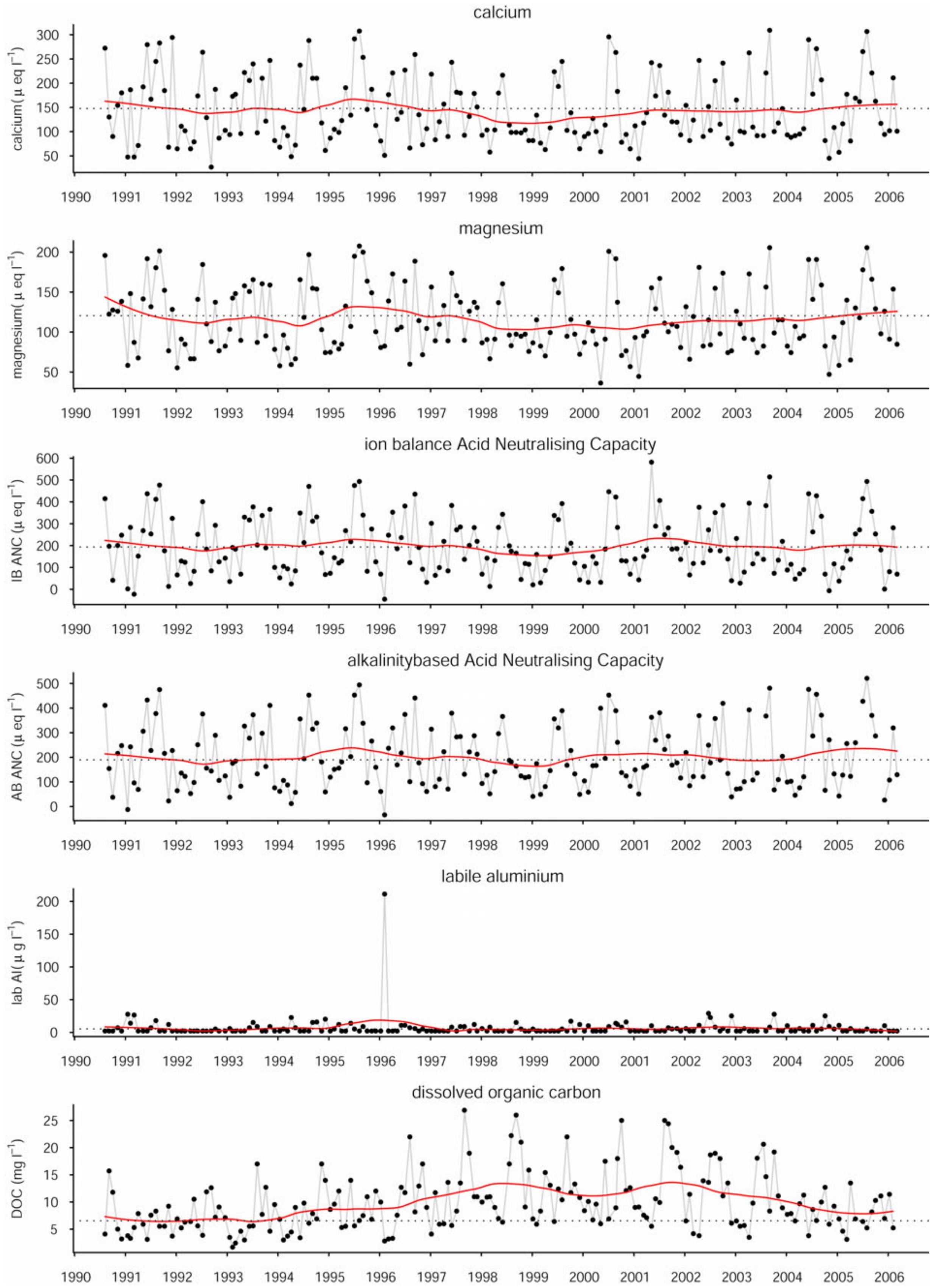

calcium
calcium(μ eq l⁻¹)
magnesium
magnesium(μ eq l⁻¹)
ion balance Acid Neutralising Capacity
IB ANC (μ eq l⁻¹)
alkalinitybased Acid Neutralising Capacity
AB ANC (μ eq l⁻¹)
labile aluminium
lab Al(μ g l⁻¹)
dissolved organic carbon
DOC (mg l⁻¹)
1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006

Table 4.22.1 Water Chemistry Summary Data and Trend Statistics: Coneyglen Burn

Determinand		xSO_4^{2-}	NO_3^-	Cl^-	pH	alk	IB-ANC	AB-ANC	cond	Ca^{2+}	Mg^{2+}	Na^+	K^+	sol. Al	lab._Al	DOC
period		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$		$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu eq\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$
Aug 1990 - Mar 1993	mean	26.5	1.4	274.6	6.54	157.9	193.8	189.6	56.0	147.8	120.4	248.0	8.8	34.3	5.3	6.5
	st. dev	19.0	0.6	75.0	0.75	132.5	136.9	127.3	12.9	77.7	42.7	42.9	2.0	17.5	7.0	3.3
	min	-0.5	1.3	158.0	4.60	-26.0	-22.3	-12.0	37.0	26.9	55.1	182.7	5.4	6.0	2.0	1.7
	max	86.4	4.0	496.5	7.42	448.0	477.3	475.3	78.0	294.4	201.5	374.1	12.8	82.0	28.0	15.7
Apr 1993 - Mar 1998	mean	32.7	3.8	245.9	6.49	162.2	206.4	206.4	54.8	149.4	119.9	234.6	10.5	43.9	9.0	9.3
	st. dev	29.5	7.0	46.9	0.74	134.7	130.8	127.5	11.5	68.6	41.0	28.9	3.5	35.1	27.0	4.9
	min	4.1	1.3	104.4	4.62	-24.0	-44.6	-34.8	31.0	48.9	57.6	139.2	2.6	7.0	2.0	2.8
	max	206.2	52.0	411.9	7.44	461.0	494.3	493.8	83.0	307.9	207.3	304.5	18.9	264.0	211.0	26.9
Apr 1998 - Mar 2003	mean	14.6	2.0	235.9	6.39	134.2	188.7	193.6	50.2	132.3	108.0	215.8	9.6	40.4	5.7	12.2
	st. dev	8.1	1.4	71.0	0.59	116.8	123.7	111.9	11.2	59.4	36.4	34.9	3.6	16.2	6.2	5.9
	min	-1.7	1.3	53.6	5.20	2.0	20.3	38.7	32.0	43.9	36.2	143.6	3.8	12.0	2.0	3.8
	max	38.4	7.4	496.5	7.37	419.0	581.4	452.5	73.0	295.9	200.7	352.4	21.7	88.0	29.0	26.0
Apr 2003 - Mar 2006	mean	13.0	3.5	264.9	5.89	175.5	202.6	223.3	57.1	151.4	120.0	231.9	8.4	25.7	5.2	9.2
	st. dev	11.9	10.8	75.2	5.54	152.6	147.1	151.0	11.7	75.1	43.0	41.7	2.4	14.2	6.1	4.2
	min	-1.6	1.3	146.7	4.80	-16.0	-6.5	26.1	33.0	45.4	46.9	152.3	3.3	8.0	2.0	3.1
	max	62.0	66.1	555.7	7.49	486.0	513.6	521.4	80.0	309.4	205.7	387.2	15.3	74.0	28.0	20.6
Seasonal-Kendall statistics	Sen-slope	-1.279	0.036	-0.208	0.006	-0.635	-1.693	-0.271		-0.733	-0.788				-0.066	0.215
	P- val	**0.007**	0.755	0.541	0.674	0.894	1.000	0.457		0.906	0.795				0.705	**0.050**

alk = Gran or Dual Endpoint Alkalinity; IB-ANC = Ion balance Acid Neutralising Capacity (see Chapter 5); cond = Conductivity (20 °C); sol. Al = soluble monomeric aluminium, lab. Al = labile soluble monomeric aluminium; DOC = dissolved organic carbon

Figure 4.22.2 Epilithic Diatom Percentage Abundance Summary: Coneyglen Burn

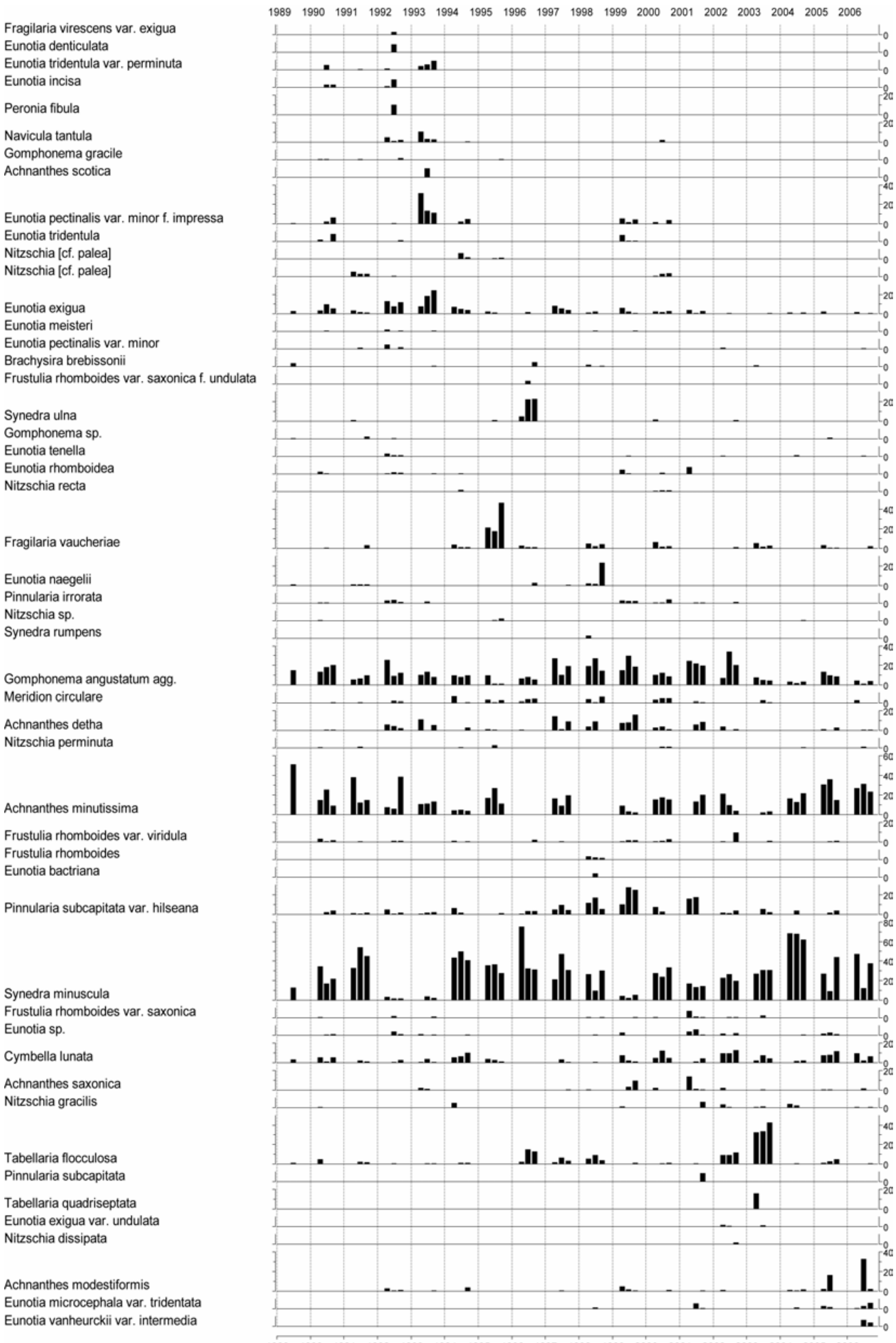
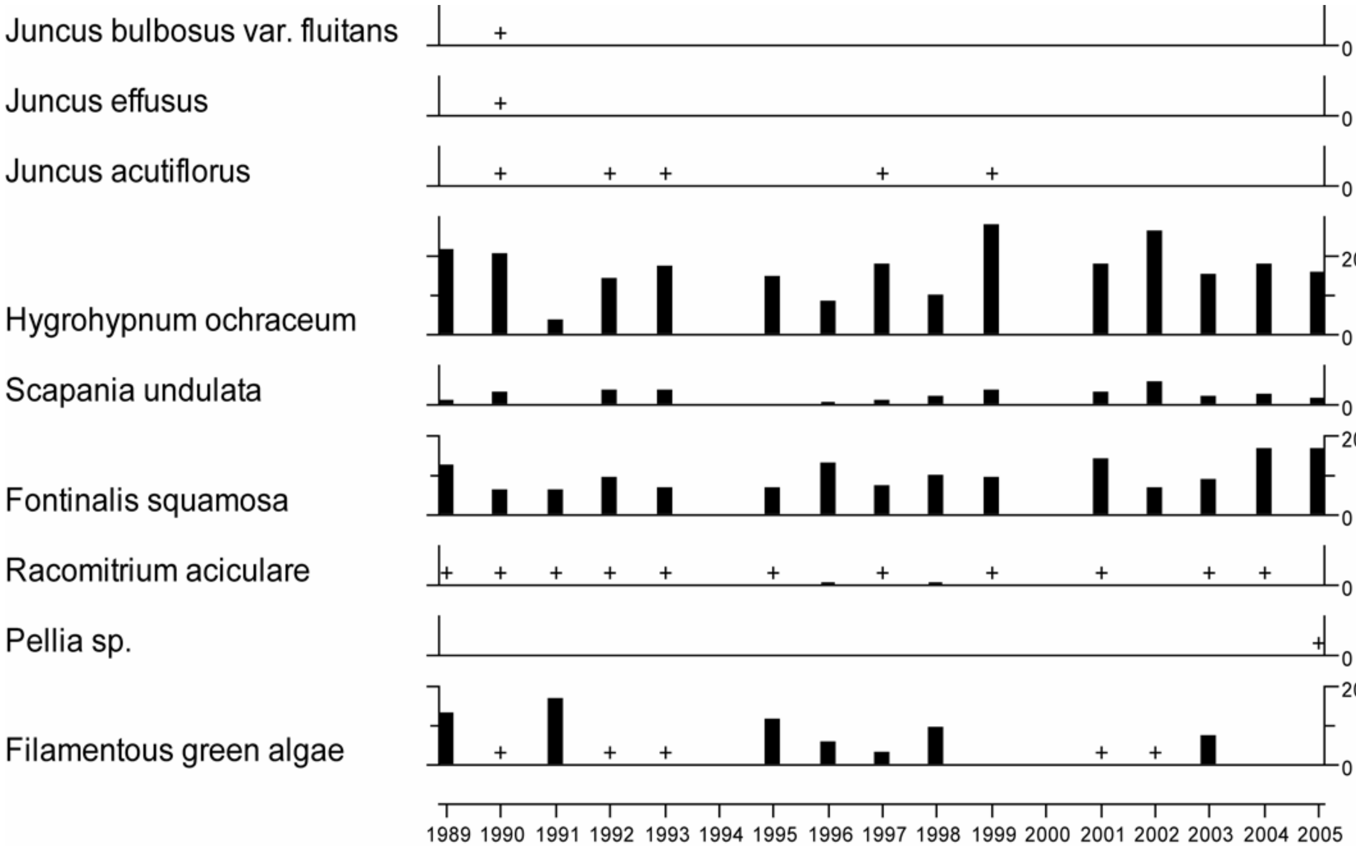
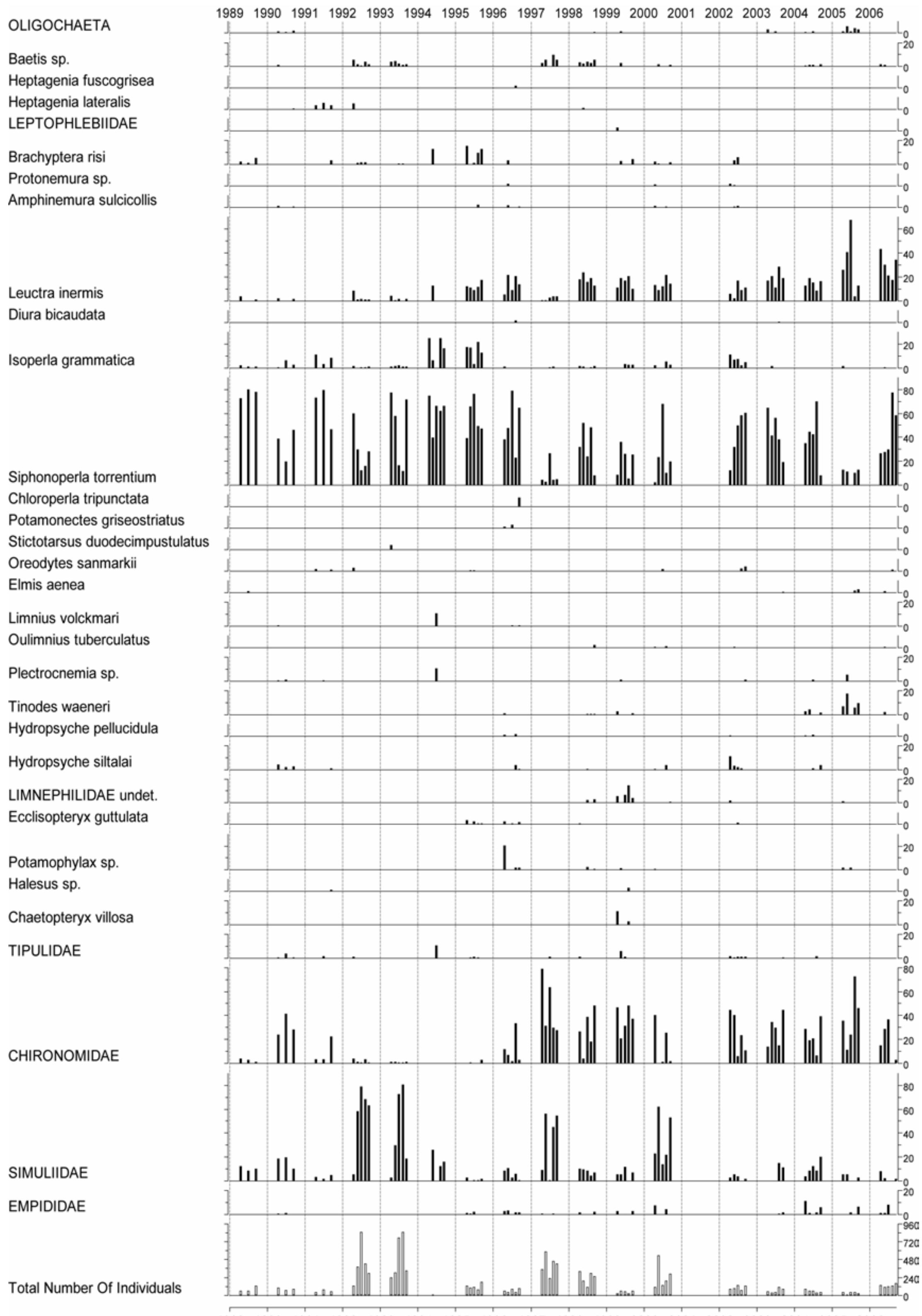


Figure 4.22.3 Aquatic Macrophyte Percentage Species Cover: Coneyglen Burn



+ Represents <0.25% abundance

Figure 4.22.4 Macroinvertebrate Percentage Abundance Summary: Coneyglen Burn

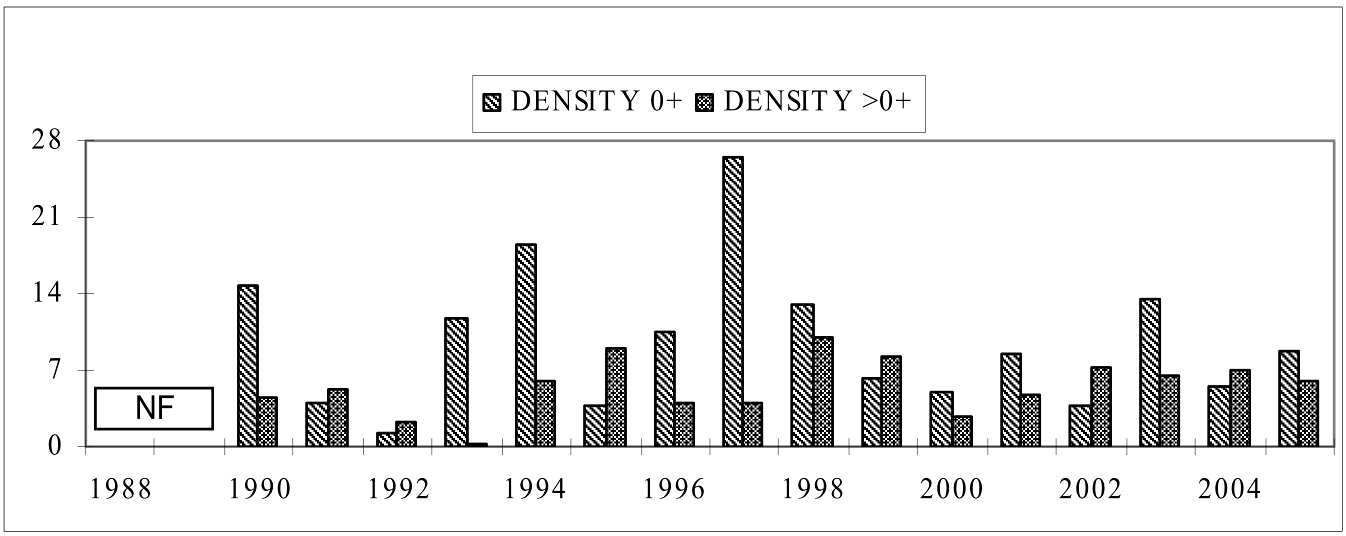


No sampling in 2001 due to Foot and Mouth restrictions.

Table 4.22.2 Trend Statistics for Macroinvertebrates and Epilithic Diatoms: Coneyglen Burn

	Total Sum Of Squares	Number of Taxa	Variance Explained Within Year	Variance Explained Between Years	Linear Trend (λ_1RDA)	λ_1RDA /λ_2RDA	P unrestricted	P restricted
Epilithic Diatoms	1711.2	126	29.9	70.1	0.06	0.30	0.001	0.289
Invertebrates	2309.43	46	40.7	59.3	0.16	0.55	0.001	0.024

Figure 4.22.5 Summary of Mean Trout Density (numbers 100m^{-2}): Coneyglen Burn



NF = Not fished

5. CONCLUSIONS

5.1 Introduction

At the time of release of this report the UK Acid Waters Monitoring Network (AWMN) will have been in operation for 20 years. Over this period, substantive interpretative reports have been produced every 5 years (i.e. Patrick *et al*., 1995; Monteith and Evans, 2000; Monteith 2005). These have reviewed the operation of the Network, summarised trends in the data and integrated the information at site and national levels. The next interpretative report of this type, that will summarise data from June 1988 to March 2007, is scheduled for 2008.

In the following sections we review site performance, summarise site-level observations provided in Chapter 4, draw conclusions with respect to the current evidence for ecosystem responses to acid emissions controls, describe the metals monitoring programme, and comment on the wider value of the AWMN to national and international monitoring programmes and scientific research.

5.2 AWMN Site Performance

With one exception, there have been no major unanticipated disturbances at AWMN sites since monitoring began in 1988, or soon after. Most Network sites have the advantage of being relatively remote and are well protected from the changes in land-use, intensive agriculture and industrial development that can threaten the ecology of lowland waters.

Some felling and replanting has occurred in several catchments with managed forestry (i.e. Allt na Coire nan Con, Loch Chon, Loch Grannoch, Llyn Cwm Mynach, Afon Hafren), however the inclusion of these systems was an intentional part of the Network design. In all cases it would seem that the regional scale pattern of sulphur deposition has continued to dominate trends in the acidity of these sites, although it is clear that the presence of forest increases significantly the interception of acidic pollutants and seasalt. Recently, there has been a change in grazing management within the catchments of the Round Loch of Glenhead and the Dargall Lane Burn in Galloway, with sheep having being replaced with cattle. Currently there is no indication of any direct affect on these AWMN sites.

The only significant damage to an AWMN site, the installation of a dam on the outflow of the most northerly site, Loch Coire nan Arr, and subsequent water level management, has been documented previously (see Monteith, 2005). Perhaps surprisingly it has been difficult, until very recently to detect any substantial effect of water level manipulation on water chemistry – variation in dissolved organic carbon (DOC) concentration for example continues to resemble that of the nearest stream site, Allt na Coire nan Con. Loch Coire nan Arr has, therefore, remained an effective control site for the Network with respect to water chemistry, and continues to provide a standard for levels of non-marine sulphate (xSO_4) and nitrate (NO_3) in a minimally impacted region. The physical disturbance of the loch however has been hugely deleterious to the aquatic flora and fauna, to the extent that biological monitoring has now ceased. Parallel monitoring of a neighbouring site, Loch Coire Fionnaraich, which shares many physical, geological, and chemical characteristics of Loch Coire nan Arr, began in 2001 and this site will now assume the role of a low-deposition control for the Network.

5.3 Methodological and Analytical Performance

The Water Research Centre (WRC) in Medmenham has maintained an AQC system for the AWMN throughout its operation. This system has been extremely important, not only for the Network, but also for several other laboratories throughout the UK involved in the analysis of softwater chemistry. It was essential in identifying analytical problems at local laboratories (unstable determinand analysis) during the first two years of operation and has demonstrated a consistently high standard of precision and accuracy at all remaining AWMN labs.

The remaining laboratories on the Network, CEH Wallingford, FRS Pitlochry and EA Llanelli, also participate in an international AQC programme operated by the UNECE International Cooperative Programme Focal Centre for the Assessment of Acidification in Rivers and Lakes (ICP Waters) in Norway and have again shown consistently high performance.

Biological sampling within the AWMN has been conducted by the same groups, and often by the same individuals, ever since its inception. Similarly, the same analysts, for taxonomic identification of diatoms, aquatic macrophytes and macroinvertebrates, have been involved from the outset and this has resulted in a high level of consistency over time. In all cases, however, samples are archived and new data is screened in the context of the longer records during the annual reporting procedure in order to identify outliers or missing values. Where necessary the raw data, or even the original samples, are re-examined.

Fisheries scientists at FRS Pitlochry are currently undertaking an assessment of AWMN fish records at all sites. This has revealed problems in the suitability of a minority of sites (e.g. Loch Grannoch and Loch Tinker) for the identification of possible long-term responses to changes in water quality and these sites will no longer be fished under any future contract.

5.4 Trends in Water Chemistry

5.4.1 Non-marine sulphate

The summaries in Chapter 4 demonstrate that anthropogenically derived, or non-marine, sulphate (xSO_4) remains the dominant acidifying agent throughout the Network. Non-marine sulphate concentrations have declined substantially across the Network. However, despite national statistics that show a relatively linear decline in SO_2 emissions over the last 20 years, trends in xSO_4 concentration in runoff from AWMN sites have been distinctly non-linear. For most sites this reflects non-linear changes in deposition – see for example Cooper (2005). Very few significant trends in xSO_4 concentration were detected over the first 10 years of monitoring (Monteith and Evans, 2000) but many sites showed dramatic reductions in concentrations between 1995 and the end of the last assessment period (Monteith, 2005).

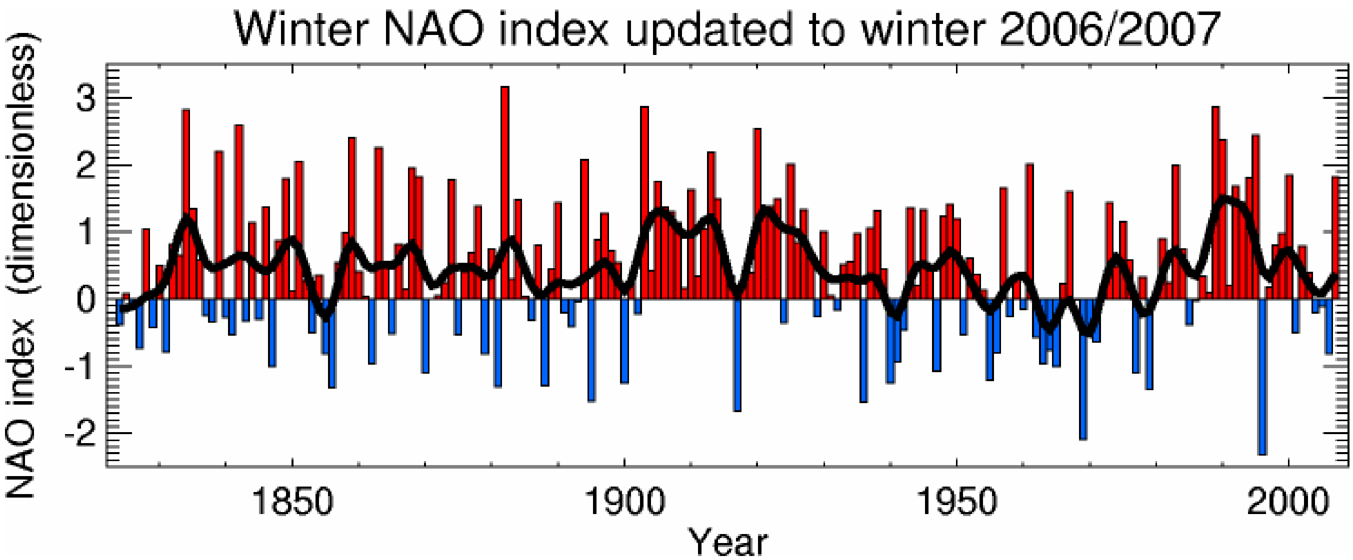


Figure 5.4.1. Temporal variability in the winter NAO index

Source: the University of East Anglia Climatic Research Unit website; url: http://www.cru.uea.ac.uk/~timo/projpages/nao_update.htm. Positive phases bring relatively warm wet and less polluted air masses over the UK. Note the tendency for approximately decadal scale variation throughout much of the last century, the elevated levels in the early 1990s, and a tendency toward negative values (i.e. more easterly dominated conditions) throughout most of the last 20 years.

Non-linearity with SO_2 emissions is perhaps best explained by decadal scale variability in climate. At the onset of monitoring the UK was dominated by westerly conditions, associated with a high winter North Atlantic Oscillation (NAO) Index (Hurrell, 1995) which brought relatively clean air across the country (see Figure 5.4.1). Declines in SO_2 emissions during the first half of the 1990s were countered by a progressive switch to more easterly conditions during winter, which brought an increasing supply of more contaminated easterly air masses. In the mid 1990s flue gas desulphurisation (FGD) plant was fitted to some large sulphur emitting power stations in the UK, and, after 1995-1996, westerly conditions began to dominate again. This combination of effects may explain the subsequent sharp decline in sulphur deposition and an almost 50% decline in the xSO_4 concentrations of runoff from some AWMN sites. This was reported as the first indication of national improvement in the sulphate load in the last AWMN assessment (Monteith, 2005a; Monteith and Evans, 2005).

Over the period since March 2003 (the termination point for the last report) there is little indication of further reductions in the xSO_4 concentrations in runoff from AWMN sites; indeed at most sites concentrations reached minimum levels in around 2000 and at a minority there has been a slight reversal since 2003. Again, this may in part reflect a recent return to more negative winter NAO conditions (Figure 5.4.1). Perhaps more importantly for ecological recovery, however, xSO_4 concentrations at the majority of AWMN sites remain well above those experienced at sites in the low deposition regions of northwest Scotland (Loch Coire nan Arr / Loch Coire Fionnaraich) and northwest Northern Ireland (Coneyglen Burn). This is illustrated in Figures 5.4.2 and 5.4.3 which summarise trends in five yearly mean (or for the last period a three yearly mean) concentration for lakes and streams respectively.

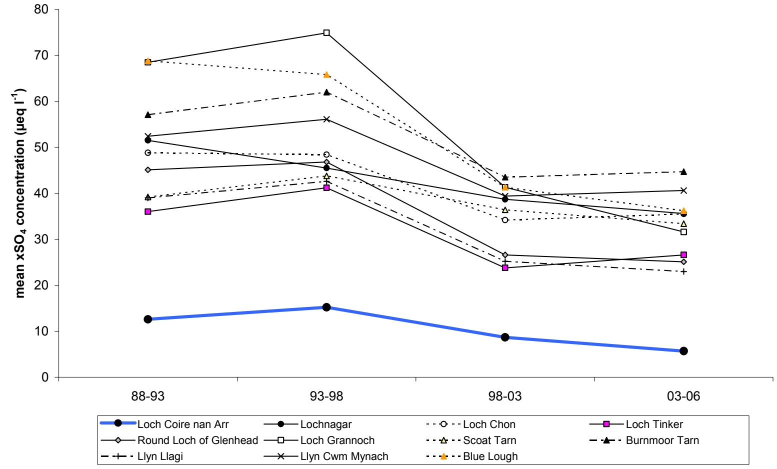


Figure 5.4.2 Trends in five yearly mean concentrations of non-marine sulphate in runoff from AWMN lakes.

The last period represents three years only. Note that all sites show a similar temporal pattern with most of the decline occuring in the middle of the record. Note also that in 2003-2006 the concentration in most lakes is circa 4-7 times higher than that for Loch Coire nan Arr - representing the low deposition region of northwest Scotland.

The sites that have shown the highest concentrations historically, as a consequence of their proximity to emission sources, the River Etherow in the Pennines and Old Lodge in southeast England, show large absolute declines but continue to exhibit concentrations far in excess of those ever recorded for the more remote sites on the Network (Figure 5.4.3). Cooper (2005) showed that even for these two stream sites, runoff fluxes of xSO_4 equate largely to those in deposition, and, clearly, waters in these high deposition regions are continuing to receive very high loads of acidity from sulphur deposition.

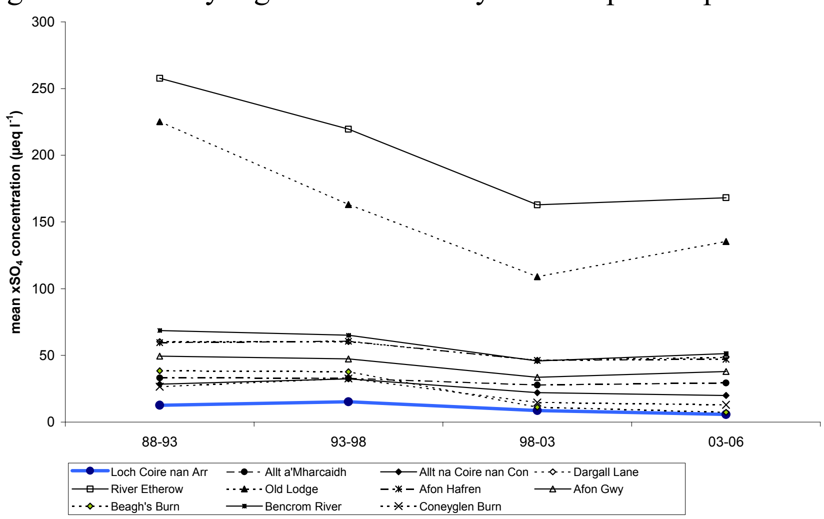


Figure 5.4.3 Trends in the five yearly mean concentrations of non-marine sulphate in AWMN streams and Loch Coire nan Arr.

The last period represents three years only. Note that the y-axis scale is different from that for Figure 5.4.2. All sites show a similar temporal pattern with most of the decline occurring in the middle of the record. There is greater variation in 2003-2006 concentrations between sites in comparison with AWMN lakes. Beagh's Burn and Coneyglen Burn in northwest and northeast Northern Ireland, show similar 2003-2006 concentrations to Loch Coire nan Arr, representing the low deposition region of northwest Scotland. However, concentrations in most streams remain more than four times higher, and in the case of Old Lodge and the River Etherow, are 23 and 29 times higher respectively.

5.4.2 Nitrate

Nitrate represents a second source of acidity for acid-sensitive freshwaters, but unlike sulphate there is little indication of downward trends across the Network to date. Currently, NO_3 levels alone are sufficient to cause critical load exceedence in over half of all UK waters where the critical load for acidity is deemed to be exceeded by the FAB model (Curtis and Simpson, 2007). Even the complete elimination of anthropogenic sulphur deposition, therefore, would be insufficient to protect these sites while NO_3 concentrations remain elevated.

Unlike sulphate, which behaves relatively conservatively in catchments, the NO_3 reaching surface waters has mostly undergone biological cycling within the soil and fluxes in runoff do not follow fluxes of N in deposition so closely. Short-term variation in NO_3 tends to be governed by climatic variability as demonstrated, for example, by Monteith *et al*. (2000) who showed a strong link between peak winter concentrations and the strength of the NAO.

There is a strong spatial correlation between average N deposition flux and freshwater concentrations. Nitrate concentrations in runoff from sites in low deposition regions such as Loch Coire nan Arr and Coneyglen Burn are often below the limit of detection (particularly during the growing season), and never exceed a few microequivalents per litre. For sites in high deposition areas, such as the River Etherow in the southern Pennines, and sites in more moderate deposition areas with poorly developed soils and therefore lower potential for N retention, such as Scoat Tarn in the English Lake District, NO_3 concentrations are high all year round and represent a particularly important contribution to the total acid load.

Curtis *et al*. (2005) demonstrated that as xSO_4 continues to fall at AWMN sites, NO_3 will become an increasingly important acidifying agent unless its concentrations begin to decline also. However, if anything, NO_3 concentrations have increased at some sites. Stoddard (1994) predicted that soils subject to anthropogenic N deposition would progressively accumulate N to a point of "nitrogen saturation" with year round N retention (the reference case) developing into seasonal leaching, and eventually year round leaching. It is possible that the Round Loch of Glenhead, Loch Chon, Lochnagar, and Loch Grannoch exemplify this process (Figure 5.4.4).

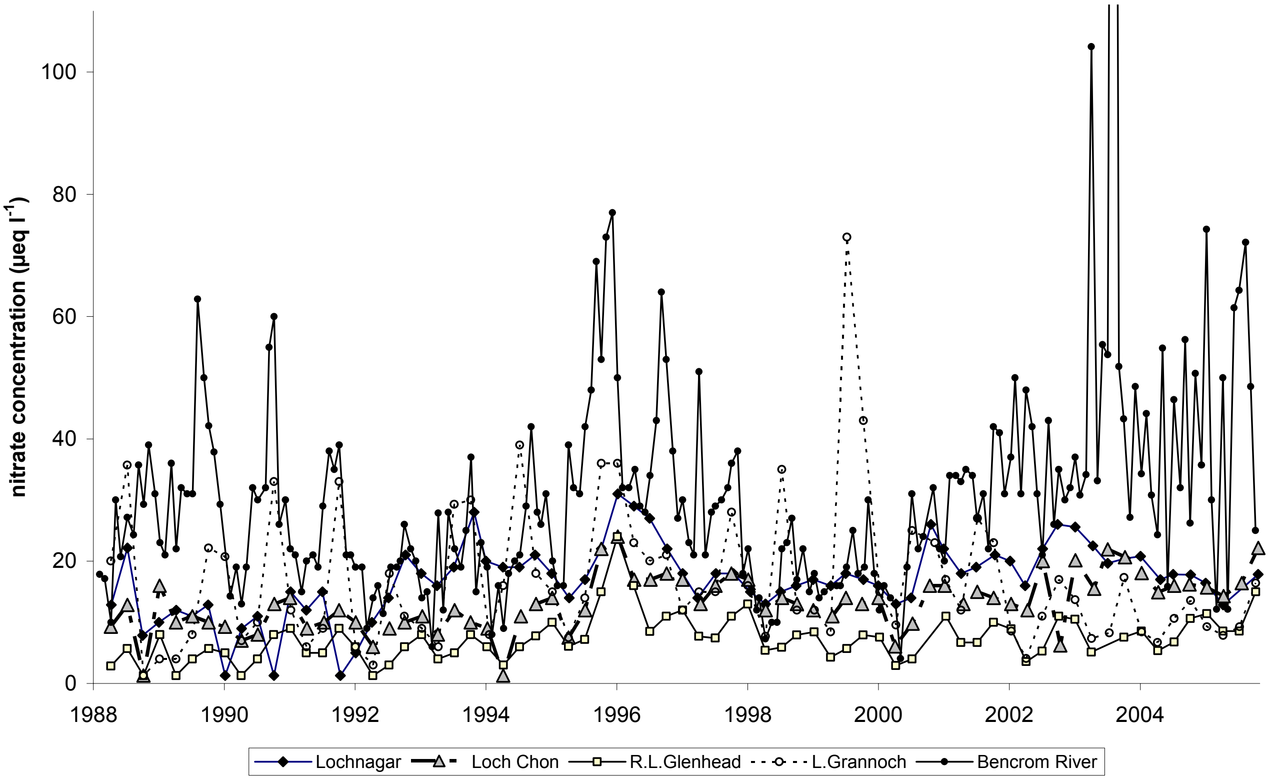


Figure 5.4.4 Trends in nitrate concentrations at AWMN sites that are broadly consistent with the nitrogen saturation hypothesis of Stoddard (1994).

Note there is some indication of a coherent signal with a shift away from seasonal retention at some sites from around 1994.

However, there is evidence for some coherence in temporal patterns in NO_3 concentration between these sites and it is also feasible, therefore, that this behaviour is linked to climatic variation. The exceptionally elevated winter NAO Index during the early years of monitoring resulted in some of the warmest winters on record. The relatively low winter NO_3 concentrations in runoff from these sites in these years may reflect this climatic anomaly with greater retention of N by catchment soils. On balance however, the tendency for an apparent increase in NO_3 in approximately one AWMN site in four gives considerable cause for concern with respect to potential future recovery. Importantly, the AWMN provides the only regional-scale long term record of this behaviour for upland waters in the UK; continuation of these records is crucially important to develop a better understanding of the dominant drivers of these trends, and track future changes.

Finally, NO_3 also represents an important nutrient in these upland waters, and there is increasing concern that aquatic ecosystems in remote environments are acutely sensitive to its effects. It has been suggested that rising nitrogen inputs may have led to shifts toward more mesotrophic, plankton-dominated algal assemblages in lakes as remote as the Arctic and many high mountain regions, with as yet unknown consequences for wider aquatic biodiversity. Recent palaeolimnological work conducted within DEFRA's Freshwater Umbrella programme has shown that several AWMN lakes have undergone a significant shift in $\delta^{15}N$ over the past 150 years which is most likely explained by an increased contribution from anthropogenic N deposition (Curtis and Simpson, 2007). Future work based at AWMN sites is planned to facilitate a better understanding of processes.

5.4.3 Seasalt

Because of the westerly location of many geologically sensitive upland regions of the England, Scotland and Wales, the chemistry of many AWMN sites is strongly influenced by inputs of seasalt, derived from sea spray generated during coastal storms. This is indicated by the concentration and variability in the chloride ion – which tends to be derived almost solely from seasalt in most AWMN sites. Chloride is considered to be relatively conservative in catchments and is not retained significantly by the soil. However, the accompanying base cations in seasalt exchange with soil cations on negatively charged surfaces. In non-acidified catchments this normally leads only to base cation exchange and, therefore has little effect on acid neutralising capacity (ANC) or acidity status of runoff. However, when deposited on acidified soils, marine base cations may displace hydrogen (H^+) and aluminium ions, leading to acidic pulses that can be extremely damaging to aquatic biota. As recently as January 2003, a seasalt deposition event in southwest Norway lead to a major fish kill in some rivers for this reason (Larssen and Holme, 2006).

The temporal pattern of seasalt deposition across the AWMN has been linked to the state of the NAO during winter (Evans *et al*., 2001). Large pressure gradients over the North Atlantic associated with a positive NAO Index lead to high winds, an increase in wave height, and an increase in the generation and entrainment of a seasalt aerosol as waves break on the coast. In the early 1990s the winter NAO was in a persistently elevated state, and the effect of the resulting storminess is evident in peaks in many chloride records over this period. Chloride records for some AWMN sites appear to be even more strongly linked to the Arctic Oscillation (AO), effectively an alternative expression of the same North Atlantic phenomenon but based on multiple sea level pressure monitoring stations rather than just two (Thompson and Wallace, 1998). Figure 5.4.5 demonstrates that that the chloride concentration in the Dargall Lane Burn in southwest Scotland reflects variation in the daily AO Index throughout the monitoring record.

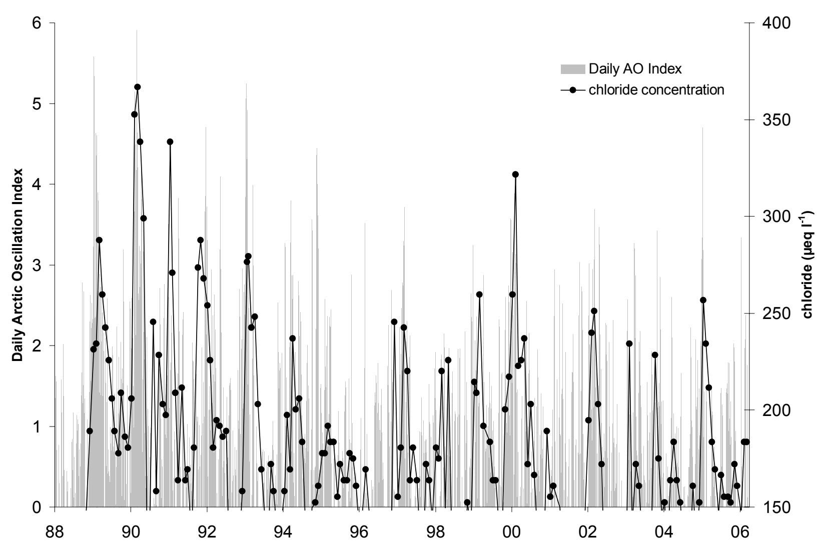


Figure 5.4.5 Comparison of the monthly chloride concentration record of the Dargall Lane Burn with the daily Arctic Oscillation Index

Both y-axes scales have been truncated to emphasise the relationship between peak levels. Note that the largest peaks in chloride (e.g. 1989, 1990, 1993 and 2000) often coincide with a periods of a sustained (continuous grey hatching) and elevated AO Index.

On short timescales therefore, the effect of North Atlantic storminess dominates variation in acidity. This is illustrated for the forested site Allt nan Coire nan Con in Figure 5.4.6. and indicates that the high aluminium levels recorded in the early 1990s were linked to an intense and prolonged period of storminess. (It should be noted however, that acidity during stormy periods is also enhanced by the increased rate of runoff that is also associated with these conditions (see Section 5.4)).

Despite the overall downward trend in the AO Index over the past 18 years, there are indications that in the longer term the AO has been increasing since the 1970s (Figure 5.4.7) and may continue to increase in response to global warming. The potential implication for many AWMN sites is that not only will the conditions experienced during the early 1990s be repeated, but that they could be even more severe in future. Under such a scenario any recent biological recovery could be retarded or even reversed. These effects may be felt particularly in the forested water courses of the UK uplands which, although widespread, are relatively poorly served by long term monitoring records (particularly with respect to labile aluminium measurements).

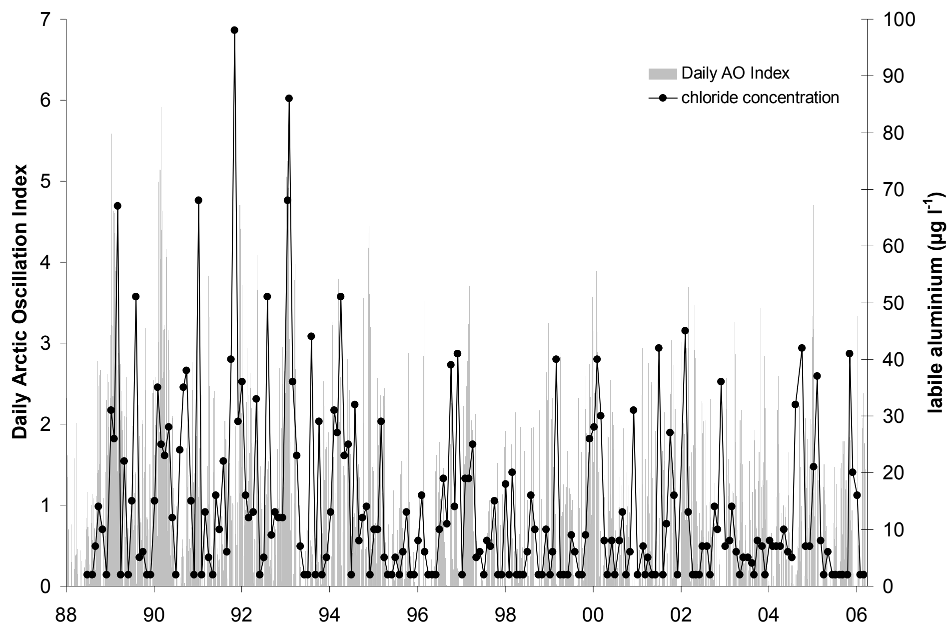


Figure 5.4.6Comparison of the monthly labile aluminium concentration record of Allt na Coire nan Con (a forested site in northwest Scotland) with the daily Arctic Oscillation Index

The y-axes scale for the AO Index is truncated to emphasise the relationship between peak levels. The plot suggests that under current sulphur deposition levels, a return to climatic conditions experienced in the early 1990s could drive labile aluminium levels during episodes back toward potentially toxic concentrations. The apparent sensitivity of this site to seasalt may have been enhanced by the depletion of soil base cations by forest growth and harvesting and the increased interception of the seasalt aerosol by the forest canopy.

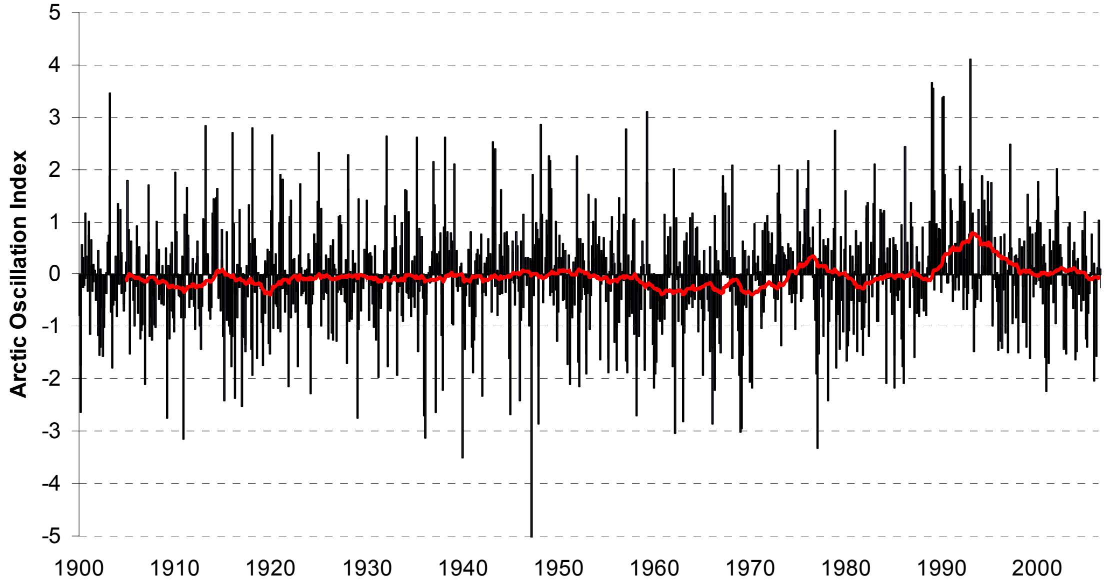


Figure 5.4.7 Monthly mean Arctic Oscillation (AO) Index since 1900

The trend line represents a 10 year moving average. Note the tendency for an increase over the last few decades and the unprecedentedly high levels in the early 1990s (i.e. the early years of the AWMN).

5.4.4 Acidity

The AWMN data described in Chapter 4 demonstrate that water acidity, as represented by labile aluminium (Al_{lab}), pH and alkalinity, has declined at all sites where xSO_4 concentrations, and by inference sulphur deposition, have fallen. Responses are site specific, reflecting differences in the acidity status of these systems, and in the case of streams, differences in hydrological pathways.

Labile aluminium

In the more acidic systems that exhibited chronically high Al_{lab} concentrations at the onset of monitoring (such as Blue Lough, Bencrom River, Loch Grannoch and Scoat Tarn), the primary response to falling levels of acid deposition has been a reduction in these levels (Figures 5.4.8 and 5.4.9 respectively). Rosseland *et al*. (1990) proposed that concentrations of between 25 µg l^{-1} and 75 µg l^{-1} represented a toxicological threshold for fish in low pH and low calcium surface waters. Some AWMN sites show downward movement across this threshold over the past 18 years.

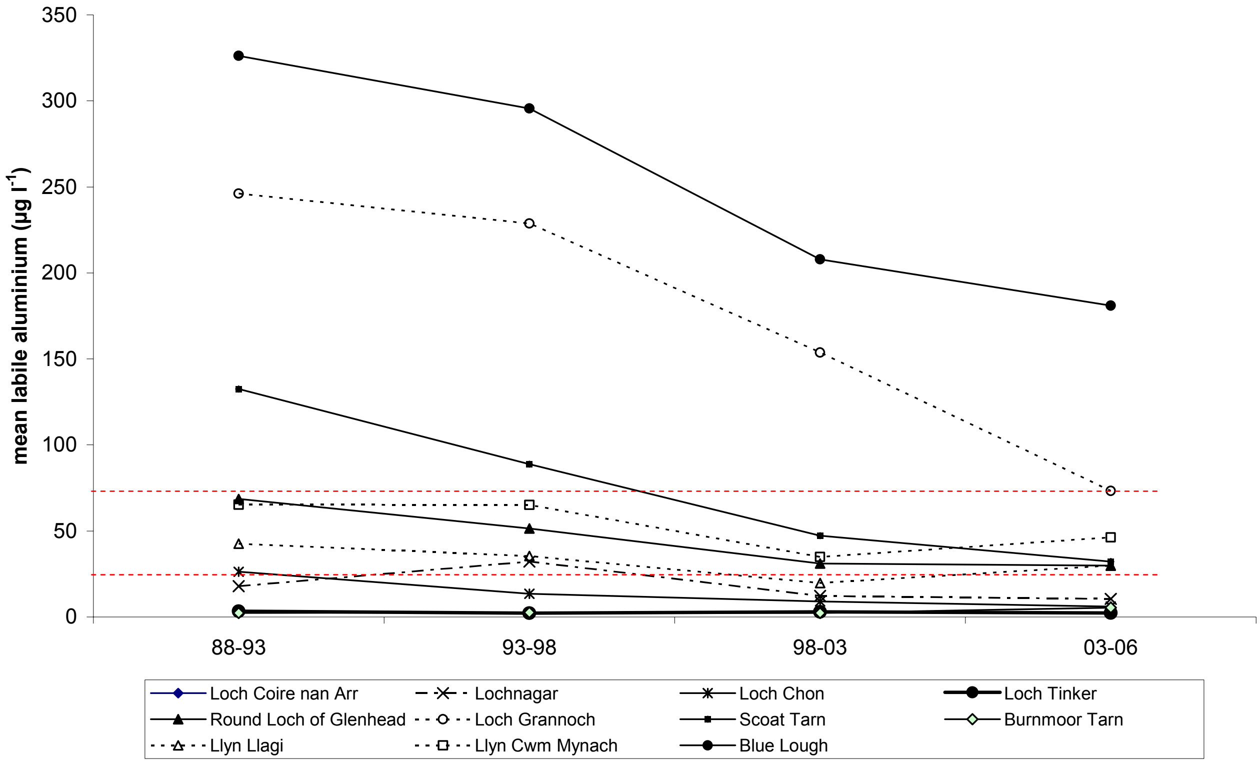


Figure 5.4.8 Trends in five yearly mean concentrations of labile aluminium concentration (in runoff from AWMN lakes. The last period represents three years only.

Horizontal dotted lines represent a band of labile aluminium concentration proposed by Rosseland *et al*. (1990) to represent a toxicity threshold for salmonids. Note from Chapter 4 however, that labile aluminium concentrations show high variability and maxima during episodes can greatly exceed the long term mean presented here.

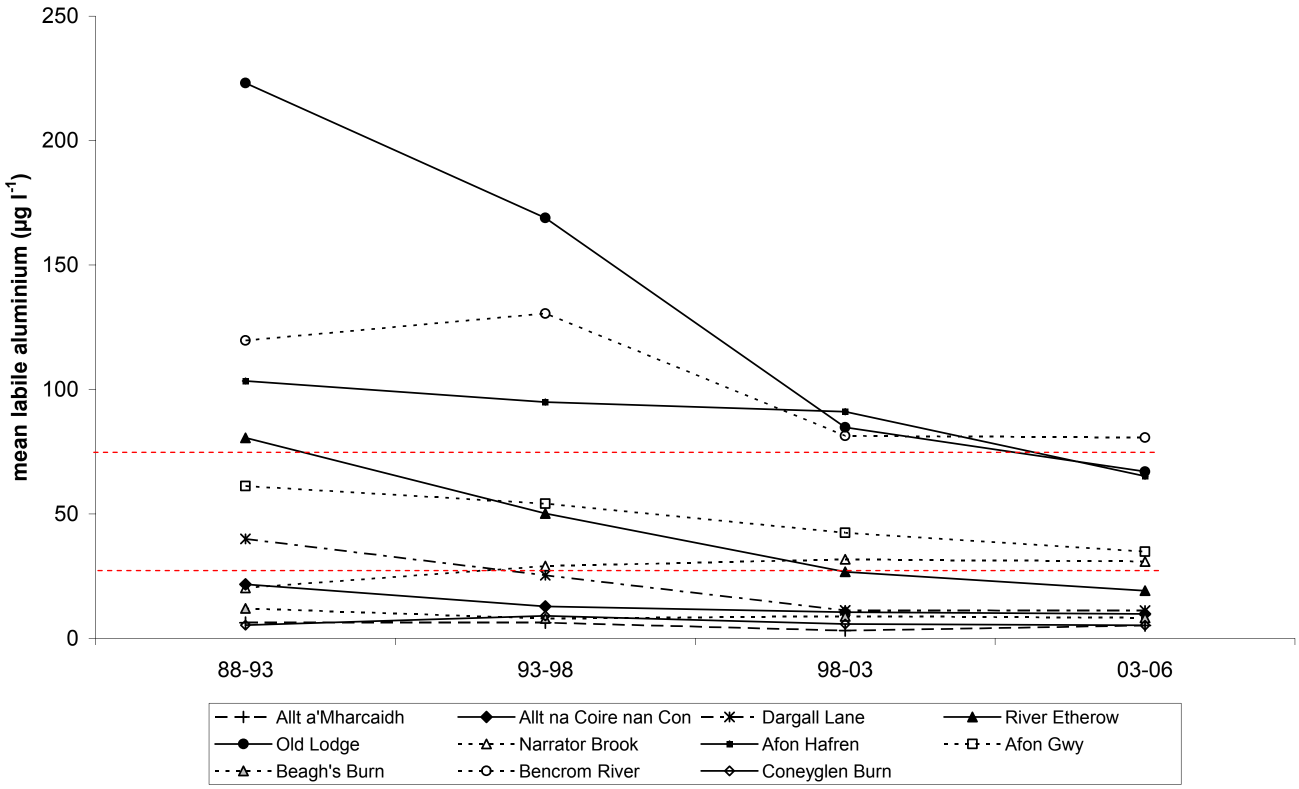


Figure 5.4.9 Trends in five yearly mean concentrations of labile aluminium concentration in AWMN streams. The last period represents three years only.

Horizontal dotted lines as in Figure 5.4.8. Note from Chapter 4 however, that labile aluminium concentrations show high variability and maxima during episodes can greatly exceed the long term mean presented here.

Between 2003-2006 approximately half of AWMN sites show average Al_{lab} concentrations within or above the band of 25 - 75 µg l^{-1} at which Rosseland et al (1990) argue toxic effects on salmonids become likely, while three sites, Blue Lough and Bencrom River in the Mourne Mountains and Loch Grannoch, an afforested site in southwest Scotland, have mean concentrations above 75 µg l^{-1}. Several more sites continue to show episodic concentrations of this magnitude, and these tend to coincide with the most sensitive stages of salmonid life cycles in winter and early spring.

Further reductions in the acid load may be necessary to bring aluminium concentrations down to benign levels in some sites, while increased inputs of seasalt would potentially exacerbate the situation.

pH/hydrogen ion concentration

Trends in pH have not been as clear across the Network as had perhaps been anticipated at the onset of monitoring. In part this is due to the strong response in labile aluminium at some of the more acidic sites, while at the least acidic sites hydrogen (and aluminium) ion concentrations were already low at the onset of monitoring, and here the primary response is most likely to be in bicarbonate alkalinity. Trends in pH in more acidic sites will inevitably be relatively subtle due to the logarithmic relationship with H^+ concentration, and for this reason we have illustrated trends in terms of H^+ in Figures 5.4.10-5.4.12.

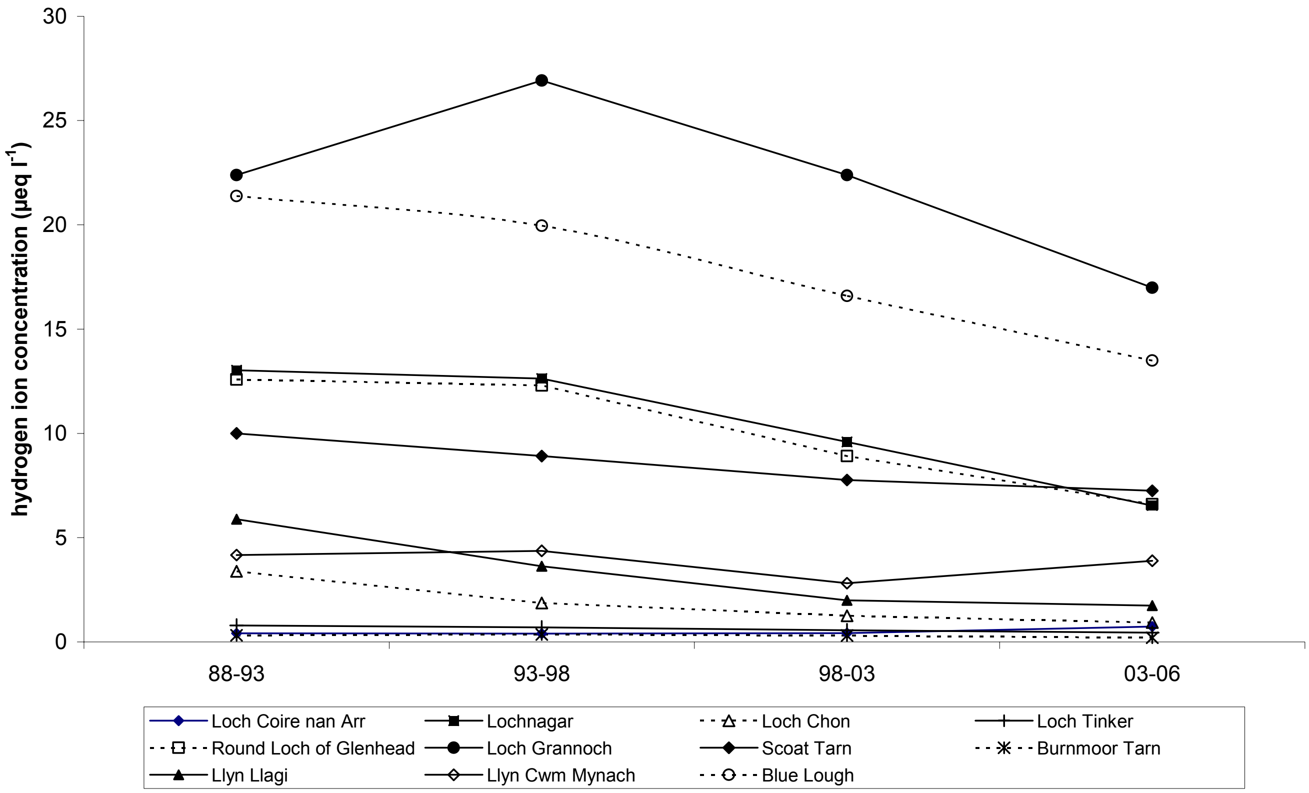


Figure 5.4.10 Trends in five yearly mean concentrations of hydrogen ion concentration in runoff from AWMN lakes. The last period represents three years only.

While trends in pH in more acid sites are sometimes hard to detect when plotted using a common scale for all sites, several have undergone clear reductions in hydrogen ion concentration. Llyn Cwm Mynach, an afforested lake, is unusual for a more acid site in showing no response, but this site has undergone a decline in labile aluminium concentration.

Trends in mean H^+ are less obvious in AWMN streams with only Old Lodge and the Dargall Lane Burn showing progressive improvement. The water chemistry records for flowing waters are more sensitive to variation in hydrology (due to the extent that water reaches stream channels by relatively acidic surficial routes - that may dominate during high rainfall – a opposed to more buffered groundwater). Site summaries in Chapter 4 illustrate that stream pH shows considerably greater temporal variation than lake pH as retention within the lake serves to smooth the chemistry of input streams.

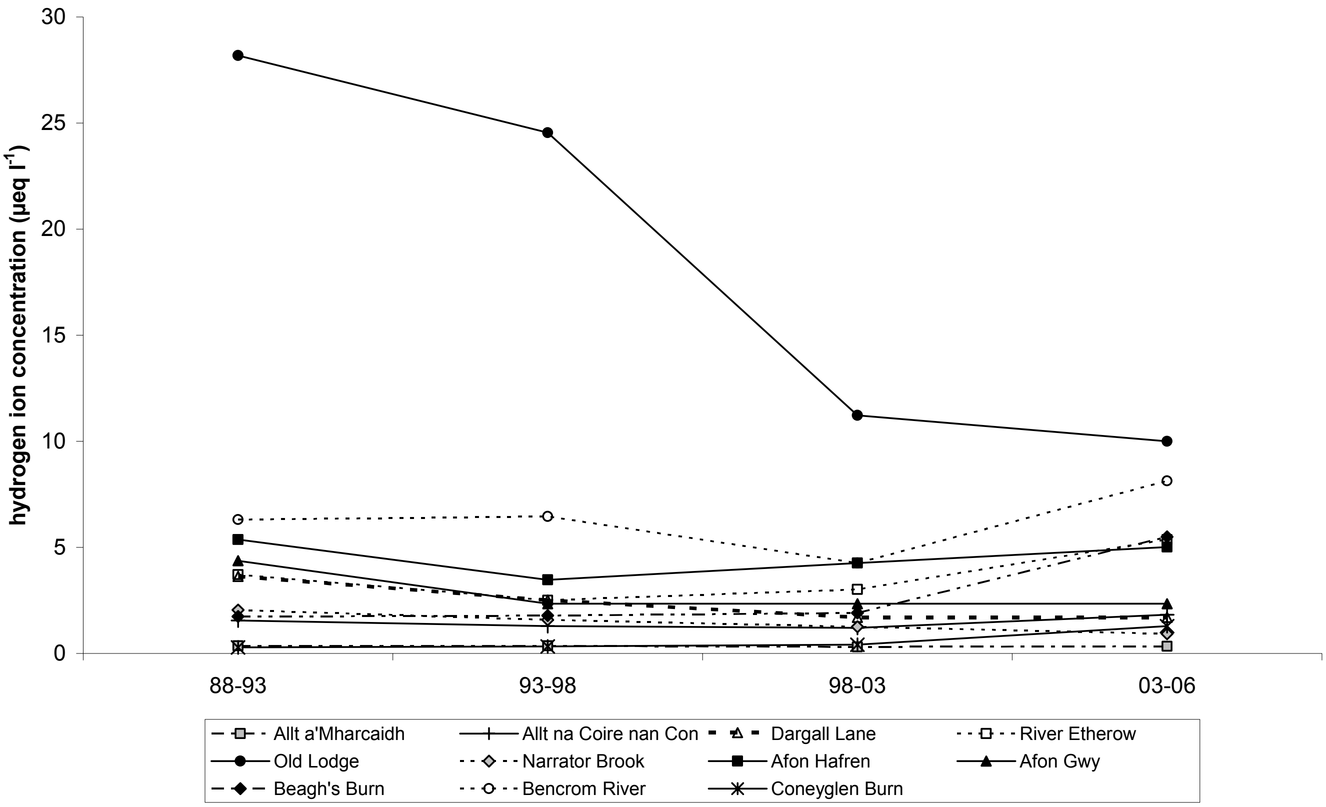


Figure 5.4.11 Trends in five yearly mean concentrations of hydrogen ion concentration in AWMN streams.

Trends are mostly less obvious than for lakes. In part this reflects much greater temporal variability, although a minority of streams may not be acidic enough for pH to respond to declining acid deposition. Note that the clearest trend is for the chronically acidic Old Lodge stream that is not influenced by more alkaline chemistry at base-flow. The last period represents three years only.

Despite the absence of obvious trends in mean H^+ in most AWMN streams there are clear trends in pH minima (or H^+ maxima) associated with hydrological or seasalt episodes over the monitoring period. This is illustrated in Figure 5.4.12, showing progressive declines in H^+ maxima between the four periods of measurements. The sharpest improvement has been in the River Etherow (Site 12). It is likely that peak acidity during episodes imposes the chief restriction on the recovery potential of macroinvertebrates (see for example Lepori and Ormerod (2005)) as well as salmonids, so this progressive lowering of peak acidity levels might be expected to be biological beneficial.

As stream acidity is sensitive to the amount of precipitation, any long term trend in precipitation has the potential to either confound or accentuate apparent acidity responses to falling sulphur deposition. While there have not been any clear hydrological trends across the UK over the 1988-2006 period, it is possible to control for hydrological effects by examining trends in the relationship of chemistry and flow through time. This is illustrated in Figure 5.4.13 that demonstrates how pH, for a given flow, has increased over the past 20 years in the Afon Gwy.

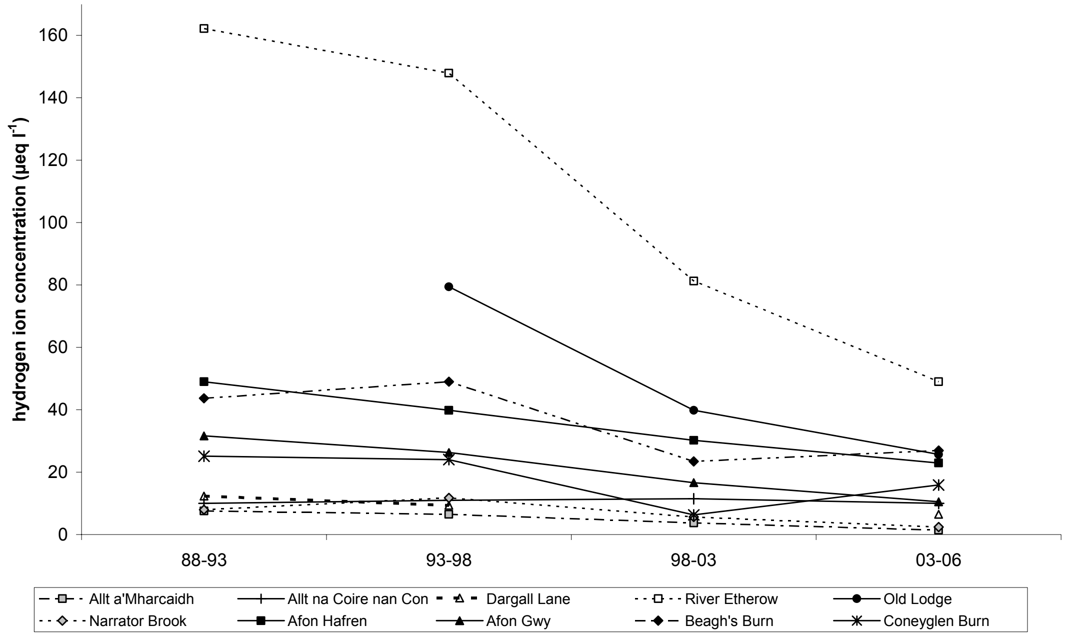


Figure 5.4.12 Trends in five yearly maximum concentrations of hydrogen ion concentration in AWMN streams.

The data show a steady decline in the acidity of the most acidic sample over time in almost all sites. The last period represents three years only.

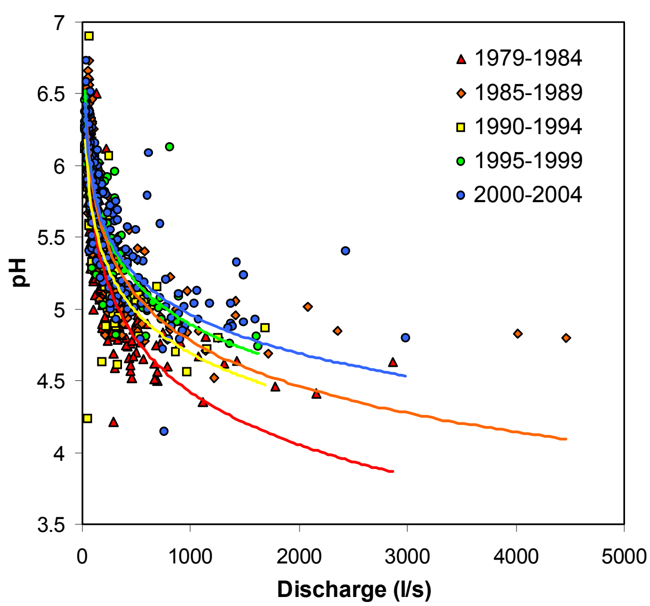


Figure 5.4.13 Long-term decreases in severity of discharge-driven acid episodes at the Afon Gwy catchment (incorporated into the AWMN in 1988)

From a figure in Evans CD, Reynolds B, Hinton C *et al.* (2007). Effects of decreasing acid deposition and climate change on acid extremes in an upland stream. Hydrological Earth System Sciences, in press.

Finally, with respect to pH trends, an unexpected consequence of chemical recovery appears to have been a rise in organic acid concentration (as indicated by rising DOC – see Section 5.4.5). The contribution of H^+ from these organic acids will inevitably have dampened the recovery in pH expected at AWMN sites.

Acid Neutralising Capacity

Physico-chemical models such as MAGIC predict that any reduction in the input of sulphate and nitrate to acidified sites should result in an increase in concentrations of base cations relative to acid anions in runoff, resulting in an increase in Acid Neutralising Capacity (ANC). Ion balance ANC is calculated as follows:

Ion balance ANC = $[Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]) - ([SO_4^{2-}] + [NO^{3-}] + [Cl^-]$

Currently, UK government freshwater critical loads assessments are based on the concept that an ANC of 20 μeq l^{-1} represents the "critical limit" for freshwaters in the UK. Evidence from Norway suggests that below an ANC of 20 μeq l^{-1} damage to brown trout populations becomes likely (Lien et al., 1996), while it also seems that very few UK lakes and streams would have experienced ANC levels below this prior to anthropogenic acidification. There is some debate as to whether this limit should actually be higher; the Norwegian government currently applies a limit of 40 μeq l^{-1} for biological protection.

Many AWMN sites show increases in ANC over the monitoring period although, for most, rates of increase are slow (Figure 5.4.14 and 5.4.15). Only four AWMN lakes currently (i.e. the 2003-2006 mean) show an ANC greater than 20 μeq l^{-1} and three of these are unlikely to have ever acidified below this level historically. Lochnagar shows no upward trend, probably as a result of the increase in NO_3 that offset the reduction in xSO_4. The absence of ANC response at the severely acidified Scoat Tarn is more difficult to interpret but perhaps is related to the dominance of seasalt deposition, and occasional large releases of NO_3, on the ion-balance. By the 2003-2006 period Scoat Tarn, the Round Loch of Glenhead, Loch Grannoch and Blue Lough still showed mean ANCs of less than zero. If these sites are representative of their heavily acidified sub-regions in the Lake District, Galloway and Mourne Mountains, the implication is that the 20 μeq l^{-1} target has not been met by the reductions in sulphate deposition achieved to date. Note, however, that Blue Lough is an exception in that MAGIC and palaeoecological assessment suggests this site never had an ANC as high as 20 μeq l^{-1} and 0 μeq l^{-1} is normally considered an appropriate target here.

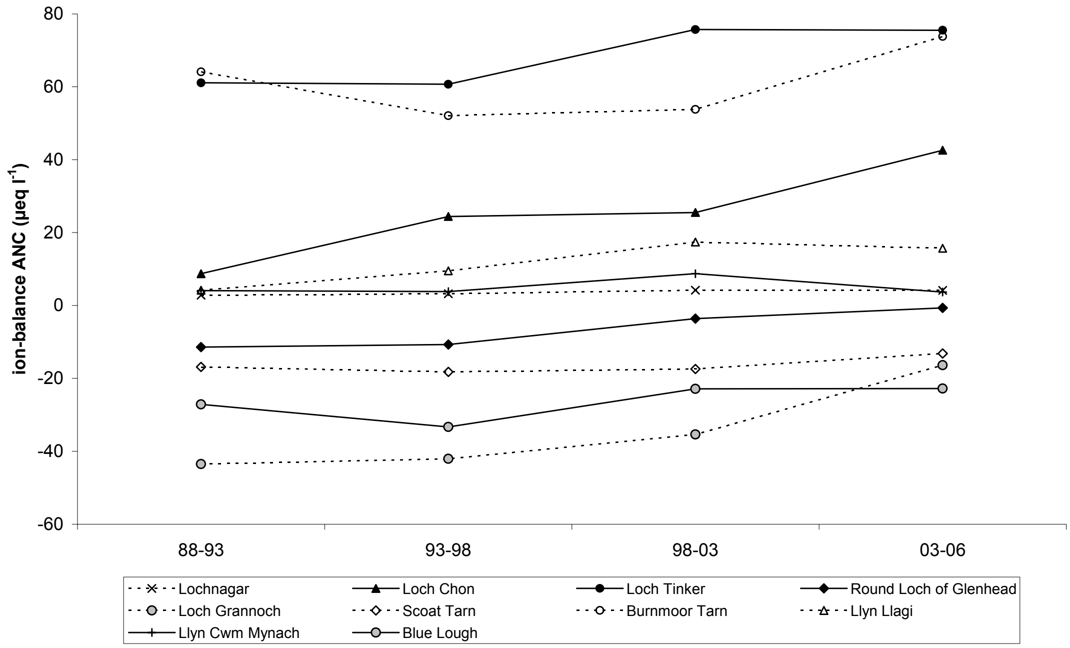


Figure 5.4.14 Trends in five yearly mean concentrations of Acid Neutralising Capacity according to the ion-balance method in runoff from AWMN lakes.

The trace for the unacidifed Loch Coire nan Arr has been omitted in order to improve clarity. Loch Coire nan Arr experienced two major seasalt events in the last period which depressed ANC severely. It is likely that water level manipulation at the site contributed to this uncharacteristic response. The last period represents three years only.

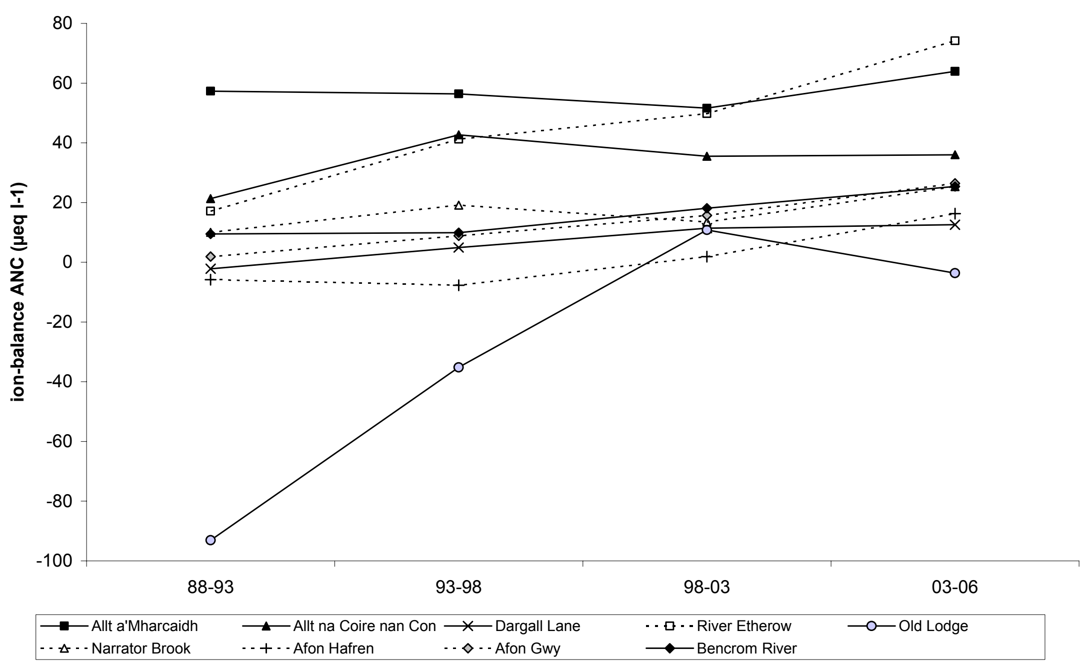


Figure 5.4.15 Trends in five yearly mean concentrations of Acid Neutralising Capacity according to the ion-balance method in AWMN streams. The last period represents three years only.

The traces for Coneyglen Burn and Beagh's Burn, sites with relatively high ANC levels and no long term trends, have been omitted to improve overall clarity. The last period represents three years only.

5.4.5 Dissolved Organic Carbon (DOC)

Perhaps the most striking Network-wide observation from the AWMN has been the substantial increase in DOC in nearly all sites. The AWMN has been fundamental in revealing the geographical extent of these changes throughout the UK, and demonstrates the wider importance of the Network in documenting environmental change in UK source waters. The increase in DOC has had major implications for the water industry and DOC treatment has become the single largest treatment cost in some areas.

The national tendency for DOC increases was first reported in the 10 Year Interpretative Report (Monteith and Evans, 2000) and was the subject of debate within the journal *Nature* (Freeman *et al*., 2001; Tranvik and Jansson, 2002; Evans *et al*., 2002). Initially, it was proposed that the UK DOC trends might be linked to the effects of a gradual rise in air temperatures (since the 1970s) on soil processes (Freeman *et al*., 2001) but the magnitude of change was shown later to be much greater than could be supported by laboratory studies. Since then, similar trends have been reported for surface waters across large areas of northern Europe and North America and attributed to factors as wide-ranging as changing hydrology, land-use, nitrogen deposition and rises in atmospheric CO_2. Recent assessments of AWMN data however, have indicated that the key driver of DOC trends across these regions has been the changing solubility of organic matter (and hence DOC) as a result of changes in deposition chemistry (Evans *et al*., 2006). Organic matter solubility is known to be dependent both on soil pH and the ionic strength of the soil solution. Soil pH is expected to have risen and ionic strength reduced in response to both a reduction in seasalt inputs, that dominated the chemistry of many sites in the early 1990s, and a reduction in sulphate deposition in the late 1990s.

The hypothesis of a dominant control of deposition chemistry on DOC has recently been tested by AWMN scientists in collaboration with colleagues in North America and Scandinavia (Monteith et al., 2007). This international study provided very strong evidence that DOC concentrations were depressed during acidification and that recent trends (Figure 5.4.16 and 5.4.17) represent a return to more natural levels.

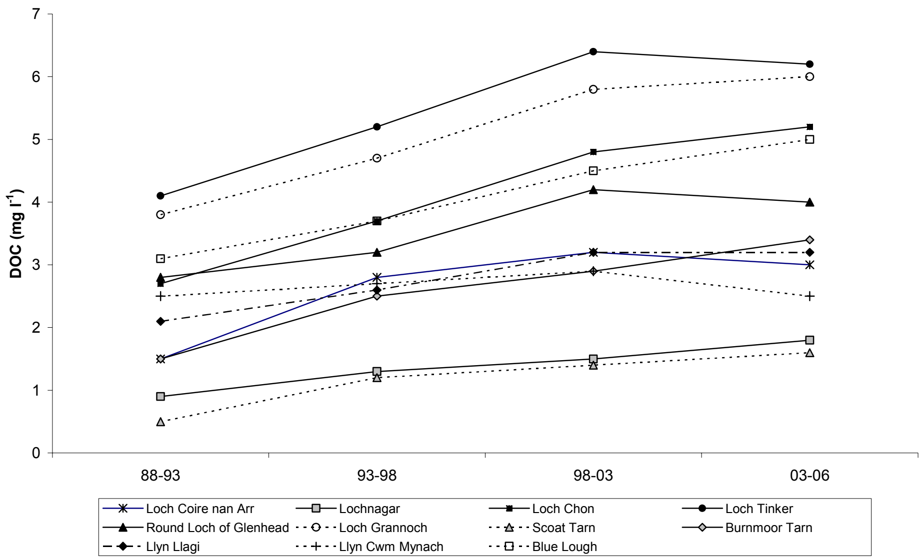


Figure 5.4.16 Trends in five yearly mean concentrations of Dissolved Organic Carbon concentration in runoff from AWMN lakes.

Trends are thought to represent responses both to declining seasalt inputs in the early part of the record and, more recently, to declines in sulphur deposition. Note an apparent tailing off of concentrations in the most recent period, during which sulphate concentrations have stabilised. The last period represents three years only.

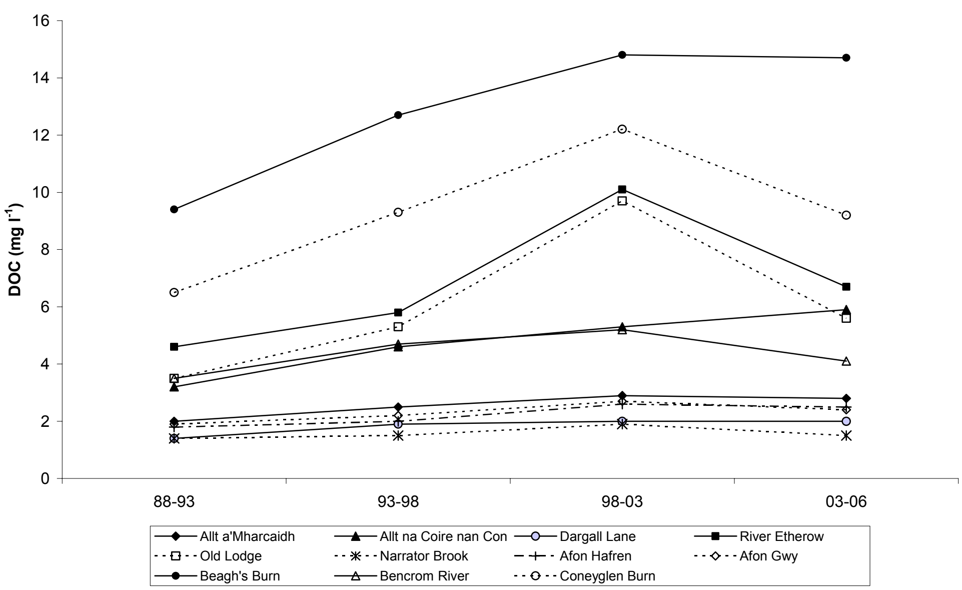


Figure 5.4.17 Trends in five yearly mean concentrations of Dissolved Organic Carbon concentration in AWMN streams.

Trends are thought to represent responses both to declining seasalt inputs in the early part of the record and, more recently, to declines in sulphur deposition. Note that the apparent downturn in concentrations in the most recent period at a minority of sites coincides with a slight upturn in either/or sulphate or chloride concentrations. The last period represents three years only.

5.5 Biological Trends

Evidence for widespread, albeit very gradual, biological change across the AWMN consistent with early stages of biological recovery was first reported in the 15 Year Interpretative Report (Monteith, 2005; and see Monteith *et al*., 2005). The site summaries outlined in Chapter 4 demonstrate that most of these trends have persisted, and further indications of biological "improvement" have been detected. A summary of the occurrence of long-term biological trends on the Network is provided in Table 5.5.1.

	Epilithic diatoms	Sed trap diatoms	Macro-invertebrates	Aquatic macrophytes	brown trout density	
					0+	>0+
Loch Coire nan arr	✓	x	x	↓	not fished since 2000	
Allt a' Mharcaidh	↓	NA	x	✓	x	x
Allt na Coire nan Con	✓	NA	↑	↓	x	x
Lochnagar	✓	✓	x	x	x	x
Loch Chon	↑	↑	↑	↑	x	x
Loch Tinker	↑	↑	x	↑	✓	↓
R. Loch Glenhead	↑	↑	x	↑	↑	x
Loch Grannoch	✓	✓	x	X	x	x
Dargall Lane Burn	↑	NA	x	↑	x	x
Scoat Tarn	↑	↑	↑	x	x	x
Burnmoor Tarn	↑	↑	✓	↑	x	x
River Etherow	↑	NA	↑	↑	not fished	
Old Lodge	x	NA	x	↑	↑	↑
Narrator Brook	x	NA	✓	x	x	x
Llyn Llagi	↑	↑	↑	↑	↓	x
Llyn Cwm Mynach	↓	↓	✓	↑	x	x
Afon Hafren	↑	NA	↑	↑	not fished until 1995	
Afon Gwy	↑	NA	↑	x	x	x
Beagh's Burn	x	NA	x	↑	x	x
Bencrom River	x	NA	x	x	x	↓
Blue Lough	↑		↑	x	x	↑
Coneyglen Burn	x	NA	✓	x	x	x

Table 5.5.1 Summary of biological trends at AWMN sites over the full monitoring period

Sites shaded grey have undergone increases in pH and alkalinity, and or reductions in labile aluminium concentration over the monitoring period. ↑ = trend indicative of a biological response to a reduction in acidity; ↓ = trend indicative of a biological response to an increase in acidity of other reduction in biological quality; ✓ = long term trend not indicative of overall change in biological quality; x = no trend. Trends in diatoms and macroinvertebrates determined by Redundancy Analysis (explanatory variable = sample year) and restricted permutation test (only $p<0.05$ accepted). ↑ for aquatic macrophytes = detection of acid-sensitive species after 1995 only. Trends in 0+ and >0+ brown trout populations determined by linear regression with sample year (only $p<0.05$ accepted).

5.5.1 Diatoms

Species Trends

Table 5.1.1 shows a clear relationship between those sites where the species balance of diatom assemblages has shifted toward more acid-sensitive taxa and those where acidity has declined.

There is little evidence for biological improvement in sites in northern Scotland, where sulphate levels have historically been low and do not show large reductions. Epilithic diatom communities do show significant trends in sites in this region, i.e. Loch Coire nan Arr, the Allt a'Mharcaidh, Allt na Coire nan Con and Lochnagar, but none of these involve a rise in the proportion of relatively acid-sensitive species. Water level manipulation is the most likely driver of change in Loch Coire nan Arr, while trends at the two streams (allt a'Mharcaidh and Allt na Coire nan Con) may reflect a trend toward more acidic periods in summer in recent years (linked to increasing summer precipitation). At Lochnagar, the species trends in both epilithon and sediment trap samples do not appear to be linked to acidity, which shows no clear change over the full period. At this stage we cannot rule out the potential importance of the rise in NO_3 (as a nutrient) on the flora and more work is necessary to ascertain the possible influence of the reduction in the period Lochnagar is covered by ice each winter. Trends in diatom assemblages were not detected in the relatively low sulphur deposition stream sites Beagh's Burn and Coneyglen Burn in Northern Ireland.

Away from these relatively unimpacted parts of the UK the evidence for diatom responses to falling acidity is very clear. Eleven sites show statistically significant trends in epilithic diatom assemblages that are characterised by a rise in the relative abundance of taxa with pH optima higher than for those species on the decline. At some sites the extent of change is particularly dramatic and unambiguous with respect to the cause of environmental response. For example, the epilithic diatom flora of Llyn Llagi was dominated by the acidophilous species *Tabellaria quadriseptata* over the first few years of monitoring. Palaeoecological work shows that this species was very rare in UK lakes prior to the industrial period, but in many cases became dominant as lakes acidified. This species is now undetectable in the stony habitats of Llyn Llagi where it grows, and at very low abundances in the annually collected sediment collected in the deep water traps. Significant reductions in the proportional abundance of *T. quadriseptata* (in either or both epilithon or sediment trap samples) have also been found in Loch Chon, the Round Loch of Glenhead and Blue Lough, although at Llyn Cwm Mynach it has remained at relatively steady and low proportions in trap samples throughout the last 18 years.

The specific diatom community response to changing acidity depends on the starting point of the site on an acidity gradient and the extent of chemical improvement. Hence in Loch Chon one of the primary changes has been a decline in *Navicula leptostriata*, whereas this species has replaced *T. quadriseptata* in the more acidic, but also recovering, Round Loch of Glenhead.

In the 15 year interpretative report (Monteith, 2000) no trends in epilithic diatom communities were found in diatom assemblages in some of the most acidic, or at least episodically acidic, streams (namely, the Afon Hafren, Bencrom River, and Old Lodge) despite a clear reduction in acidity. We speculated that the continued relatively high levels of labile aluminium might provide some barrier to recovery. In our new assessment, the floras of the Afon Hafren and Bencrom River do now show statistically significant long term trends toward more acid-sensitive communities. Perhaps significantly, Old Lodge has exhibited the highest labile aluminium concentrations of any other stream on the Network until the last three years (see

Figure 5.4.9). Here there are clear indications of shifts in the flora indicative of improvement since around 2002 (Figure 4.13.4), although these are not currently sufficient for a trend in the full time series to be deemed statistically significant using our most stringent (restricted) permutation test.

Sediment traps

The sediment trap diatom data are particularly important to the AWMN with respect to determining the current state of biological recovery. The modern sediment trap assemblage (indicative of the ecological condition of the lake today) can be compared directly with assemblages that pre-date lake acidification, and the difference can provide some indication of ecological gap closure. Assessment of this process using AWMN data is currently underway at UCL (Battarbee *et al.*, in prep).

Initial indications are that acid-sensitive taxa are regaining dominance in the majority of lakes. However, while certain acidification indicators, e.g. *T. quadriseptata*, are declining in relative abundance, and some species that were previously common are returning, the most recent assemblages often differ markedly in composition from those existing at any point in the past. The reasons for this are currently far from clear but hypotheses include:
1) water chemistry of recovering waters is not returning along the path followed as these lakes acidified, for example, due to rising nitrogen inputs;
2) biological controls - for example, some acid tolerant species that became established as acid-sensitive species were lost may persist;
3) warmer water temperatures, particularly summer temperatures since the mid-1990s may influence the species balance.

Clearly, these observations have important implications for the development of acidification assessment under the Water Framework Directive. Current indications are that a full return to the “reference state” may be unrealistic and unattainable, and that appropriate recovery targets may have to be based more on the return of functional groups rather than on species.

5.5.2 Aquatic Macrophytes

AWMN data show that acid-sensitive taxa have been recorded for the first time only recently in AWMN sites. There have been no major changes since the last report (Monteith, 2005). The most visible changes over the last seven years have been the rapid expansion of the Water Starwort, *Callitriche hamulata*, in Llyn Llagi, and the Water Milfoil, *Myriophyllum alterniflorum*, in the Round Loch of Glenhead. The latter species was recorded in one isolated location in the loch in 2003 but has since spread throughout the loch. Previously these sites were dominated by isoetid taxa, that derive inorganic carbon for photosynthesis from the sediment. Both *C. hamulata* and *M. alterniflorum* derive their inorganic carbon from the water column and their establishment is consistent with an increase in the availability of dissolved inorganic carbon as alkalinity returns to these systems. These species have much wider importance to lake ecosystems, since they contribute to the underwater “architecture”, thus providing a new substrate for epiphytic algae, a new food source and shelter from predation for a range of zooplankton.

The primary changes observed in AWMN streams have been the recent detection of aquatic mosses, albeit in very small amounts, in sites previously dominated almost solely by acid tolerant liverworts. The extent to which these headwater streams would have been dominated by liverworts prior to acidification is still unclear, but aquatic mosses tend to dominate the least acidic streams on the Network. Perhaps one of the most striking recent records has been the detection of very small amounts of the moss *Hygrohypnum ochraceum*, previously only found in the relatively unacidified sites, Allt a'Mharcaidh, Coneyglen Burn and Allt na Coire nan Con, in the heavily acidified River Etherow.

5.5.3 Macroinvertebrates

Species trends

The statistically significant trends in macroinvertebrate assemblages identified in the last assessment are still apparent at over half of the sites on the AWMN. After 15 years of monitoring there was a remarkably strong relationship between sites showing trends in macroinvertebrates and those showing increases in ANC and reductions in labile aluminium (Monteith *et al.*, 2005). Some common patterns were also noted, particularly with respect to increases in the relative abundance of certain predatory taxa such as net spinning caddis and some stoneflies.

The majority of these trends have persisted to the spring of 2006 with the exception of Loch Grannoch. Here the net spinning caddis genus *Cyrnus* sp., that had been increasing in proportional abundance in the late 1990s, has not been recorded in the last two years (Figure 4.8.4). This apparent stalling of macroinvertebrate recovery in Loch Grannoch is surprising, given a clear improvement in pH and reduction in labile aluminium concentration in recent years. However, labile aluminium levels remain the second highest on the Network and the 2003-2006 mean concentration was just below the 75 $\mu g\ l^{-1}$. In the neighbouring moorland site, the Round Loch of Glenhead, there are recent changes in the fauna, namely the occasional detection of *Lymnaea peregra* and *Pisidium* sp. and the increased occurrence of the net spinning caddis *Polycentropus* sp., that although currently not significant, are indicative of the early stages of recovery from a severely acidified state.

Trends in macroinvertebrate biodiversity

The biodiversity of freshwater lakes and streams has been shown to be strongly positively correlated with pH for many species groups (Petchey *et al*., 2004). A recent assessment of macroinvertebrate community structure in acid and acidified lakes has concluded that ANC is a particularly powerful indicator of species richness and suggests that labile aluminium concentration (for which data are often not available, but which tends to be high in lakes with very low or negative ANC), rather than pH, may exert the most important chemical control on the faunal diversity of these systems (SNIFFER WFD60 project, pers comm.).

Many sites on the AWMN show upward trends in species richness (determined as the total number of taxa (to mixed taxon level) recorded each year (Figures 5.5.1 and 5.5.2). Perhaps surprisingly, trends in streams are more common than trends in lakes; one lake site, Loch Grannoch, shows a clear reduction in species richness over time. It is feasible that the increase in species richness in AWMN streams is linked (directly or indirectly through the wider food chain) to a reduction in the severity of acid episodes. However, one of the sites to show the strongest increase is Narrator Brook (Site 14) where there is relatively little chemical change. Alternative explanations for this apparent improvement in biodiversity include recent changes in water temperature, changes in flow at critical periods in the year, and phenological responses to changes in the timing of spring. Further analysis is required to test these hypotheses.

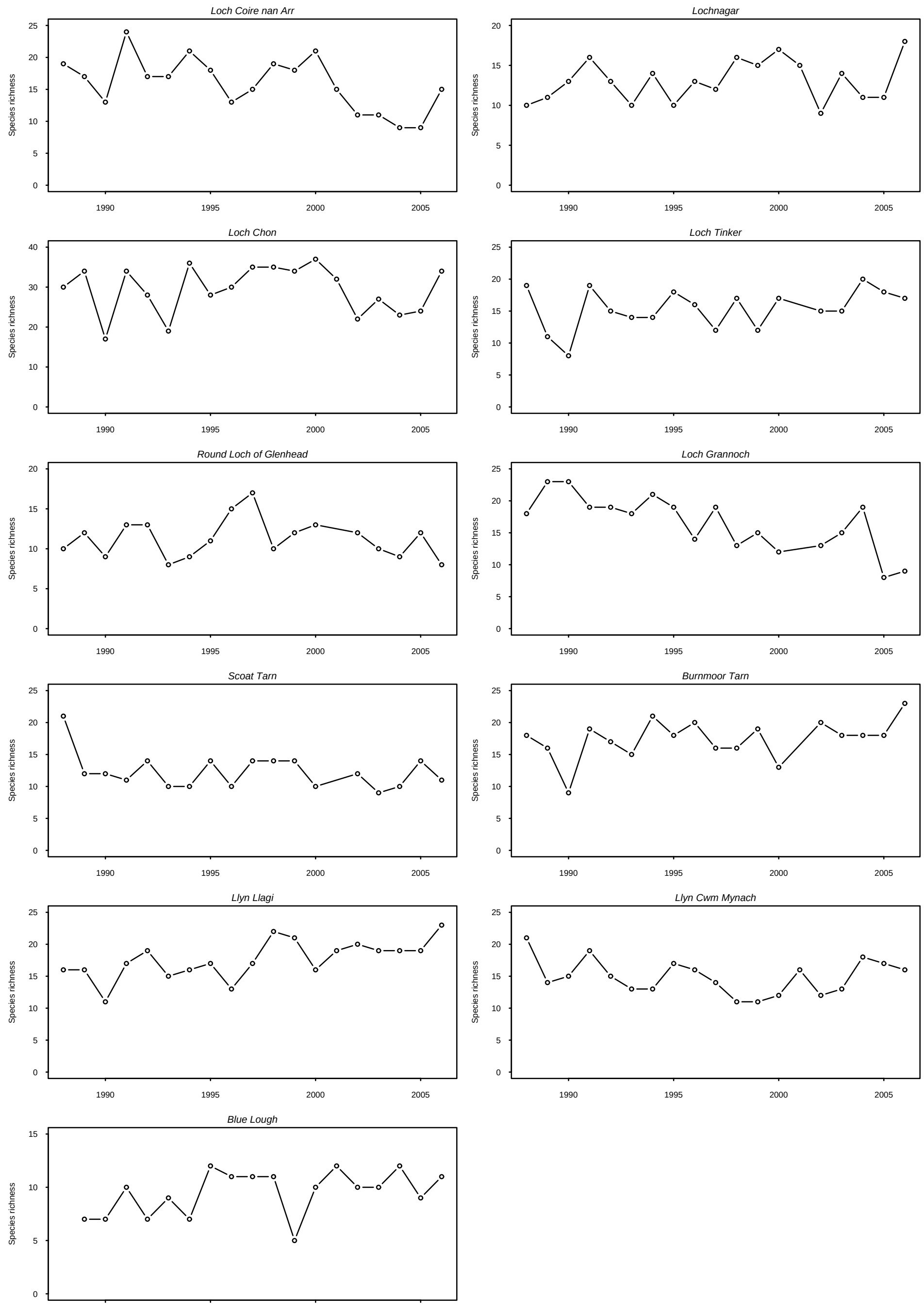


Figure 5.5.1 Trends in the minimum number of effective macroinvertebrate taxa in kick net sampling of AWMN lakes

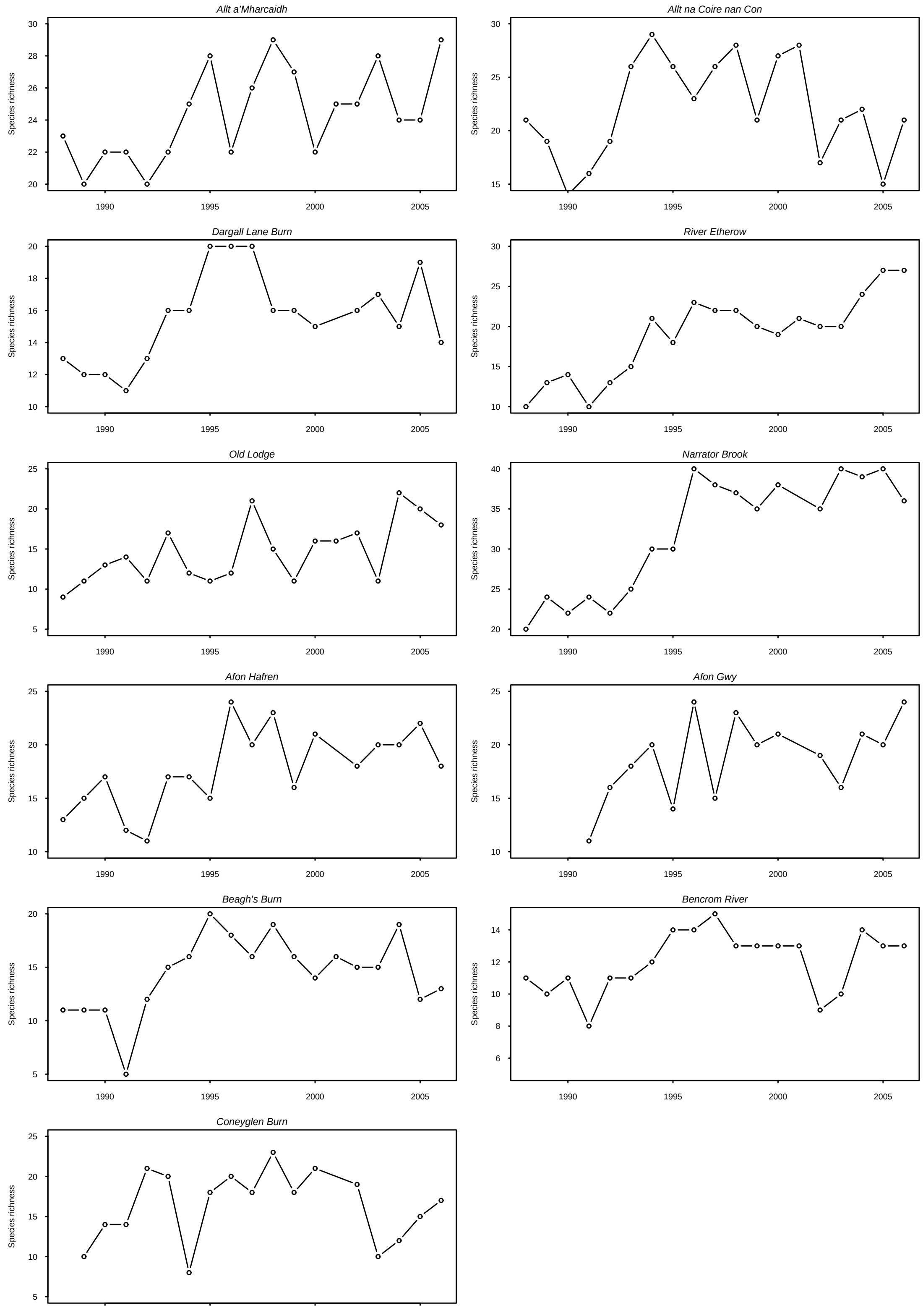


Figure 5.5.2 Trends in the minimum number of effective macroinvertebrate taxa in kick net sampling of AWMN lakes - Contd

5.5.4 Fish

The AWMN salmonid time series represent an unparalleled long term national record of salmonid density, age and condition factor for the upland waters of the UK. Detailed analysis of these AWMN data by members of the Fisheries Research Services Freshwater Laboratory, Pitlochry is currently in progress. Density data only are presented in this report. Most sites do not show any obvious change in density over the last 18 years, although there are upward trends in one or both age groups in three sites. It is likely that climatic variability (particularly with respect to water temperature) represents the primary driver of short term variability in these data, and it is possible that even after 18 years of monitoring "natural" variability may be masking subtle responses to changing water chemistry. It is intended to monitor (continuously) water temperature of AWMN stream sites in future in order to establish an air temperature – water temperature calibration that may then be applied to determine historic fluctuations in the latter.

Perhaps the most important observations relate to the recent arrival of juvenile brown trout in some of the most acidic sites on the AWMN. The most striking example of this is from the Old Lodge stream in the Ashdown Forest that has undergone a very large reduction in non-marine sulphate and labile aluminium concentration and a recent rise in pH (Figure 5.5.3).

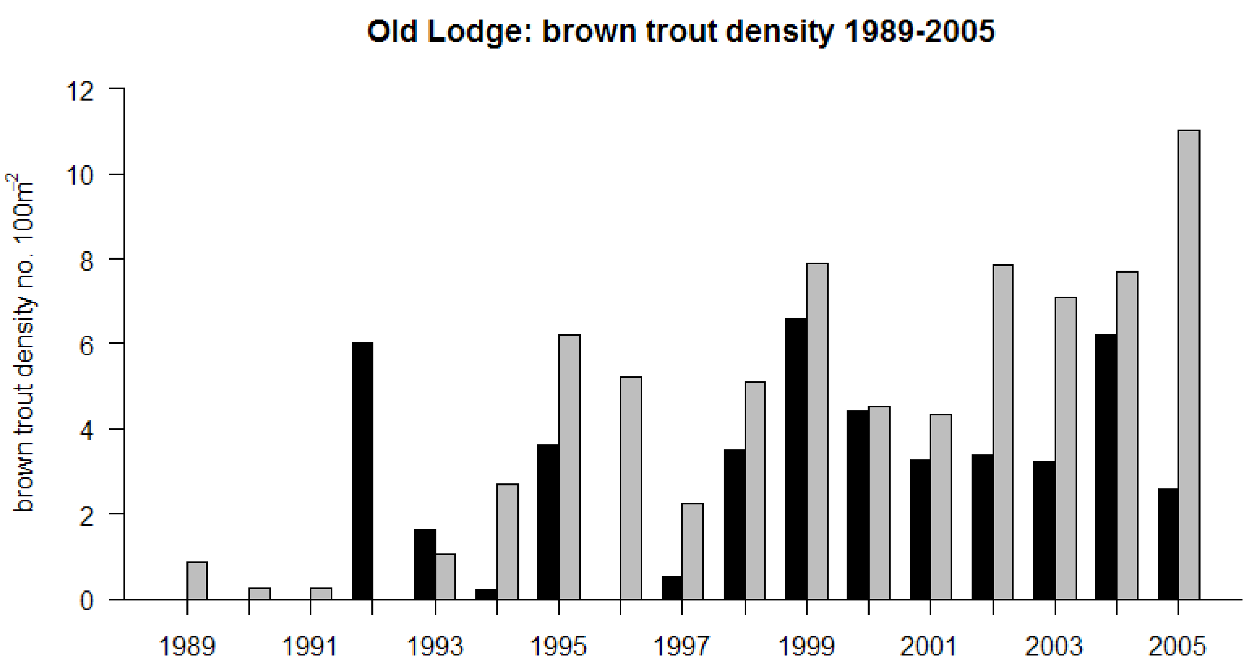


Figure 5.5.3 Trends in the density of juvenile (less than one year old; black bars) and older (grey bars) brown trout in the AWMN stream Old Lodge, Ashdown Forest

Note that juvenile fish, indicative of local spawning, were not detected until 1992 and have since been caught in most years. Older fish show a gradual rise in density from very low levels in the first five years of monitoring.

5.6 AWMN monitoring of trace metals and spherical carbonaceous particles

The trace metals Pb, Cd, Cu, Ni and Zn have been monitored in bulk deposition, lake water sediment traps and a range of biota at Lochnagar since 1996. Mercury was included in the water, deposition and biota monitoring from 1997 and in the sediment trapping programme from 2000. This work was initiated under the EU funded MOLAR project, and subsequently continued via funding through DEFRA's (then DETR) 'Critical Loads for Acidity and Metals' (CLAM) project, then the 'Freshwater Umbrella' and most recently the UK Acid Waters Monitoring Network. These measurements have continued to the present. Sampling and analysis have been amended periodically to improve the range of biotic groups included in the sampling (i.e. removal of poor performers; addition of 'new' classes), but the root analyses of water, sediment traps and terrestrial and aquatic plants has remained throughout.

At the other AWMN sites, the monitoring of trace metals has been more restricted. Metals (Hg, Pb, Cd, Cu, Ni and Zn) in the terrestrial mosses *Hylocomium splendens* and *Pleurozium schreberi* have been monitored from all sites (lakes and streams) since 2000 while the same suite of metals have been measured in the trapped sediments of the lake sites on an annual basis since 2000. The flux of spherical carbonaceous particles (SCPs) to AWMN lakes is also estimated from these sediment samples.

5.6.1 Deposition

Direct measures of trace metals in deposition and lake waters are only undertaken at Lochnagar. In general the pattern of deposition is one of a low but detectable level of contamination punctuated with irregular higher values (e.g. Pb - Figure 5.6.1). However, in the winter of 2005-2006 Hg began to increase markedly in deposition and reached concentrations considerably higher than any previously recorded (Figure 5.6.2). This was followed by high lake water concentrations a few weeks later. The source of this 'additional' Hg remains unclear; although concentrations of some other metals were periodically elevated in deposition and / or lake water at Lochnagar over the same period, the temporal pattern differed (e.g. Figure 5.6.4). Mercury concentrations in deposition have declined sharply since the end of 2006 but the latest concentration data remain higher than 'pre-event' values, while the concentrations in lake water have returned to those observed at the end of 2005. Although sample contamination cannot be completely ruled out, the complete change of all sampling and analytical equipment, rigorous cleaning protocols and the similar trends in both deposition and lake water samples point to a real depositional event. Continued long-term monitoring is clearly necessary before it can be ascertained whether this event is an isolated incident. Plots of annual mean concentrations and deposition fluxes of Hg highlight the recent period of elevated Hg, but show also that this event occurred on the background of a declining trend (in concentration) over recent years (Figure 5.6.3).

In 2001, methyl mercury (MeHg) measurements in deposition and lake water samples were initiated at Lochnagar. These data show winter peaks in MeHg deposition while loch water values have remained below the limit of detection. High winter measurements have continued to the present but there are no other data in the UK against which to compare, and this seasonal pattern is not observed elsewhere in Europe. Currently it is unknown why this occurs as MeHg is derived from microbial activity and hence is not produced by reaction in the atmosphere and should be less common in the winter due to the temperature limitation in its production. These episodes may be derived from marine production combined with scavenging by snow to be deposited over mountainous regions. A study under the EU funded Euro-limpacs project intends to attempt daily resolution sampling at Lochnagar over the winter 2007-2008 to determine the cause. However, these data are unique for the UK uplands and so the extent to which they are representative of the wider Grampian Mountains and upland UK more generally is unknown.

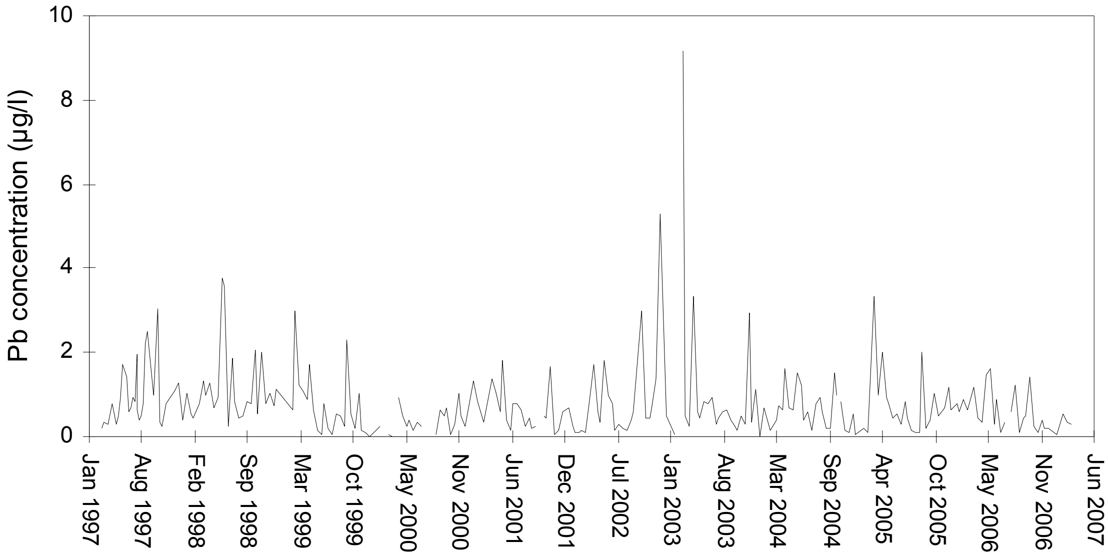


Figure 5.6.1 Deposition concentrations of Pb at Lochnagar 1997 – 2007

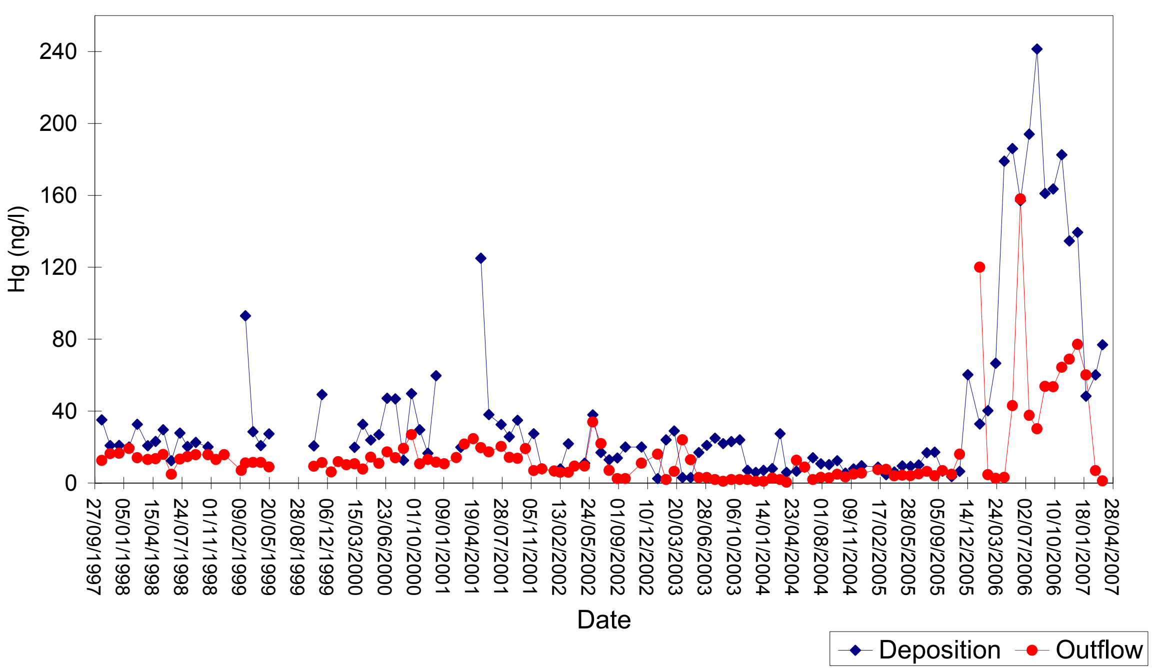


Figure 5.6.2 Deposition and lake water concentrations of Hg at Lochnagar 1997 – 2007

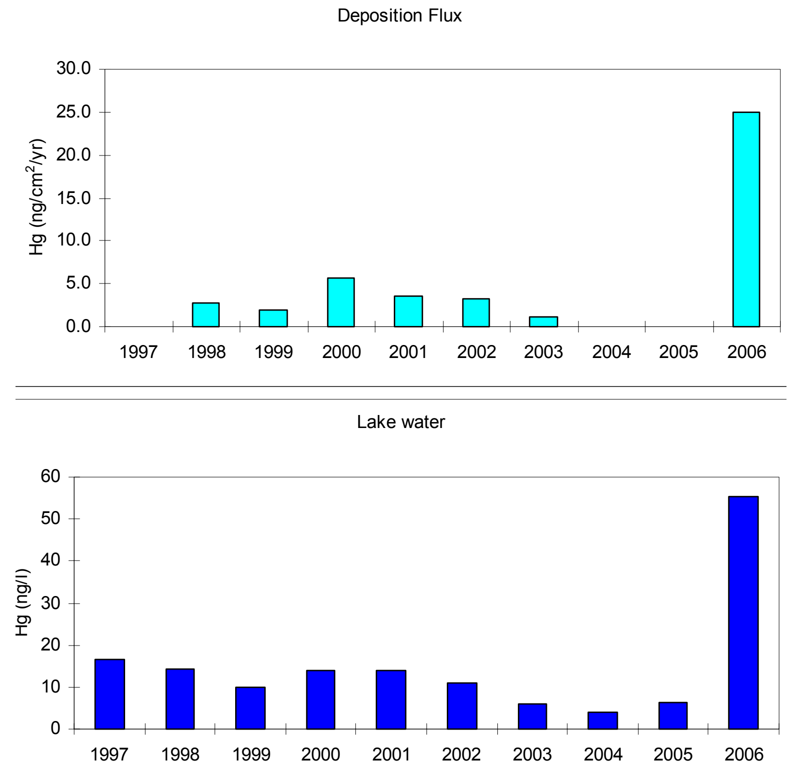


Figure 5.6.3 Mean annual Hg deposition fluxes and lake water Hg concentration, Lochnagar

Power problems with the Automatic weather station in the winters of 2004 and 2005 preclude the conversion of the Hg deposition concentrations to fluxes.

MeHg is the biologically available form of Hg and hence determining the source and extent of this contamination is urgent.

5.6.2 Metals in Biota

A range of terrestrial and aquatic plants and aquatic invertebrates from Lochnagar have also been analysed for the same suite of trace metal analysis. Annual measurements of the Hg concentration in a selection of these biotic components is provided in Figure 5.6.4. Although the dataset is currently too short to identify temporal trends, the consistency in concentrations in certain biota both inter-annually and between related species within the same year (e.g. the terrestrial mosses *Hylocomium splendens* and *Pleurozium schreberi*) provide reassurance that this approach, the sampling methods and the analytical techniques are repeatable and robust. This suggests that given a sufficiently long monitoring period, temporal trends in deposition and inputs to the loch (i.e. catchment inputs in addition to atmospheric inputs – see below) should be detectable.

Some aquatic species appear to show similar declining trends to lake water concentrations and depositional fluxes and so it will be of particular interest to whether 2006 - 2007 data provide any indication of the observed depositional event. It is also interesting to observe an increase in Hg in the sediment of the deepwater traps at Lochnagar, although again the time series is short.

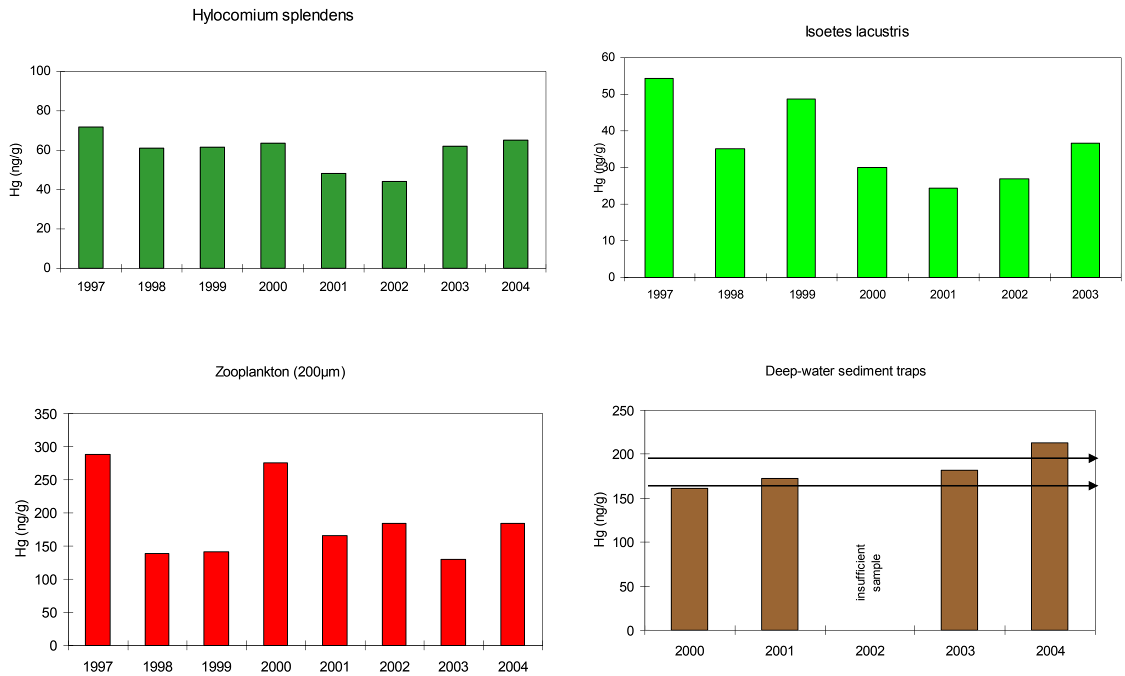


Figure 5.6.4 Hg concentrations for a range of Lochnagar biota

Hg concentrations in deepwater sediment traps have been seen to exceed freshwater sediment quality values for total Hg (e.g. MacDonald et al, 2000; Avocet Consulting, 2003)

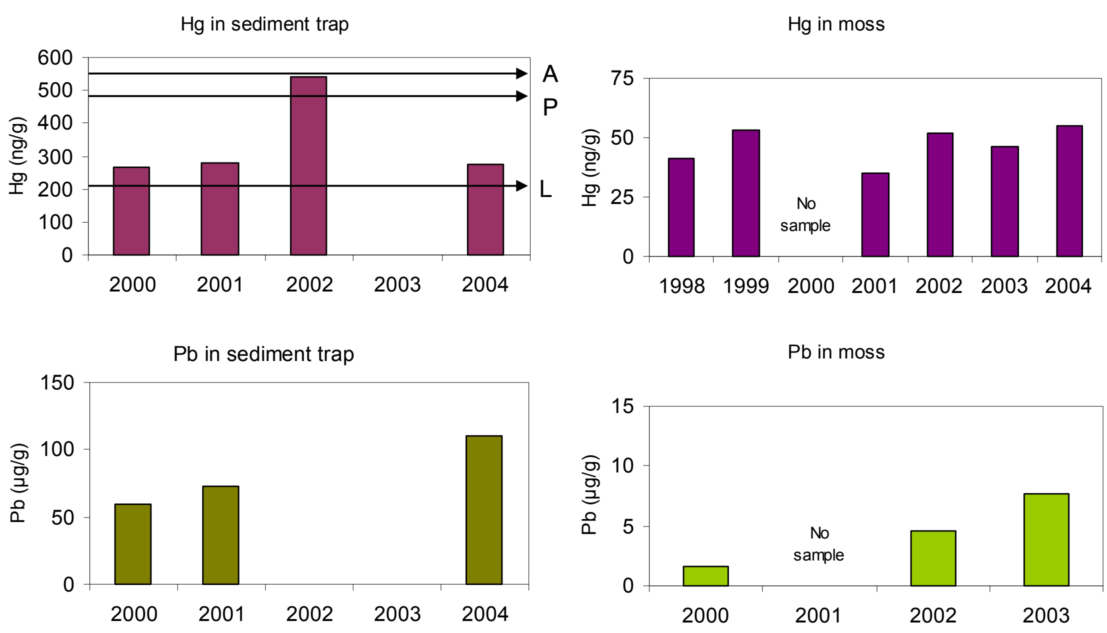


Figure 5.6.5 Hg and Pb in sediment traps and terrestrial moss samples at Scoat Tarn

Sediment in deep water traps exceeds more limits than Lochnagar sediment (A = 560 ng g^{-1} is the 'Apparent threshold level' above which biological effects have always been observed; P = 490 ng g^{-1} is the 'Probable effects level' at which adverse biological effects are frequently seen; L = 200 ng g^{-1} is the 'Lowest effects level' at which adverse biological effects are seen in 5% of benthic species).

If this increase is sustained, despite decreases in atmospheric flux, then it would provide support for hypotheses that climate change (e.g. changing frequency of drought or high rainfall events) may be exacerbating a release of previously deposited and stored pollutants, including trace metals, to the loch. Alternatively the increase might be related to the deposition-driven rise in DOC concentrations (see Section 5.4.5). The study of these phenomena is currently being undertaken as part of the EU funded project Euro-limpacs.

In other AWMN sites the trace metals work is restricted to the analysis of terrestrial mosses (again *Hylocomium splendens* and *Pleurozium schreberi)* at both lake and stream sites and the analysis of sediment trap material in lake sites. This has been undertaken since 2000 but there are some gaps in the dataset due to some loss of traps at some sites and the limited availability of trapped material for all analyses. The data from Scoat Tarn (Figure 5.6.5) show that Hg guideline values (e.g. MacDonald *et al*, 2000; Avocet Consulting, 2003) are frequently exceeded at this site and to a far higher level than that observed in Lochnagar. Sediment Hg exceedences are also observed at Llyn Llagi, Blue Lough and the Round Loch of Glenhead. This raises the possibility of a much broader impact of climate- or recovery-enhanced release of catchment stored pollutants than previously considered i.e. this is the first evidence beyond Lochnagar that metal concentrations in upland waters may be increasing despite reduced depositional fluxes. Monitoring over the next few years would therefore be particularly valuable as the dataset becomes long enough to test these observed trends.

5.6.3 The need for wider monitoring of trace metals and other pollutants in the uplands

While the value of this monitoring increases with each year, the value of the work, particularly that undertaken at Lochnagar, would be greatly increased by undertaking the same in-depth monitoring at a range of other AWMN sites across the UK. The lack of pollutant data for UK upland waters prevents us from placing the observed levels and trends observed at Lochnagar in any regional context. Certainly, contamination (trace metals and POPs) in Lochnagar, both in the sediment record and in biota (including fish), is high when compared with mountain lakes across Europe. Given that exceedences are observed in sediment Hg at a number of the AWMN sites a much larger scale of contamination may exist than that of which we are currently aware. Ignorance of the levels of pollutants in upland lakes across the UK is severe and needs to be addressed as a matter of urgency.

5.6.4 Fluxes in spherical carbonaceous particles

Spherical carbonaceous particles (SCPs) provide an unambiguous indication of atmospherically deposited contamination from industrial sources (see Rose and Monteith, 2005). AWMN data indicate major reductions in SCP deposition in all AWMN lakes, including Loch Coire nan Arr (Site 1) in northwest Scotland (Figure 5.6.6).

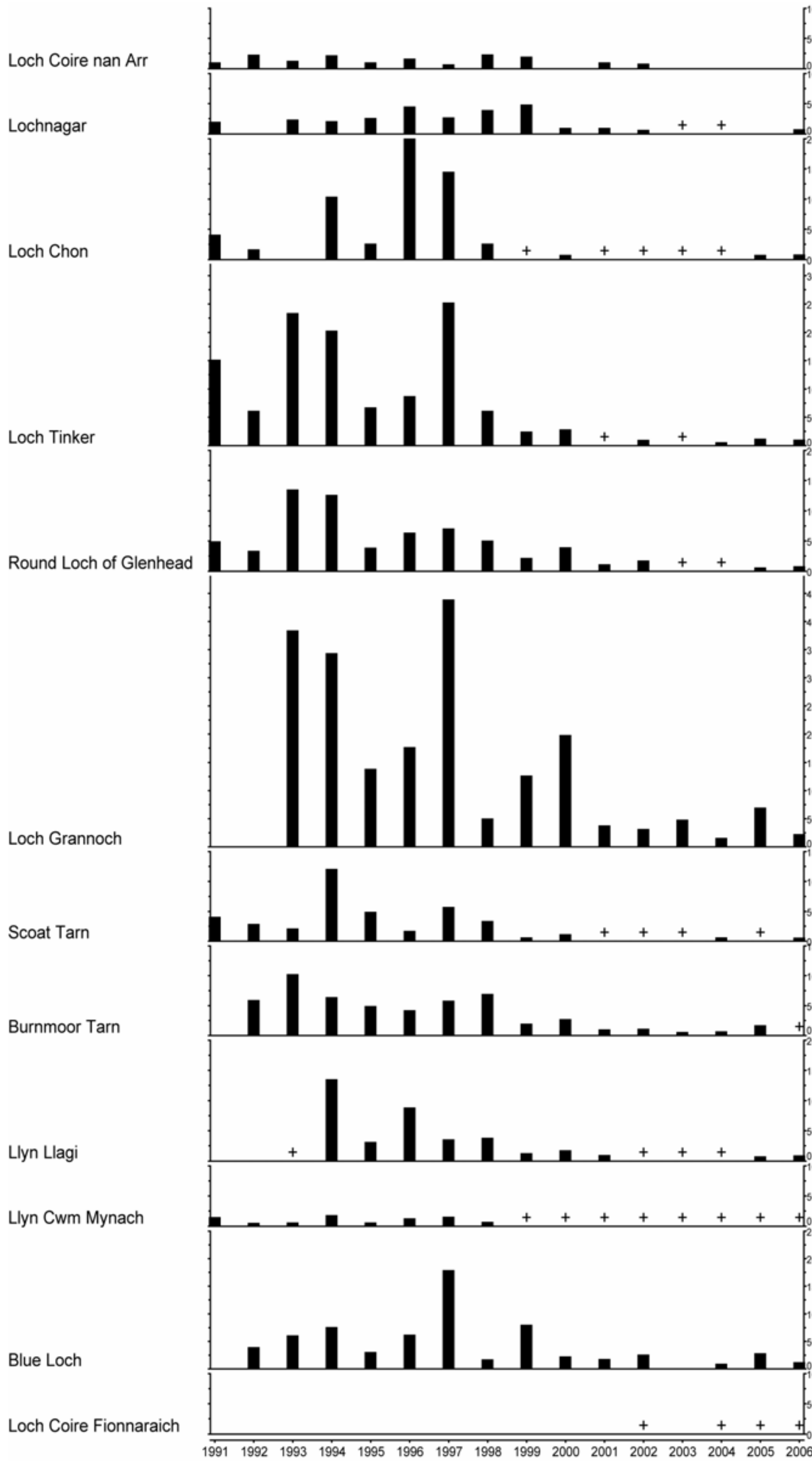


Figure 5.6.6 Sediment trap carbonaceous particle flux (no. cm^{-2} yr^{-1}) for AWMN lakes + represents < 50 cm^{-2} yr^{-1}

Note: Sediment trap monitoring in Loch Coire Fionnaraich began in 2002 – no trap recovered in 2003. Monitoring terminated in Loch Coire nan Arr in 2002.

5.7 Contributions to other Networks and wider research

The AWMN has continued to deliver water chemistry and macroinvertebrate data annually to the UNECE Cooperative Programmes (ICPs) for the Assessment of Acidification of River and Lakes, and Integrated Monitoring. AWMN personnel have played an active role in both programmes and have recently been involved in a major ICP Waters supported assessment of trends in DOC in acid-sensitive waters, leading to the publication in the journal Nature (Monteith et al., 2007). Data also continue to be provided for three lakes and one stream to the UK Environmental Change Network (ECN).

AWMN data are becoming increasingly central to other research programmes funded by DEFRA and NERC. AWMN data have underpinned, and continue to support, work under DEFRA's Freshwater Umbrella and Dynamic Modelling programme. Currently, AWMN sites are the focus of a NERC standard grant (PI: Dr Pippa Chapman, University of Leeds) that seeks to determine the influence of deposition chemistry on DOC concentration, and a NERC Ecology and Hydrology Funding Initiative grant (CEH Bangor) concerned with inter-relationships between sulphur, nitrogen and carbon dynamics in upland soils.

A succession of EU Framework projects, including ALPE, MOLAR, STAR, and most recently REBECCA and EURO-LIMPACS, and PhD projects at UCL, Queen Mary University of London and CEH have been and/or are dependent on AWMN data and sites.

At its current size and with the current breadth of measurements it has huge potential to address issues not only relating to acidification, but also eutrophication by deposited nitrogen, climate change, aquatic biodiversity and upland land management in the UK source water regions.

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